A Systematic Investigation into the Performance of
Nanocrystal and Hierarchical ZSM-5 Zeolites in MTG

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School of Mechanical and Chemical Engineering
Chemical Engineering
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THESIS DECLARATION

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ABSTRACT

Methanol to gasoline (MTG) is a promising alternative to the Fisher–Tropsch process for utilisation of small scale, stranded and associated gas resources and for the production of synthetic liquid transportation fuel. MTG typically uses ZSM-5 zeolite catalysts however, owing to the strong acidity and unique pore structure, ZSM-5 zeolite is easily deactivated during the reaction. Nanocrystal and hierarchical ZSM-5 zeolites have been proposed to further enhance the catalytic performance in MTG while greatly suppress the deactivation issue, inspiring intense research efforts in the literature. In spite of this, there is a lack of information about the effect of the SiO₂/Al₂O₃ ratio and the reaction conditions on the performance of nanocrystal zeolites. Moreover, the superior performance of the nanocrystal ZSM-5 zeolite over its microcrystal counterpart still lacks an in-depth scientific understanding. On the other hand, none of the reported methods for synthesising hierarchical ZSM-5 zeolites are economically feasible. The overall aim of this thesis research was to systematically investigate the performance of nanocrystal and hierarchical ZSM-5 zeolites in MTG.

The specific objectives of this thesis research are to: (i) develop methods to synthesise ZSM-5 zeolites with varying crystal sizes but similar SiO₂/Al₂O₃ ratios and nanocrystal ZSM-5 zeolites with similar crystal sizes but varying SiO₂/Al₂O₃ ratios; (ii) investigate the effect of catalyst properties (crystal size and SiO₂/Al₂O₃ ratio) on the performance of ZSM-5 catalyst in MTG; (iii) study the effect of reaction conditions on the performance of nanocrystal ZSM-5 catalyst in MTG; (iv) provide an insight into coke formation and characteristics in relation to catalyst deactivation and (v) directly synthesise hierarchical ZSM-5 zeolite and investigate its performance in MTG.
A series of nanocrystal ZSM-5 samples with similar crystal sizes of ~100 nm and varying SiO$_2$/Al$_2$O$_3$ ratios of 23, 47, 107, 217 and 411 were synthesised. The effect of the SiO$_2$/Al$_2$O$_3$ ratio on the performance of nanocrystal ZSM-5 zeolite in MTG was then examined. A steady methanol conversion was sustained with increasing the SiO$_2$/Al$_2$O$_3$ ratio and a progressive decrease in methanol conversion was observed over catalysts with SiO$_2$/Al$_2$O$_3$ ratios ≤107 after 5 h on stream. Decreasing the SiO$_2$/Al$_2$O$_3$ ratio promoted C$_1$–C$_4$ selectivity and thus decreased gasoline yield. It was also noted that decreasing the SiO$_2$/Al$_2$O$_3$ ratio promoted aromatisation reactions and hence higher durene selectivity and greater coking tendency, resulting in rapid catalyst deactivation. The sample with the SiO$_2$/Al$_2$O$_3$ ratio of 217 showed the best overall performance.

The effect of reaction conditions on the catalytic performance was studied using the nanocrystal catalyst with a SiO$_2$/Al$_2$O$_3$ ratio of 47 over a range of reaction conditions (temperature from 300 to 450 °C, pressure from 0.1 to 2.0 MPa and WHSV from 1 to 4 h$^{-1}$). Increasing temperature promoted methanol conversion, while a rapid decrease in the methanol conversion occurred at temperatures below 350°C. Increasing temperature also decreased durene selectivity, increased coking tendency and increased C$_1$–C$_4$ formation leading to a relatively low gasoline yield. The main effect of increasing pressure was to decrease the C$_1$–C$_4$ selectivity but increase the durene selectivity. Increasing pressure also promoted coke formation and thus led to rapid catalyst deactivation. WHSV had a similar effect on catalytic performance as the pressure.

The coke formation and characteristics were investigated using the nanocrystal catalyst with a SiO$_2$/Al$_2$O$_3$ ratio of 47 in comparison with that of a microcrystal catalyst at the times when the methanol conversion decreased to 50%. The nanocrystal catalyst incurred 31.1 wt% coke deposition while the microcrystal counterpart only incurred 14.1 wt% coke formation. The nanocrystal catalyst also showed a lifespan almost seven times
longer than the microcrystal catalyst. It was found that the internal coke was quickly formed in the microcrystal catalyst leading to rapid coverage of the active sites and blockage of the pores, resulting in rapid deactivation. In contrast, for the nanocrystal catalyst, coke formed preferentially on the external surface, which also had a porous graphitic structure that was found not to be detrimental to the catalytic performance.

A simple method was then developed to synthesise hierarchical ZSM-5 zeolite with intercrystalline mesopores using TPAOH as a sole structure directing agent. The hierarchical structure was formed by self-assembly of highly crystalline, nanosized primary crystals, resulting in mesopores in the range of 10–90 nm and intact microporous framework. The hierarchical zeolite exhibited almost 100% methanol conversion and 59% gasoline yield over 24 h. In addition, the hierarchical ZSM-5 zeolite had 2% coke formation, was much less as compared to the microcrystal zeolite with nearly 8% carbon deposition under the same reaction conditions.
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- The candidate worked closely with Professor Dongke Zhang, Professor Hong Yang and Dr Gang (Kevin) Li to critically review the manuscript. The manuscript is now ready for submission

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<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CNG</td>
<td>compressed natural gas</td>
</tr>
<tr>
<td>CTAB</td>
<td>cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>CTO</td>
<td>coal to olefins</td>
</tr>
<tr>
<td>DCM</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>DME</td>
<td>dimethyl ether</td>
</tr>
<tr>
<td>EFAL</td>
<td>extra framework aluminium</td>
</tr>
<tr>
<td>EIA</td>
<td>Energy Information Administration</td>
</tr>
<tr>
<td>FCC</td>
<td>fluid catalytic cracking</td>
</tr>
<tr>
<td>FID</td>
<td>flame ionisation detector</td>
</tr>
<tr>
<td>FT</td>
<td>Fisher–Tropsch synthesis</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatograph</td>
</tr>
<tr>
<td>GC–MS</td>
<td>gas chromatography mass spectrometry</td>
</tr>
<tr>
<td>GTL</td>
<td>gas to liquids</td>
</tr>
<tr>
<td>HAADF STEM-EDS</td>
<td>high angle annular dark field scanning transmission electron microscopy image and energy dispersive X-ray spectroscopy elemental maps</td>
</tr>
<tr>
<td>HMB</td>
<td>hexamethylbenzene</td>
</tr>
<tr>
<td>ICP–AES</td>
<td>inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>IZA</td>
<td>International Zeolite Association</td>
</tr>
<tr>
<td>LNG</td>
<td>liquefied natural gas</td>
</tr>
<tr>
<td>MAS NMR</td>
<td>magic angle spinning nuclear magnetic resonance</td>
</tr>
<tr>
<td>MCF</td>
<td>million cubic feet</td>
</tr>
<tr>
<td>MTG</td>
<td>methanol to gasoline</td>
</tr>
<tr>
<td>MTH</td>
<td>methanol to hydrocarbon</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>MTO</td>
<td>methanol to olefine</td>
</tr>
<tr>
<td>MTP</td>
<td>methanol to propene</td>
</tr>
<tr>
<td>NGH</td>
<td>natural gas hydrate</td>
</tr>
<tr>
<td>NH$_3$–TPD</td>
<td>ammonium temperature programmed desorption</td>
</tr>
<tr>
<td>PSS</td>
<td>product shape selectivity</td>
</tr>
<tr>
<td>RF</td>
<td>radio frequency</td>
</tr>
<tr>
<td>RON</td>
<td>research octane number</td>
</tr>
<tr>
<td>RSS</td>
<td>reactant shape selectivity</td>
</tr>
<tr>
<td>SAED</td>
<td>selected area electron diffraction</td>
</tr>
<tr>
<td>SDA</td>
<td>structure directing agent</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>TBAOH</td>
<td>tetrabutylammonium hydroxides</td>
</tr>
<tr>
<td>TCD</td>
<td>thermal conductivity detector</td>
</tr>
<tr>
<td>TCF</td>
<td>trillion cubic feet</td>
</tr>
<tr>
<td>TEAOH</td>
<td>tetraethylammonium hydroxide</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>tetraethylorthosilicate</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analyser</td>
</tr>
<tr>
<td>TMAOH</td>
<td>tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>TMS</td>
<td>tetramethylsilane</td>
</tr>
<tr>
<td>TPA$^+$</td>
<td>tetrapropylammonium cation</td>
</tr>
<tr>
<td>TPAOH</td>
<td>tetrapropylammonium hydroxide</td>
</tr>
<tr>
<td>TSS</td>
<td>transition–state shape selectivity</td>
</tr>
<tr>
<td>WGSR</td>
<td>water gas shift reaction</td>
</tr>
<tr>
<td>WHHSV</td>
<td>weight hourly space velocity</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
1.1 Background

The global demand for liquid transportation fuels is continuously increasing due to the rising global population and living standards and, thus, the number of automobiles, while the primary source for the production of transportation fuels, the conventional crude oil, is rapidly depleting. Moreover, more than half of the world oil reserves are geographically located in inhospitable regions. This imposes great uncertainties to future oil supplies and prices. Finding alternative solutions that would liberate us from the reliance on crude oil is certainly of urgent interest, particularly for oil-importing countries.

Precautions must be taken in order to satisfy the humankind’s ever-increasing energy needs. Thankfully, technologies have already been developed to produce transportation fuels independent of conventional sources, namely synthetic fuels. One of the prominent technologies is known as methanol to gasoline (MTG) conversion, first developed by Exxon Mobil in the 1970s. As the name implies, the MTG process uses methanol as feedstock, which can be catalytically converted over a ZSM-5 zeolite catalyst into a mixture of hydrocarbons within the gasoline boiling range, having research octane number (RON) comparable to the conventional gasoline and is sulphur free, more environmentally friendly. Furthermore, methanol is easy to transport and store, and more importantly, easy to obtain from natural gas steam reforming or gasification of coal or biomass. Even the greenhouse gas, CO2, could be made available for methanol production. A methanol based route for the production of transportation fuel is very promising. A schematic is shown in Figure 1.1.

The methanol based route for the production of transportation fuels also has the potential to monetise half of the natural gas reserves, which are either in a small capacity or located
in remote areas, being non-profitable based on current options for natural gas monetisation and thus remained stranded, known as stranded gas. Methanol can be readily produced from natural gas via synthesis gas (syngas). Based on present technologies, methanol production plant is easily constructed, and no high capital investment and large infrastructure are required. On site plants for methanol production at the stranded gas fields are thus made possible. The produced methanol can be easily transported to the consumer end, and thus indirectly monetising the stranded gas.

![Diagram of methanol based route for gasoline production.](image)

Figure 1.1 A schematic of the methanol based route for the production of gasoline.

Nevertheless, like many catalysis processes, the catalyst used for MTG is progressively deactivated by coke formation over the reaction time, and ultimately needs to be either regenerated or replaced by a fresh batch. A catalyst having enhanced performance has always been the goal of the scientific community since the advent of MTG. Reducing crystal size of the catalyst into nanoscale and creating mesopores, namely, synthesis of nanocrystal and hierarchical ZSM-5 zeolites have been acknowledged to greatly improve the catalytic performance and suppress the deactivation issues. Massive efforts have thus been dedicated into this regard.

However, early studies have mainly focused on developing synthesis methods for the two types of catalysts. Little has been devoted to studying some deeper level factors which are also recognised to play an important role in determining the catalytic performance, such as SiO$_2$/Al$_2$O$_3$ ratio and reaction conditions in terms of the development of
nanocrystal ZSM-5 zeolite. In addition, although nanocrystal ZSM-5 zeolite having enhanced catalytic performance over its microcrystal counterpart (conventional ZSM-5) has been well documented, little is known about the coke formation and characteristics related to the enhanced catalytic performance as a result of crystal size reduction into nanoscale. Furthermore, for the reported synthesis methods developed for hierarchical ZSM-5 zeolite, none has been found to have potential to be commercialised in terms of economic and environmental concerns. It is therefore imperative and essential to study these research gaps identified.

1.2 Research scope and aims

The overall aim of this research is to achieve an improved understanding about MTG with respect to catalyst development, with particular attentions dedicating to study the effect of SiO$_2$/Al$_2$O$_3$ ratio and reaction conditions on catalytic performance, coke formation and characteristics related to catalyst deactivation in terms of the development of nanocrystal ZSM-5 zeolite, as well as develop method for direct synthesis of hierarchical ZSM-5 zeolite.

The present research began with studying the effect of crystal size on the catalytic performance, following by a systematic study on the intrinsic effect of SiO$_2$/Al$_2$O$_3$ ratio on catalytic performance based on developing method to synthesise nanocrystal ZSM-5 catalysts with various SiO$_2$/Al$_2$O$_3$ ratios but identical crystal sizes and structural properties. Nanocrystal ZSM-5 zeolite having enhanced catalytic performance was then studied in relation to coke formation and characteristics. Finally, a method for direct synthesis of hierarchical ZSM-5 zeolite was developed, and its catalytic performance was studied and compared with a microcrystal counterpart.
1.3 Thesis outline

The thesis embraces a total of nine chapters designed to a set of logically sequenced topics of work and discussion, and its structure is schematically shown in Figure 1.2, in the form of a chemical engineering “process block diagram” or the thesis map.

- **Chapter 1** defines the scope, overall aims and structure of this thesis
- **Chapter 2** reviews the nature gas reserves, the current status of options to monetise natural gas, and methods for methanol production, leading to the concept of a methanol based route for the production of transportation fuel via MTG. Ultimately, tremendous efforts have been devoted into reviewing the MTG process and catalyst used, the synthesis of catalyst, mechanism and catalyst deactivation of MTG, and catalyst development to enhance catalytic performance. Finally, the research gaps and specific objectives of this research have been identified
- **Chapter 3** illustrates the methodology and approaches for the synthesis and evaluation of catalyst, techniques used for characterisation of the catalysts and coke
- **Chapter 4** presents the characteristics of the nanocrystal ZSM-5 zeolite, the effect of crystal size and SiO$_2$/Al$_2$O$_3$ ratio on the performance of nanocrystal ZSM-5 zeolite in MTG
- **Chapter 5** demonstrates the effect of reaction conditions (temperature, pressure and WHSV) on the performance of nanocrystal ZSM-5 zeolite in MTG
- **Chapter 6** investigates coke formation and characteristics in relation to the enhanced catalytic performance of nanocrystal ZSM-5 zeolite used in MTG
- **Chapter 7** displays the characteristics and catalytic performance of a directly synthesised hierarchical ZSM-5 zeolite.
- **Chapter 8** evaluates the findings from the present study and discusses their implication, and raises the new gaps identified for future research
Chapter 9 draws conclusions from the present study and outlines the recommendations for future research.

Figure 1.2 Thesis map.
Chapter 2 Literature Review

2.1 Introduction

The liquid transportation fuels we use daily are primarily processed from the refining of crude oil. However, as the cost of exploring remaining crude oil reserves are increasing and the known conventional crude oil sources are diminishing, we will increasingly confront a rising and volatile price of liquid fuels. In addition, oil reserves are mostly found in regions where are politically unstable. The political uncertainties have contributed and will continue to significantly impact on the oil market, with oil supplies being abruptly cut off and prices being artificially manipulated. This would have serious consequences on oil-importing countries. Nevertheless, the dependence on crude oil will need to lessen.

Searching for alternative routes for the production of transportation fuels is certainly urgent. Methanol to gasoline conversion (MTG) and Fisher–Tropsch synthesis (FT) are two known technologies to produce synthetic transportation fuels (synthetic fuels) independent of crude oil. The major advantage of MTG over FT is the use of liquid feedstock—methanol which is easy to obtain, transport and store. This chapter provides an overview of MTG, not only the MTG reaction itself, but also a variety of knowledge from methanol production to the catalyst used.

As methanol is mainly manufactured from synthesis gas (syngas) derived from natural gas, this chapter begins with a general review of natural gas reserves around the world followed by options for monetising natural gas. The inherent challenges in each option are identified, leading to the proposal that the methanol based route should be chosen to monetise natural gas and produce transportation fuels. The next section covers a number of methods of methanol production. The subsequent section is the major part of this
chapter with focus on MTG, including a brief induction to MTG, catalyst use, catalyst synthesis, MTG mechanisms, coke formation leading to catalyst deactivation, and catalyst development to overcome catalyst deactivation. All this eventually leads to identify a number of key research gaps in this area, enabling us to define the scope and specific objectives of this PhD study.

2.2 Natural Gas Reserves and Market

2.2.1 World gas reserves
The worldwide proven natural gas reserves in 2014 were estimated to be 6972.5 trillion cubic feet (TCF) according to U.S. Energy Information Administration (EIA). Table 2.1 shows 15 countries with the largest gas reserves in the world. Of these countries, Russia and Iran account for over 40% of the total gas reserves. However, most of the gas reserves are found in places where no one lives, with roughly half of the total gas reserves located in small scale fields, deep under the ocean floor or in complex geologic formations, remaining stranded and generally known as stranded gas. Moreover, a large quantity of gases produced along with oil or coal exploration are often reinjected or flared, known as associated or flared gas. These gases are uneconomic to deliver to market based on current technologies.

2.2.2 Options for monetising natural gas
Natural gas is of little value unless it can be brought from the wellhead to the customer, who may be several thousand kilometres away. As natural gas is relatively low in energy content per unit volume under ambient conditions, the cost to transport energy in the form of gas is significantly more expensive than that of liquid. This is one of the key hurdles to the increased use of gas.
Table 2.1 Top 15 countries with largest gas reserves of the world (Source: U.S. EIA, 2014)

<table>
<thead>
<tr>
<th>Country</th>
<th>Reserves (TCF)</th>
<th>% of World Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russia</td>
<td>1688</td>
<td>24.2</td>
</tr>
<tr>
<td>Iran</td>
<td>1201</td>
<td>17.2</td>
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<tr>
<td>Qatar</td>
<td>872</td>
<td>12.5</td>
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<tr>
<td>Saudi Arabia</td>
<td>294</td>
<td>4.2</td>
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<td>Turkmenistan</td>
<td>265</td>
<td>3.8</td>
</tr>
<tr>
<td>United Arab Emirates</td>
<td>215</td>
<td>3.1</td>
</tr>
<tr>
<td>Venezuela</td>
<td>197</td>
<td>2.8</td>
</tr>
<tr>
<td>Nigeria</td>
<td>180</td>
<td>2.6</td>
</tr>
<tr>
<td>China</td>
<td>164</td>
<td>2.4</td>
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<tr>
<td>Algeria</td>
<td>159</td>
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<tr>
<td>Iraq</td>
<td>112</td>
<td>1.6</td>
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<tr>
<td>Indonesia</td>
<td>103</td>
<td>1.5</td>
</tr>
<tr>
<td>Mozambique</td>
<td>100</td>
<td>1.4</td>
</tr>
<tr>
<td>Kazakhstan</td>
<td>85</td>
<td>1.2</td>
</tr>
<tr>
<td>Malaysia</td>
<td>83</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Currently, there are five major options to bring natural gas to the consumers: pipeline, liquefied natural gas (LNG), compressed natural gas (CNG), natural gas hydrate (NGH) and gas to liquids (GTL):

**Pipeline:** The gas is treated to meet pipeline quality requirements and compressed for transportation and distribution through a network of pipelines. The pipeline option is generally considered to be the cheapest and most efficient option for monetising natural gas when transportation distance is less than 2000 km, preferably on land. As building up pipelines depends on the terrain and distance, the cost is approximately proportional to
the distance. Pipelines become uneconomical for small gas fields and when the distance is above 2000 km.

LNG: The gas is treated, liquefied, shipped and re-gasified at the destination. Natural gas is in liquid phase when it is cooled to around -162 °C and has a volume of ~ 1/600 that of gas at ambient temperature[1]. At the gas fields, complex machinery is required to cool the gas to -162 °C, and special refrigerated facilities are also needed for transporting the LNG to the consumers. At the consumer end, storage and reprocessing of LNG can be also complex and costly. Large tanks with cryogenic capacity are needed to store the LNG, which requires continuous running to keep natural gas in liquid form so that to prevent warming up that causes tragedy. LNG is competitive with pipeline at distances between 2500 and 4000 km for large gas fields having production volume above 3 metric tonnes per annum (MTPA) [2].

CNG: The gas is treated, compressed and shipped to consumers in containers at high pressures, usually at 20–25 MPa (2900–3600 psi). CNG has a volume less than 1% of its original volume at standard atmospheric pressure. However, filling a container with natural gas to that high pressure is very slow, and the placement and maintenance of storage tank is often very expensive. CNG can be competitive with LNG for gas fields of ~ 500 million cubic feet (MCF) when the transportation distance to the consumers is low.

NGH: The natural gas molecule can be trapped to stabilise within crystalline ice-like hydrates. By mixing the gas with water at 80–100 bar and 2–10 °C, one ton of hydrate can trap up to 160 sm³ of natural gas. As this hydrate is solid, it can then be transported in simple insulated carriers which are significantly cheaper than LNG tanks. At the consumer end, the gas hydrate is warmed up and the natural gas is released. NGH has
lower capital and operating costs compared to other options of monetising natural gas. This promising technology has yet to be commercialised [2].

**GTL:** The natural gas undergoes chemical reactions to be converted to liquids, such as methanol and ammonia. The transportation and storage of these liquids is much easier than the natural gas. More importantly, the converted liquid can be further converted to other valuable chemicals via well-known processes, such as methanol to hydrocarbon (MTH), including methanol to olefine (MTO), methanol to propene (MTP), and methanol to gasoline (MTG).

Among those five options for monetising natural gas, GTL currently seems to be the most attractive method to bring stranded gas to the consumers, particularly for small and/or remote gas fields (Figure 2.1) [3].

Figure 2.1 Comparison of existing methods for monetising natural gas, reproduced from [2].
2.2.3 Gas to liquid

GTL is generally referred to a refinery process that first converts natural gas into synthesis gas or syngas (CO + H₂) and then to other value-added hydrocarbons and oxygenates. FT and methanol synthesis are two main process routes of the GTL technology.

FT synthesis is a collection of chemical reactions that converts syngas into liquid hydrocarbons mainly consisted of saturated linear hydrocarbons with carbon number higher than 40 (C₄₀). The hydrocarbons in the range of C₁₀–C₂₀ are ideal for use as diesel fuel, which is free of sulphur and nitrogen, and is more environmentally friendly than conventional diesel. The chemical reactions for FT synthesis can be represented as follows:

\[
\text{nCO} \, + \, (2n+1)\text{H}_2 \, \rightarrow \, \text{C}_n\text{H}_(2n+2) + n\text{H}_2\text{O}
\]

First discovered by Franz Fischer and Hans Tropsch in the 1920s, FT synthesis has been very successful. A number of F-T plants have been commercialised, although some have been shut down due to economic concerns or other issues [4]. The popularity of FT synthesis has been hampered by the high costs and the large scale infrastructures required.

Methanol is another GTL fuel option which can be readily prepared from syngas or by direct oxidative conversion of natural gas. With the progressive technological improvements over the past 100 years, and in particular the development of “Mega Methanol” technology, the cost of methanol production has come down to US$ 65 per ton for production capacity up to 7,500 ton per day [5]. Methanol as a liquid can be easily transported and stored, and large scale infrastructures, large pipelines or special tanks are not required. Methanol with an octane number of 106 can be used as a transportation fuel or gasoline blend [6]. Pure methanol (M100) or methanol blended with conventional
gasoline in an 85/15 mix (M85) have been used as fuel in some vehicles since 1965 [7]. However, progress in the development of methanol as a fuel in the past few decades has been slow and the process has not fully mature. Methanol fuels are problematic because the polar character of methanol means it has great affinity for water and poor solubility in gasoline [8]. Also large investments are required to modify engine systems due to the unique physical and chemical properties [9]. Overall, it is more economical to convert methanol into a transportation fuel than to use it alone or blend it with conventional gasoline [10].

GTL via methanol is a worthy alternative compared to FT synthesis. Commercial methanol plants are generally an order of magnitude smaller in scale than commercial FT plants [11]. Commercial methanol plants have a wider and more diverse distribution with the smallest plant being only approximately 1/30 the scale of the largest methanol plant, whereas for a F-T commercial plant, the plant size varies only by a factor of 10. This implies that the much smaller and diverse scale of methanol synthesis makes natural gas to methanol conversion a more applicable and accessible GTL technology for the stranded, associated and flared gases.

2.3 Methanol Production

Methanol has the chemical formula CH₃OH, and is also known as methyl alcohol (MeOH) or wood alcohol. It is a colorless liquid with slight alcoholic odor. Methanol containing only one carbon atom can be made at various scales from various sources such as natural gas, coal and/or biomass or even the utilisation of greenhouse gas, CO₂ [12]. In fact, any hydrocarbon sources can be used for methanol production via syngas derived from steam gasification or reforming of the hydrocarbons. Methanol production is a mature process
and most exiting plants have production capacities ranging from $1 \times 10^5$ to $8 \times 10^5$ ton per year. In addition, plants with capacities of $1 \times 10^6$ ton per year will become the norm [13].

2.3.1 Methanol production from syngas

Today, methanol is mainly manufactured via syngas derived from natural gas or coal, according to the equation below:

$$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} \quad \Delta H^{\text{298K}} = -21.7 \text{ kcal mol}^{-1} \quad (2-2)$$

The reaction is exothermic and reversible, with decreasing temperature favouring the formation of methanol. The ideal stoichiometry for methanol synthesis requires the syngas to have a H$_2$/CO ratio of 2.

Another reaction that also occurs during methanol synthesis is the reverse water-gas shift reaction (RWGSR):

$$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H^{\text{298K}} = 9.8 \text{ kcal mol}^{-1} \quad (2-3)$$

This reaction can produce carbon monoxide (CO) that will further react with hydrogen to produce methanol.

The feedstock syngas for methanol production can be obtained by reforming or partial oxidation of virtually any carbon-containing materials, such as natural gas, coal or biomass. Natural gas is the preferred feedstock as it has high hydrogen content, low energy consumption, and low operating costs. Furthermore, natural gas has few impurities compared to other sources, such as sulphur and halogenated compounds, which act as “catalyst poisons” and greatly reduce catalyst performance. In our study, syngas produced from natural gas is explored as a means of monetising stranded gas.
2.3.1.1 Syngas from natural gas

Steam reforming of methane

In the presence of steam, methane can be converted into syngas at high temperature (800–1000 °C) and pressure (20–30 atm). The catalyst is typically nickel based. The produced CO can also react with steam to form H2 and CO2 via the water gas shift reaction (WGSR), the resulted gas is thus a mixture of H2, CO and CO2:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3\text{H}_2 & \Delta H_{298K}^\circ &= 49.1 \text{ kcal mol}^{-1} \quad (2–4) \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 & \Delta H_{298K}^\circ &= -9.8 \text{ kcal mol}^{-1} \quad (2–5)
\end{align*}
\]

The syngas produced from the above reactions has a H2/C0 ratio of 3, which is much higher than the ideal stoichiometric ratio of 2 for methanol synthesis. This can generally be corrected by the addition of CO2 that directs the WGSR to consume excessive H2 and produce CO. The overall ratio of the gas mixture depends on the reaction conditions such as temperature, pressure and CH4/H2O ratio. Increasing temperature curbs the WGSR and reduces CO2 production. The overall efficiency of syngas production is found to increase with increasing temperature and decreasing pressure.

Partial oxidation of methane

Partial oxidation is the reaction of methane with insufficient oxygen:

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2 \quad \Delta H_{298K}^\circ = -8.6 \text{ kcal mol}^{-1} \quad (2–6)
\]

The reaction can proceed at high temperature 800–1500 °C with or without a catalyst. The produced syngas has a H2/CO ratio of 2 according to the equation, ideal for methanol synthesis. However, CO and H2 can further react with O2 to form CO2 and water, in reality
Chapter 2 Literature Review

the H₂/CO ratio is typically below 2. Moreover, safety concerns are also raised as the reactions are highly exothermic:

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 & \rightleftharpoons \text{CO}_2 \quad \Delta H_{298K} = -67.6 \text{ kcal mol}^{-1} \\
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightleftharpoons \text{H}_2\text{O} \quad \Delta H_{298K} = -57.7 \text{ kcal mol}^{-1}
\end{align*}
\] (2–7) (2–8)

2.3.1.2 Syngas from coal

Coal was the original feedstock used for production of town gas for residential and commercial applications and later, syngas for industrial applications by steam gasification. Coal gasification is still widely used, particularly in China and South Africa for the production of methanol and ammonia, and may also become a major source for syngas production in the future in other countries with abundant coal. Combining partial oxidation and steam treatment, syngas can be formed by coal gasification:

\[
\begin{align*}
\text{C} + \frac{1}{2} \text{O}_2 & \rightleftharpoons \text{CO} \quad \Delta H_{298K} = -29.4 \text{ kcal mol}^{-1} \\
\text{C} + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + \text{H}_2 \quad \Delta H_{298K} = 31.3 \text{ kcal mol}^{-1} \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H_{298K} = -9.8 \text{ kcal mol}^{-1} \\
\text{CO}_2 + \text{C} & \rightleftharpoons 2\text{CO} \quad \Delta H_{298K} = 40.8 \text{ kcal mol}^{-1}
\end{align*}
\] (2–9) (2–10) (2–11) (2–12)

The process for syngas production by coal gasification has been commercialised over years. As coal is rich in carbon and has a low H/C ratio, the produced syngas generally has a high ratio of CO. To meet the ideal H₂/CO ratio of 2 for methanol synthesis, the obtained syngas is usually subject to WGSR to produce more H₂ and in the meantime
reduce the amount of CO. In addition, the produced CO₂ also needs to be removed before methanol synthesis, as well as sulphur containing gas (such as H₂S) which is highly detrimental to the catalyst performance.

2.3.2 Methanol direct from methane

Although methanol synthesis via syngas is the most favourable process for methanol production at present, it requires a massive amount of energy for the initial highly endothermic step of methane steam reforming. From the point of view of energy saving, it is not efficient to first transform methane into CO and then reduce it again to methanol with hydrogen. Instead, direct methane conversion into methanol would be more efficient. Extensive efforts have been directed towards this goal and considerable progress has been made in recent years, particularly for direct oxidation of methane into methanol:

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{OH} \quad \Delta H_{298K}^\circ = -30.4 \text{ kcal mol}^{-1}
\]

(2–13)

Methane can be directly converted into methanol by selective oxidation. This process eliminates the need for producing syngas, greatly reducing capital costs. However, the major problem associated with this process is the high reactivity of the products themselves. This reaction favours the complete combustion of methane, producing CO₂ and water:

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_{298K}^\circ = -191.9 \text{ kcal mol}^{-1}
\]

(2–14)

Reaction conditions to mitigate complete methane combustion and achieve high methane conversion into methanol have been explored. Unfortunately, a process with high methanol yield and selectivity, and high catalyst stability has yet to be developed that is competitive with the conventional method (syngas based method of methanol production).
2.3.3 Methanol from biomass

Methane is the primary feedstock for methanol synthesis at present. However, although natural gas reserves are still considerable, they are inevitably diminishing. Therefore, the exploitation of unconventional sources for methanol production is increasing in popularity.

Biomass, namely, any type of plant or animal material (including wood and wood wastes, agricultural crops and wastes, and animal waste) can be used to produce syngas by means of pyrolysis, and therefore to produce methanol. The technology to convert biomass into methanol is quite similar to that used for coal gasification for methanol production. Biomass is first transformed to syngas followed by methanol synthesis processes identical to the natural gas processes.

One of the major challenges for utilisation of biomass for methanol production is the collection and transportation of the biomass. About 1.5 million ton of biomass would be needed to feed a methanol plant with production capacity of 2500 ton per day. Such a large amount of biomass needs to be collected over a vast area of land and transportation of this biomass to the methanol production plant then become a challenge. The technology thus needs to be further developed before commercialisation.

2.3.4 Methanol from recycling of carbon dioxide (CO₂)

Own to the impact of CO₂ on climate change, recycling CO₂ by means of reversing the combustion process to produce valuable chemicals is being explored, as shown in Figure 2.2. In fact, CO₂ conversion to methanol has been known by researchers since the early twentieth century.

\[ \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]  \hspace{1cm} (2–15)
Catalysts, commonly copper and zinc based, which are very similar to those used for the process of methanol production via syngas have been developed and found to be efficient. Pilot scale production of methanol from CO$_2$ with a capacity of 50 kg per day and selectivity of 99.8% has been demonstrated in Japan [14]. More recently, Javier and co-workers [15] developed a novel catalyst of ZrO$_2$ supported In$_2$O$_3$ which showed 100% methanol selectivity from CO$_2$ conversion and remarkable catalyst stability up to 1000 h on stream.

The major challenge for the commercialisation of methanol production from CO$_2$ is the availability of feedstock, the capital costs and the extra energy required. Nevertheless, methanol from CO$_2$ recycling provides us with an alternative option to liberate from the dependence on depleting and non-renewable fossil fuels.

![Carbon dioxide recycling for methanol production and other value-added chemicals](image)

**Figure 2.2** Carbon dioxide recycling for methanol production and other value-added chemicals, adopted from [16].

In summary, methanol can be obtained from various sources and processes and almost all hydrocarbons currently produced from crude oil can be practically obtained from methanol. A methanol based route for gas to liquid has the potential to monetise the
stranded gases, and is also promising for the production of transportation fuel in responding to the depletion of crude oil.

2.4 Methanol to Gasoline

2.4.1 History of MTG

MTG uses methanol as feedstock and ZSM-5 zeolite as catalyst to produce gasoline range hydrocarbons. It is the first major breakthrough in the development of synthetic fuel since the advent of FT synthesis, providing a new route for the production of synthetic transportation fuel from sources that are independent of conventional petroleum sources.

The first reported observation of synthetic gasoline from methanol is credited to Exxon Mobil in early 1970s [17-19], when two teams accidentally discovered the formation of hydrocarbons from methanol over ZSM-5 zeolite. Aromatic hydrocarbons were observed by one team at Mobil Chemical who were trying to convert methanol to ethylene oxide. Another team at Mobil’s Central Research Laboratory also discovered the formation of hydrocarbons when working on isobutene methylation with methanol in the presence of ZSM-5 zeolite. The aromatic hydrocarbons produced by both were found to be similar to premium gasoline, and virtually absent of hydrocarbons higher than C_{10}, suitable for use as gasoline fuel [18].

Extensive development of MTG was initiated owing to the first oil crisis in 1973 and second oil crisis in 1978, eventually leading to the commercialisation of MTG. The first commercial MTG plant was built in New Zealand with a fixed–bed process shown in Figure 2.3. The plant had a production capacity of 14500 barrels per day (bpd; 1 barrel=159 L) based on methanol converted from syngas via natural gas [19-21]. The MTG process used was a two-stage reaction as illustrated below:
The first stage involved the dehydration of crude methanol over a slightly acidic catalyst (typically alumina based) to produce an equilibrium mixture of methanol, dimethyl ether (DME) and water. In the second stage, the resulting mixture was introduced over ZSM-5 catalyst to produce light olefins (primarily ethylene and propylene) which underwent further transformation into higher hydrocarbons rich in iso-paraffins and aromatics, with C₅⁺ (benzene fraction) selectivity of about 80%. The hydrocarbons were sulphur free, with an unleaded Research Octane Number (RON) of 90–96, comparable with conventional gasoline.

Figure 2.3  Schematic of typical MTG fixed bed process flow, adopted from [19].
Table 2.2  Typical products for MTG reaction [18, 23, 24]

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Formula</th>
<th>Chemical Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>p-xylene</td>
<td>C₆H₄(CH₃)₂</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>1,2,3-trimethylbenzene</td>
<td>C₆H₃(CH₃)₃</td>
</tr>
<tr>
<td>Ethene</td>
<td>C₂H₄</td>
<td>1,2,4-trimethylbenzene</td>
<td>C₆H₃(CH₃)₃</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>1,3,5-trimethylbenzene</td>
<td>C₆H₃(CH₃)₃</td>
</tr>
<tr>
<td>Propene</td>
<td>C₃H₆</td>
<td>α-ethyltoluene</td>
<td>C₆H₅CH₂CH₃</td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>m-ethyltoluene</td>
<td>C₆H₅CH₂CH₃</td>
</tr>
<tr>
<td>Butene</td>
<td>C₄H₈</td>
<td>p-ethyltoluene</td>
<td>C₆H₅CH₂CH₃</td>
</tr>
<tr>
<td>C₅⁺ aliphatics*</td>
<td>*</td>
<td>Isopropylbenzene</td>
<td>C₆H₅CH(CH₃)₂</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>1,2,3,4-tetramethylbenzene</td>
<td>C₆H₂(CH₃)₄</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₆H₅CH₃</td>
<td>1,2,3,5-tetramethylbenzene</td>
<td>C₆H₂(CH₃)₄</td>
</tr>
<tr>
<td>o-xylene</td>
<td>C₆H₄(CH₃)₂</td>
<td>1,2,4,5-tetramethylbenzene</td>
<td>C₆H₂(CH₃)₄</td>
</tr>
<tr>
<td>m-xylene</td>
<td>C₆H₄(CH₃)₂</td>
<td>Others</td>
<td>*</td>
</tr>
</tbody>
</table>

*C₅⁺ aliphatics represent non-aromatic liquid hydrocarbons with carbon number no less than 5; others represent aromatics higher than tetramethylbenzene.

Typical products are summarised in Table 2.2. Unfortunately, the New Zealand MTG plant was shut down shortly after the operation started due to the plummet in crude oil prices. In the mid-nineties, the plant reduced operations to methanol production alone [21]. Today, MTG and alike (MTO, MTP) are again receiving attention, particularly the use of coal as feedstock to produce olefins (CTO). In 2010, two CTO units with a total capacity of $1.1 \times 10^6$ ton per year were built in China by Shenhua Group. In 2011, Datang
International Power Generation also built a MTP unit with capacity of $4.6 \times 10^5$ ton per year [22].

### 2.4.2 ZSM-5 zeolite

The earliest report of hydrocarbon formation from methanol can be dated back to 1880, when Lebel and Greene observed the formation of hexamethylbenzene (HMB) and light gases (predominantly CH$_4$) from methanol decomposition using molten ZnCl$_2$. In 1962, Mattox reported trace amounts of C$_2$–C$_5$ olefins formed during methanol dehydration to dimethyl ether (DME) over NaX zeolite; higher hydrocarbons (such as substituted aromatics) were also reported from methanol dehydration over P$_2$O$_5$ [10, 23]. It was not until the advent of ZSM-5 zeolite in the 1970s that highly selective production of gasoline range hydrocarbons were first obtained from methanol.

The term “zeolite” is derived from the Greek for “boiling stone” as they release water upon heating [25]. Zeolite can be formed naturally and about 40 natural zeolites are known. The first discovered zeolite can be tracked back to 1756 [26]. However, the application of natural zeolite is limited by their impurities and low surface areas that impede their catalytic activity and absorption capability. It was not until the development of synthetic zeolites, particularly the synthesis of ZSM-5 zeolite and the discovery of its extraordinary catalytic activity in methanol conversion in the 1970s, that zeolites became widely used in various applications [27, 28], and thereafter escalating further development of synthetic zeolites. According to the International Zeolite Association (IZA, http://www.iza-online.org), there are now 231 known zeolite framework structures. ZSM-5, derived from Zeolite Socony Mobil–five, is a microporous crystalline aluminosilicate material composed of SiO$_4$ and AlO$_4$ tetrahedra. The building units of the
ZSM-5 framework are pentasil unit consisting of 8 five-member rings, as shown in Figure 2.4a. The pentasil units with vertices of Si or Al are linked to form pentasil chains (Figure 2.4b). These chains are interconnected via shared O to form corrugated sheets with 10-ring holes (in grey perpendicular to \( a \) in Figure 2.4c). The sheets are bridged by O to form a three-dimensional framework named MFI (Mobil–Five) type. Shown in Figure 2.4 (c) is the skeletal diagram of the [010] face of ZSM-5 zeolite. This produces straight channels parallel to [010] having openings defined by 10-ring size of 5.3×5.6 Å based on oxygen
radii of 1.35 Å, and sinusoidal channels along [100] with openings of 5.1×5.5 Å. Along the [001] direction, diffusion can readily occur between the overlapping channels parallel to [100] and [010] [23, 25-27, 29, 30]. The represented channel structure is shown in Figure 2.4 (d).

### 2.4.2.1 Synthesis of ZSM-5 zeolite

The systematic synthesis of zeolite was first established by Richard Barrer and Robert Milton in the 1940s by investigating the conversion of known mineral phases at high temperatures (~170–270 °C) [27, 31]. These materials were later determined to be zeolite ZK-5 with a KFI structure. The synthesis conditions were later optimised by Milton and co-workers in late 1940s when zeolites A, X and P were produced hydrothermally at low temperatures (~ 100 °C) under autogenous pressures. Significant developments in zeolite synthesis then occurred over the next few decades, particularly when quaternary ammonium cations were introduced as structure directing agent for the formation of zeolites. Following the first successful synthesis of high–silica zeolite—zeolite beta with Si/Al ratios ranging from 5 to100, the ZSM-5 zeolite was synthesised using tetrapropylammonium cation (TPA⁺) by Argauer and Landolt in 1972 [32]. The general chemical formula of ZSM-5 zeolite with Na⁺ as the charge compensation cation is shown below:

\[
\text{Na}_n\text{Al}_{12}\text{Si}_{96-n}\text{O}_{192} \cdot 16\text{H}_2\text{O} \quad (0<n<27)
\]  

(2–16)

The hydrothermal synthesis technique has since become the most common route for zeolite synthesis. A typical hydrothermal zeolite synthesis involves [27]: (1) Reactants as silica and alumina sources are mixed with a cation source in a basic (usually pH>12) aqueous medium; (2) the reaction mixture is heated usually at temperatures above 100 °C
in a sealed autoclave; (3) Crystallisation starts to occur during the hydrothermal treatment and eventually leads to the final zeolite product with its properties (framework type, crystallinity, crystal size, microporosity and surface area) depending on various parameters. The product is finally recovered by filtration, washing and drying. An overview of typical hydrothermal zeolite synthesis is shown in Figure 2.5.

While the procedure for hydrothermal zeolite synthesis is seemingly simple, the chemistry involved is rather complicated. The process of zeolite crystallisation during crystal nucleation and growth involves very complex chemical reactions, such as solution–precipitation, polymerisation–depolymerisation and nucleation–crystallisation, and this process is affected by various factors, such as silica and alumina sources, type of structure directing agent, Si/Al ratio, water content, pH of solution, stirring, aging, hydrothermal temperature and duration. Subtle changes in any parameters can produce zeolite products with dramatically different properties. For example, it has been reported that an increase in SiO$_2$/Al$_2$O$_3$ ratio can lead to a substantial decrease in the crystal size under otherwise identical conditions [33-36].

Figure 2.5 schematic of typical hydrothermal zeolite synthesis.
2.4.2.2  **Synthesis mechanism**

The research community has always been endeavour to answer a series of questions such as how the crystals grow during the hydrothermal treatment, how the quaternary ammonium cation can direct the crystal growth towards the desired framework structure. Massive efforts have been devoted to investigate the mechanism of zeolite synthesis [33, 34, 37-45] and more detailed discussions could be found in the reviews [33, 34].

![Diagram of zeolite crystallisation process](image_url)

**Figure 2.6**  Schematic of sequential steps in the evolution of zeolite crystallisation, adopted from [27, 37].

Zeolite synthesis could be considered as a process of nucleation and crystallisation involving very complex chemical reactions. A schematic for the evolution of zeolite crystallisation is shown in Figure 2.6 [27, 37]. Briefly, the reactants form as *meta*-stable phases under hydrothermal conditions, leading to the formation of monomers, which undergo condensation and association to form large clusters, eventually leading to nucleation and crystallisation to form stable phases. Once the crystallisation process gets started, the conversion of the gel or solution is very fast. This is in agreement with studies reporting that the addition of seed crystals can short the induction time [46].
Figure 2.7  A schematic of TPA$^+$ directing to the formation of ZSM-5 framework, adopted from [38-40].
In the 1990s, Chang and Bell investigated the role of structure directing agent in zeolite formation using XRD, ²⁹Si MAS NMR and ion exchange [47]. In the presence of tetrapropylammonium cations (TPA⁺), they found channel intersections with clathrate–like units were first formed. These units which contained essentially one TPA⁺ cation were initially randomly connected but progressively became rearranged and ordered, eventually leading to the formation of the ZSM-5 framework. Later, Burkett and Davis built upon the work of Chang and Bell [38-40], and provided a better understanding of how TPA⁺ directed the zeolite structure (Figure 2.7). First, clathrate-like water structures form around the template. Isomorphous substitution of silicate for water then leads to the formation of inorganic–organic composites resembling ZSM-5 channel intersections. These composites progressively aggregate and become more ordered, resulting in the crystal growth that ultimately forms the ZSM-5 framework.

2.4.2.3 Properties of ZSM-5 zeolite

Ion–exchange property— acidity

The ZSM-5 zeolite framework is silicate based with some Si atoms substituted with Al atoms (Si⁴⁺ → Al³⁺). This imposes a negative charge on the framework and therefore cations are needed (usually Na⁺) to keep the framework neutrally charged. More importantly, the cations are ion–changeable, in principle by all other kind of cations. This enables ZSM-5 to be widely used as ion-exchange agents, such as water softening agents in the detergent industry. Once the Na⁺ is exchanged with NH₄⁺ and subsequently decomposed by calcination (usually at 500 °C), a pronated ZSM-5(H-ZSM-5) is produced. Figure 2.8 shows the ion-exchange process. The [H] in the framework of ZSM-5 is highly acidic, with the acidity of each [H] roughly equivalent to 70% sulphuric acid aqueous solution [48]. The [H] is thus known as the acid site, and its total density is proportional
to the Al content of the ZSM-5 zeolite as each Al substitution requires one cation to balance the framework charge.

There are two types of acid sites in the ZSM-5 zeolite, the Brønsted and Lewis acid sites. The Brønsted acid sites are believed to be ascribed to the bridging hydroxyl groups (Si–OH–Al) between the Si and Al tetrahedrals. The Lewis acid sites, however, are believed to be associated with the Al presented on the extra framework (EFAL) which is octahedrally coordinated. The generation of EFAL is believed to be attributed to the lattice instability caused by the introduction of Al to the silicate based framework, leading to a tendency of Al to migrate to outside of the lattice and thus form octahedrally coordinated Al species [49]. It has been reported that ZSM-5 zeolite with high Al content is more prone to develop EFAL as confirmed by $^{27}$Al NMR [49-51]. ZSM-5 zeolite with lower Si/Al ratio has higher peak intensity around ~0 ppm which is corresponding to Al at the octahedral coordination.

In general, the acidity of Brønsted acid sites is higher than that of the Lewis acid sites, which is usually determined by ammonium temperature programmed desorption (NH$_3$–TPD). Two distinct desorption peaks could be usually observed for the NH$_3$–TPD profiles of ZSM-5 zeolite. The one centred around 200 °C is categorised as low temperature peak (LT–peak) attributed to desorption of weakly bound NH$_3$, and the peak area is generally considered to correspond to the density of weak (Lewis) acid sites. Similarly, the one at
~400 °C is known as high temperature peak (HT-peak) resulted from desorption of strongly bound NH₃, with its area corresponding to the density of strong (Brønsted) acid sites [52-54].

The total acid strength of ZSM-5 zeolite composes of those contributed by Brønsted and Lewis acid sites, and is closely related to the Al content. It is believed the total acidity increases linearly with increasing Al content in the zeolite. On the other hand, zeolite with high Al content are more likely to generate EFAL, and this kind of sample is expected to have a high density of weak acid sites [49]. However, this is not indicative of high EFAL compromising the total acid strength of the zeolite sample. In fact, it has been observed there exists a synergy effect between EFAL and Bronsted acid sites, resulting in an increase in the acid strength. A similar phenomenon is also found in liquid acids, in which the combination of Brønsted and Lewis acid sites greatly enhance the acid strength [49].

Shape selectivity

Zeolite catalysed reactions predominantly take place in the channels and thus follow the process of: reactants enter into the channels → reactants reach the active sites to initiate the reactions → products exit the channels to appear as final products. Therefore, the mass transfer from the external surface to the interior of the catalyst particles is regulated by the overall pore size which is defined by the framework of the catalyst. In other words, the shape and diameter of the reactant and product molecules are not random but selected—shape selectivity.

Shape selectivity is a concept that when the diameter of the molecules reaches the structural dimensions of the intracrystalline pores during the mass diffusion process, the molecules may either be excluded to enter the pores or subject to configuration to fit the pore size. It was first proposed by Paul Weisz in 1960 [55-57], and the basis of the concept
has been widely utilised in many aspects of industry applications since then. A few theories of shape selectivity have been developed and three are commonly acknowledged and accepted: reactant shape selectivity (RSS), product shape selectivity (PSS) and transition–state shape selectivity (TSS) [58-61].

Figure 2.9 An example of reactant selectivity of ZSM-5 zeolite: selective cracking of n-octane but not 2,2,4-trimethylpentane, adopted from [62].

**RSS**: Whether the reactants can enter into the pores depends on the geometry of the pore opening and diameter of the reacting molecules. Only those reactants having diameter not larger than the size of pore mouth can access the channels. Accordingly, those exhibiting higher mass diffusion limitations would be inhibited and remained virtually intact. A typical example for RSS is the competitive cracking of n-octane and 2,2,4-trimethylpentane (Figure 2.9) [31, 62]. n-octane with linear chain is free to enter the channel and access the active sites. However, 2,2,4-trimethylpentane with branched chain has too big diameter and thus is deterred. It may only be converted at the active sites located at the external surface, or exit the reactor without any reaction.
Figure 2.10  An example of product shape selectivity of ZSM-5 zeolite: alkylation of toluene with ethylene to selectively form \textit{para}-ethyltoluene, adopted from [62].

\textit{PSS}: For heterogeneous catalysis, various products could be formed during the reaction but only those with shape and diameter fitting the pore size will be preferentially and selectively diffused out as final products. This is the reason why products are found to possess exclusive shapes and dimensions. An example of PSS is catalytic ethylation of toluene (Figure 2.10) [31, 62]. There is no restriction for the two reactants to enter the channels to react further. However, for the possible products, \textit{ortho}-, \textit{meta}- and \textit{para}-ethyltoluene, only the \textit{para}-isomer (\textit{para}-ethyltoluene) can traverse through the channels. The other two isomers might only be formed at the channel intersections (with size of \(~0.8\) nm) but are too big to diffuse out. They may only exist as a transition state during the reaction, and ultimately be transformed into smaller molecules.

\textit{TSS}: the reactions taking place in the channels are constrained by the geometry of the pores. Reactions which occurred in a homogeneous catalysis process may be restricted in zeolite catalysed process. A typical example of TSS is alkylation of benzene, as shown in Figure 2.11. Only the reaction to form ethylbenzene can occur, and the formation of \textit{1,3,5}-triethylbenzene is not allowed.
It is the combination of the two properties that enable ZSM-5 zeolite to be widely used as a heterogeneous catalyst in petroleum industries. The possession of high acid strength enables its catalytic activity and the framework structure together with the pore size inhibit the hydrocarbons to grow within a certain range, generally not larger than C\textsubscript{11} \cite{63}. ZSM-5 is used in a large number of applications, such as improving gasoline octane in fluid catalytic cracking (FCC), xylene isomerisation, toluene disproportionation, catalytic dewaxing, methanol conversion to hydrocarbons (gasoline, olefins and propene) \cite{64, 65}.

### 2.4.3 Mechanisms of MTG reactions

The conversion of methanol to gasoline is a reaction involving the formation of assorted hydrocarbons (with carbon number typically up to 10) from a single carbon compound (CH\textsubscript{3}OH). The overall stoichiometry could be represented as follows:

\[
\text{CH}_3\text{OH} \rightarrow [\text{CH}_2] + \text{H}_2\text{O}
\]  

(2–17)
where $[\text{CH}_2]$ is the average composition of the hydrocarbon product.

The main reaction steps of methanol conversion to gasoline could be summarised as:

methanol dehydration to DME $\rightarrow$ formation of primary products (olefin and propene) $\rightarrow$ formation of higher hydrocarbons (iso-paraffins and aromatics). The first step of methanol dehydration over solid acid catalysts is a well-known reaction, which is subject to nucleophilic attack by methanol. The conversion of light olefins to higher hydrocarbons is also well-known from the chemistry point of view. However, the second step which is the formation of primary products, and how the initial C–C bond is formed has been a rebated topic over the years.

Mechanistic studies of MTG have been a core research for several decades, and more than 20 possible mechanisms have been proposed. The first and also the easiest mechanistic proposal is the formation of the initial C–C bond via carbenium ion ($\text{CH}_3^+$) or carbene ($:\text{CH}_2$) [24, 66-68].

The first C–C bond formed via carbenium ion [67, 68]:

\[
\text{CH}_3\text{OH} \xrightarrow{H^+} \text{H}_2\text{O} + \text{CH}_3^+ \xrightarrow{\text{CH}_3\text{OCH}_3} \text{CH}_3\xrightarrow{\text{H}} + \text{OCH}_3 \xrightarrow{-H^+} \text{H}_3\text{C} \xrightarrow{\text{CH}_2} \text{CH}_2 \xrightarrow{\text{OCH}_3}
\]

(2–18)

The first C–C bond formed via carbene [24, 66]:

\[
\text{CH}_3\text{OH} \xrightarrow{} \text{H}_2\text{O} + \text{CH}_2 + \text{CH}_3\text{OH} \xrightarrow{\text{H}_3\text{C} \xrightarrow{\text{CH}_2} \text{CH}_2 \xrightarrow{\text{OH}}}
\]

(2–19)

However, later work has revealed direct coupling of methanol was impossible[69]. The activation energy barriers for direct methanol coupling to form C–C bond were
prohibitively high (200 kJ mol\(^{-1}\)), which ruled out the possibility of the carbenium and carbene pathways for the formation of initial C–C bond [70, 71]. In addition, the mechanisms of oxoniun ylides and free radicals were also proposed [70-73]. However, there was no experimental evidence supporting any of these proposals. Moreover, it was later found the formation of the initial C–C bond was practically not as important as expected for the overall reaction of methanol conversion [21, 74, 75].

Nowadays, a commonly accepted mechanism is an indirect route known as “hydrocarbon pool”, which was first proposed by Dahl and co-workers (Figure 2.12) [76-78]. The “hydrocarbon pool” mechanism describes that the methanol forms a hydrocarbon pool of \((\text{CH}_2)_n\), which serves as an adsorbate and subsequently produces paraffins, olefins and aromatics. Unfortunately, the chemical structure of the pool was not specified by Dahl.

![Figure 2.12](image)

Figure 2.12 The initial hydrocarbon pool mechanism proposed by Dahl and co-workers, adopted from [76-78].

The “hydrocarbons pool” mechanism has significantly contributed to the general understanding of methanol conversion to hydrocarbons on zeolite catalysts. Later work on the relevant topic has been largely based on this proposed mechanism, leading to the discovery that polymethyl benzenes are actually the active hydrocarbon pool species. Haw and co-workers found that methyl benzenes could act as organic centres for MTO
reaction using SAPO-34 catalyst (Silico-aluminophosphate material with chabasite CHA structure) [81-83]. Similarly, this has also been observed by other researchers [79, 80, 84]. Eventually, a dual cycle mechanism (aromatics carbon pool and olefin carbon pool) has been proposed, as shown in Figure 2.13. From which, it is suggested that methanol conversion to hydrocarbons on ZSM-5 catalyst involves two mechanistic cycles running simultaneously: one cycle for the formation of methyl benzenes and another is responsible for the formation of C3+ alkenes [79, 80]. The dual cycle mechanism has given a new insight into the understanding of hydrocarbon pool [85, 86].

![Dual cycle mechanism for methanol to hydrocarbon conversion](image)

Figure 2.13  Dual cycle mechanism for methanol to hydrocarbon conversion, adopted from [79, 80].
2.4.4 Coke formation and catalyst deactivation

During the MTG reaction, loss of catalyst activity is often found over the time. Eventually, the catalyst needs to be replenished by a new batch or deposited if the catalyst activity is completely lost. For a commercial MTG plant, a few reactors are typically needed to operate in parallel to ensure a continuous production [87]. The loss of activity is called deactivation, which has a great impact on the application of ZSM-5 zeolite. Therefore, considerable motivation has been devoted towards understanding catalyst deactivation.

Deactivation of ZSM-5 zeolite catalyst in MTG is of great technical and economic concerns in the practice of industrial processes. In general, there are two main deactivation mechanisms [20, 88]. One is the removal of Al (dealumination) during reaction and regeneration, leading to a decrease in the number of active sites thus the catalyst activity. Another major reason for catalyst deactivation is coverage of active sites and blockage of pores by coke that is gradually formed during the reaction. The activity loss by dealumination is permanent, however, deactivation by coke is reversible, as coke can be removed by combustion heated to 500–600 °C in air [88-90], and hence, efforts have been devoted to understanding coking mechanism in order to develop catalysts less prone to deactivation.

Coking is a complex mechanism and in-depth understanding of this requires an investigation of coke characteristics and factors affecting coke formation, which is believed to be intrinsically due to the microporous framework structure of ZSM-5 zeolite [65, 91, 92]. This pore system renders the passage of gasoline components. However, it causes mass diffusion problems to large aromatics formed in the pores as a side product and subsequently trapped in the channels as coke [93, 94]. Generally, coke is categorised as soluble and insoluble based on its solubility in dichloromethane (DCM) [95-98].
Soluble coke is comprised of carbonaceous residues with molecular weight in the range of 200 to 300. Insoluble coke is comprised of more carbonaceous polyaromatics.

On the other hand, coke characteristics can also vary with factors such as the nature of catalyst and reaction conditions, particularly reaction temperature and SiO$_2$/Al$_2$O$_3$ ratio of the catalyst [99-105]. The reaction temperature can greatly impact on coke formation and thus catalyst deactivation. Previous studies have revealed that coke formed at low temperatures was soluble in DCM but not polyaromatics, and as the temperature increases to above 350 °C, the reactive coke precursors tend to form more carbonaceous coke molecules [99, 100]. In addition, it is peculiar to find that ZSM-5 zeolite tested at low temperatures (< 300 °C) deactivated much more rapidly than that performed at high temperatures. For example, a ZSM-5 catalyst tested at 290 °C had a catalytic lifetime of 0.5 h and 10% coke deposition. While, when tested at 380 °C, the same catalyst had a catalytic lifetime up to 400 h and only 0.3% coke deposition [106]. Furthermore, temperature programmed desorption (TPD) of the spent catalyst (tested at 290 °C) showed desorption of alkenes and lighter polymethyl benzenes at temperatures above 350 °C, indicating dealkylation involving hydrogen transfer begins to take place at this temperature, which means the retained compounds become more carbonaceous, in agreement with the statement above.

The SiO$_2$/Al$_2$O$_3$ ratio (also can be referred to Al content or density of acid sites) of the catalyst is also found to have a great effect on coke formation and catalyst deactivation [103-105]. A statement given by Guisnet and co-workers well explains the relation between acidity and coking phenomena in a general term: “(i) the stronger the acidic sites, the faster the chemical steps and the more pronounced the retention of coke precursors and coke molecules, hence the faster the coking rate; (ii) the higher the density of the acid sites, thus the closer these sites are to each other, the larger the number of
successive chemical steps undergone by reactant molecules along the diffusion path within the zeolite crystallites and the more favourable the condensation reactions, hence the faster the coking rate.” [101]. With increasing the density of acid sites, coke compounds are rapidly formed and the growth of these compounds tends to be extended. This is more pronounced when the reaction is performed at high temperatures [105]. There is a common consensus that a low SiO$_2$/Al$_2$O$_3$ ratio (high Al content) promotes aromatisation, and in turn, the overall rate of coke formation and catalyst deactivation.

Coke can be formed in the microporous channels and on the external surface, deactivating the catalyst by covering active sites and blocking pores [20, 105]. In general, coverage of active sites occurs when molecule species have strong chemisorption capability with the active sites, and therefore, the active sites are occupied and no longer active. Pore blockage occurs at the point when pore access is blocked by the accumulated coke or even a single coke molecule. Once the pore is blocked, the reactant had no longer accesses to the active sites even though there are still active sites remaining uncovered in the pores. In principle, pore blockage is more detrimental to the catalyst activity [107].

Whether it is the internal coke or external coke predominantly causing catalyst deactivation, however, is still a disputed subject. Studies have reported that coke predominantly formed in the internal channels of ZSM-5 catalyst and at the intersections between the straight and sinusoidal channels, eventually leading to catalyst deactivation [20, 89, 95, 102]. Benito and co-workers [95] suggested this was due to the high branching micropore structure of the zeolite. Active sites partially remained accessible from lateral channels in spite of some were progressively covered, and deactivation by pore blockage did not occur. This is in agreement with a study conducted by Müller and co-workers very recently [102], from which the authors reported the catalyst was deactivated by coke covering individual active sites in the catalyst but not pore blockage by external coke, as
the overall methanol conversion decreased linearly with time on stream and the Brønsted acid sites were also found to decrease with time on stream. Those uncovered still remained accessible for pyridine adsorption after testing.

5 to 22 h:

![Chemical structures](image)

47 to 92 h:

![Chemical structures](image)

Figure 2.14 Possible routes for the coke formation on the external surface of ZSM-5 zeolite with time on stream from 5-22 h and 47-92 h, respectively, adopted from [102].
In contrast, Bjørgen and co-workers [80] concluded that the catalyst deactivation was caused by external coke only. In line with this, Mores and co-workers [105] reported that the formation of coke progressed from the external surface towards the inside of the bulky crystals, particularly formed rapidly on the triangular edges of the crystals. A further study from this group has also revealed the straight channels were responsible for the formation of polyaromatic coke molecules and eventually built up on the external surface of ZSM-5 zeolite, while those retained in the sinusoidal channels were relatively smaller. A possible route for the formation of external coke was proposed by Müller and co-workers [102], as shown in Figure 2.14. In addition, Shulz correlated coke deposition to reaction temperature, suggesting the catalyst deactivation could be attributed to internal coke below 350 °C and external coke above this temperature.

2.5 Catalyst Development

As catalyst deactivation is inevitable for most industrial processes, finding ways to mitigate deactivation by coking is economically important. The ever-increasing attention towards the cost and efficiency of the industrial processes is thus directing the scientific community towards developing zeolite catalysts that are less prone to deactivation.

The unique pore structure, shape and size of ZSM-5 zeolite give it shape selectivity but also create diffusion limitations. The overall MTG reaction is restricted by these diffusion limitations. Reactant(s) needs to enter and diffuse in the zeolites channels to reach active sites, and intermediates also need to traverse through the pores before the final products are formed. Some intermediates may undergo further reactions and thus further increases in diameters that are larger than the pore size, constraining their diffusion in the channels. Ultimately, these large intermediates become trapped in the channels resulting in coke.
A potentially simple way to overcome diffusion limitations within ZSM-5 zeolites is to reduce their crystal size to the nanoscale, namely, via synthesis of nanocrystal ZSM-5 zeolite. In this study, the term of nanocrystal zeolites is used to refer to those zeolites with single crystals. A reduction in the crystal size provides these ZSM-5 zeolites with an increased external surface area and more micropore entrances per weight, providing more active sites accessible to reactants. More importantly, it greatly shortens the diffusion paths in these nanocrystals, leading to significantly enhanced mass transfer for both reactant and product species. This allows these species to enter and exit the micropores and reduces the possibility of second reactions such as coke formation and dealkylation.

Nanocrystal ZSM-5 zeolites have been reported to outperform their microcrystal counterparts in various catalytic reactions [108-110]. For example, Rownaghi and co-workers [109] developed a nanocrystal ZSM-5 sample with long-term catalytic stability and sustained complete methanol conversion within 10 h on stream. However, the methanol conversion of the microcrystal catalyst was only ~65% to start with and dropped to 50% over the same reaction time.

Another promising strategy to improve the catalytic performance of ZSM-5 zeolite is to synthesise ZSM-5 zeolites with a hierarchical pore structure. Here, ‘hierarchical’ refers to the presence of at least two levels of porosities in the ZSM-5 zeolite; the primary intrinsic micropores and the secondary pores that are usually in the mesopore size range (2 to 50 nm). These secondary mesopores provide not only more accessible active sites for the reactants, but also more adequate spaces for diffusion of the reaction products, and mesopores have diffusion rates several orders of magnitude faster than micropores [57, 111-113]. Consequently, hierarchical ZSM-5 zeolites often have higher catalytic activity and longer lifespan. For example, Bjørgen and co-workers [114] described using a hierarchical ZSM-5 catalyst for the MTG reaction which increased the gasoline fraction.
by a factor of 1.7, and increased the catalytic lifetime by a factor of 3.3 compared with a conventional counterpart.

Figure 2.15  A typical profile of a hierarchical zeolite particle comprised of nanosized crystals, reproduced from [126].

Tremendous efforts have thus been dedicated to the synthesis of nanocrystal and in particular hierarchical ZSM-5 zeolites. However, while several reviews focusing on the synthesis strategies of hierarchical ZSM-5 can be found in the literature [115-124], this is not the case for nanocrystal ZSM-5 zeolites. One possible reason for the lack of research in this area is ZSM-5 zeolites with nanosized crystals are difficult to be collected by conventional filtration methods, so high-speed centrifugation is often required. Another possible reason is this type of ZSM-5 sample is often found to have mesoporous
properties. Once the sizes of the ZSM-5 crystals come down to the nanoscale, particularly those below 100 nm, such crystals are easily aggregated to form bulky particles having intercrystalline mesopores according to sorption technique. Therefore these materials are often categorised as hierarchical zeolites [125-128]. A typical profile of hierarchical zeolite particle consisting of nanosized crystals is illustrated in Figure 2.15 [126].

However, to our best knowledge, the size and shape of the mesopores in hierarchical zeolites are not related to the framework structure of the zeolite crystals. Their existence does not contribute to the X-ray diffraction (XRD) patterns of the hierarchical zeolites. Therefore, the mesopores cannot be considered to be part of an intrinsic pore system. In fact, almost all the hierarchical zeolites reported in the literature still reserve intact microporosity identical to their main porous structure, same as their corresponding microcrystal counterparts. In principal, a genuine hierarchical material could have crystallographic mesopore structure and distinctive XRD patterns. Good examples of this are the silica-based mesoporous materials SBA-15 and MCM-41 which have intrinsic mesopores and their own characteristic XRD patterns that are not related to any known zeolite framework structure. These two materials are not collected by IZA (http://www.iza-structure.org/).

Nevertheless, hierarchical zeolites indeed show improved catalytic performance compared to their corresponding conventional counterparts, even nanocrystal ones. This is particularly true for organic synthesis involving bulky molecules [120, 129], but not always for the case of methanol conversion [109]. Rownaghi and co-workers [109] compared the catalytic performances of nanocrystal (single crystals with an average size of ~ 120 nm), hierarchical (~ 300 nm hierarchical particles consisting of 5–10 nm crystals) and conventional (varied sizes) ZSM-5 zeolites in the MTG reaction. Both nanocrystal and hierarchical samples showed higher overall methanol conversion than that of the
conventional sample (50%) under the same reaction conditions, but the nanocrystal
catalyst had 100% methanol conversion over the 10 h reaction time, whereas the
hierarchical catalyst had only 70% conversion over the same period. Rownaghi suggested
this was due to differences in the density of strong active sites in the two samples, as
confirmed by NH3–TPD. The nanocrystal catalyst had a higher density of strong active
sites (0.27 mmol g⁻¹) than that of the hierarchical one (0.12 mmol g⁻¹). The observation
that a reduction in crystal size to the nanoscale often compromises crystallinity supports
this finding.

2.5.1 Synthesis of nanocrystal ZSM-5 zeolite

Currently, methods for the synthesis of nanocrystal ZSM-5 zeolites are not as well
developed as those for hierarchical ZSM-5 zeolites. A review of nanocrystal ZSM-5
zeolite shows there are three main methods of synthesis: (i) conventional hydrothermal
synthesis where all the crystallisation processes are carried out in an autoclave under
autogenous pressures; (ii) confined space synthesis where crystallisation is conducted by
hydrothermal treatment but crystal growth is confined by a porous hard template which
directs crystal size [130, 131]; (iii) static atmospheric pressure synthesis where
crystallisation is performed in open vessels at low temperature and ambient pressure [46].
Of these three methods, conventional hydrothermal synthesis is the preferred method in
terms of cost and efficiency.

The crystal size of ZSM-5 zeolites are extremely sensitive to changes in synthesis
parameters, including silica and alumina sources, SiO₂/Al₂O₃ ratio and other composition
ratios, aging duration and temperature, alkalinity and hydrothermal treatment conditions
[132, 133]. Subtle changes in these parameters often lead to zeolite samples with
dramatically different crystal sizes, in particular changing the SiO₂/Al₂O₃ ratio (Al
content). Generally, an increase in the SiO$_2$/Al$_2$O$_3$ ratio leads to a decrease in the crystal size under otherwise identical conditions [35, 36, 134]. Wang and co-workers [135] synthesised a series of ZSM-5 zeolites with the SiO$_2$/Al$_2$O$_3$ ratio in the range of 26–110 and the resulting crystal sizes of these samples ranged from 1000 to 200 nm. The only difference in the preparation of these samples was the amount of Al added, which was aimed at varying SiO$_2$/Al$_2$O$_3$ ratio of these samples. In addition, this method used sodium aluminate and tetraethylorthosilicate (TEOS) as alumina and silica sources, respectively, and tetra propylammonium hydroxide (TPAOH) was used as structure directing agent. The crystal size increased with increasing Al content probably because more addition of Al consumed more alkali, reducing the alkalinity of the solution.

Alkalinity, also referred to as the OH/SiO$_2$ ratio, is one of the most important parameters in zeolite synthesis and an increase in alkalinity leads to an increase in crystal size [134, 136, 137]. Grieken and co-workers found that increasing alkalinity of the solution from 12.5 to 14 resulted in an increase in crystal size from 60 to 170 nm. The incorporation of Al was thought to decrease with increasing alkalinity, affecting the Al species in the nucleation process.

Water content is also found to significantly impact crystal size by promoting crystal growth [134, 137]. Grieken and co-workers found an increase in the H$_2$O/SiO$_2$ ratio from 11 to 50 correspondingly increased the crystal size from 70 to 1000 nm and decreased crystallinity from 97% to 72.7%. Clearly, an increase in water content will dilute the concentration of the solution system, including concentration and alkalinity of the structure directing agent. A decrease in the structure directing agent concentration will reduce the solubility of the silica and alumina sources, and thus form a supersaturated solution, which leads to an increase in crystal size [35, 138].
Fouad and co-workers [139] also investigated the effect of structure directing agent (SDA) on the crystal sizes of ZSM-5 zeolite. Four samples were prepared with a molar composition of: 40 SiO₂/Al₂O₃, 0.215 SDA/ SiO₂, 9.5 H₂O/ SiO₂, 0.133 Na₂O/ SiO₂ and 22 CH₃OH/ SiO₂. Four difference structure directing agents were used, including tetramethylammonium hydroxide (TMAOH), tetraethylammonium hydroxide (TEAOH), TPAOH and tetrabutylammonium hydroxides (TBAOH). The crystal sizes of the samples synthesised from these four SDA varied from 56 to 160 nm.

Changes in reaction time and temperature also dramatically influence the crystal growth. For example, Firoozi and co-workers [140] prepared two ZSM-5 samples using the same reactants and sources, hydrothermal conditions, and composition molar ratio—5 TPAOH:0.03 Al₂O₃:25 SiO₂:480 H₂O:100 EtOH:0.1 Na₂O and following almost identical procedures. The final solution mixtures were then either statically heated in an oil bath at 100 °C under reflux condition for 60 h before hydrothermal treatment or directly hydrothermally treated. The sample synthesised with static heating produced crystal of 150–200 nm whereas the one synthesised form direct hydrothermal treatment resulted in crystal of 1000–2000 nm.

2.5.2 Synthesis of hierarchical ZSM-5 zeolite

Over the past few decades, significant efforts have been directed towards developing synthesis methods to hierarchical ZSM-5 zeolite materials. These synthesis methods can be classified into three broad categories; (i) post-treatment methods (removal of framework atoms) such as dealumination and desilication [93, 141-145], (ii) soft-template synthesis methods such as dual templating and amphiphilic organosilanes [108, 146-149], and (iii) hard-template synthesis methods [150, 151].
2.5.2.1 Post-treatment method

Post-treatment methods are the most common method used for synthesising hierarchical zeolites because they are low cost and simple. These methods involve dealumination by acid treatment or desilication by alkaline treatment. Some of the Si or Al atoms are leached from the framework structures, leading to the formation of vacancies and partial collapse of the zeolite structure. The vacancies create porosity in the mesopore range.

Of the post-treatment method, desilication is more efficient at creating mesopores than delumination [93, 114, 141-145, 152-155]. The first reported generation of mesopores in ZSM-5 zeolite by NaOH treatment was by Ogura and co-workers [152, 153], from which 4 nm mesopores were created using 0.2 M NaOH aqueous solution. More importantly, the crystallinity of the resulting sample was preserved, and mesopore volume was greatly increased and micropore volume was slightly decreased.

As mesopores are thought to form when framework atoms are removed by alkaline treatment (commonly NaOH), it is not surprising that the concentration of the alkaline medium, the treating temperature and time play a pivotal role in determining zeolite properties. One of the remarkable observation is an alteration of the crystal morphologies. Figure 2.16 shows changes in morphologies of ZSM-5 zeolites by increasing NaOH concentration and treating conditions [153]. Clearly, high NaOH concentrations, high temperatures and long treatment times are detrimental to the ZSM-5 crystals, with more crack and faults forming on the external surface of the zeolite grains. It was suggested the optimum treating conditions for obtaining relatively uniform mesopores without altering the original crystallinity and acidity are: NaOH concentration of 0.2 M, treating time of 30–120 min at 65 °C [120].
Figure 2.16 Changes in ZSM-5 zeolite morphology with changing treatment conditions: (a) pristine ZSM-5 sample; (b) 0.1 M NaOH at 65 °C for 120 min; (c) 0.1 M NaOH at 65 °C for 300 min; (d) 0.2 M NaOH at 80 °C for 300 min, adopted from [153].

While NaOH (or alkaline) treatment predominantly extract Si from the framework, a small portion of Al can also be leached. Therefore, the concentration of Al also plays an important role in the creation of mesopores [154]. As shown in Figure 2.17, high Al content (Si/Al $\leq 15$) prevents the extraction of Si and thereby limits the formation of mesopores. When the Al content is very low (Si/Al $\geq 200$), there is more damage to the crystals and relatively large pores are observed. The optimal Si/Al ratio is thought to be 25–50.
Despite post-treatment methods being simple and inexpensive, the chemical treatment often results in significant zeolite loss due to chemical dissolution and undesired changes to the SiO$_2$/Al$_2$O$_3$ ratio.

![Simplified schematic representation of the influence of the Al content on the desilication treatment of MFI zeolites in NaOH solution and the associated mechanism of pore formation, adopted from [154].](image)

Figure 2.17  Simplified schematic representation of the influence of the Al content on the desilication treatment of MFI zeolites in NaOH solution and the associated mechanism of pore formation, adopted from [154].

### 2.5.2.2 Soft-template method

In general, soft-template methods use a conventional structure directing agent for the formation of micropores and a second template to generate mesopores [146]. The underlying idea is the structure directing agent directs the formation of the zeolite framework structure while the second template generates the micelles which serve as the template for the formation mesostructure. The second template generally has a
characteristic diameter in the mesopore range, and forms mesopores with essentially the same size and shape as the template after its removal. This makes it possible to tailor the mesopore size by varying the size of the template.

The first attempt of using a second template for the synthesis of hierarchical ZSM-5 zeolite was conducted by Karlsson and co-workers [156]. However, phase segregation occurred during the synthesis. As a result, physically mixed products were obtained, that is, the structure directing agent led to the formation of a zeolite structure separated from a mesoporous silica material formed from the second template.

Xiao and co-workers [147] overcame this segregation problem by designing a hydrophilic cationic template prepared from the treatment of polystyrene-co-polyvinyl pyridine using methyl iodide. Using this meso–scale soft template, a hierarchical ZSM-5 sample having mesopores of two sizes (about 13 and 55nm) was synthesised. More importantly, the orientation of the mesopores in the sample was found to be in the [010] direction. The [010] face is known to be the most energetically favourable face according to the \textit{ab initio} DFT calculation. Accordingly, the sample had high hydrothermal stability and high catalytic activity in the processing of large molecules.

Ryoo and co-workers [149] later synthesised hierarchical ZSM-5 zeolites using a poly quaternary ammonium surfactant serving as both structure directing agent and meso–scale template. This surfactant has a \([\text{C}_{22}\text{H}_{45}\text{N}^+(\text{CH}_3)_2\text{C}_6\text{H}_{12}\text{N}^+(\text{CH}_3)_2\text{C}_6\text{H}_{13}\text{C}_{22-6-6}]\) molecule structure with three ammonium moieties, which are believed to be essential for crystallisation of zeolite structure inside the mesopore walls. These hydrophobic moieties can undergo aggregation with other template molecules to form the micelles necessary for the generation of the meso–structure. By also changing the length of the hydrophobic alkyl chain of the template and adding swelling agents such as 1,3,5-trimethylbenzene, a
wide range of mesopores of controlled sizes ranging from ~ 3.8 nm to 21 nm were synthesised. The zeolites had extremely high BET surface areas (up to 1190 m$^2$/g), high total pore volumes (up to 1.58 cm$^3$/g), and enhanced catalytic activity. However, this method of creating mesopores requires specially designed templates, which often incur high costs.

Synthesis of hierarchical ZSM-5 zeolites using conventional surfactants, such as the commonly available and low cost surfactants cetyltrimethylammonium bromide (CTAB) and Pluronic F127 have also been reported [157-159]. Zhou and co-workers [157] used a direct strategy for the synthesis of hierarchical ZSM-5 zeolite (with the assistance of post-steaming). Mesopores of 9.8 nm in size could be generated. In addition, the mesopore size and volume could be tuned by changing the amount of meso-template. This study illustrated how a conventional surfactant could be used to lower the cost of hierarchical ZSM-5 zeolite synthesis.

Compared to the post-treatment method for the synthesis of hierarchical ZSM-5, the soft-template method has better control over mesopore size and SiO$_2$/Al$_2$O$_3$ ratio. However, the soft-template method often requires mesopore directing agents that are expensive or commercially unavailable. Furthermore, the synthesis procedure often involves multiple steps, where zeolite crystal seedlings have to be produced first and then assembled using additional templating agents.

### 2.5.2.3 Hard-template method

The hard-template methods involve the use of porous or hollow solid particles as matrices into which ZSM-5 zeolite crystals grow and confined within the confines of the templates cavities [150, 151]. The first synthesis of hierarchical ZSM-5 zeolite using hard-template method was given by Jacobsen and co-workers [150]. As shown in Figure 2.18, pre-
treated carbon nanoparticles by acidic or alkaline solution were used as the mesoporous template. The carbon nanoparticles were embedded in the crystals during crystal growth. After removing the nanoparticles by calcination, mesopores with the size and shape of the nanoparticles were generated. More recently, the use of carbon nanotubes, ordered mesoporous carbon and carbon aerogels have also been used as hard templates.

As an alternative to carbon materials, polymers can also be used as hard templates for hierarchical ZSM-5 zeolite production. Compare to carbon materials, removal of polymers by calcination is relatively easy. Xu and co-workers [160] synthesised hierarchical ZSM-5 zeolites with a macroporous wall mainly formed by nanosized ZSM-5 crystals. The sample was obtained by hydrothermal treatment (100°C for 16 h) of a highly packed composite formed by a ZSM-5 gel precursor and the polystyrene spheres. Unfortunately, amorphous aluminosilicate was observed, possibly due to the low hydrothermal crystallisation temperature. This is a major drawback of this method as it requires the polymer to be thermally stable.

![Figure 2.18 Hierarchical ZSM-5 zeolite prepared using carbon nanoparticles as a mesoscale template, adopted from [150].](image)

\[ \text{Carbon particles ca. 12 nm} \quad \overset{\text{O}_2}{\rightarrow} \quad 550 \, ^\circ \text{C} \quad \overset{+ \text{CO}_2}{\rightarrow} \quad \text{Mesoporous zeolite single crystal} \]

\[ \text{Ca. 1 \, \mu m zeolite crystal grown in pores system of carbon} \]

\[ \text{Pores created by combustion of carbon particles} \]
Starch has also been used as a hard template for the synthesis of hierarchical ZSM-5 zeolites. Wang and co-workers [161] prepared these zeolites using a starch–derived white bread as the meso–scale template. The hydrothermal treatment was carried out at 180 °C for 48–168 h, producing 5–40 nm mesopores and a total pore volume of 0.68 cm³ g⁻¹, which was four times higher than the conventional counterpart (had a total pore volume of 0.17 cm³ g⁻¹). Furthermore, the hierarchical sample has similar BET surface area as the conventional one, indicating a high crystallinity.

The main drawback of using a hard template as a meso–scale template to obtain hierarchical ZSM-5 zeolite is the removal of carbon materials by combustion at high temperatures. This removal of carbon induces damage to the microporous properties of the sample. Svelle and co-workers [162] found a high amount of defects and internal silanol groups were generated due to the locally high temperature attributed to the template combustion. This will have a detrimental effect on the properties and catalytic performance of the ZSM-5 zeolite.

Although hierarchical ZMS-5 zeolites have shown superior catalytic performance than their conventional counterparts, the templating synthesis routes are largely inadequate to support the production for industrial applications, mainly due to the increased cost involved in the use of a second template. Post-treatment method is often more efficient in cost saving, but this method also causes mass loss of the zeolite product, making it hard to control the SiO₂/Al₂O₃ of the resulting sample. Therefore, more research needs to be directed towards the development of a more economical, efficient and environmentally friendly method for the synthesis of hierarchical ZSM-5 zeolites.
2.6 Conclusions from Literature Review and Specific Objectives of This Thesis

A methanol based route for transportation fuel production is promising because (i) methanol is easy for transportation and storage; (ii) methanol is easily obtained from natural gas, biomass and CO₂ recycling, and (iii) MTG has the potential to make use of stranded gas reserves.

MTG is a promising technology for the production of transportation fuel. The gasoline from MTG attains the properties of the conventional gasoline fuel, but is more environmentally friendly as it is sulphur and nitrogen free. The major challenge for MTG is catalyst deactivation during the reaction which requires frequent regeneration that increases operation costs. Reduction of crystal size of the catalyst to the nanoscale and creation of mesopores in the catalyst are two effective ways to suppress the deactivation issues to a large extent. While many methods for the synthesis of nanocrystal and hierarchical ZSM-5 zeolite have been reported extensively, there seems to be a lack of information about MTG with respect to the development of nanocrystal ZSM-5 zeolite, such as the intrinsic effect of SiO₂/Al₂O₃ ratio and reaction conditions on catalytic performance, coke formation and deactivation in relation to catalyst deactivation, particularly the effect of coke location on catalyst deactivation is still a disputed topic. In addition, methods for the synthesis of hierarchical ZSM-5 zeolite are not yet suitable for commercial production, and the costs need to be reduced.

Specific objectives of the thesis research:

- To synthesise ZSM-5 zeolites with similar SiO₂/Al₂O₃ ratios but various crystal sizes and nanocrystal ZSM-5 zeolites with various SiO₂/Al₂O₃ ratios but almost identical
crystal sizes and structural properties. This would lead to a successful control of the crystal size and SiO₂/Al₂O₃ ratio for the synthesis of ZSM-5 zeolite.

- To investigate the effect of SiO₂/Al₂O₃ ratio on the performance of nanocrystal ZSM-5 zeolite in MTG. This method will contribute to a better understanding of the sole effect of acidity on activity and deactivation of ZSM-5 catalyst.

- To study the effect of reaction conditions (temperature, pressure and WHSV) on the performance of nanocrystal ZSM-5 zeolite in MTG. The performance of nanocrystal ZSM-5 catalysts at different temperatures, pressures, and WHSV will be assessed. This will allow a better understanding of the effect of reaction conditions on catalytic performance when nanocrystal ZSM-5 zeolite was used in MTG.

- To provide an insight into coke formation and characteristics in relation to catalyst deactivation when using nanocrystal ZSM-5 catalyst in MTG. This work will give an in-depth understanding about how nanocrystal ZSM-5 zeolite has superior catalytic performance compared to the microcrystal counterpart.

- To develop a method to directly synthesise hierarchical ZSM-5 catalyst. This work will demonstrate a simple method for the synthesis of hierarchical ZSM-5 zeolite and its superior performance in MTG in comparison with a conventional ZSM-5 catalyst.
Chapter 3 Methodology, Approach and Techniques

3.1 Introduction

This chapter covers methodology, approach and techniques employed in this thesis work to fulfill the research gaps identified from Chapter 2. Detailed methods for the synthesis of nanocrystal, hierarchical and microcrystal (conventional) ZSM-5 catalysts, and their associated characterisation approaches and techniques are summarised. In addition, methodology and approaches for evaluating catalytic performance of ZSM-5 zeolite in MTG, analysis of coke formation and characteristics are also included.

3.2 Synthesis of ZSM-5 zeolites

- Materials

All reagents were acquired from Sigma-Aldrich and used as supplied. These include NaAlO$_2$ (sodium aluminate anhydrous, AR) as the Al source, TEOS (tetraethyl orthosilicate, $\geq$99.0%) as the Si source, TPABr (tetrapropylammonium bromide, 98%) as the structure directing agent for the synthesis of conventional ZSM-5 zeolites, and TPAOH (1.0 M in water) as the structure directing agent for the synthesis of hierarchical ZSM-5 zeolites. In addition, pellets of NaOH (sodium hydroxide, AR) for creating the alkaline environment required for the zeolite synthesis were obtained from Chem Supply.

- Synthesis of ZSM-5 zeolites with various crystal sizes

Four ZSM-5 samples with different crystal sizes and a nominal SiO$_2$/Al$_2$O$_3$ ratio of 50 were synthesised using different procedures.
(1) Synthesis of ZSM-5_0.1µm

0.1 g of NaAlO₂ and 12 g of TPAOH in a 100 mL Schott–Duran bottle were stirred at room temperature for 0.5 h before 6.4 g of TEOS was added drop-wise. The resulting gel was stirred at room temperature for 1 h, and then transferred to an oil bath and heated up to 100 °C under stirring for 3 h. The mixture was then continuously stirred at room temperature for a further 20 h before being transferred to a Teflon-lined autoclave and hydrothermally treated at 180 °C for 48 h. After cooling, the product was collected by centrifugation and washed thoroughly with deionised water.

(2) Synthesis of ZSM-5_0.65µm

ZSM-5_0.65µm was prepared by modifying the procedure reported by Zhu and co-workers [163]. 0.3 g of NaAlO₂, 19.2 g of TEOS and 20 g of TPAOH were mixed and stirred at 60 °C for 24 h. The mixture was then hydrothermally treated at 180 °C for 48 h. The resulted white powder was collected by filtration and washed thoroughly with deionised water.

(3) Synthesis of ZSM-5_1.5µm

6.4 g of TEOS was added to a solution of 0.1 g of NaAlO₂ and 4 g of TPAOH to form a mixture. After becoming a dense gel, the mixture was added to a solution containing 1.0 g of TPABr, 4.9 mL of 2.0 M NaOH and 50 mL of deionised water. The resulting mixture was stirred at room temperature for 20 h, and finally hydrothermally treated at 180 °C for 48 h. The white powder product was collected by filtration and washed thoroughly with deionised water.

(4) Synthesis of ZSM-5_30µm

ZSM-5_30µm was prepared following a similar procedure as of ZSM-5_0.1µm, with the addition of 0.6 g of NH₄F before adding TEOS [146].
• **Synthesis of nanocrystal ZSM-5 zeolites with various SiO$_2$/Al$_2$O$_3$ ratios**

A series of nanocrystal ZSM-5 zeolites with SiO$_2$/Al$_2$O$_3$ ratios of 23, 47, 107, 217 and 411 were prepared using a hydrothermal synthesis method, and denoted as NZ$_{23}$, NZ$_{47}$, NZ$_{107}$, NZ$_{217}$ and NZ$_{411}$, respectively. The samples were synthesised from a sol–gel solution with a molar composition of \( x \) Na$_2$O: \( x \) Al$_2$O$_3$: 100 SiO$_2$: 25 TPAOH: 1157 H$_2$O, where \( x \) is 4, 2, 1, 0.5 or 0.25, as calculated from a predetermined amount of NaAlO$_2$ used in the synthesis. The amount of NaAlO$_2$ used was 0.2 g, 0.1 g, 0.05 g, 0.025 g and 0.0125 g, respectively. For each sample, the predetermined amount of NaAlO$_2$ and 8 g of 1.0 M aqueous TPAOH solution were added to a 100 mL Schott-Duran bottle and stirred at room temperature for 0.5 h before 6.4 g of TEOS was added drop-wise. The resulting gel was continuously stirred at ambient temperature for 0.5 h, then in an oil bath at 80 °C for 1 h, and finally back to ambient temperature for another 20 h. The prepared gel was transferred to a Teflon-lined autoclave to allow for the hydrothermal reaction at 180 °C for 48 h. After cooling, the sample was collected by centrifugation and washed thoroughly using deionised water three times.

• **Synthesis of a microcrystal ZSM-5 catalyst as a comparison with nanocrystal ZSM-5 zeolite for the investigation of coke formation and characteristics in relation to catalyst deactivation**

The microcrystal ZSM-5 sample was synthesised by modifying the synthesis method for nanocrystal ZSM-5 zeolite with SiO$_2$/Al$_2$O$_3$ ratios of 47. Briefly, 20 g (instead of 8 g) of 1.0 M TPAOH aqueous solution was used and the hydrothermal synthesis was carried out for 72 h (instead of 48 h).
• **Synthesis of hierarchical ZSM-5 zeolite**

The synthesis of hierarchical ZSM-5 zeolites, thereafter denoted as Hi-ZSM-5, consisted of five simple steps including the preparation of the clear solution of NaAlO$_2$, TEOS, TPAOH and H$_2$O, aging, hydrothermal processing, filtration and calcination. Specifically, 0.05 g of NaAlO$_2$, 12.0 g of 1.0 M aqueous TPAOH solution and 30.0 mL of deionised water were mixed and stirred at room temperature for 0.5 h before 6.4 g of TEOS was added drop-wise. The resulting mixture had a molar composition of 1 Na$_2$O: 1 Al$_2$O$_3$: 101 SiO$_2$: 39 TPAOH: 7215 H$_2$O, and a pH of 13.1. The clear solution was stirred at room temperature for a further 20 h before being transferred to a Teflon-lined autoclave, sealed and hydrothermally treated at 180 °C for 48 h. After cooling, the product was recovered by filtration and washed thoroughly with deionised water.

• **Calcination and ion–exchange**

All samples synthesised were dried at 100 °C for 20 h before calcination at 550 °C in air for 5 h to remove the structure directing agent. Ion–exchange was then performed to replace Na$^+$ with NH$_4^+$ by mixing 1.0 g of sample in 10 mL of 1.0 M NH$_4$NO$_3$ solution at 50 °C for 24 h. The procedure was repeated twice to ensure complete ion exchange. The ion-exchanged samples were again collected by centrifugation and washed in deionised water three times, dried at 100 °C for 20 h and calcined at 500 °C for 5 h to obtain the final H$^+$ type ZSM-5 samples.

### 3.3 Catalyst Characterisation

• **XRD**

Powder X-ray diffraction (XRD) is used to confirm the formation of the zeolites as compared to the typical XRD patterns (Figure 3.1) [164, 165]. The XRD patterns were
obtained using a PANalytical Empyrean X-ray Diffractometer employing Cu Kα 
(λ=1.54439 Å) radiation. The patterns were collected at a scan rate of 2.2° min⁻¹ over a 
2θ range of 5–50 °.

Figure 3.1 Standard powder XRD patterns of calcined ZSM-5 zeolite, reproduced 
from [164, 165].

- **SEM and TEM/STEM–EDS**
Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) 
were used to determine the size of the crystals and particles and morphology of the ZSM- 
5 samples. SEM images were obtained using a Zeiss 1555 VP-FESEM instrument 
operating at 15 kV and FEI Verios XHR operating at 10 kV. The SEM samples were 
prepared by loading a small quantity of a ZSM-5 powder onto a conducting carbon tape 
adhered to a standard Al stud. The sample was coated with 3 nm of platinum to ensure 
surface conductivity. TEM images were obtained using a JEOL 2100 TEM operating at 
120 kV. The TEM sample was prepared by dispersing a small amount of the ZSM-5
samples in ethanol and placing one droplet onto a carbon-coated copper grid. The samples were then allowed to dry in air prior to imaging.

In addition, the high angle annular dark field scanning transmission electron microscopy image and energy dispersive X-ray spectroscopy elemental maps (HAADF STEM-EDS) of the spent nanocrystal ZSM-5 sample were obtained using a Titan G2 80-200 TEM at 200 kV.

- **ICP–AES**
  Inductively coupled plasma atomic emission spectroscopy (ICP–AES) was used to determine the total SiO$_2$/Al$_2$O$_3$ ratio of the synthesised samples using a Thermo Scientific iCAP 6500 Duo ICP–AES

- **MAS NMR**
  Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) was used to investigate the coordination of Al and Si atoms in the ZSM-5 framework. The measurements were performed on a Varian 400 wide-bore NMR spectrometer equipped with two radio frequency (RF) channels. $^{27}$Al MAS NMR spectra were recorded at 104.2 MHz at a spinning frequency of 5 kHz and 2.05 s intervals between successive accumulations. $^{29}$Si MAS NMR spectra were recorded at 79.4 MHz at a spinning frequency of 5 kHz and 6.05 s intervals between successive accumulations. The standard references of $^{27}$Al and $^{29}$Si were [Al(H$_2$O)$_6$]$^{3+}$ and tetramethylsilane (TMS), respectively.

- **NH$_3$–TPA/TPD**
  In-situ ammonia temperature programmed adsorption/desorption (NH$_3$–TPA/TPD) was also carried using a Quantachrome ChemBET PULSAR TPR/TPD. Specifically, under
high purity helium at a flow rate of 15 mL min\(^{-1}\), approximately 0.1 g of each sample was heated from room temperature at a heating rate of 10 °C min\(^{-1}\) to 500 °C and maintained at this temperature for 60 min to remove any absorbed species. The sample was then cooled down to 120 °C and flushed with a mixture of 5% NH\(_3\) (v/v) in helium at a flow rate of 15 mL min\(^{-1}\) for 40 min. The gas atmosphere was then changed to helium at a flow rate of 15 mL min\(^{-1}\) to remove the physisorbed NH\(_3\). After 40 min, the sample was heated again to 650 °C at a heating rate of 10 °C min\(^{-1}\) to remove NH\(_3\) absorbed on the acid sites by desorption. The desorbed NH\(_3\) was recorded every 5 s using a thermal conductivity detector (TCD).

- **Nitrogen physisorption**
  The nitrogen adsorption behaviours of the samples were measured at -196 °C using a Micromeritics TriStar II instrument. Before each measurement, the sample was degassed under vacuum at 200 °C for 12 h. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area using the adsorption data in the range of \(p/p_0=0.05–0.2\) \([166, 167]\). The t-plot method was used to calculate the external surface area, micropore area and micropore volume using the adsorption data in the range of \(p/p_0=0.2–0.5\)\([167]\). The total pore volume was determined from the amount of nitrogen adsorbed at \(p/p_0=0.995\).

### 3.4 Evaluation of Catalytic Performance in MTG

- **Method 1**
  This method was applied to evaluate the catalysts used to investigate the effect of crystal size on catalytic performance (Chapter 4), hierarchical ZSM-5 zeolite and its corresponding conventional counterpart (Chapter 7).
The MTG reaction was carried out in a high pressure fixed-bed reactor with a cooling trap to collect liquid product and an on-line GC for C\textsubscript{1}–C\textsubscript{4} gaseous products analysis, as shown in Figure 3.2. In a typical reaction run, 0.4 g of pelletised and sieved ZSM-5 catalyst (pellet size \~1 mm) was loaded into a middle section of a vertically located quartz tube (with an internal diameter of 10 mm and a total length of 450 mm). The quartz tube was placed in a 500 mm furnace and aligned so that the catalyst was sitting at the centre of the isothermal zone. The catalyst was first activated at 350 °C for 2 h under high purity N\textsubscript{2} gas purge at a flow rate of 28 mL min\textsuperscript{-1}, prior to the start of the MTG reaction. After catalyst activation, liquid methanol at a flow rate of 0.01 mL min\textsuperscript{-1} was evaporated at 350 °C and introduced into the reactor with a flow of high purity N\textsubscript{2} at 28 mL min\textsuperscript{-1}, giving a 16.5% methanol in nitrogen mixture. The reaction was allowed to proceed for 24 h at a relatively low temperature of 350 °C and pressure of 1.1 MPa and weight hourly space velocity (WHSV) of 1.2 h\textsuperscript{-1}.

![Figure 3.2](image)

Figure 3.2 A schematic of the high pressure fixed bed reactor with a cooling trap to collect liquid product and an on-line GC for C\textsubscript{1}–C\textsubscript{4} gaseous products analysis.

The reactor exit stream was allowed to pass through a trap containing 25 mL of ethyl acetate cooled with ice (~ 0 °C), in which liquid products were collected. The gas stream was analysed on-line at a 4 h interval for composition. An Agilent 7890A gas
chromatograph (GC) equipped with a Gas–Pro capillary column, a Hayseep Q column, two 5A capped columns, two Hayseep T columns, a Flame Ionisation Detector (FID) and two thermal conductivity detectors (TCD) was used for this purpose. The liquid product collected in the ethyl acetate trap was analysed for its chemical composition using an Agilent 7890A gas chromatograph equipped with one HP–5 column (30 m × 0.25 µm × 0.32 mm) and an FID. By using acetone as the GC internal standard for the quantification of methanol, the unreacted methanol in the reactor effluent could be determined. The methanol conversion was calculated using:

\[
\text{Methanol Conversion} \, (\%) = \frac{M_{in} - M_{out}}{M_{in}} \times 100\%
\] (3-1)

where \(M_{in}\) and \(M_{out}\) are the amount of pumped in and unconverted methanol, respectively.

The following naming conventions were used when describing the reaction products: C1-C4 for the sum of gaseous hydrocarbons with carbon numbers between 1 and 4, and aliphatics for the sum of liquid non-aromatics, TMB stands for trimethylbenzene. By using N2 and hexadecane as the GC internal standard for the quantification of gas and liquid hydrocarbon products, the selectivity of a given product was calculated using:

\[
\text{Product Selectivity} \, (\%) = \frac{M_i}{M_{HC}} \times 100\%
\] (3-2)

where \(M_i\) is the amount of the product of interest and \(M_{HC}\) is the total amount of hydrocarbon products.

All the liquid hydrocarbon products were considered as gasoline product, the gasoline selectivity was then calculated using:

\[
\text{Gasoline Selectivity} \, (\%) = \frac{M_{HC} - M_{C1-C4}}{M_{HC}} \times 100\%
\] (3-3)

where \(M_{C1-C4}\) is the amount of gas products (C1-C4).
• Method 2
This method was applied to evaluate nanocrystal ZSM-5 zeolite with various SiO₂/Al₂O₃ ratios (Chapter 4), the catalysts used for the investigation of effect of reaction conditions on catalytic performance (Chapter 5) and coke formation and deactivation (Chapter 6).

![Figure 3.3 A schematic of the high pressure fixed bed reactor equipped with an on-line GC for all products analysis.](image)

The catalytic performance of the ZSM-5 catalysts was evaluated in MTG conversion using a high pressure fixed-bed reactor equipped with an on-line GC for all products analysis. A schematic of the reactor system is shown Figure 3.3. The ZSM-5 catalyst was pelletised, crushed and sieved into pellets of ~1 mm in diameter. In a typical run, 0.24 g of the catalyst pellets were loaded into the middle section of the reactor—a quartz tube (8 mm) equipped with a stainless steel tube jacket. The reactor was placed in a 400 mm vertical furnace and aligned to ensure the catalyst sit at the centre of the isothermal zone. Prior to the start of the MTG reaction, the catalyst was activated at 375 °C for 2 h under high purity nitrogen purge at a flow rate of 44 mL min⁻¹(STP). Then, liquid methanol (Sigma-Aldrich, HPLC grade, 99.9%) at a flow rate of 0.01 mL min⁻¹ was vapourised at 375 °C in a preheater, and then introduced into the reactor using high purity nitrogen as carrier gas at a flow rate of 44 mL min⁻¹, giving a 10% (v/v) methanol in nitrogen mixture.
The reactions were allowed to continue for 24 h under a set of constant conditions of temperature 375 °C, pressure 1 MPa and weight hourly speed velocity (WHSV) 2 h⁻¹, unless otherwise specified.

It must be noted the reaction for the investigation of coke formation was ceased when methanol conversion decreased by 50%, at which the lifetime of the catalyst was defined (denoted as \( t_{1/2} \)).

A split sample of the reactor exit stream was directed to an Agilent 7890A gas chromatograph (GC) and analysed online at a 1 h interval for its composition. To avoid condensation, the reactor’s entire downstream tubes were maintained at 180 °C. The GC was equipped with two capillary columns, VF-1 ms and PoraBOND Q, connected to a thermal conductivity detector (TCD), and three additional capillary columns, CP Ms 5A, CP-Sil 8 CB and PoraBOND Q, connected to a flame ionisation detector (FID). The GC results allowed the calculation of methanol conversion and product selectivity [128, 168, 169].

High catalytic performance should be indicated by high methanol conversion, high gasoline yield and low coke formation. The following naming conventions were used when describing the reaction products: ‘C1−C4’ for the sum of gaseous hydrocarbons with carbon numbers between 1 and 4, namely, C1−C4 alkanes and C2=C4 alkenes, ‘C5+ aliphatics’ for the sum of liquid nonaromatics, ‘aromatics’ for the sum of all aromatic products including durene. The liquid products, namely, all products except C1−C4 were considered as gasoline.
3.5 Coke Analysis

- Total coke content

The total coke content on all the spent ZSM-5 catalysts was determined by thermogravimetric analyser (TGA) using a SDT600 TGA (TA Instrument). Two methods were established for the analysis.

**Method 1**

The following procedure was applied to determine the total coke content on the spent catalysts used to investigate the effect of crystal size on catalytic performance (Chapter 4) and the spent hierarchical ZSM-5 zeolite (Chapter 7). Typically, the experiments were conducted in air at a flow rate of 100 mL min\(^{-1}\) with a temperature-programmed heating profile. A used sample (i.e. the ZSM-5 sample after the MTG reaction) of about 6 mg was first placed in an alumina crucible and kept at room temperature for 5 min to allow the balance to stabilise. The sample was first heated at a heating rate of 20 °C min\(^{-1}\) to 105 °C and maintained there for 15 min to remove the surface moisture. It was then further heated to 550 °C at a heating rate of 10 °C min\(^{-1}\) and held there for 360 min. The mass loss below 105 °C was due to the loss of moisture. The mass loss between 105 and 300 °C was ascribed to the loss of absorbed volatile residues on the catalysts. The mass loss between 300–550 °C was considered to be the coke deposition on the catalyst during the MTG reaction [90, 170].

**Method 2**

The following procedure was applied to determine the total coke content on the spent nanocrystal ZSM-5 zeolite with various SiO\(_2\)/Al\(_2\)O\(_3\) ratios (Chapter 4), the catalysts used for the investigation of the effect of reaction conditions on catalytic performance (Chapter
5) and coke formation and deactivation (Chapter 6). Specifically, the measurements were first conducted in an inert nitrogen atmosphere to vaporise absorbed organic volatiles and then followed by air to burn off hard coke. Specifically, with high purity nitrogen at a flow rate of 100 mL min$^{-1}$, about 10 mg of the spent sample was placed in an alumina crucible and heated to 105 °C at a heating rate of 20 °C min$^{-1}$ and maintained for 15 min to remove any surface moisture. The sample was then heated to 550 °C at a heating rate of 10 °C min$^{-1}$ and kept for 15 min. Subsequently, the gas atmosphere was switched to air with a flow rate of 100 mL min$^{-1}$, and the sample was held for 40 min to allow for coke combustion. Finally, the temperature was increased to 800 °C at a heating rate of 30 °C min$^{-1}$ and kept for 10 min. The mass loss in nitrogen above 105 °C was ascribed to removal of volatile species absorbed on the catalyst. The mass loss in air was associated with combustion of the hard coke.

- **Coke characteristics**

The coke composition and morphology was studied using gas chromatography mass spectrometry (GC–MS), $^1$H and $^{13}$C NMR and high-resolution TEM (HRTEM). Before analysis coke was completely extracted from the catalyst by dissolving the spent catalyst in a solution of NaOH and EtOH, a schematic of the coke extraction is shown in Figure 3.4. Specifically, 0.2 g of the spent catalyst, 1.5 g of NaOH and 15mL of EtOH (15mL) were mixed in a Teflon-lined autoclave, and the resulting mixture was treated at 100 °C for 24 h. After cooling to room temperature, the solution was transferred to a polypropylene beaker and heated to 70 °C in an oil bath until the EtOH fully vaporised. The sample was then added with deionized water and dichloromethane (DCM), and filtered to give a black solid which was collected and dried to be analysed by TEM. The filtrate was transferred to a separating funnel and extracted twice using DCM. The
recovered DCM phase was concentrated and subsequently analysed by GC–MS and $^1$H and $^{13}$C NMR.

The amount of internal and external coke was quantified using a method reported in the literature [100, 104]. Briefly, assuming the decrease in micropore volume of the spent sample compared with the pristine counterpart is attributed to the deposition of internal coke, thus the amount of internal coke can be calculated by referring the coke density to 1.22 g cm$^{-3}$ of coal having H/C ratio of 0.8 [100, 104]. The amount of external coke then can be calculated by subtracting the internal coke from the total coke content determined by TGA analysis. In this study, the volatile species were considered as coke as they also contributed to the reduction in micropore volume. The total coke content comprised the amount of volatiles and hard coke.

![Figure 3.4 Schematic of coke extraction using EtOH/NaOH solution](image)

**3.6 Data Collection and Analysis**

In order to ensure the validity of the methods for the synthesis and characterisation of all the ZSM-5 zeolite samples, all experimental procedures were repeated and confirmed to be reliable. In addition, catalyst characterisation strictly followed the standard operation procedures of each instrument and facility.
To determine the statistical validity of the catalytic performance data obtained, the entire experimental system, including the pump for methanol feeding, the mass flow meter for carrier gas control and the thermocouple for temperature control of the furnace were all calibrated, and the thermocouple was placed at the middle of the furnace where the catalyst was loaded to ensure the temperature was measured for the catalyst. For each run of the testing, the quartz reactor was cleaned thoroughly before use.

**Figure 3.5** A schematic of GC configurations and columns

The GC for product analysis was configured as desired and stringently calibrated according to standard protocols. Figure 3.5 shows the schematic of the GC configurations and columns equipped. Summarised in Table 3.1 are the specifications and functions of the columns. In addition, calibrated GC-FID signal of typical MTG product is shown in Figure 3.6.
### Table 3.1 The specifications and functions of the columns equipped with the GC

<table>
<thead>
<tr>
<th>Columns</th>
<th>Specifications</th>
<th>Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Col 1: VF-1 ms</td>
<td>$30\text{m} \times 530\text{µm} \times 0.5\text{µm}$</td>
<td>For separating light hydrocarbons ($\text{C}_1-\text{C}_4$) and permanent gases from the product mixture</td>
</tr>
<tr>
<td>Col 2: PoraBOND Q</td>
<td>$25\text{m} \times 530\text{µm} \times 10\text{µm}$</td>
<td>For separating light hydrocarbons ($\text{C}_1-\text{C}_4$) from the gaseous mixture</td>
</tr>
<tr>
<td>Col 3: CP Ms 5A</td>
<td>$30\text{m} \times 530\text{µm} \times 15\text{µm}$</td>
<td>For separating permanent gases ($\text{N}_2$ and $\text{CH}_4$)</td>
</tr>
<tr>
<td>Col 4: CP-Sil 8 CB</td>
<td>$30\text{m} \times 530\text{µm} \times 0.5\text{µm}$</td>
<td>For separating heavy hydrocarbons ($\text{C}_{5+}$)</td>
</tr>
<tr>
<td>Col 5: PoraBOND Q</td>
<td>$25\text{m} \times 530\text{µm} \times 10\text{µm}$</td>
<td>For separating light hydrocarbons ($\text{C}_1-\text{C}_4$) and oxygenates (MeOH, EtOH, PrOH)</td>
</tr>
</tbody>
</table>

Figure 3.6 Calibrated GC-FID signal of typical MTG product
3.7 Summary

- Five nanocrystal ZSM-5 catalysts with various SiO$_2$/Al$_2$O$_3$ ratios were synthesised and evaluated in MTG. This is to investigate the intrinsic effect of SiO$_2$/Al$_2$O$_3$ ratio on the catalytic performance in MTG when nanocrystal ZSM-5 catalyst is used. In addition, four ZSM-5 catalysts with distinctly different crystal sizes were prepared to investigate the effect of crystal size on their performance in MTG. These two pieces of work are to study the effect of catalyst properties on the catalytic performance in MTG with respect to the development of nanocrystal ZSM-5 catalyst. This is detailed in Chapter 4.

- The nanocrystal catalyst with mediate SiO$_2$/Al$_2$O$_3$ ratio of 47 was used to investigate the effect of reaction conditions (Chapter 5), coke formation and characteristics in relation to deactivation (Chapter 6) in responding to catalyst development of using nanocrystal ZSM-5 catalyst in MTG.

- A simple method for direct synthesis of hierarchical ZSM-5 zeolite is developed, namely, no additional template is used for the generation of mesopores. Its characteristics and catalytic performance in MTG is discussed in Chapter 7.
4.1 Introduction

This chapter illustrates the effect of catalyst properties (crystal size and SiO$_2$/Al$_2$O$_3$ ratio) on catalytic performance of ZSM-5 zeolite in MTG.

Four catalysts with distinctively different crystal sizes ranging from 0.1–30 µm and five with various SiO$_2$/Al$_2$O$_3$ ratio in the range of 23–411 were synthesised, and their physical and structural properties were characterised and discussed, comparisons were also made where was necessary. Their catalytic performances in MTG were evaluated. The differences in methanol conversion, product distribution and coke formation were discussed and compared with respect to the changes in crystal sizes and SiO$_2$/Al$_2$O$_3$ ratio.

4.2 Effect of Crystal Size

Crystal size of ZSM-5 catalyst directly affects the diffusion length so that to impact on the mass diffusion in the microporous channels of the catalyst. Reducing crystal size of ZSM-5 catalyst has been reported as an effective way to shorten the diffusion paths for easy access and exit of activity sites in ZSM-5 [9-14]. Reduction in crystal size has also been linked to higher resistance to coke formation in ZSM-5 [9,15,16].

In this contribution, we present experimental results showing how the crystal size of ZSM-5 influenced its catalytic activity and the extent of coking in the MTG reaction. ZSM-5 with four different crystal sizes and a nominal SiO$_2$/Al$_2$O$_3$ ratios of 50 were synthesized by facile routes as presented in Chapter 3 and their catalytic performance are discussed in the present work.
4.2.1 Characteristics of ZSM-5 catalysts with various crystal sizes

The XRD patterns for the four ZSM-5 samples prepared are shown in Figure 4.1. These patterns confirmed the formation of ZSM-5, as all diffraction peaks obtained can be indexed to ZSM-5 [171].

![XRD patterns of ZSM-5 samples](image)

Figure 4.1 Typical XRD patterns of ZSM-5 samples with various crystal sizes ranging from 0.1–30 µm

The SEM images shown in Figure 4.2 display the crystal morphology and sizes of the ZSM-5 samples. As can be seen from Figure 4.2a, the ZSM-5_0.1 µm sample consisted of single crystals of rather a uniform size distribution, with average crystal size estimated to be 0.1 µm (100 nm). Similarly, the ZSM-5_0.65 µm sample (Figure 4.2b) also consisted of single crystals with narrow size distribution and averaged at about 0.65 µm. The crystal size of the ZSM-5_1.5 µm (Figure 4.2c) was not as uniformly distributed as the other samples, ranging from 1 to 2 µm. The average crystal size for the sample was estimated at approximately 1.5 µm. The ZSM-5_30 µm sample, on the other hand, consisted of rod-shaped crystals with average dimensions of 30×5×2 µm.
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Figure 4.2 Typical SEM images of ZSM-5 samples with various crystal sizes ranging from 0.1–30 µm: (a) ZSM-5_0.1 µm; (b) ZSM-5_0.65 µm; (c) ZSM-5_1.5 µm; and (d) ZSM-5_30 µm

Figure 4.3 Nitrogen physisorption isotherms of ZSM-5 samples with various crystal sizes ranging from 0.1–30 µm. Solid symbols denote adsorption and hollow ones for desorption
The nitrogen physisorption isotherms of the ZSM-5 samples are shown in Figure 4.3. From which, the BET surface area and micropore volumes were calculated and summarized in Table 4.1. The BET surface area is found to increase with decreasing crystal size of the ZSM-5 samples, with ZSM-5_0.1µm exhibiting the highest BET surface area of 464 m²g⁻¹. In comparison, the variation of micropore areas due to the change in crystal sizes is evidently less significant. This agrees with the observation in the nitrogen physisorption isotherms shown in Figure 4.3, in which all samples displayed a sharp nitrogen uptake at a low pressure of \( p/p_0 < 0.02 \), indicating similar micropores existed in the samples.

ZSM-5_0.1µm was shown to possess a typical type–IV isotherm, with a hysteresis loop starting at \( p/p_0 = 0.80 \), suggesting relatively large mesopores existed in the sample. It is also worth noting that the total pore volume of ZSM-5_0.1µm was more than double of that of other samples, indicating ZSM-5_0.1µm would have a strong adsorption capacity.

Table 4.1  Nitrogen physisorption characteristics of ZSM-5 catalysts with various crystal sizes ranging from 0.1–30 µm

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{BET} ) (m²g⁻¹)</th>
<th>t-Plot ( S_{Micro} ) (m²g⁻¹)</th>
<th>t-Plot ( S_{Exter} ) (m²g⁻¹)</th>
<th>( V_{Total} ) (cm³g⁻¹)</th>
<th>t-Plot ( V_{Micro} ) (cm³g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5_0.1µm</td>
<td>464</td>
<td>327</td>
<td>137</td>
<td>0.38</td>
<td>0.15</td>
</tr>
<tr>
<td>ZSM-5_0.65µm</td>
<td>386</td>
<td>313</td>
<td>73</td>
<td>0.19</td>
<td>0.12</td>
</tr>
<tr>
<td>ZSM-5_1.5µm</td>
<td>351</td>
<td>301</td>
<td>50</td>
<td>0.17</td>
<td>0.14</td>
</tr>
<tr>
<td>ZSM-5_30µm</td>
<td>288</td>
<td>245</td>
<td>43</td>
<td>0.17</td>
<td>0.14</td>
</tr>
</tbody>
</table>

*Note: \( S_{BET} = \) BET surface area, which was calculated using the BET method; t-Plot \( S_{Micro} = \) micropore area, which was determined using the t-plot method; t-plot \( S_{Exter} = \) external surface area calculated by subtracting the micropore area from the BET area.
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\[ V_{\text{Total}} = \text{total pore volume, which was determined from the adsorbed amount at } \frac{p}{p_0}=0.995. \]

\[ t-\text{plot } V_{\text{Micro}} = \text{micropore volume was calculated using the t-plot method; } V_{\text{Meso}} = \text{mesopore volume was calculated by subtracting micropore volume from the total pore volume.} \]

4.2.2 Catalytic performance of ZSM-5 catalysts with various crystal sizes

4.2.2.1 Effect of crystal size on methanol conversion and product distribution

Table 4.2 summarises the products formed and their distribution during the screening tests of the synthesised ZSM-5 catalysts. The methanol conversion was found to decrease with increasing crystal size of the ZSM-5 catalysts, with the highest methanol conversion of 99.2% obtained from ZSM-5_0.1 µm, and the lowest of 73.0% from ZSM-5_30 µm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZSM-5_0.1µm</th>
<th>ZSM-5_0.65µm</th>
<th>ZSM-5_1.5µm</th>
<th>ZSM-5_30µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol conversion (%)</td>
<td>99.2</td>
<td>94.2</td>
<td>89.7</td>
<td>73.0</td>
</tr>
<tr>
<td>C1–C4</td>
<td>52.2</td>
<td>65.2</td>
<td>68.3</td>
<td>75.0</td>
</tr>
<tr>
<td>Aliphatics</td>
<td>11.1</td>
<td>11.3</td>
<td>12.4</td>
<td>5.3</td>
</tr>
<tr>
<td>Toluene</td>
<td>4.2</td>
<td>3.3</td>
<td>2.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Xylene</td>
<td>12.2</td>
<td>7.2</td>
<td>7.2</td>
<td>5.6</td>
</tr>
<tr>
<td>TMB</td>
<td>11.9</td>
<td>8.0</td>
<td>5.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Durene</td>
<td>3.2</td>
<td>2.4</td>
<td>1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Others</td>
<td>3.0</td>
<td>1.3</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Gasoline Selectivity</td>
<td>46.4</td>
<td>33.5</td>
<td>28.4</td>
<td>15.3</td>
</tr>
</tbody>
</table>

Table 4.2 Methanol conversion and product distribution of ZSM-5 catalysts with various crystal sizes tested at 350 °C, 1.0 MPa and WHSV of 2 h⁻¹
Chapter 4 Characterisation and Effect of Catalyst Properties on Performance of Nanocrystal ZSM-5 Catalyst in MTG

In addition, as seen from the product distribution data in Table 4.2, ZSM-5_0.1 µm offered the highest gasoline yield of 46.4%, mainly due to its high selectivity towards aromatics. Among the aromatics distribution shown in Figure 4.4, xylene and TMB were the main components in all reaction products. This is due to the unique selectivity of ZSM-5. It can also be observed that the selectivity of durene, being a larger molecule among the products decreased with increasing crystal size of the ZSM-5 catalysts. This observation suggests larger product molecules would have more difficulty exiting the micropores of ZSM-5 zeolite with large crystals that extend diffusion paths. Consequently, the large products would remain in the pores during the reaction and ultimately result in coke. This is also consistent with the observation that large crystal ZSM-5 displayed the lowest activity.

Figure 4.4 Effect of crystal size on aromatics distribution of ZSM-5 catalysts with various crystal sizes tested at 350 °C, 1.0 MPa and WHSV of 2 h⁻¹
Table 4.2 also shows that the selectivity towards C₁–C₄ was relatively higher than that towards other hydrocarbons. This is because the MTG reactions in this study were a one-step process without recycling of the light products. It is well known that there are two steps involved in the conventional MTG process [172, 173], where light gaseous components are recycled as part of the reactant. It is expected that the gasoline selectivity would increase if the light hydrocarbons were recycled back to the reactor.

On the other hand, it was also observed that C₁–C₄ selectivity increased with increasing crystal size, with ZSM-5_0.1µm having 52.2% of C₁–C₄ selectivity while this was 75.0% for ZSM-5_30µm, respectively. This could be understood by the molecule diffusion in the microporous channels of the catalyst. The catalyst with larger crystal size has longer diffusion paths, thus molecules traverse in the microporous channels would take longer time to exit. This promotes molecules having more chances to contact with active sites and therefore more reactions to occur, such as dealkylation, which results in higher selectivity of C₁–C₄.

![Figure 4.5 TGA curves of the spent catalysts with different crystal sizes tested at 350 °C, 1.0 MPa and WHSV of 2 h⁻¹ for 24 h.](image-url)
4.2.2.2 Effect of crystal size on coke formation

The TGA curves shown in Figure 4.5 suggest that with increasing crystal size, more coking occurred during the catalytic reaction, with weight losses of 3.1%, 4.4%, 6.7% and 8.5% correspond to ZSM-5_0.1 µm, ZSM-5_0.65 µm, ZSM-5_1.5 µm and ZSM-5_30 µm, respectively. This suggests that the ZSM-5 catalyst with a larger crystal size would have a shorter catalytic life time. As reported by Sahoo and co-workers [174] and Abdullah and co-workers [175], the gradually accumulated coke would cover the acidic sites and eventually block the channels in ZSM-5, thus prevent the reactants from accessing the pores. It is well known that the number and strength of acidic sites dictate the catalytic activity of the ZSM-5 catalysts [176] and as such, once the acidic sites are covered, the activity of ZSM-5 catalyst is lost.

In summary, the crystal size of ZSM-5 zeolite was found to play a vital role in determining its catalytic performance in methanol conversion, product distribution, and coke formation. The nanosized ZSM-5 catalyst showed the best catalytic activity and lest coke formation within the reaction time studied. This is believed to be resulted from the high BET surface area and short diffusion paths due to the small crystal size, providing reactant molecules with easy access of the active sites within the micropores of the catalyst, and more importantly, increasing chances for the larger product molecules to exit the pores. The latter was vital in retaining the catalytic activity of the catalyst, thus extending the catalytic lifespan.
4.3 Effect of SiO$_2$/Al$_2$O$_3$

It is believed the activity of ZSM-5 zeolite is determined by the strength and density of its acid sites, more precisely, the number of accessible Brønsted acid sites per unit cell, which are proportional to the tetrahedrally coordinated Al content in the zeolite framework [49, 177]. Therefore, the SiO$_2$/Al$_2$O$_3$ ratio of ZSM-5 zeolite plays an important role in determining its catalytic activity and lifespan. A ZSM-5 zeolite with a low SiO$_2$/Al$_2$O$_3$ ratio (i.e. high Al content) generally has a high amount of acid sites, and thus high activity. However, the high Al content in a zeolite will also lead to high coke formation that results in fast catalyst deactivation [20, 136, 178]. This trade-off between the acidity and lifespan of the ZSM-5 zeolite implies a suitable SiO$_2$/Al$_2$O$_3$ ratio is pivotal to ensure the zeolite to have high activity as well as a long lifespan. A suitable range of SiO$_2$/Al$_2$O$_3$ ratio was reported to be 30-70 for microcrystal zeolite catalysts in MTG conversion [168, 179].

The above study (Section 4.2) clearly demonstrates nanocrystal ZSM-5 catalyst possesses superior performance in MTG. The question then arises if nanocrystal ZSM-5 zeolite is used for MTG reaction, will the suitable SiO$_2$/Al$_2$O$_3$ ratio be different from that of the conventional microcrystal ZSM-5 zeolite? To address this question, nanocrystal ZSM-5 zeolites of different SiO$_2$/Al$_2$O$_3$ ratio but the same crystal size and structural properties have to be used. However, synthesis of such materials is challenging due to the interplay between crystal size and SiO$_2$/Al$_2$O$_3$ ratio and, it has not been reported before to the best of our knowledge. In this work, we prepared a series of nanocrystal ZSM-5 zeolites with almost identical crystal size and structural properties but different SiO$_2$/Al$_2$O$_3$ ratios of 23, 47, 107, 217 and 411. Furthermore, we used these materials in MTG reaction to systematically investigate the intrinsic effect of SiO$_2$/Al$_2$O$_3$ ratio on the catalyst performance independent of crystal size.
4.3.1 Strategy of synthesising nanocrystal ZSM-5 samples with various SiO$_2$/Al$_2$O$_3$ ratios

The synthesis of nanocrystal ZSM-5 samples has been extensively studied and many synthesis methods have been developed. These studies have shown that the crystal sizes of resultant ZSM-5 zeolite products depend greatly on the precursor composition and synthesis conditions, including factors such as silica and alumina sources, temperature, alkalinity and aging duration of the gel, hydrothermal treatment conditions and SiO$_2$/Al$_2$O$_3$ ratio [132, 133]. Changing SiO$_2$/Al$_2$O$_3$ ratio was observed to have great impact on the crystal size of ZSM-5 zeolite. Generally, an increase in the SiO$_2$/Al$_2$O$_3$ ratio leads to a decrease in the crystal size under otherwise identical conditions [35, 36, 134], therefore making it difficult to prepare ZSM-5 zeolites of various SiO$_2$/Al$_2$O$_3$ ratios and similar crystal size from the same method. On the other hand, it is well known that crystal size of the ZSM-5 zeolite can have a significant impact on its catalytic performance, particularly on the catalyst deactivation [109, 180]. Thus it is challenging to investigate the effect of SiO$_2$/Al$_2$O$_3$ ratio alone on the catalytic performance of the zeolite and in the past such study has been often performed by ignoring the effect of crystal size [110, 181, 182].

A simple method was developed (as presented in Chapter 3) to synthesise a series of nanocrystal ZSM-5 samples with various SiO$_2$/Al$_2$O$_3$ ratios but almost identical crystal sizes and structural properties. Changing the SiO$_2$/Al$_2$O$_3$ ratios without affecting the crystal sizes of the samples was achieved by varying the amount of the alumina source (NaAlO$_2$) and using an excessive amount of TPAOH, while keeping the amount of other precursor components unchanged. The amount of TPAOH used in the synthesis was relatively high, thus ensuring there was sufficient OH$^-$ in the precursor solutions for all samples. This overrode the effect of varying Al contents on the nuclei formation, and the
alkalinity of the gel solutions was almost unaffected. Consequently, nucleation and growth rate of framework structure was not significantly affected during the synthesis when SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio was varied, enabling the production of ZSM-5 samples with almost identical crystal sizes but of various SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios.

### 4.3.2 Characteristics of nanocrystal ZSM-5 samples with various SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios

The powder XRD patterns of the five samples are shown in Figure 4.6. Evidently, these diffraction patterns are almost identical and consistent with that of typical ZSM-5 zeolite reported in the literature [183], confirming that highly crystalline ZSM-5 were produced at all the five different SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios.

![Figure 4.6 Typical XRD patterns of nanocrystal ZSM-5 samples with various SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios ranging from 23–411](image)

Representative SEM and TEM images of the five samples are shown in Figure 4.7. All samples consisted of crystals of almost identical size of \(\sim100\) nm with a narrow size...
distribution. The lattice fringes observed along different axis under high-resolution TEM further confirmed that each nanocrystal was a high crystalline single crystal with micropore structures of typical ZSM-5 zeolite.

Figure 4.7 Typical SEM and TEM images of nanocrystal ZSM-5 samples with various SiO₂/Al₂O₃ ratios ranging from 23–411
The chemical environment of the framework aluminium in these five samples was verified through $^{27}$Al MAS NMR spectra. As shown in Figure 4.8, the spectrum was dominated with the main resonance peak at ~55.5 ppm for all samples and a minor resonance at ~0 ppm for the samples with SiO$_2$/Al$_2$O$_3$ ratio $\leq$ 107. According to the literature [184], the former can be attributed to the tetrahedrally coordinated Al within the framework structure, whereas the latter one is associated with the octahedrally coordinated Al on the extra framework. Therefore, the majority of the Al in the framework of the synthesised samples was tetrahedrally coordinated, with only a very minor proportion on the extra framework for the samples with low SiO$_2$/Al$_2$O$_3$ ratio. The resonance at ~ 0 ppm dropped substantially with increasing SiO$_2$/Al$_2$O$_3$ ratio suggesting ZSM-5 zeolites with high Al content (thus low SiO$_2$/Al$_2$O$_3$ ratio) are more prone to develop extra-framework Al [49, 50].

![Figure 4.8 $^{27}$Al MAS NMR spectra of nanocrystalline ZSM-5 samples with various SiO$_2$/Al$_2$O$_3$ ratios ranging from 23–411]

The acid site distributions of the five samples obtained via NH$_3$–TPD are shown in Figure 4.9. As can be seen, all samples exhibited two well-resolved desorption peaks typical of
ZSM-5 zeolite, with the low-temperature peaks at 150–320 °C corresponding to weak acid sites and the high-temperature peaks at 320-550 °C corresponding to strong acid sites, respectively [185-187]. The intensity of a desorption peak representing the amount of acid sites decreased with increasing SiO₂/Al₂O₃ ratio, indicating the amount of acid sites was indeed proportional to the Al content in the catalyst. Clearly, NZ_23 had the highest Al content and thus the highest amount of acid sites, in good agreement with the literature [188, 189]. In this study, a low SiO₂/Al₂O₃ ratio was indicative of a high acid site density, and vice versa.

Figure 4.9  NH₃–TPD profiles of nanocrystal ZSM-5 samples with various SiO₂/Al₂O₃ ratios ranging from 23–411

The nitrogen physisorption isotherms of all five samples presented in Figure 4.10 show all samples exhibited very similar adsorption/desorption behaviour. The steep uptake observed for all isotherms in low relative pressure region (p/p₀ < 0.01) reflects a high microporosity in the samples, indicating an intact microporous framework and high crystallinity, consistent with the results of XRD and TEM. The sudden rise in the adsorption capacity at high relative pressures (p/p₀>0.9) along with the hysteresis loops
suggestions the existence of mesopores in the samples. These mesopores were created by intercrystal spaces and are commonly observed in zeolites with nanosized crystals [109, 190]. The adsorption properties of the samples extracted from the isotherms are summarised in Table 4.3. The BET surface areas, micropore areas and volumes were
found to increase slightly (by ~5%) with increasing SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio, consistent with existing understanding on the aluminium content effect [191, 192]. The total pore volume for all the samples was determined to be \( \approx 0.35 \) cm\textsuperscript{3}g\textsuperscript{-1}, in good agreement with that of typical nanocrystal ZSM-5 zeolite with high crystallinity [190].

Table 4.3  Nitrogen physisorption characteristics of nanocrystal ZSM-5 samples with various SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios ranging from 23–411

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>t-Plot</th>
<th>( S_{\text{Micro}} ) (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>t-Plot</th>
<th>( V_{\text{Total}} ) (cm\textsuperscript{3}g\textsuperscript{-1})</th>
<th>t-Plot</th>
<th>( V_{\text{Micro}} ) (cm\textsuperscript{3}g\textsuperscript{-1})</th>
<th>( V_{\text{Meso}} ) (cm\textsuperscript{3}g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NZ_23</td>
<td>418</td>
<td>302</td>
<td>116</td>
<td>0.33</td>
<td>0.12</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NZ_47</td>
<td>420</td>
<td>304</td>
<td>116</td>
<td>0.33</td>
<td>0.12</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NZ_107</td>
<td>426</td>
<td>308</td>
<td>118</td>
<td>0.34</td>
<td>0.13</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NZ_217</td>
<td>430</td>
<td>310</td>
<td>120</td>
<td>0.35</td>
<td>0.13</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NZ_411</td>
<td>435</td>
<td>311</td>
<td>124</td>
<td>0.35</td>
<td>0.13</td>
<td>0.22</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is clear that for the five ZSM-5 samples produced, although their SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios varied significantly from 23 to 411, their crystal sizes and structural properties remained almost identical. This thus provided a unique opportunity to independently investigate the effect of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio on the catalytic performance of these samples in MTG conversion which is discussed in the following.

4.3.3  Catalytic performance of nanocrystal ZSM-5 zeolite catalysts

4.3.3.1  Effect of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio on methanol conversion and product distribution

The effect of SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio on methanol conversion versus time on stream is shown in Figure 4.11. With the exception of NZ_411, all other ZSM-5 samples showed complete methanol conversion (100%) during the first 5 h reaction period. After that, a decrease in methanol conversion was observed in the samples with low SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios (NZ_107, NZ_47, NZ_23), and this reduction became increasingly pronounced with decreasing
SiO$_2$/Al$_2$O$_3$ ratio, indicating the samples having higher aluminium content thus higher acidity were deactivated more rapidly. In addition, the extra-framework Al observed for those three samples might also contribute to the fast deactivation [50, 193, 194]. The methanol conversion remained complete and steady for NZ_217 over the 24h time period studied. However, further increasing SiO$_2$/Al$_2$O$_3$ ratio to 411 resulted in incomplete methanol conversion (~94%) even from the very beginning of the reaction. This was most likely due to the reduced number of active sites in NZ_411. As the number of active sites is proportional to the aluminium content in the ZSM-5 zeolite, a catalyst with a highly increased SiO$_2$/Al$_2$O$_3$ ratio of 411 led to insufficiency in active sites and hence incomplete methanol conversion under the reaction conditions enforced. Note that methanol conversion for NZ_217 and NZ_411 remained steady over the reaction time studied, suggesting a sustained catalyst activity on ZSM-5 with high SiO$_2$/Al$_2$O$_3$ ratios (due to less coking as elaborated in next section).

Figure 4.11  Effect of SiO$_2$/Al$_2$O$_3$ ratio on methanol conversion of nanocrystal ZSM-5 zeolite catalysts tested at 375 °C, 1 MPa and WHSV of 2 h$^{-1}$
Figure 4.12  Effect of SiO$_2$/Al$_2$O$_3$ ratio on product distribution and gasoline yield of nanocrystal ZSM-5 zeolite catalysts tested at 375 °C, 1 MPa and WHSV of 2 h$^{-1}$

The product distribution and gasoline yield of the catalysts with different SiO$_2$/Al$_2$O$_3$ ratios are shown in Figure 4.12. Aromatics decreased with increasing SiO$_2$/Al$_2$O$_3$ ratio. The zeolite catalyst with the highest aluminium content (NZ_23) had the highest aromatics selectivity, suggesting a high amount of acid sites clearly promoted the aromatisation reaction. An important effect of increasing SiO$_2$/Al$_2$O$_3$ ratio was a significant decrease in the durene selectivity, from 10.8% to 3.9% as SiO$_2$/Al$_2$O$_3$ ratio increased from 23 to 411. It was also evident that increasing SiO$_2$/Al$_2$O$_3$ ratio facilitated the formation of C$_5$+ aliphatics, consequently contributed to an increase in the gasoline yield. The gaseous products that cannot be considered as gasoline, was found to decrease with increasing SiO$_2$/Al$_2$O$_3$ ratio.
The term of C₁‒C₄ in this study includes C₁‒C₄ alkanes (paraffins) and C₂=C₄ alkenes (olefins). The latter, particularly ethylene (C₂H₄) and propylene (C₃H₆), are believed to be the primary products for methanol conversion to hydrocarbons (MTH) catalysed by zeolitic catalysts [170, 195]. Under the reaction conditions for MTG, as demonstrated in the reaction path shown in Figure 4.13, methanol (CH₃OH) is first catalytically dehydrated to form an equilibrium mixture of dimethyl ether (DME), the mixture undergoes further reactions to form the primary products. These primary products subsequently undergo oligomerisation, cyclisation, aromatisation, aromatic methylation, hydrogen transfer and aromatic dealkylation to form the final product.

Figure 4.13  Proposed reaction pathways for methanol conversion on ZSM-5 catalyst

The reactions involved in MTH are catalysed by the acid sites arising from the bridging hydroxyl group (Si‒OH‒Al), shown in Figure 4.13. Apparently, high amount of acid sites would direct the reactions towards to formation of high hydrocarbons, in agreement with the high aromatic selectivity for NZ_23 discussed above. It also can be inferred that C₂=C₄ alkenes, being the primary products, should have low selectivity at low SiO₂/Al₂O₃ ratio. This is revealed in the selectivity of C₂=C₄ alkenes as a function of SiO₂/Al₂O₃ ratio displayed in Figure 4.12b, increasing SiO₂/Al₂O₃ ratio led to an increase in C₂=C₄ alkenes. Therefore, a high SiO₂/Al₂O₃ ratio is preferred for the production of light olefins, and is widely reported in the literature for methanol/ethanol to olefins (M/ETO) [181, 196-199].
In contrary, C\textsubscript{1}–C\textsubscript{4} alkanes were found to decrease with increasing SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio, shown in Figure 4.12b. This can be understood by the unique shape selectivity of ZSM-5 zeolite [200]. It is well known that ZSM-5 zeolite has an intermediate pore size of ~0.55nm, only small and intermediate organic molecules can traverse through these pores [65]. The growth of the molecules formed during the reaction is regulated by the pores, leading to the occurrence of aromatic dealkylation and thus the formation of light hydrocarbons (C\textsubscript{1}–C\textsubscript{4}). C\textsubscript{2}=C\textsubscript{4} alkenes can further react to form other hydrocarbons; however, C\textsubscript{1}–C\textsubscript{4} alkanes are saturated and thus relatively stable, remaining as effluent gas. Low SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio promoted the further reaction of C\textsubscript{2}=C\textsubscript{4} alkenes and also aromatic dealkylation, resulted in C\textsubscript{1}–C\textsubscript{4} alkanes being the predominant light hydrocarbons at a low SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio and the overall C\textsubscript{1}–C\textsubscript{4} selectivity decreasing with increasing SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio.

Figure 4.14 shows the product distributions as a function of time on stream for the five catalysts. All the catalysts showed a decrease in the selectivity of C\textsubscript{1}–C\textsubscript{4}, aromatics and durene, and an increase in C\textsubscript{5+} aliphatics, reflecting a similar phenomenon as the effect of increasing SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio on product distribution. This can be understood by the active sites in the catalysts being progressively covered by coke formed during the reaction, and consequently, the effective amount of active sites decreased with time on stream. Furthermore, the changes in product distributions with time on stream were found to be more stable for NZ_217 and NZ_411, and more pronounced with decreasing SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio, indicating a faster coverage of active sites at lower SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratios, in line with the more rapid catalyst deactivation with decreasing SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio aforementioned.

Overall, NZ_217 had the highest gasoline yield through the course of the test, as a consequence of its complete and steady methanol conversion and relatively low C\textsubscript{1}–C\textsubscript{4} selectivity. It is worth noting that NZ_217 had an acceptable durene selectivity of 4.6%,
as durene concentration in the gasoline higher than 5% will cause rough engine operation [10].

![Figure 4.14](image)

Figure 4.14   Product selectivity as a function of time for the nanocrystal ZSM-5 zeolite catalysts with various SiO$_2$/Al$_2$O$_3$ ratios tested at 375 °C, 1 MPa and WHSV of 2 h$^{-1}$

### 4.3.3.2 Effect of SiO$_2$/Al$_2$O$_3$ ratio on coke formation

Deactivation of catalysts is mainly caused by the formation of carbonaceous residues and subsequent deposition on the catalyst surfaces and/or pores, thus covering the active sites. These carbonaceous residues are commonly known as coke, constituting polycyclic aromatic hydrocarbons [95]. During the catalytic reaction, coke is gradually formed and retained in the catalyst. A small proportion of volatile compounds are also trapped in the catalyst thus not considered as “real coke” but the precursors [106]. Therefore,
specifically quantifying the “real coke” was studied by thermal gravimetric analysis conducted first in an inert nitrogen atmosphere below 550 °C to remove volatile molecules and then followed by in air for the combustion of the “real coke”.

![TGA curves of the spent catalysts with different SiO2/Al2O3 ratios tested at 375 °C, 1 MPa and WHSV of 2 h⁻¹ for 24 h](image)

Figure 4.15 TGA curves of the spent catalysts with different SiO2/Al2O3 ratios tested at 375 °C, 1 MPa and WHSV of 2 h⁻¹ for 24 h

The weight loss curves of the spent catalysts are shown in Figure 4.15. It can be found the amount of coke on the spent catalysts was 3.3, 3.2, 1.7, 0.4 and 0.1 wt% for NZ_23, NZ_47, NZ_107, NZ_217 and NZ_411, respectively, after subtracting the trapped volatile components. It is also noticed that the proportion of volatile compounds relative to the total removable organics/cokes was more significant for catalysts with higher SiO2/Al2O3 ratios, e.g. around 80% of the removals in the spent NZ_411 sample was volatile compounds whereas only about 25% in NZ_23. Evidently, catalysts with lower SiO2/Al2O3 ratios were more prone to coke formation, suggesting samples with high aluminium content would deactivate more rapidly, which was clearly reflected by the time-dependent methanol conversion results shown in Figure 4.11. In addition, typical
SEM and TEM images shown in Figure 4.16 of the spent catalysts revealed virtually identical morphologies as their pristine counterparts, suggesting coking was the dominant cause of catalyst deactivation. NZ_217 showed higher sustained activity towards methanol conversion, desirable product selectivity and also the highest gasoline yield. It was also expected that NZ_217 would have a longer lifespan due to its relatively low coke formation. Collectively, the analysis of the five samples showed the one with the relatively high SiO$_2$/Al$_2$O$_3$ ratio (217) had the best overall catalytic performance. In comparison, previous studies reported a preferred SiO$_2$/Al$_2$O$_3$ ratio of 30-70 for zeolitic catalysts in MTG conversion [168, 179]. This difference is actually a reflection of the effect of crystal size on the catalytic performance of ZSM-5 zeolite. The earlier studies were based on conventional ZSM-5 zeolites that had crystal size in the micrometre range, in which a certain proportion of active sites were inaccessible to reactants due to its long diffusion path. Thus high Al content (low SiO$_2$/Al$_2$O$_3$ ratio) was required for micron-sized ZSM-5 zeolite to provide sufficient accessible active sites to enable good methanol conversion. In contrast, by reducing the crystal size of the zeolite from micron to nanometre scale, the number of accessible active sites is greatly increased leading to higher activity of nanocrystal ZSM-5 zeolite than its conventional counterpart. In other words, nanocrystal ZSM-5 zeolite with the same aluminium content as a micron-sized counterpart would show better catalytic performance [180, 201].

An unbiased study of the effect of SiO$_2$/Al$_2$O$_3$ ratio on the catalytic performance of nanocrystal ZSM-5 in the MTG conversion was systematically conducted. Five nanocrystal ZSM-5 samples with different SiO$_2$/Al$_2$O$_3$ ratios ranging from 23 to 411 but of similar crystal sizes and structural properties were successfully synthesised. This allowed for the investigation into the intrinsic effect of SiO$_2$/Al$_2$O$_3$ ratio on catalytic performance of ZSM-5 zeolite in MTG.
Figure 4.16  Typical SEM and TEM images of spent nanocrystal ZSM-5 samples. The sample name is corresponding to their pristine counterparts with various SiO$_2$/Al$_2$O$_3$ ratios ranging from 23–411
It was shown that decreasing SiO$_2$/Al$_2$O$_3$ ratio facilitated higher methanol conversion whereas the catalyst activity was better sustained with increasing SiO$_2$/Al$_2$O$_3$ ratio. C$_2$=C$_4$ alkenes decreased and C$_1$–C$_4$ alkanes increased with decreasing SiO$_2$/Al$_2$O$_3$ ratio, leading to an increase in the overall C$_1$–C$_4$ selectivity and thus low gasoline yield. Decreasing SiO$_2$/Al$_2$O$_3$ ratio also promoted aromatisation reaction, thus high durene selectivity and coke formation, leading to rapid catalyst deactivation. The nanocrystal catalyst with a moderate SiO$_2$/Al$_2$O$_3$ ratio of 217 showed a sustained 100% methanol conversion, high gasoline yield and low coke formation under the reaction conditions studied. By using nanocrystal ZSM-5 catalyst in MTG, the preferred SiO$_2$/Al$_2$O$_3$ ratio is much higher than that for the microcrystal counterparts.

4.4 Summary

It is evident that properties of ZSM-5 catalyst have a significant impact on its performance in MTG. Reduction of crystal size into nanoscale not only facilitated methanol conversion but also enhanced gasoline selectivity and mitigated coke formation. Furthermore, by using nanocrystal ZSM-5 catalyst in MTG, a decrease in SiO$_2$/Al$_2$O$_3$ ratio was also found to be very effective in improving its performance. It is therefore anticipated the combination of reducing crystal size and SiO$_2$/Al$_2$O$_3$ ratio would synergistically lead to great improvement in the performance of ZSM-5 catalyst in MTG.
Chapter 5 Effect of Reaction Conditions on Performance of Nanocrystal ZSM-5 Catalyst in MTG

5.1 Introduction

Following Chapter 4 on the investigation of the effect of catalyst properties on performance of nanocrystal ZSM-5 zeolite in MTG with respect to the development of nanocrystal ZSM-5 zeolite, this chapter discusses the effect of reaction conditions on catalytic performance of nanocrystal ZSM-5 zeolite synthesised in this work, namely, temperature, pressure and weight hourly speed velocity (WHSV).

Table 5.1 A summary of experimental conditions for MTG conversion

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>WHSV (h⁻¹)</th>
<th>Amount of catalyst loading (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>300</td>
<td>1</td>
<td>2</td>
<td>0.24</td>
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<tr>
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<td>350</td>
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<td>Pressure</td>
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<tr>
<td>WHSV</td>
<td>375</td>
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<td>4</td>
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</tbody>
</table>

Reaction conditions can also play a pivotal role in determining the performance of ZSM-5 catalyst in MTG. It is therefore necessary to review this topic based on a non-conventional catalyst in responding to catalyst development. In this contribution, the nanocrystal ZSM-5 catalyst with SiO₂/Al₂O₃ ratio of 47 was used for this purpose, as it was in the range of 30–70 which was commonly used in the literature [168, 179]. This
enabled us to make necessary comparison to the previous studies with reaction conditions of temperature from 300 to 450 °C, pressure from 0.1 to 2.0 MPa and WHSV from 1 to 4 h⁻¹. In addition, more detailed characteristics of this catalyst are also discussed.

The effect of temperature was investigated first, followed by the effect of pressure, and then WHSV which was determined with respect to the catalyst loading amount. The reaction conditions and catalyst loading amount for each reaction are summarised in Table 5.1.

5.2 Characteristics of Nanocrystal ZSM-5 Catalyst

Representative SEM and TEM images of the sample are shown in Figure 5.1. Figure 5.1a and b show that the sample consisted of single crystals with well-defined morphology and a uniform size of ~100 nm. This was further confirmed by the TEM images (Figure 5.1c). The lattice fringes displayed in the high-resolution TEM (Figure 5.1d) and selected area electron diffraction (SAED) (inset) are indicative of high crystallinity of the sample, in good agreement with the powder XRD patterns.

Figure 5.2a shows ⁷¹Al MAS NMR spectra of the sample. The weak resonance peaked at chemical shift of about 0 ppm suggested only a small amount of Al (approx. 4%, calculated by the relative peak area) was octahedrally coordinated in the extra-framework positions. The strong resonance centred at ~55.5 ppm suggested most of the Al (approx. 96%) was tetrahedrally coordinated in the framework [202-204]. Tetrahedral Al is believed to account for the Brønsted acidity in the zeolite catalyst. As the strength of Brønsted acid sites is much higher than that of Lewis acid sites which are ascribed to octahedral Al [49], the higher amount of tetrahedral Al, the higher acidity of the catalyst, and thus such catalyst generally has high activity. Figure 3a therefore indicates the sample
possessed a high density of Brønsted acid sites and the effect of the Lewis acid sites was negligible.

![Image](image_url)

Figure 5.1 Typical SEM images (a and b), TEM images (c and d), and a selected area electron diffraction (SAED) image (inset) of the nanocrystal ZSM-5 catalyst

Figure 5.2b shows the $^{29}\text{Si}$ MAS NMR spectra of the sample. The resonances centred at -116.1 and -113.0 ppm could be assigned to the Si(4Si, 0Al) sites, which indicated the Si sites were not surrounded by Al. The resonance centred at 108.9 ppm could be attributed to Si(3Si, 1Al) sites, suggesting the Si sites had one neighbouring Al connected via oxygen. Since the introduction of each Al into the Si coordination results in a characteristic $^{29}\text{Si}$ resonance with well-resolved chemical shift, the intensity of the resonance can be used to determine the amount of Al substituted in the framework, and
thus the framework SiO$_2$/Al$_2$O$_3$ ratio, which can be calculated using the equation Si/Al=\(I/0.25I_1\), where \(I\) is the total intensity of the $^{29}$Si resonance and \(I_1\) is the intensity corresponding to the Si(3Si, 1Al) coordination [65]. Applying the intensity of each resonance shown in Figure 5.2b to the equation, the framework SiO$_2$/Al$_2$O$_3$ ratio of the sample was calculated to be 56, consistent with that determined by ICP–AES (SiO$_2$/Al$_2$O$_3$ =47).

Figure 5.2 $^{27}$Al (a) and $^{29}$Si (b) MAS NMR spectra of the nanocrystal ZSM-5 catalyst. The dashed curves are Gaussian bands corresponding to the individual resonances
The nitrogen physisorption isotherms of the sample are shown in Figure 5.3. The isotherms are type IV with H3 hysteresis [167]. The sharp uptake observed at low relative pressure ($p/p_0 < 0.01$) could be attributed to nitrogen condensation in micropores, and the high adsorption volume at this pressure indicated the sample had high microporosity and an intact microporous framework, suggesting the ZSM-5 catalyst were well crystallised, in good agreement with the XRD and TEM results. The hysteresis loop started at $p/p_0=0.9$ indicated large mesopores existed in the sample. This is further confirmed by the pore size distribution shown in Figure 5.3 (inset), in which mesopores with an average pore size of ~50 nm were present. The mesopores were believed to be the inter-crystal voids created by the nanosized crystals of the sample.

The above results demonstrated the sample had characteristics typical of nanocrystal ZSM-5 zeolite. This sample is a good candidate allowing us to ignore the effect of catalyst properties on catalyst performance when discussing the effect of reaction conditions on the performance of nanocrystal ZSM-5 catalyst below.

![Figure 5.3](image_url)
5.3 Effect of Reaction Conditions on Performance of Nanocrystal ZSM-5 Catalyst

5.3.1 Effect of temperature

The effect of temperature on catalyst performance was conducted at 300 °C, 350 °C, 375 °C, 400 °C, and 450 °C, under pressure of 1.0 MPa and WHSV of 2 h\(^{-1}\). Figure 5.4 shows the methanol conversion against time on stream. At 450 °C, the methanol conversion was complete (100%) and sustained over the time studied. At 400 °C, the methanol conversion decreased to ~99% after 4 h and remained steady thereafter. Similar results were observed at 375 °C, where the methanol conversion started to decrease after 4 h and progressively to 98% by 24 h. Interestingly, a rapid decrease in methanol conversion was observed when the reaction temperature decreased to 350 °C, where the methanol conversion was ~93% by 24 h. The rapid decrease in methanol conversion became more pronounced at 300 °C, where the methanol conversion was only ~87% by 24 h.

![Figure 5.4 Effect of temperature on methanol conversion of the nanocrystal ZSM-5 catalyst in MTG. The experimental conditions were temperature: 300 °C, 350°C, 375 °C, 400 °C and 450 °C, pressure: 1.0 MPa and WHSV: 2 h\(^{-1}\)](image)
Figure 5.5 Effect of temperature on product distribution and gasoline yield of the nanocrystal ZSM-5 catalyst in MTG. The experimental conditions were temperature: 300 °C, 350 °C, 375 °C, 400 °C and 450 °C, pressure: 1.0 MPa and WHSV: 2 h⁻¹.

The product distribution and gasoline yield for the MTG reactions conducted at different temperatures are presented in Figure 5.5. Increasing the reaction temperature resulted in an increase in C₁–C₄ hydrocarbons from 22.8 to 39.3%, and a significant decrease in durene selectivity. At 300 °C, the durene selectivity was 19.4%, more than 10 times higher than that at 450 °C, which had a durene selectivity of only 1.9%. In addition, DME was only observed at 300 °C, as at this low reaction temperature, some methanol could only be dehydrated to DME instead of being further converted to higher hydrocarbons. It also can be seen from Figure 5 that the gasoline yield first increased then decreased with increasing temperature. This was due to decreased methanol conversion at low temperature and increased C₁–C₄ selectivity at high temperature. Although the reaction conducted at low temperature had low C₁–C₄ selectivity, the methanol conversion was also low, leading to a low gasoline yield. Increasing temperature facilitated methanol conversion but also promoted the formation of C₁–C₄, resulting in low gasoline yields.
The reaction conducted at 375 °C had the highest gasoline yield as a result of its high methanol conversion and relatively low C₁–C₄ selectivity.

It was very interesting to note that the durene selectivity was distinctively high at 300 °C. According to the widely supported ‘hydrocarbon pool’ mechanism for methanol to hydrocarbon conversion [21, 69, 80, 170, 195, 205], poly methylated benzenium cations (such as 1,1,2,4,6-pentamethylated benzenium) would act as active centres. These active centres undergo dealkylation and intramolecular rearrangement to form ‘primary products’ (such as ethylene and propylene). The ‘primary products’ then undergo further reactions (such as olefin methylation, olefin cracking, hydrogen transfer, cyclization, aromatic methylation) to eventually form the final product.

For methanol conversion using a ZSM-5 zeolite catalyst, it can be inferred from the ‘hydrocarbon pool’ mechanism that this type of conversion should have a very strong tendency to form large aromatics. However, the product distribution is eventually governed by reaction conditions and other factors such as the nature of the catalyst. At 300 °C, the temperature was so low that it had less impact on the tendency to form large aromatics and the product was more likely kinetically controlled. Therefore the durene selectivity was much higher at this temperature. As the temperature increased we found durene selectivity significantly decreased and C₁–C₄ selectivity increased. This is possibly because the product became increasingly thermodynamically controlled causing secondary cracking.

Figure 5.6 shows the TGA curves for the catalyst after use tested at different reaction temperatures. The TGA experiments were carried out first in an inert nitrogen atmosphere to remove any adsorbed volatile species and then in an oxidising atmosphere for coke combustion. The mass loss after 105 °C in nitrogen atmosphere could be attributed to
vaporisation of volatiles. Clearly, less volatile species were retained in the catalyst with increasing reaction temperature. In stark contrast, the amount of hard coke ( coke being a carbon-rich phase) whose amount was determined from the mass loss in air atmosphere, was 3.4, 3.5, 3.7, 5.0 and 9.7 wt% for the catalyst tested at 300 °C, 350 °C, 375 °C, 400 °C and 450 °C, respectively. Increasing temperature promoted coke formation.

![TGA curves of the nanocrystal catalyst spent at different temperatures.](image)

The experimental conditions were temperature: 300 °C, 350 °C, 375 °C, 400 °C and 450 °C, pressure: 1.0 MPa and WHSV: 2 h⁻¹

Coke formation usually correlates well with deactivation of the catalyst; the higher the coke formation, the faster the catalyst deactivation. It was expected more sustained methanol conversion should be observed with decreasing temperature. However, it was found the catalyst tested at 300 °C deactivated most rapidly regardless of the formation of lowest amount of hard coke. While it was a completely different phenomenon at 450 °C, where the catalyst had the highest coke formation but also had the slowest deactivation with complete and steady methanol conversion over the time studied. This may be explained by the composition of the compounds retained on the catalyst at different
temperatures. At 300 °C, the catalyst had the highest amount of volatile species (3.2 wt%), accounting for nearly half of the compound retained on the catalyst. This ratio decreased dramatically with increasing temperature, and was only 0.7% when the reaction temperature increased to 450°C. These volatile species were believed to be non-polyaromatics and would be chemically absorbed in the catalyst bonding to active sites, leading to coverage of active sites. As these volatiles generally had molecular sizes larger than the pores of the catalyst, they would have also blocked the channels of the catalyst. The deposition of the volatile species was apparently highly detrimental to the activity of the catalyst as evident in the rapid deactivation observed during MTG conversion at 300 °C.

At 450 °C, the amount of hard coke was more than ten times higher than that of volatiles. This could be explained by hydrogen transfer and secondary cracking occurred at this high temperature, making the organic compounds increasingly carbonaceous by splitting off hydrogen-rich compounds such as light hydrocarbons, which was evident in the high C1–C4 selectivity observed at high temperature. The carbonaceous residues were believed to be condensed poly-aromatics attributed to the hard coke that could not be thermally removed under inert atmosphere, and accumulated preferentially on the external surface of the catalyst [100, 102]. This could explain the slow deactivation of the catalyst at high temperatures. Until the coke accumulated to the point where it blocked the pore mouth, the pores were still accessible and the catalyst remained active despite the coke formation. Despite these observations, it is believed that high coke formation would eventually lead to deactivation, and if the catalyst was tested at 450 °C for a longer period, deactivation would likely be observed.

The catalyst tested at 375 °C showed high methanol conversion, high gasoline yield and relatively low coke formation. The volatile species retained on the catalyst at this
temperature was at a low level, reducing the possibility of active site coverage and pore blockage. As this temperature was also not too high to facilitate the formation of hard coke, deactivation of the catalyst was slow. Further studies of the effect of pressure and WHSV on the MTG reaction were conducted at 375 °C.

### 5.3.2 Effect of pressure

The effect of pressure on the catalyst performance was evaluated at 375 °C, WHSV of 2 h\(^{-1}\), under pressure of 0.1 MPa, 1.0 MPa and 2.0 MPa, respectively. The profiles of methanol conversion versus time-on-stream are shown in Figure 5.7. The catalyst tested at 0.1 MPa showed complete and sustained methanol conversion within the time studied. A decrease in methanol conversion was observed with increasing pressure, this was more pronounced at a pressure of 2.0 MPa, where the methanol conversion decreased to 95% by 24 h, indicating an increase in pressure prompted catalyst deactivation.

![Figure 5.7 Effect of pressure on methanol conversion of the nanocrystal ZSM-5 catalyst in MTG. The experimental conditions were temperature: 375 °C, WHSV: 2 h\(^{-1}\), pressure: 0.1 MPa, 1.0 MPa and 2.0 MPa](image-url)
Figure 5.8 shows the product distribution of the catalyst tested at different pressures. The main effect of increasing pressure was to decrease C₁–C₄ selectivity and promote the formation of higher aromatics (such as durene), in agreement with the findings of Chang and co-workers [10, 206].

![Product Distribution Chart]

Figure 5.8 Effect of pressure on product distribution and gasoline yield of the nanocrystal ZSM-5 catalyst in MTG. The experimental conditions were temperature: 375 °C, WHSV: 2 h⁻¹, pressure: 0.1 MPa, 1.0 MPa and 2.0 MPa

![TGA Curves Chart]

Figure 5.9 TGA curves of the nanocrystal catalyst spent at different pressures. The experimental conditions were temperature: 300 °C, 350°C, 375 °C, 400 °C and 450 °C, pressure: 1.0 MPa and WHSV: 2 h⁻¹
Chapter 5 Effect of Reaction Conditions on Performance of Nanocrystal ZSM-5 Catalyst in MTG

The TGA curves for the catalyst tested at different pressures are shown in Figure 5.9. The amount of hard coke derived from the mass loss occurred in air atmosphere was 2.6, 3.7 and 5.0 wt% for the catalyst tested at 0.1 MPa, 1.0 MPa and 2.0 MPa, respectively. Increasing pressure played a role in promoting coke formation. It was also found that in contrast to the effect of temperature on the retention of volatile species, there was virtually no difference between the mass loss in nitrogen. This suggested pressure had little impact on the formation of volatiles and the retention of the volatiles in the catalyst was more likely to be temperature controlled.

While it was expected that the catalyst tested at 0.1 MPa would have longer lifespan than the catalysts tested at higher pressures due to slower coke formation, the catalyst tested at this pressure had high C₁–C₄ selectivity (~42.8%), resulting in low gasoline yield, as shown in Figure 5.8. In terms of methanol conversion, durene selectivity, coke formation and gasoline yield, the performance of the catalyst tested at 1.0 MPa was more desirable. Therefore, the MTG reaction for the investigation of WHSV was conducted at 1.0 MPa.

5.3.3 Effect of WHSV

The effect of WHSV on catalyst performance was conducted at 375 °C, 1.0 MPa, and WHSV of 1 h⁻¹, 2 h⁻¹ and 4 h⁻¹, respectively. The methanol conversion based on time-on-stream was shown in Figure 5.10. At 1 h⁻¹, the methanol conversion was complete and sustained (100%) over the 24 h time period studied. At 4 h⁻¹, methanol was not completely converted even at the beginning of the reaction, suggesting that a small proportion of methanol did not even make contact with the catalyst, WHSV of 4 h⁻¹ was too high for full reaction to take place. It was also found that methanol conversion decreased during the reaction period, indicating the catalyst was slowly deactivated.
Figure 5.10 Effect of WHSV on methanol conversion of the nanocrystal ZSM-5 catalyst in MTG. The experimental conditions were temperature: 375 °C, pressure: 1.0 MPa, and WHSV: 1 h⁻¹, 2 h⁻¹ and 4 h⁻¹

Figure 5.11 Effect of WHSV on product distribution and gasoline yield of the nanocrystal ZSM-5 catalyst in MTG. The experimental conditions were temperature: 375 °C, pressure: 1.0 MPa, and WHSV: 1 h⁻¹, 2 h⁻¹ and 4 h⁻¹

Figure 5.11 shows the product distribution of the catalyst tested at different WHSV and the main effect of increasing WHSV was to decrease C₁‒C₄ selectivity and promote the
formation of higher aromatics such as durene, similar to the study of the effect of pressure discussed above, as increasing WHSV was in turn to increase methanol partial pressure.

The TGA curves for the catalyst tested at different WHSV in Figure 5.12 also showed that WHSV had little impact on the formation of volatiles. As WHSV increased the amount of hard coke also increased, and was most pronounced when the catalyst was tested at 4 h⁻¹, which had 9.2 wt% coke content, while this was only 3.2 and 3.7 wt% for the catalyst tested at 1 h⁻¹ and 2 h⁻¹, respectively. Increasing WHSV also tended to promote coke formation.

Overall, taking into account high methanol conversion and gasoline yield, low durene selectivity and low coke formation, the results obtained at different MTG reaction conditions indicated that the best overall catalytic performance of ZSM-5 was achieved at 375 °C, pressure of 1.0 MPa and WHSV of 2 h⁻¹.

Figure 5.12  TGA curves of the nanocrystal catalyst spent at different WHSV The experimental conditions were temperature: 375 °C, pressure: 1.0 MPa, and WHSV: 1 h⁻¹, 2 h⁻¹ and 4 h⁻¹.
5.4 Summary

Reactions temperature played a very important role in determining the catalyst performance. Increasing temperature facilitated a more sustained high methanol conversion but also promoted the formation of hard coke. However, the retention of volatile species was found to be more detrimental to the catalyst activity and the retention of these species increased with decreasing temperature, a rapid decrease in methanol conversion was observed at lower temperatures (<350 °C). It was also found increasing temperature caused an increase in C₁–C₄ selectivity, resulted in a decrease in gasoline yield. Increasing pressure led to a decrease in methanol conversion with time on stream and coke formation, sustained methanol conversion was observed at low pressure (0.1 MPa). A decrease in C₁–C₄ selectivity and an increase in durene were found with increasing pressure, enhancing gasoline yield. The effect of WHSV was found to be similar to the effect of pressure; increasing WHSV caused a decrease in methanol conversion. The formation of durene and coke increased with increasing WHSV while the formation of C₁–C₄ decreased.
6.1 Introduction

This chapter demonstrates two different coke deposition mechanisms using two catalysts only differed in crystal sizes, that is, they were of the same ZSM-5 type with similar structure properties and amounts of active sites, with an effort to peek into the relationship between coke formation behaviour and deactivation on catalyst with different diffusion paths. The nanocrystal ZSM-5 zeolite with SiO$_2$/Al$_2$O$_3$ of 47 (crystal size of $\sim$ 100 nm) and a microcrystal counterpart (crystal size of $\sim$ 13 µm) were used for this purpose. The characteristics of the nanocrystal catalyst were discussed for convenience when comparing with the microcrystal catalyst.

The coke location and characteristics, which were determined using TGA, nitrogen physisorption technique and TEM, were discussed in relation to the difference in performance of the two catalysts. In addition, the coke fouled nanocrystal ZSM-5 catalyst was regenerated and the activity of the regenerated sample was also evaluated and compared with the pristine nanocrystal catalyst.

6.2 General Characteristics of Nanocrystal and Microcrystal ZSM-5 Catalysts

The crystal structures of the nano- and microcrystal ZSM-5 samples were verified by powder XRD patterns. As shown in Figure 6.1, both samples exhibited diffraction patterns corresponding to the reference standard of a highly crystalline ZSM-5 zeolite[183]. It was also observed that the nanocrystal ZSM-5 sample had slightly less resolved peaks than the microcrystal sample in the 22.5–25° 2$\theta$ angle range. This can be
understood according to the Scherrer equation that nanosized crystals would show broad peaks in a diffraction pattern [204, 207].

![XRD patterns](image)

**Figure 6.1** Typical powder XRD patterns of the fresh nanocrystal and microcrystal ZSM-5 catalysts

The morphologies of the two samples are shown by representative SEM and TEM images in Figure 6.2. The nanocrystal sample displayed clean and segregated particles consisting of single crystal with a uniform size of ~100 nm (Figure 6.2a and b). The microcrystal sample consisted of twined crystals with average size of ~13 µm (Figure 6.2 c), and it must be noted these crystals were partially crushed after pelletising, producing irregular particles but remained largely same crystal size (Figure 6.2 d).

The NH\textsubscript{3}–TPD profiles of the fresh nanocrystal and microcrystal ZSM-5 samples are shown in Figure 6.3. Both samples had two distinct desorption peaks. The one at 150–320 °C is categorised as low temperature peak (LT–peak) attributed to desorption of
weakly bound NH$_3$, and the peak area is generally considered to correspond to the density of weak acid sites.

Figure 6.2 Typical SEM (a) and TEM (b) images of the nanocrystal sample; and SEM images of the microcrystal sample before (c) and after (d) pelletising

Figure 6.3 NH$_3$–TPD profiles of the fresh nanocrystal and microcrystal ZSM-5 catalysts
Similarly, the one at 320–550 °C is known as high temperature peak (HT–peak) resulted from desorption of strongly bound NH₃, with its area corresponding to the density of strong acid sites [52-54]. The nanocrystal sample had lower peak area in LT–peak but higher peak area in HT–peak than those of the microcrystal sample. The overall peak area is very similar for the two samples, indicating these samples had comparable amount of total acid sites, in good agreement with their almost identical SiO₂/Al₂O₃ ratio as determined by ICP–AES, which is 47 and 51 for the fresh nano- and microcrystal samples, respectively.

![Figure 6.4 Nitrogen physisorption isotherms of the fresh nanocrystal and microcrystal ZSM-5 catalysts, where solid symbols denote adsorption and hollow ones for desorption](image)

The nitrogen physisorption isotherms of the fresh nanocrystal and microcrystal ZSM-5 samples are shown in Figure 6.4. The nanocrystal sample showed type–IV isotherms with increased nitrogen uptake and hysteresis loops at high relative pressures (p/p₀>0.9), indicating the existence of mesopores in the sample which can be attributed to the
intercrystal voids between nanosized crystals. The microcrystal sample exhibited type I
isotherms, indicating it was a solely microporous material. The two samples also had
almost the same steep uptakes at low relative pressure region ($p/p_0 < 0.01$) indicative of
high microporosity, suggesting both samples had virtually the same intact microporous
framework with high crystallinity. As further evidenced by the pore characteristic in
Table 1, the two samples had very similar micropore areas and volumes typical of highly
crystalline ZSM-5 zeolites. The nanocrystal ZSM-5 had doubled external surface areas
and total pore volumes of the microcrystal sample as a result of its nanosize.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$g$^{-1}$)</th>
<th>t-Plot</th>
<th>t-Plot</th>
<th>$V_{\text{Total}}$ (cm$^3$g$^{-1}$)</th>
<th>t-Plot $V_{\text{Micro}}$ (cm$^3$g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh nanocrystal ZSM-5</td>
<td>420</td>
<td>304</td>
<td>116</td>
<td>0.33</td>
<td>0.12</td>
</tr>
<tr>
<td>Spent nanocrystal ZSM-5</td>
<td>248</td>
<td>101</td>
<td>147</td>
<td>0.23</td>
<td>0.05</td>
</tr>
<tr>
<td>Fresh microcrystal ZSM-5</td>
<td>352</td>
<td>302</td>
<td>50</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td>Spent microcrystal ZSM-5</td>
<td>99</td>
<td>75</td>
<td>24</td>
<td>0.05</td>
<td>0.03</td>
</tr>
</tbody>
</table>

### 6.3 Performance of Nanocrystal and Microcrystal ZSM-5 Catalysts in MTG

The performance of the two catalysts in MTG was evaluated in a fixed bed reactor under
identical reaction conditions of temperature 375 °C, pressure 1 MPa and WHSV 2 h$^{-1}$. 
This set of reaction condition is similar to that applied for the commercial MTG process [20, 87], thus providing some insights into a commercial MTG process.

Figure 6.5 Methanol conversion with time on stream for the fresh nanocrystal and microcrystal ZSM-5 catalysts tested in MTG under reaction conditions of 375 °C, 1 MPa and WHSV 2 h⁻¹

Methanol conversion with time on stream for the two catalysts is illustrated in Figure 6.5. The nanocrystal catalyst showed $t_{1/2}$ of 270 h, almost seven times longer than its microcrystal counterpart which had $t_{1/2}$ of 40 h. ZSM-5 catalysts with smaller particle size have been known for improved catalytic lifetime as a result of shortened diffusion path[180, 208]. Similarly, as observed in this study, the enhanced catalytic lifetime may be easily assigned to the obvious differences in crystal size of the two catalysts considering both had similar structural properties and active site density. The lingering question is could the stark differences in $t_{1/2}$ for the two catalysts be solely explained by their size differences.
6.4 Coke Formation and Characteristics

To understand the mechanism of deactivation of these two catalysts due to coking, detailed study and analysis on coke formation and characteristics are required. The analysis aimed to not only quantify the total amount of coke formed, but also understand the nature and locations of coke.

6.4.1 Internal and external coke

The total amount of coke formed during the MTG reaction for both catalysts was determined using TGA, and the TGA curves are shown in Figure 6.6. The total mass losses were 23.7 and 12.6 wt% for the spent nanocrystal and microcrystal catalysts, respectively. It corresponds to 31.1 wt% of coke formed per gram of the pristine nanocrystal catalyst during the reaction. In other words, 1 g of the fresh nanocrystal catalyst could lead to the formation of 0.31 g of coke at the time when methanol conversion decreased by 50%. Similarly, 14.4 wt% of coke formed per gram of fresh microcrystal catalyst. In the following discussions, coke content is represented as weight percent per gram of the fresh catalyst, unless specified otherwise.

![TGA curves of the spent nanocrystal and microcrystal ZSM-5 catalysts](image)

Figure 6.6 TGA curves of the spent nanocrystal and microcrystal ZSM-5 catalysts
Figure 6.7 Nitrogen physisorption isotherms of two spent samples compared with their fresh counterparts

The amount of internal and external coke was determined by combining the nitrogen physisorption and TGA results. Internal coke content was estimated by (i) assuming its density is 1.22 g cm$^{-3}$ (typical of coal having H/C ratio of 0.8) and (ii) assuming the reduction in micropore volume of the catalyst before and after use is purely due to the formation of internal coke. The micropore volume of the spent catalyst was measured by nitrogen physisorption. The adsorption/desorption isotherms for the two spent catalysts are shown in Figure 6.7 b and c, respectively, together with their pristine counterparts. Comparing with the pristine samples, both spent catalysts showed a significantly reduced adsorption capability in the low relative pressure region. This was indicative of a substantial reduction in micropore volume, revealing the micropore channels for the two spent samples were largely occupied by coke. Calculated from the micropore volumes summarised in Table 1, the nanocrystal catalyst had a reduction in micropore volume of 0.07 cm$^{3}$g$^{-1}$. The amount of internal coke was thereby determined to be 0.09 g, that is, the nanocrystal catalyst had 9 wt% of internal coke, and herein 22.1 wt% of external coke. Similarly, the internal coke for the microcrystal catalyst was determined to be 0.10 g, that is, the microcrystal catalyst had 10 wt% of internal coke and 4.4 wt% of external coke,
respectively. These results are summarised in Figure 6.8. Clearly, nanocrystal ZSM-5 catalyst favoured the formation of external coke whilst coke was predominantly deposited internally within microcrystal ZSM-5.

![Coke Content Chart]

Figure 6.8  Amount of internal and external coke for the two spent catalysts as calculated based on 1 g of fresh catalyst

The differences in coke formation for the two catalysts were also reflected by the change in their morphologies before and after use. Figure 6.9 shows the SEM and TEM images of the spent nanocrystal and microcrystal catalysts. In contrast to segregated particles of single crystal (Figure 6.2 a and b), the spent nanocrystal catalyst showed agglomerates of crystals ‘glued’ together by amorphous substances on the external surface of the crystals (Figure 6.9 a and b). These substances were further examined and a typical HAADF STEM image and associated EDS elemental maps of the spent sample are shown in Figure 6.10. The element distribution of carbon is evident in Figure 6.10 b presenting a mapping area identical to the samples observed in the STEM. In particular, some areas of the map show highly concentrated carbons (highlighted in Figure 6.10 b) but no trace of Si and Al as shown in Figure 6.10 c and d. Such observation is consistent with the SEM
characteristics of coke deposited on the external surface of the catalyst. Since we can rule out the possibility of residual carbon from the synthesis process due to thorough calcination of the catalyst at 550 °C for 5 h prior to each use, we confirm this carbon is the coke formed during the MTG reaction and a significant fraction was external coke when nanocrystal ZSM-5 catalyst was used. Unlike the case of nanocrystal catalyst, the spent microcrystal catalyst displayed morphology almost identical to that of the pelletised fresh sample (Figure 6.9c); clear visual evidence of coke on the external surface was not observed (Figure 6.9d), confirming little external coke was formed on microcrystal catalyst.

Figure 6.9 Typical SEM and TEM images of the spent nanocrystal and microcrystal catalysts: (a) and (b) showed significant amount of coke formed on the external surface nanocrystal catalyst, the spent microcrystal catalyst displayed morphology almost the nanocrystal catalyst; (c) and (d) showed the spent microcrystal sample had similar features as its fresh counterpart.
The stark difference in the coke formation behaviour of the two catalysts may be explained in terms of their variations in crystal size. The diffusion paths of the nanocrystal catalyst were greatly shortened owing to its nanosized crystals, leading to markedly enhanced mass diffusion. Coke precursors (e.g. aromatic species) initially formed in the micropore channels could readily migrate to the external surface, resulted in the predominant formation of external coke (~1.5 times higher than the internal coke). In the case of the microcrystal catalyst, the migration of coke precursors was sluggish due to its microcrystal crystals. Coke precursors would further undergo condensation reactions to polymerise and ultimately be trapped in the micropore channels. The external coke for
the microcrystal catalyst was 56% lower than the internal coke. Evidently, coke formation behaviour could be very different even though the same type of catalysts was used.

### 6.4.2 Coke composition and properties

Studying coke composition and properties requires the carbonaceous compounds to be separated from the spent zeolite catalyst. Therefore, the spent catalyst needs to be completely dissolved, normally through leaching by hydrofluoric acid (HF) aqueous solution [100, 104]. However, HF is a notorious highly corrosive chemical and the handling of HF must follow a series of stringent requirements which is not adaptable for most chemistry laboratories. In this study, we adopted a greener and safer method using NaOH/EtOH solution to dissolve the catalyst, successfully avoiding the use of HF.

![Figure 6.11 GC-MS spectrum for the soluble coke extracted by dichloromethane. The first peak is likely to be a molecule of C_{14}H_{12} according to the NIST standard reference database. The later one is identified to be from contamination by plasticizer.](image-url)

Figure 6.11   GC–MS spectrum for the soluble coke extracted by dichloromethane. The first peak is likely to be a molecule of C_{14}H_{12} according to the NIST standard reference database. The later one is identified to be from contamination by plasticizer.
The soluble coke extracted by DCM was subsequently subjected to GC–MS and $^1$H and $^{13}$C NMR analysis as shown in Figure 6.11 and Figure 6.12. A molecule of $\text{C}_{14}\text{H}_{12}$ was identified by the NIST standard reference database of the GC–MS. Unfortunately, the overall data obtained were insignificant due to the extremely low concentration of soluble coke despite that the solution was concentrated to the minimal volume required for the
GC vial and NMR tube. This is indicative of a trace amount of soluble coke formed during the reaction. Indeed, coke would tend to be more carbonaceous due to aging under such long reaction time and high temperature, ultimately promoting the formation of more hard coke (insoluble coke). This is also echoed in the TGA curve (Figure 6.6), in which the mass loss under nitrogen atmosphere (before combustion) was very low, particularly before 300 °C (less than 1 wt%), indicating a little amount of volatile species which could be associated with soluble coke formed in the spent nanocrystal sample.

Figure 6.13 Typical TEM images of insoluble coke separated from the spent nanocrystal ZSM-5 catalyst (a–c), and HRTEM image showed the existence of localised graphitic structures (d).

The coke insoluble in DCM (insoluble coke) was collected by filtration, dried and analysed by TEM. As shown in Figure 6.13, the insoluble coke appeared in a form of randomly entangled coil with a thread width of ~ 11 nm. The structure of the “thread”
was further revealed by the high-resolution TEM (HRTEM) in Figure 6 d in which clear lattice fringes with space of ~ 0.33 nm was observed, indicating the existence of localised graphitic structures in the insoluble coke.

![Typical TEM images of the spent nanocrystal ZSM-5 catalyst with coke encapsulating and falling off but still keeping the same shape of the crystals.](image)

**Figure 6.14** Typical TEM images of the spent nanocrystal ZSM-5 catalyst with coke encapsulating and falling off but still keeping the same shape of the crystals.

![Schematic of isolation and collection of coke formed on the spent nanocrystal ZSM-5 catalyst.](image)

**Figure 6.15** Schematic of isolation and collection of coke formed on the spent nanocrystal ZSM-5 catalyst.
It is worthwhile noting that during TEM imaging for the spent nanocrystal catalyst, the crystals were often found to be heavily encapsulated with coke, and some of these coke casings were found to be isolated but still remained the contour shape of the crystals, as shown in Figure 6.14. Moreover, it was also observed the external coke had a similar width as the isolated insoluble coke shown in Figure 6.13. The insoluble coke observed was thus likely to have formed following a mechanism as schematically shown in Figure 6.15. Firstly, coke layers were formed wrapping or partially wrapping the crystals. After removal of zeolites, coke was segregated as a suspension in the NaOH/EtOH solution. During the subsequent filtration step, internal coke was highly likely to have collapsed due to its very thin diameter (maximum ~0.55 nm); external coke separated randomly stacked together and a transmissive view would resemble those observed in Figure 6.13.

6.5 Relating Coke Formation and Characteristics to Catalyst Deactivation

The catalyst is deactivated by coke formation that leads to progressive active sites coverage and pore blockage [102, 209]. Coke is of large aromatics formed on the active sites by a reaction parallel to the main MTG reaction as a by–product. Due to the reaction of methanol conversion is predominantly taking place in the micropore channels of ZSM-5 zeolite where the majority of active sites are located [95], the deposition of coke in the channels (internal coke) can lead to direct coverage of the active sites and obstruction of diffusion paths thus has an adverse effect on the durability of the catalyst. Furthermore, the formation of coke on the external surface (external coke) of the catalyst may lead to plugging of pore mouths if the coke is non-porous. This would prevent the reactant from accessing the active sites, also can be significantly poisonous to the catalyst performance. Therefore, it can be inferred that the deactivation behaviour of the catalysts was primarily
determined by two factors: formation rate of internal coke and structural properties of external coke.

The two catalysts had very similar internal coke contents at \( t_{1/2} \). It could also be understood as when the accumulation of internal coke reached to about 10 wt\%, ZSM-5 catalyst would lose 50\% of its activity. However, taking the reaction duration into account, it took 270 h for the nanocrystal catalyst to form such an amount of internal coke, while it only took 40 h for the microcrystal counterpart do the same. The averaged formation rates of internal coke for the nanocrystal and microcrystal catalyst were thus determined to be \( 3.3 \times 10^{-4} \) g h\(^{-1} \) and \( 2.5 \times 10^{-3} \) g h\(^{-1} \), respectively. Clearly, the nanocrystal catalyst showed tremendously slow formation of internal coke, and correspondingly, much slower coverage of active sites and blockage of channels inside the nanocrystal catalyst, leading to long extended catalytic lifetime.

Figure 6.16  Nitrogen physisorption isotherms at -196 °C for the isolated coke and pore size distribution (inset). Solid symbols denote adsorption and hollow ones for desorption.
On the other hand, the nanocrystal catalyst showed great longevity with a significant amount of external coke (~1.5 times higher than the internal coke). This may imply the formation of external coke has little impact on the catalyst deactivation. As aforementioned, whether external coke is harmful to the catalyst performance really depends on its pore structure. The isolated coke was thus measured by nitrogen physisorption. The resulting isotherms (Figure 6.16) were typical of type V isotherms, indicating the external coke was a non-microporous material. The hysteresis loop at relative pressures ($p/p_0 > 0.6$) was indicative of existence of mesopores in the coke sample, which was further confirmed by the pore size distribution (Figure 6.16 inset) showing mesopores of ~10 nm. This diameter was much greater than the molecule sizes of reactant and products, and thus no extra mass transfer limitation was imposed. It was therefore ascertained that external coke was harmless to the catalyst performance.

It was also observed the methanol conversion of the nanocrystal ZSM-5 catalyst showed a steep decrease after being sustained at ~ 98% for approximately 200 h (Figure 6.5). This might imply a sudden change in the pore network of the catalyst that impedes the accessibility of active sites and the diffusion of reactant and products. ZSM-5 zeolite is known to have a three-dimensional interconnected tubular network. Since coke is accumulated as a function of time, such deposition inside the ZSM-5 crystals may change the interconnectivity of the network affecting the pore accessibility. It is anticipated that the entire pore network gradually loses the diffusivity with time on stream and eventually become non-through at the end of catalysts’ lifetime. However, as evidenced by our experimental data, the transition of catalyst deactivation was rather abrupt well before the micropores were fully blocked in the spent ZSM-5 catalysts. This phenomenon may be explained by the percolation theory.
The percolation theory hypothesises that when the fraction of blocked pore volume approaches a threshold, the remaining pores are no longer accessible, and diffusion through the pore network is terminated. A percolation probability, \( P \), is used to describe the probable faction inside the network, and thus can be related to the accessibility of the pore network [210, 211]. Hence, \( P \) decreases with the increase of number of blocked pores, and becomes zero at the percolation threshold. In the case of ZSM-5 zeolite, as internal coke causes the pore blockage, the accessibility of the pore network or \( P \) decreases with increasing internal coke content, and becomes zero when the internal coke accumulates to a certain amount, by means of reaching the percolation threshold. This could lead to a dramatic impact on the catalyst activity, causing the sudden drop in methanol conversion aforementioned. We found the nanocrystal ZSM-5 catalysts lost 58% of its initial micropore volume at the time of sharp decrease in methanol conversion, indicating a percolation threshold of 0.58, in line with the value (0.64) predicted by the dynamic Monte Carlo simulation [212].

6.6 Catalytic Performance of the Regenerated Nanocrystal Catalyst

The loss of catalyst activity in most catalysis processes is inevitable. Instead of discarding the fouled catalyst, restoring its activity is normally preferred. In the industrial practice of MTG, coke fouled ZSM-5 catalysts are often subjected to thermal treatment in air (500-600 °C) to remove the coke by combustion [88-90]. However, it is frequently found the activity of the catalyst cannot be fully restored [88, 213]. Such degradation is believed to be mainly due to the loss of Al by hydrolysis during the reaction and regeneration.

The spent nanocrystal sample was also regenerated and the properties and activity of the regenerated catalyst was investigated in this study. The regeneration of the deactivated catalyst was carried out at 550 °C in air for 4 h. Figure 6.17 shows the SEM and TEM of
the regenerated catalyst. After combusting the spent catalyst in air, the morphologies of the regenerated sample were almost identical to the fresh one. In addition, the nanocrystal sample had very similar adsorption/desorption isotherms (Figure 6.18) as the fresh one, suggesting no significant damage occurred during the reaction and regeneration of the nanocrystal catalyst. However, a decrease in the total amount of acid sites was evident by the NH$_3$–TPD profiles for the regenerated sample shown in Figure 6.19, compared with that of the fresh one. This is in agreement with an increase in the SiO$_2$/Al$_2$O$_3$ ratio determined by ICP-AES which was 61 (the fresh sample had a SiO$_2$/Al$_2$O$_3$ ratio of 47), revealing approximately 30% Al was lost after one cycle of reaction and regeneration.

Figure 6.17  Typical SEM and TEM images of the regenerated nanocrystal catalyst

Figure 6.18  Typical SEM and TEM images of the regenerated nanocrystal catalyst
Chapter 6 Relating Coke Formation and Characteristics to Catalyst Deactivation

Figure 6.19  Typical NH$_3$–TPD profiles of the regenerated nanocrystal catalyst

![Typical NH$_3$–TPD profiles of the regenerated nanocrystal catalyst](image)

**Figure 6.19**  Typical NH$_3$–TPD profiles of the regenerated nanocrystal catalyst

Figure 6.20  Methanol conversion with time on stream for the fresh and regenerated nanocrystal ZSM-5 catalysts tested in MTG under reaction conditions of 375 °C, 1 MPa and WHSV 2 h$^{-1}$

![Methanol conversion with time on stream for the fresh and regenerated nanocrystal ZSM-5 catalysts](image)

**Figure 6.20**  Methanol conversion with time on stream for the fresh and regenerated nanocrystal ZSM-5 catalysts tested in MTG under reaction conditions of 375 °C, 1 MPa and WHSV 2 h$^{-1}$

The rejuvenated sample was subsequently tested under the reaction conditions same as those of the fresh one. The methanol conversion with time on stream is shown in Figure 6.20. The regenerated catalyst showed a trend of methanol conversion with time on stream analogue to that of the fresh counterpart. However, instead of causing activity loss, the
regenerated catalyst had an increased catalytic lifetime $t_{1/2}$ of 300 h, 10% longer than the fresh one. This may be understood by the effect of Al concentration on the performance of the catalyst.

It is well documented that Al concentration (commonly represented as Si/Al or SiO$_2$/Al$_2$O$_3$ ratio) of ZSM-5 catalyst or zeolitic catalyst plays a pivotal role in determining its catalytic performance [49, 177]. ZSM-5 zeolite is an aluminosilicate material, its protonated type (HZSM-5) possesses strong acidity that enables it to have high catalytic activity herein be widely used in heterogeneous catalysis [214]. The acid strength is determined by the number of acid sites which are proportional to the Al concentration in the zeolite catalyst. Generally, the higher Al concentration, the stronger acidity and thus the higher activity the catalyst has. However, coke formation is also a function of the acidity, coke formation increases with increasing acid strength and concentration. The high concentration of Al would also increase coke formation rate that leads to rapid catalyst deactivation [209, 215]. Catalyst with low concentration of Al can extend its lifetime but may sacrifice its catalytic activity. A suitable range of Al concentration is thus essential to ensure the catalyst has desirable lifetime and also preserve its high activity. As discussed in Section 4.3 of Chapter 4, the nanocrystal ZSM-5 catalyst with SiO$_2$/Al$_2$O$_3$ ratio of 217 had the best performance among those with SiO$_2$/Al$_2$O$_3$ ratio from 23–411.

The regenerated sample had a decrease in the total amount of acid sites, resulting in enhanced catalytic lifetime. More importantly, in our work, the activity of the regenerated nanocrystal ZSM-5 was not significantly compromised, and it was still sufficient to sustain a 98% MeOH conversion in the MTG process. However, as the loss of Al is irreversible, we believe the catalyst would eventually lose its activity for an effective MTG when Al level drops below a certain threshold after many repeated cycles, thereafter due for replenishment.
6.7 Summary

This study demonstrated two coke deposition mechanisms and the relationship between the behaviour of coke formation and catalyst deactivation in ZSM-5 zeolite catalysed MTG reaction. It was demonstrated that a nanocrystal ZSM-5 catalyst (crystal size of ~100 nm) had more than double coke content but surprisingly sustained a catalytic lifetime seven times longer than its microcrystal counterpart (~13 µm). The total amount coke formed thus was not simply indicative of catalyst lifetime.

An insight into the coking behaviour was revealed, in that, it was the formation rate of internal coke that directly determined the catalytic lifetime while the formation of external coke had little impact on catalyst performance. The improved lifetime in nanocrystal was attributed to the slow accumulation of internal coke as a result of short diffusion paths, which allowed coke precursors to readily migrate to the outer surface and form external coke. Such external coke mainly found on the surface of nanocrystal catalyst was porous and thus less detrimental to the catalyst activity.

Removal of Al during the reaction and regeneration could also lead to an increase in the catalyst performance depending on the optimal Al range. The Al concentration of the nanocrystal ZSM-5 catalyst was decreased by 30% after the first cycle of reaction and regeneration. However, the regenerated catalyst had a longer lifetime than its pristine counterpart. This finding implies that starting the MTG process with a nanocrystal ZSM-5 having marginally higher Al content may significantly extend the overall cyclic lifetime of the catalyst while not compromising the catalytic performance.
Chapter 7 Direct Synthesis of Hierarchical ZSM-5 Zeolite and Its Performance in MTG

7.1 Introduction

This chapter reports a simple method for the direct synthesis of hierarchical ZSM-5 zeolite without the need of additional template or zeolite seeding crystals. The method was relatively simple compared to the literature reported methods [114, 146-148]. The zeolite was synthesised by hydrothermal processing of a clear solution of NaAlO₂, TEOS, TPAOH and deionised water at 180 °C for 48 h. The characteristics, catalytic performance and coke formation of the Hi-ZSM-5 zeolite are discussed in detail, and are compared with its conventional ZSM-5 counterpart with crystal sizes in the micrometre range.

7.2 Characteristics of Hierarchical ZSM-5 Zeolite

Typical powder XRD patterns of two typical samples of an Hi-ZSM-5 and a conventional ZSM-5 zeolite, respectively, are shown in Figure 7.1. Both samples showed a characteristic diffraction pattern typical of the MFI framework [183], confirming that ZSM-5 zeolites were successfully synthesised.

Representative SEM images of typical Hi-ZSM-5 and conventional ZSM-5 samples are shown in Figure 7.2. Hi-ZSM-5 clearly consisted of aggregated particles assembled from nanosized primary zeolite crystals, conforming to the features of hierarchical ZSM-5 zeolites. The primary crystals had an average crystal size of ~ 70 nm, whilst the aggregates had an average size of ~ 800 nm. In comparison, for the conventional ZSM-5 zeolite, each particle was a single crystal with an average size of ~ 1.5 µm. The TEM imaging analysis further confirmed the presence of the hierarchical structure of the Hi-
ZSM-5 synthesised. As shown in Figure 7.3, the nanosized primary particles were indeed single crystals of high crystallinity, as evident by the lattice fringes and the

![Graph showing XRD patterns](image)

**Figure 7.1** Typical XRD patterns of the conventional ZSM-5 and hierarchical ZSM-5 (Hi-ZSM-5) zeolite samples

![SEM images](image)

**Figure 7.2** Typical SEM images: (a) and (b) for the Hi-ZSM-5 sample; (c) and (d) for the conventional ZSM-5 zeolite sample
selected area electron diffraction (SAED) pattern shown in Figure 7.3 (c) and (d), respectively. It is also evident from Figure 7.3 (c) that the primary crystals were well aligned when assembled into the hierarchical particles, allowing the inter-primary crystal mesopores to be created within the hierarchical particle structures. As an added benefit, the sub-micron to micron sized aggregated particles could be easily collected by traditional filtration methods after the synthesis.

Figure 7.3 Typical TEM images of the Hi-ZSM-5 sample obtained under three different magnifications (a-c) and its SAED image (d), (c) is the zoom in image of the dash oval area in (b)

It is known [50, 184, 216] that the activity of an aluminosilicate zeolite is mainly dependent on its acidity, largely determined by the strength and number of the Brönsted acid sites available in the zeolite framework. For ZSM-5, the Brönsted acid sites directly correspond to the number of tetrahedrally coordinated Al atoms in the MFI framework
Chapter 7 Direct Synthesis of Hierarchical ZSM-5 Zeolite and Its performance in MTG

In this study, the MAS NMR spectroscopy was used to reveal the coordination of Si and Al atoms, determining how Al atoms were associated with the Si atoms at the T positions, and calculated the Si/Al ratios of the synthesised zeolites [65, 217]. Shown in Figure 7.4 (a) and (c) are the $^{27}$Al MAS NMR spectra of the Hi-ZSM-5 and conventional ZSM-5 zeolites, respectively. Both samples exhibited a main resonance at about 55.5 ppm and a negligible resonance at 0 ppm, suggesting that the vast majority of Al atoms in the framework of both Hi-ZSM-5 and conventional ZSM-5 zeolites were indeed tetrahedrally coordinated. Fig. 7.4 (b) and (d) shows the $^{29}$Si MAS NMR spectra of Hi-ZSM-5 and conventional ZSM-5 zeolites. For both samples, the resonances around 116.5 and 113.0 ppm could be assigned to the Si (4Si, 0Al) sites [65, 203], and those at 105.0 and 106.5 ppm could be assigned to the Si (3Si, 1Al) sites, i.e., one Al atom was incorporated at each T–position. The additional resonance at 100.9 ppm of Hi-ZSM-5 corresponded to the Si (3Si, 1OH) sites, which could be attributed to the hydroxyl groups on the large external surface of Hi-ZSM-5 [218]. Resonances with chemical shifts below 100 ppm
representing Si (2Si, 2Al) sites were not observed in either of the samples, indicating that (Al-O-Si-O-Al) sequences were not present in these samples.

$^{29}$Si MAS NMR can also be used to calculate the framework Si/Al ratio, as the introduction of Al atoms into the Si coordination sphere results in progressive chemical shifts away from Si(OSi)$_4$ in the local environment. Typically, up to five resonances can be observed corresponding to Si (4Si, 0Al), Si (3Si, 1Al), Si (2Si, 2Al), Si (1Si, 3Al) and Si (0Si, 4Al), respectively. The intensity of each resonance can then be used to quantify the number of Al atoms substituted into the framework, so the Si/Al ratio can be calculated using:

$$\frac{Si}{Al} = \frac{\sum_{n=0}^{4} I_{Si(nAl)}}{\sum_{n=0}^{4} 0.25 \cdot n \cdot I_{Si(nAl)}} \quad (7-1)$$

where $I_{Si(nAl)}$ is the intensity of the Si(nAl) signal and $n$ is the number of Al atoms in the coordination sphere [65, 202]. Using this equation, the Si/Al ratio of the Hi-ZSM-5 and conventional ZSM-5 samples was calculated, and the results are summarised in Table 7.1. The values were very close to the nominal Si/Al ratio of the samples at the initial stage of synthesis.

![Figure 7.5 N₂ physisorption isotherms of the fresh and used Hi-ZSM-5 and conventional ZSM-5 zeolite samples](image-url)
Figure 7.5 presents the N₂ physisorption isotherms of the Hi-ZSM-5 and conventional ZSM-5 zeolites. The conventional sample showed a type-I isotherm, typical of microporous materials with relatively low external surface areas [219]. The pore size distribution curve as shown in Figure 7.6 further confirmed that no mesopore existed in the conventional ZSM-5 sample. On the other hand, the Hi-ZSM-5 sample showed a profile typical of a type-IV isotherm. A hysteresis loop starting from about $p/p₀=0.7$ and strong N₂ adsorption were evident for Hi-ZSM-5 at high pressure, indicating the presence of mesopores. This is further proven by the pore size distribution curve presented in Figure 7.6, showing mesopores over a broad range of pore sizes from 10 to 90 nm, peaking at ~ 30 nm. Both Hi-ZSM-5 and conventional samples had sharp uptakes in the adsorption capacity at low pressures and ended at almost the same adsorption levels, suggesting these samples had the similar amounts of micropores. This suggests that the nanosized primary crystals in Hi-ZSM-5 were well-crystallised, the reduction in the crystal size did not affect the crystallinity, and thus the intrinsic micropores were well preserved. The N₂ physisorption behaviour is consistent with the TEM results presented previously.

Table 7.1  
N₂ physisorption characteristics of the fresh and used Hi-ZSM-5 and conventional ZSM-5 zeolite samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio</th>
<th>S$_{BET}$ (m²/g)</th>
<th>t-plot S$_{Micro}$ (m²/g)</th>
<th>t-plot S$_{Exter}$ (m²/g)</th>
<th>V$_{Total}$ (cm³/g)</th>
<th>t-plot V$_{Micro}$ (cm³/g)</th>
<th>V$_{Meso}$ (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi-ZSM-5</td>
<td>55</td>
<td>433</td>
<td>299</td>
<td>133</td>
<td>0.3</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>Used Hi-ZSM-5</td>
<td>-</td>
<td>366</td>
<td>229</td>
<td>137</td>
<td>0.29</td>
<td>0.10</td>
<td>0.19</td>
</tr>
<tr>
<td>Conventional ZSM-5</td>
<td>52</td>
<td>352</td>
<td>302</td>
<td>50</td>
<td>0.17</td>
<td>0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>Used conventional ZSM-5</td>
<td>-</td>
<td>124</td>
<td>91</td>
<td>33</td>
<td>0.06</td>
<td>0.04</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Figure 7.6  Pore size distributions of the fresh and used Hi-ZSM-5, and fresh and used conventional ZSM-5 zeolite

The adsorption properties of both samples are summarised in Table 7.1. Hi-ZSM-5 had a high BET surface area as expected. The micropore areas and volumes calculated by the t-plot method [167] for both samples were very similar, in agreement with their adsorption capabilities at low pressures. Consequently, the external surface area of the Hi-ZSM-5 sample, calculated by subtracting the micropore area from the BET area, was greater than that of the conventional ZSM-5 zeolite. As the external surface area of zeolite corresponds to the number of pore entrances, this may have some bearing on the deactivation characteristics of these zeolites. Zeolites with higher external surface areas are likely to have longer endurance in catalytic reactions [220, 221].

7.3  Catalytic Performance of Hierarchical ZSM-5 Zeolite in MTG

7.3.1  Methanol conversion and product distribution
MTG over the Hi-ZSM-5 and conventional ZSM-5 zeolite samples, respectively, was performed at 350 °C for 24 h with ca. 16.5% methanol in nitrogen at a total pressure of
1.1 MPa and WHSV of 1.2 h\(^{-1}\). The results of methanol conversion and product distribution are summarised in Table 7.2. Hi-ZSM-5 showed a higher methanol conversion and gasoline selectivity than the conventional ZSM-5 zeolite. From the gasoline product distribution, xylene and trimethylbenzene were found to be the main components for conventional ZSM-5 zeolite. This could be attributed to the unique shape selectivity of ZSM-5 zeolites. For a conventional ZSM-5 zeolite, the majority of the active sites are located inside the micropores, it thus has the unique shape selectivity dictated by its micropore features [113, 222]. As the reactions mostly take place within these pores, only species formed with size less than the pore size can diffuse out as reaction products. Species of large molecules formed would either be cracked into smaller molecules or trapped and forming coke. As such, the MTG products are determined to a great extent by the pore structure of the catalyst. A good example of this is xylene isomerisation, where \(p\)-xylene can diffuse out of ZSM-5 zeolites more readily than \(o\)- and \(m\)-xylene [223, 224]. On the other hand, Table 7.2 shows durene (1,2,4,5-tetramethylbenzene) was the main component of the gasoline product for Hi-ZSM-5. Durene has 10 carbon atoms and is not usually a main component in the product of MTG catalysed by ZSM-5 zeolites [225].

The high durene selectivity observed for Hi-ZSM-5 might be due to its nanosized crystals. As Hi-ZSM-5 had a much higher external surface area than conventional ZSM-5 zeolite due to the reduction in the crystal size. Since the active sites on the external surfaces of ZSM-5 zeolites are independent of shape selectivity, the overall shape selectivity of this hierarchical catalyst is likely to be significantly affected by nonselective reactions taking place on the external surfaces [222, 226]. In addition, a decrease in the crystal size would reduce the diffusion path length and therefore the diffusional resistance, relatively large
aromatics (such as durene) formed in the methanol to gasoline reaction should be able to easily diffuse out of the pores in Hi-ZSM-5 sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hi-ZSM-5</th>
<th>Conventional ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol Conversion (%)</td>
<td>99.6</td>
<td>89.7</td>
</tr>
<tr>
<td>C₁–C₄</td>
<td>41.2</td>
<td>68.3</td>
</tr>
<tr>
<td>Aliphatics</td>
<td>2.8</td>
<td>12.4</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Xylene</td>
<td>11.5</td>
<td>7.2</td>
</tr>
<tr>
<td>TMB</td>
<td>15.7</td>
<td>5.3</td>
</tr>
<tr>
<td>Durene</td>
<td>18.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Other aromatics</td>
<td>4.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Gasoline Selectivity</td>
<td>58.9</td>
<td>28.4</td>
</tr>
</tbody>
</table>

The mesopores formed by the inter-crystal spaces is believed to also play a major role in the diffusion of large aromatics (such as durene). Reactions taking place in the mesopores are not expected to be sterically hindered [227], as the products have more space to grow and diffuse. Bjørgen et al [228] synthesised hierarchical ZSM-5 zeolites by treating a parent ZSM-5 zeolite with aqueous NaOH solution (dealumination). The samples were evaluated using the MTG reaction and it was found that large aromatics were produced as a result of the creation of mesopores.

It may be noted that the high durene selectivity in MTG is undesirable for industrial applications due to its high melting point of 79 °C and boiling point of 192 °C. Durene may crystallise out when its concentration is high and cause rough engine operation when
its concentration in gasoline is higher than 5 wt% [10]. However, this can be overcome as durene can be converted to a low melting point petrol component, such as isodurene (1,2,3,5-tetramethylbenzene) that has a melting point of -23.7 °C and boiling point of 198 °C [87]. In addition, this constrain could also be solved by blending the MTG gasoline with conventional gasoline to maintain an acceptable durene level [10].

7.3.2 Coke Formation on hierarchical ZSM-5 zeolite during MTG

Figure 7.7  TGA curves of the used Hi-ZSM-5 and conventional ZSM-5 zeolite samples. The coke content was determined by the mass loss above 300 °C.

Figure 7.7 shows the TGA curves for the Hi-ZSM-5 and conventional zeolite samples after being used in the MTG for 24 h. The amounts of coke on the used Hi-ZSM-5 and conventional ZSM-5 zeolites were determined to be 1.7 and 7.7wt%, respectively, indicating that significantly less coke was formed on Hi-ZSM-5 than on the conventional ZSM-5 zeolite. The much lower coke deposition in Hi-ZSM-5 was believed to be due to its hierarchical particle structure offering easy diffusion of large molecules from the catalyst during MTG, thus reducing the chance of coke formation. In addition, the
nanosized primary crystals also effectively shortened the micropore channels, reducing the diffusion path length for large molecules to escape. In contrast, the reaction products would have to diffuse through much longer paths to escape the micropore channels in the conventional ZSM-5 zeolite due to the much larger crystal sizes. The products would be more likely to become trapped and eventually form coke.

The adsorption capability of the used catalysts was also investigated using a N\textsubscript{2} physisorption technique and the N\textsubscript{2} physisorption isotherms are shown in Figure 7.5. Compared to the fresh sample, the adsorption capability of used Hi-ZSM-5 at low pressures was slightly decreased, indicating that only a small proportion of micropores in Hi-ZSM-5 were blocked by coking in MTG. The adsorption capability at high pressures was almost unaffected, with adsorption reaching the same level as that of fresh Hi-ZSM-5 when the equilibrium pressure \( p \) reached the saturation pressure \( p_0 \), and the pore size distribution curve of the used Hi-ZSM-5 shown in Figure 7.6 was very similar to that of the fresh sample. This suggests that only a negligible amount of coke was deposited in the mesopores. In contrast, the adsorption capacity of the used conventional ZSM-5 zeolite decreased dramatically as compared to that of the fresh sample, suggesting that a majority of micropores of the conventional ZSM-5 zeolite were blocked by coking. The pore size distribution of the used conventional ZSM-5 zeolite was same as the one of the fresh sample shown in Figure 7.6. The adsorption properties of the used samples are summarised in Table 7.1. The reduction in the BET surface area of the used conventional ZSM-5 zeolite was much greater than that of the used Hi-ZSM-5. This was mainly caused by the decrease in the micropore area. No obvious change was seen in the external surface area and mesopore volume of Hi-ZSM-5 before and after its use in MTG. These results further confirmed that coking had predominantly taken place in the microporous channels and as such, it is therefore more pronounced in the solely microporous zeolites like the
conventional ZSM-5 zeolite. The adsorption behaviour of the used Hi-ZSM-5 agreed strongly with the TGA result, further confirming that much less coke was formed in the hierarchical ZSM-5 zeolites.

The adsorption behaviour of the used Hi-ZSM-5 also revealed that the hierarchical structure of the Hi-ZSM-5 remained unchanged after its use in the MTG reaction. This is further confirmed by the SEM and TEM images of the used Hi-ZSM-5 shown in Figure 7.8. The particles of the used Hi-ZSM-5 remained as assembled from nanosized zeolite crystals, which was same as the fresh sample. The lattice fringes in primary crystals could still be clearly seen as in Figure 7.8 (d), further confirming the hierarchical structure of Hi-ZSM-5 was not significantly affected by its use in the MTG reaction.

7.4 Summary

Hierarchical ZSM-5 zeolite has been successfully synthesised using a simple method without the need to use an additional template for creating mesopores. The hierarchical
ZSM-5 zeolite consisted of well aligned nanosized primary crystals with mesopores created in the inter-primary crystal spaces. The primary crystals were single crystals with high crystallinity and their intrinsic microporous properties were well preserved. The catalytic performance of the hierarchical ZSM-5 zeolite in methanol conversion to gasoline was studied and compared to that of the conventional ZSM-5 zeolite. The hierarchical ZSM-5 zeolite exhibited not only high methanol conversion and selectivity towards the gasoline range hydrocarbons but also high resistance to coking, indicating the zeolite had great catalytic activity.
8.1 Introduction

This chapter evaluates the findings derived from Chapters 4–7, benchmarks them against the specific objectives addressed in Chapter 2. The results are also compared with those reported in the literature detailed in Chapter 2. Moreover, new gaps are also identified, leading to recommendations for future work.

8.2 Catalyst Synthesis and Characterisation

8.2.1 Synthesis of ZSM-5 zeolites with various crystal sizes

In the present study, four ZSM-5 zeolites with similar SiO₂/Al₂O₃ ratios but different crystal sizes ranging from 0.1 to 30 µm have been successfully synthesised. XRD confirmed the four samples had characteristics diffraction peaks identical to that of the standard ZSM-5 zeolite, and SEM determined the samples had crystal sizes of 0.1, 0.65, 1.5, 30 µm, respectively.

The synthesis methods for the four samples detailed in Section 3.2 indicated there was no significant difference between the methods, i.e. the same alumina and silica sources, the same hydrothermal conditions, particularly for samples ZSM-5_0.1µm and ZSM-5_30µm. The only difference in their synthesis was the additional step of using NH₄F for ZSM-5_30µm, which led to a significant increase in crystal size from 0.1 to 30 µm, indicating crystal size of the zeolite was very sensitive to any changes to the synthesis parameters.
8.2.2 Synthesis of nanocrystal ZSM-5 zeolites with various SiO$_2$/Al$_2$O$_3$ ratios

A method to synthesise nanocrystal ZSM-5 zeolites with various SiO$_2$/Al$_2$O$_3$ ratios but similar crystal sizes and structural properties have been successfully developed. Five samples with SiO$_2$/Al$_2$O$_3$ ratios ranging from 23 to 411 and crystal sizes of approximately 100 nm were synthesised.

The samples were obtained by systematically controlling the synthesis conditions thorough: (i) changing the SiO$_2$/Al$_2$O$_3$ ratios by varying the amount of the alumina source (NaAlO$_2$) and (ii) using an excessive amount of TPAOH to balance the overall alkalinity of the gel solutions not to be affected by varying Al contents. The method was presented in Section 3.2 and the characteristics of the zeolites were shown in Section 4.3. XRD confirmed all the samples had diffraction patterns almost identical and consistent with that of typical ZSM-5 zeolite. ICP-AES determined the samples had SiO$_2$/Al$_2$O$_3$ ratios of 23, 47, 107, 217 and 411, respectively. SEM and TEM showed the samples had very similar morphologies and crystal sizes of ~ 100 nm and nitrogen physisorption revealed these samples also had almost same structural properties. Furthermore, these samples also had the similar coordination of Si and Al in the frameworks as investigated by MAS–NMR. The characteristics of the samples confirmed the successful synthesis of nanocrystal ZSM-5 zeolites with various SiO$_2$/Al$_2$O$_3$ ratios but similar crystal sizes and structural properties.

This study has overcome the challenge of varying SiO$_2$/Al$_2$O$_3$ ratio without affecting crystal size of the ZSM-5 zeolite. It was reported that an increase in the SiO$_2$/Al$_2$O$_3$ ratio could lead to a substantial decrease in the crystal size under otherwise identical conditions [33-36], see examples in Table 8.1. Thus, the synthesis of the five samples also allowed investigating the intrinsic effect of SiO$_2$/Al$_2$O$_3$ ratio on the catalytic performance of ZSM-5 zeolite in MTG, which has not been reported in the literature to our best knowledge.
Table 8.1 Effect of increasing SiO$_2$/Al$_2$O$_3$ ratio on crystal size of ZSM-5 zeolite

<table>
<thead>
<tr>
<th>Example</th>
<th>SiO$_2$/Al$_2$O$_3$ ratio</th>
<th>Crystal size (nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 1</td>
<td>100</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>260</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>800</td>
<td>[36]</td>
</tr>
<tr>
<td>Example 2</td>
<td>118</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

8.2.3 Synthesis of hierarchical ZSM-5 zeolite

The present study has also demonstrated a simple method to directly synthesise hierarchical ZSM-5 zeolite. A zeolite sample with mesopores in the range of 10–90 nm was successfully synthesised.

It can be seen from the synthesis method presented in Section 3.2 that the procedures were easy to operate and only one template (TPAOH) was used, which was for the formation of MFI structure. XRD confirmed the sample had typical diffraction patterns of ZSM-5 zeolite. SEM and TEM revealed the sample had particles (~ 800 nm) assembled from nanosized crystals (~ 70 nm), conforming the features of hierarchical ZSM-5 zeolite. The mesopore features of the sample were further confirmed by the hysteresis loop in the nitrogen physisorption isotherms and the pore size distribution curves, which showed the sample had mesopores of 10–90 nm and peaking at 30 nm. Thus, without using a second template, direct synthesis of hierarchical ZSM-5 zeolite has been successfully achieved.
Table 8.2  A summary of various templates used for the synthesis of hierarchical ZSM-5 zeolite

<table>
<thead>
<tr>
<th>Method</th>
<th>Template</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard-template</td>
<td>Nanocarbon</td>
<td>[150]</td>
</tr>
<tr>
<td></td>
<td>Carbon nanotubes/nanofibers</td>
<td>[229, 230]</td>
</tr>
<tr>
<td></td>
<td>CMK-3</td>
<td>[231-234]</td>
</tr>
<tr>
<td></td>
<td>Carbon aerogels</td>
<td>[235]</td>
</tr>
<tr>
<td></td>
<td>Starch-derived bread</td>
<td>[161]</td>
</tr>
<tr>
<td></td>
<td>Hydrophilic cationic polymers (PDADMAC)</td>
<td>[146, 236]</td>
</tr>
<tr>
<td></td>
<td>Amphiphilic organosilane</td>
<td>[237]</td>
</tr>
<tr>
<td></td>
<td>Silylated polyethyleneimine</td>
<td>[238]</td>
</tr>
<tr>
<td>Soft-template</td>
<td>CTAB</td>
<td>[158, 159]</td>
</tr>
<tr>
<td></td>
<td>Pluronic F127</td>
<td>[157]</td>
</tr>
<tr>
<td></td>
<td>Diquatamary ammonium-type surfactant</td>
<td>[108, 239]</td>
</tr>
<tr>
<td></td>
<td>Dual-porogenic surfactant</td>
<td>[149]</td>
</tr>
</tbody>
</table>

Owing to its simplicity, the synthesis method had its advantages over those reported in the literature, which was either complicated or involved using costly templates as discussed in Chapter 2 Literature review [114, 146-148]. This study was published in *Industry & Engineering Chemistry Research, 2014* [128], and has been cited in a review paper titled “Innovations in Hierarchical Zeolite Synthesis”, in section 3.3. Template-free to appreciate the creation of mesopores without a second template [122].

By comparing the synthesis methods for nanocrystal and hierarchical ZSM-5 zeolites, as illustrated below:

NaAlO₂ + TPAOH \[\text{RT, 0.5 h}\] + TEOS \[
\xrightarrow{80^\circ C, 1 \text{ h}}
\xrightarrow{\text{RT, 20 h}}
\xrightarrow{180^\circ C, 48 \text{ h}}
\] Nanocrystal ZSM-5 zeolite

NaAlO₂ + TPAOH + H₂O \[\text{RT, 0.5 h}\] + TEOS \[
\xrightarrow{\text{RT, 20 h}}
\xrightarrow{180^\circ C, 48 \text{ h}}
\] Hierarchical ZSM-5 zeolite
It can be easily drawn that the two methods are very similar. The only difference in the
methods was an additional step of heating (80 °C, 1 h) for the synthesis of nanocrystal
ZSM-5 zeolite and extra use of H2O for the synthesis of hierarchical ZSM-5 zeolite, which
led to distinctively different characteristics of ZSM-5 zeolites.

8.3 Evaluation of Catalytic Performance in MTG

8.3.1 Catalytic performance of nanocrystal ZSM-5 zeolites

8.3.1.1 Effect of crystal size

The performances of the four ZSM-5 catalysts with various crystal sizes in MTG were
evaluated and compared. As discussed in Section 4.2.2, with decreasing crystal size from
30 to 0.1 µm, methanol conversion increased from 73.0% to 99.2%, gasoline yield
increased from 15.3% to 46.4%, and coke content decreased from 8.5% to 3.1%. Clearly,
a decrease in crystal size led to significant improvement in the performances of the
catalysts. This observation is in line with the literature [109, 180].

8.3.1.2 Effect of SiO2/Al2O3 ratio

From reviewing the literature, it has been identified that there was a lack of information
about the effect of SiO2/Al2O3 ratio on the performance of nanocrystal ZSM-5 zeolite in
MTG with respect to the catalyst development. The successful synthesis of the five
nanocrystal ZSM-5 zeolites with various SiO2/Al2O3 ratios has made such study possible
and thus fulfilled the gap. Here, the effect of the SiO2/Al2O3 ratio was an intrinsic effect
owing to the five catalysts were systematically controlled to have almost identical crystal
sizes and structural properties. A similar study has not been found in the literature owing
to the interplay between SiO2/Al2O3 ratio and crystal size. Instead, studies on this topic
in the past have been often performed by ignoring the effect of crystal size [110, 181, 182].

As discussed in Section 4.3.3, increasing the SiO$_2$/Al$_2$O$_3$ ratio facilitated a steady methanol conversion, and a progressive decrease in methanol conversion was found over catalysts with low SiO$_2$/Al$_2$O$_3$ ratios ($\leq$107) after 5 h on stream. Decreasing the SiO$_2$/Al$_2$O$_3$ ratio promoted C$_1$–C$_4$ selectivity and thus decreased gasoline yield. It was also found that decreasing the SiO$_2$/Al$_2$O$_3$ ratio promoted aromatisation reactions and hence higher durene selectivity and more coke formation, resulting in rapid catalyst deactivation.

Among the five catalysts with SiO$_2$/Al$_2$O$_3$ ratio from 23–411, the catalyst with SiO$_2$/Al$_2$O$_3$ ratio of 217 had the best overall performance. This ratio value was much higher than that obtained from the microcrystal catalyst which was in the range of 30–70, indicating high SiO$_2$/Al$_2$O$_3$ ratio is preferred when nanocrystal ZSM-5 zeolite was used. On the other hand, the data also showed increasing SiO$_2$/Al$_2$O$_3$ ratio to 411 compromised methanol conversion, 100% methanol conversion could not be achieved even from the very beginning of the reaction. This suggests a suitable range of SiO$_2$/Al$_2$O$_3$ ratio is needed to ensure the catalyst not only having a long lifespan but also high activity. Therefore, future work is required to give a more specified optimal range of SiO$_2$/Al$_2$O$_3$ ratio of using nanocrystal ZSM-5 zeolite in MTG.

8.3.1.3 Effect of reaction conditions

The review of literature also revealed there was little information on using nanocrystal ZSM-5 zeolite as a catalyst to investigate the effect of reaction conditions on its performance in MTG. We thus conducted this study and the results were discussed in Chapter 5. The performance of the nanocrystal ZSM-5 catalyst in MTG was evaluated
over a range of reaction conditions of temperature from 300 to 450 °C, pressure from 0.1 to 2.0 MPa and WHSV from 1 to 4 h⁻¹.

Temperature impacted greatly on catalytic performance. Increasing temperature facilitated high methanol conversion, a rapid decrease in methanol conversion occurred at temperatures <350°C. This was believed to be caused by the high amount of volatile species retained in the catalyst as determined by TGA. These volatile species would lead to rapid coverage of active sites and blockage of pore entrances, resulting in fast catalyst deactivation. An important effect of increasing temperature was a decrease in durene and an increase in the formation of C₁–C₄ and coke, resulted in a relatively low gasoline yield. The main effect of increasing pressure was a decrease in C₁–C₄ and an increase in durene. It was also found increasing pressure promoted coke formation leading to a decrease in methanol conversion. WHSV was observed to have a similar effect on catalyst performance as pressure.

It can be concluded from the study that the reaction conditions giving the best performance for nanocrystal ZSM-5 in MTG were: 375 °C, 1.0 MPa and WHSV of 2 h⁻¹. This set of conditions was in line with that applied to the commercial MTG plant in New Zealand, which were 350–370 °C, WHSV of 2 h⁻¹ [10, 20, 23]. Unfortunately, it was not able to derive a specific pressure for the commercial MTG plant.

8.3.2 Catalytic performance of hierarchical ZSM-5 zeolite

The catalytic performance of the hierarchical ZSM-5 zeolite in MTG was studied and compared with a microcrystal counterpart, as discussed in Chapter 7.

The hierarchical catalyst was confirmed to have better performance than the conventional catalyst. Under the same reaction conditions, the hierarchical ZSM-5 catalyst had 99.6%
methanol conversion and 58.9 % gasoline yield, while these were only 89.7% and 28.4% for the conventional catalyst. Moreover, the hierarchical ZSM-5 zeolite also showed high resistance to coke formation. TGA showed the hierarchical catalyst had 1.7 wt % coke content, which was more than four times less than that of the microcrystal catalyst.

On the other hand, by comparing the performance of the hierarchical ZSM-5 zeolite with that of the nanocrystal ZSM-5 zeolite with SiO$_2$/Al$_2$O$_3$ ratio of 107 discussed in Chapter 6, it can be found that the two catalysts showed very similar methanol conversion and coke formation over 24 h reaction time. However, the nanocrystal catalyst had higher gasoline yield than the hierarchical ZSM-5 zeolite. This could be understood by the higher C$_1$–C$_4$ selectivity of the hierarchical ZSM-5 zeolite.

Overall, the performance of the hierarchical ZSM-5 catalyst was comparable to those reported in the literature [109, 180, 240, 241]. This further evidences the successful development of the synthesis method for hierarchical ZSM-5 zeolite. The catalyst was not only easy to be obtained but also possessed high catalytic performance.

### 8.4 Coking and Catalyst Deactivation

An in-depth understanding towards coking in relation to catalyst deactivation was conducted in terms of coke formation and characteristics. The study demonstrated two different mechanisms of coke formation and deposition using catalysts only differed in crystal size, as discussed in Chapter 6.

It can be drawn from reviewing the literature that the superior performance of nanocrystal ZSM-5 catalyst over its microcrystal counterpart has been commonly accepted. However, many papers only claimed the improved performance as a result of reduced coke formation attributed to the reduction in crystal size, and this coke formation was mainly
studied based on the determination of bulk coke content. Given coking is the main cause for catalyst deactivation, coke formation and characteristics in relation to catalyst deactivation has not been clearly addressed. In addition, whether it is internal coke or external coke dominating catalyst deactivation is still a disputed topic in the literature [80, 85, 97, 101, 102, 242].

In this study, the nanocrystal catalyst also evidently showed better performance than the microcrystal catalyst, with seven times longer lifespan when methanol conversion for both catalysts decreased to 50%, whereas the former also had two times higher coke content than the later. This suggests coke content could not directly correlate to catalytic lifespan. An insight into coke formation and characteristics of the two catalysts gave a better understanding of their correlation.

Figure 8.1 Morphology changes for nanocrystal and microcrystal ZSM-5 catalysts before and after use: (a) and (b) for fresh and spent nanocrystal ZSM-5 catalyst; (c) and (d) for fresh and spent microcrystal ZSM-5 catalyst.
A reduction in crystal size was found to promote coke predominantly deposited on the external surface of the nanocrystal catalyst. The SEM and TEM images of the spent nanocrystal catalyst showed distinctively different morphologies compared to its pristine counterpart, with the crystals largely encapsulated by amorphous substances after use. These substances were determined to be carbon by HAADF STEM–EDS, and herein were external coke. However, the morphologies of the microcrystal catalyst before and after use remained virtually the same. Quantitative analysis of this coke deposition further revealed the amount of external coke for nanocrystal catalyst was ~1.5 times higher than that of the internal coke. In contrast, microcrystal ZSM-5 catalyst primarily formed internal coke.

It was also found the nanocrystal catalyst had the very slow formation of internal coke compared to the microcrystal catalyst. The two catalysts had a similar amount of internal coke at the time when methanol conversion decreased to 50%. However, the nanocrystal catalyst took 270 h to form such amount of internal coke, while the microcrystal catalyst took only 40 h. Clearly, the formation of internal coke in the nanocrystal catalyst was one order of magnitude slower than the microcrystal counterpart. As the majority of active sites are located in the micropore channels of ZSM-5 zeolite, the faster formation of internal coke, the quicker coverage of active sites and thus the more rapid deactivation of catalyst. This explained the rapid deactivation of microcrystal catalyst. Additionally, nitrogen physisorption revealed the external coke was a mesoporous material, indicating the formation of external coke was not detrimental to the activity of nanocrystal catalyst, as no severe diffusion limitation shall be imposed on the reactant and product.
The study confirmed that ZSM-5 catalyst was mainly deactivated by internal coke, and more pronounced in the catalyst with micronsized crystals. In addition, the formation of external coke had little impact on the activity of the catalyst. The coke formation and characteristics in relation to catalyst deactivation of two catalysts only differing in crystal size could be illustrated in Figure 8.2.

8.5 Practical Implications

In the present study, four ZSM-5 samples with similar SiO$_2$/Al$_2$O$_3$ ratios but different crystal sizes and five nanocrystal ZSM-5 samples with different SiO$_2$/Al$_2$O$_3$ ratios but almost identical crystal sizes and structural properties have been successfully synthesised. This achievement has shed a light to a successful control of crystal size and SiO$_2$/Al$_2$O$_3$ ratio for the synthesis of ZSM-5 zeolite, and researchers can easily follow the synthesis recipes discussed in this thesis to obtain ZSM-5 zeolites with various characteristics for their purposes. The concept of the synthesis methods can also be applied to synthesise zeolites with other framework structures.
The method developed for the synthesis of hierarchical ZSM-5 zeolite has successfully eliminated the use of a second template for the generation of mesopores. The drawback of this method was the use a certain amount of TPAOH as structure directing agent. Nevertheless, this recipe has led a forward step in pursuing low-cost synthesis of hierarchical ZSM-5 zeolite, and the strategy could also be used to synthesise different types of zeolites.

The performances of the nanocrystal and hierarchical ZSM-5 zeolites in MTG again confirmed the significant advantages of using such catalysts over conventional counterparts. A systematic investigation into the effect of SiO$_2$/Al$_2$O$_3$ ratio on the performance of nanocrystal ZSM-5 zeolite in MTG has fulfilled the gap in the literature and given a preferred SiO$_2$/Al$_2$O$_3$ ratio when using nanocrystal ZSM-5 zeolite (217), which was much higher than that for microcrystal ZSM-5 zeolite (30–70). This has important practical implications for the industry applications of the catalysts, as catalysts with high SiO$_2$/Al$_2$O$_3$ ratio can greatly prolong their catalytic lifespan. More importantly, an insight into coking of the two catalysts only deferred in crystal size has illustrated two different mechanisms of coke formation and deposition. This has given an in-depth understanding towards coke formation and characteristics in relation to catalyst deactivation, which has profound significance to future catalyst development in pursuing catalysts less prone to coking.
Chapter 9 Conclusions and Recommendations

9.1 Introduction

The chapter summarises the findings from this PhD thesis research into the synthesis of ZSM-5 zeolites and their catalytic performances in MTG. In addition, findings from studying the coke formation and characteristics in relation to catalyst deactivation are concluded. Moreover, recommendations for future work based on evaluating the results discussed in Chapter 8 are also proposed.

9.2 Conclusions

9.2.1 Effect of crystal size on performance of ZSM-5 zeolite in MTG

- Four ZSM-5 catalysts with similar SiO$_2$/Al$_2$O$_3$ ratios but different crystal sizes ranging from 0.1 to 30 µm were successfully synthesised.

- The crystal size of ZSM-5 played a vital role in determining its catalytic performance for methanol conversion, product distribution, and catalyst deactivation. The nanocrystal ZSM-5 sample possessed the best catalytic activity and least coke formation within the reaction time studied.

- The high BET surface area and short diffusion paths as a result of the nanosized crystals provided reactant molecules with easy access to the active sites located in the micropores of the catalyst and, more importantly, increased chances for the larger product molecules to exit the pores, reducing possibilities of coke formation.
9.2.2 Effect of SiO$_2$/Al$_2$O$_3$ ratio on performance of nanocrystal ZSM-5 zeolite in MTG

- Five nanocrystal ZSM-5 samples with different SiO$_2$/Al$_2$O$_3$ ratios ranging from 23 to 411 but of similar crystal sizes and structural properties were successfully synthesised. It thus made possible for the investigation into the intrinsic effect of SiO$_2$/Al$_2$O$_3$ ratio on the catalytic performance of nanocrystal ZSM-5 zeolite in MTG.
- It was shown that decreasing SiO$_2$/Al$_2$O$_3$ ratio facilitated higher methanol conversion whereas the catalyst activity was better sustained with increasing SiO$_2$/Al$_2$O$_3$ ratio. C$_2$–C$_4$ alkenes decreased and C$_1$–C$_4$ alkanes increased with decreasing SiO$_2$/Al$_2$O$_3$ ratio, leading to an increase in the overall C$_1$–C$_4$ selectivity and thus low gasoline yield.
- Decreasing SiO$_2$/Al$_2$O$_3$ ratio also promoted aromatisation reaction, thus high durene selectivity and coke formation, leading to rapid catalyst deactivation.
- The nanocrystal catalyst with a moderate SiO$_2$/Al$_2$O$_3$ ratio of 217 showed a sustained 100% methanol conversion, high gasoline yield and low coke formation under the reaction conditions studied. By using nanocrystal ZSM-5 catalyst in MTG, the preferred SiO$_2$/Al$_2$O$_3$ ratio is much higher than that for the microcrystal counterparts.

9.2.3 Effect of reaction conditions on performance of nanocrystal ZSM-5 zeolite in MTG

- Temperature played a very important role in determining the catalyst performance. Increasing temperature facilitated a more sustained high methanol conversion but also promoted the formation of hard coke. However, in contrast to hard coke, the volatile species increased with decreasing temperature and was found to be more detrimental to the catalyst activity, a rapid decrease in methanol conversion was observed at lower temperatures (<350 °C).
It was also found increasing temperature caused an increase in C₁–C₄ selectivity, resulted in a decrease in gasoline yield.

Increasing pressure led to a decrease in methanol conversion with time on stream and coke formation, sustained methanol conversion was observed at low pressure (0.1 MPa). Increasing pressure was also found to promote the formation of durene but decrease C₁–C₄ selectivity.

The effect of WHSV was found to be similar to the effect of pressure; increasing WHSV caused a decrease in methanol conversion. The formation of durene and coke increased with increasing WHSV while C₁–C₄ decreased.

9.2.4 Relating coke formation and characteristics to catalyst deactivation

The study demonstrated two coke formation and deposition mechanisms and the relationship between the coke formation and characteristics and catalyst deactivation in ZSM-5 zeolite catalysed MTG reaction.

The nanocrystal ZSM-5 catalyst (crystal size of ~ 100 nm) was shown to have more than doubled coke content but surprisingly sustained a catalytic lifespan seven times longer than its microcrystal counterpart (~ 13 µm). The total amount of coke thus could not be simply indicative of the catalyst lifespan.

It was revealed that the formation rate of internal coke directly determined the catalytic lifespan while the formation of external coke had little impact on the catalyst performance. The improved lifespan of the nanocrystal ZSM-5 catalyst was attributed to the slow accumulation of internal coke as a result of the short diffusion paths, which allowed coke precursors to readily migrate to the outer surface to dispose or form external coke. The external coke found mainly on the surface of nanocrystal catalyst was porous and thus less detrimental to the catalyst activity.
9.2.5 Direct synthesis of hierarchical ZSM-5 zeolite and its performance in MTG

- Hierarchical ZSM-5 zeolite has been successfully synthesised using a simple method without the need of using an additional template for creating mesopores.
- The hierarchical zeolite particles consisted of well aligned nanosized primary crystals with mesopores created in the inter-primary crystal spaces. The primary crystals were single crystals with high crystallinity and their intrinsic microporous properties were well preserved.
- The hierarchical ZSM-5 zeolite exhibited not only high methanol conversion and selectivity towards the gasoline range hydrocarbons but also high resistance to coke formation, suggesting the zeolite had great catalytic performance.

9.3 Recommendations for future work

The overall objectives of the present research have been achieved. Following the evaluation of the findings, new gaps have also been identified, leading to the following recommendations for the future research.

- The study on investigating the effect of SiO$_2$/Al$_2$O$_3$ ratio on catalytic performance of nanocystal ZSM-5 zeolite in MTG revealed the one with SiO$_2$/Al$_2$O$_3$ ratio of 271 showed the best overall catalytic performance. In addition, the catalyst with SiO$_2$/Al$_2$O$_3$ ratio of 47 showed catalytic lifespan of 270 h based on methanol conversion decreased to 50%. It would be also interesting to know the catalytic lifespan of the catalyst with SiO$_2$/Al$_2$O$_3$ ratio of 271, which is expected to be much longer than 270 h.
- Although the catalyst with SiO$_2$/Al$_2$O$_3$ ratio of 271 (between 107 and 411) showed the best overall catalytic performance, this ratio may not be the optimal one. It is necessary
to conduct more experimental work that should lead to a more specifically optimal 
SiO$_2$/Al$_2$O$_3$ ratio range.

- Following the investigation into the effect of SiO$_2$/Al$_2$O$_3$ ratio on the performance of 
nanocrystal ZSM-5 zeolite, similar study should be conducted using hierarchical ZSM-5 
zeolite. This should also give a preferred SiO$_2$/Al$_2$O$_3$ ratio for hierarchical ZSM-5 
zeolite.

- A relatively simple method for the synthesis of hierarchical ZSM-5 zeolite has been 
successfully developed. However, the mesopore size is in a wide range of 10–90 nm. 
Fine-tuning the synthesis method to have a uniform pore size distribution might be 
interesting. Moreover, the method could also be applied for the synthesis of 
hierarchical zeolites with other framework structures.
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