Cobalt Catalysts Supported on Mesoporous Alumina for Fischer-Tropsch Synthesis

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of

The University of Western Australia

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made. This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signature: ………………………

Date: ……………………………
To My Beloved Family
Fischer-Tropsch (FT) synthesis is a well-known technology that enables the conversion of syngas, a mixture of CO and H₂, into liquid hydrocarbon fuels and chemicals. The FT derived fuels are of high quality, being almost free of sulphur, nitrogen, aromatics. However, owing to the sequential chain-growth mechanism, the hydrocarbon distribution of the FT synthesis product is usually very broad and it is extremely daunting to obtain hydrocarbon fractions with a specific carbon-chain range such as gasoline (C₅-C₉) or diesel (C₁₀-C₂₀). The present study was focused on the use of Zr- and Ce-modified mesoporous alumina (MA) supported Co catalysts for the production of diesel. In particular, it was intended to establish correlations between the product selectivity when varying the catalyst properties and the effect of process parameters, such as temperature, pressure, and space velocity.

The specific objectives of this research included a study into a new preparation method of Zr- and Ce-modified mesoporous alumina supports, an investigation into the influence of the promoter amount on the properties of the MA supported Co catalysts, and their catalytic performance in the FT synthesis, as well as a systematic evaluation of the effect of process conditions (temperature, pressure and space velocity) on the performance of these catalysts in terms of CO conversion and diesel selectivity. To achieve these objectives, two series of Zr- and Ce-modified MA supports were firstly synthesised using an isomorphic substitution and a post-impregnation methods. Co was then deposited onto these supports to generate Zr- and Ce-modified MA supported Co catalysts. Their properties were analysed using different techniques, including N₂ adsorption–desorption, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Finally, they were subjected to the evaluation of catalytic performance in the FT synthesis under different process parameters.

The study of the Zr-modified MA supported Co catalysts showed that the catalyst with 5% Zr content (10Co/5ZrMA-(s)) exhibited the highest CO conversion (38.9%) and diesel selectivity (34.6%) as well as the lowest methane selectivity (7.7%). The introduction of Zr was shown to inhibit the strong interaction of Co species with the alumina supports and improve the reducibility of Co oxides. Besides, the MA supported Co catalysts generally showed better catalytic performance than the non-mesoporous commercial alumina supported counterpart. It was also found that the Zr promoted
catalysts prepared by the isomorphic substitution method were superior over the ones prepared by the post-impregnation method in terms of catalytic performance. Meanwhile, the key process parameters including temperature, pressure, space velocity and feed composition were demonstrated to have marked effects on the catalytic performance of the as-prepared catalysts.

The investigation into the Ce-modified MA supported Co catalysts revealed that the catalyst with 2% Ce content (10Co/2CeMA-(s)) showed the best performance in the FT synthesis in terms of activity and product selectivity. By modifying the catalysts with Ce, Co dispersion on the catalysts was improved whereas the reduction of Co species was decreased. It proved, once again, the superiority of the isomorphic substitution method over the post-impregnation method as the catalysts prepared by the former showed higher catalytic activity and diesel selectivity but lower methane selectivity than the ones prepared by the latter. In addition, the catalyst 10Co/2CeMA-(s) achieved the lowest methane selectivity and highest diesel selectivity under the process condition of T = 503 K, P = 3.0 MPa, GHSV = 3.0 NL g⁻¹ h⁻¹, and H₂/CO ratio = 1.2.

The outcomes of the present research have invaluable implications in the development and deployment of these MA supported Co catalysts in the FT synthesis. The understanding of promoting mechanism was enhanced and the effects of process conditions and preparation methods on the performance of catalysts were better known. This thesis provides strong confidence in the use of this catalyst system and also a scientific base to modify the current catalysts.
ACKNOWLEDGEMENT

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<thead>
<tr>
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<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>ASF</td>
<td>Anderson–Schulz–Flory</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett–Joyner–Halenda</td>
</tr>
<tr>
<td>Ce</td>
<td>Cerium</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>Com-A</td>
<td>Commercial alumina</td>
</tr>
<tr>
<td>con.</td>
<td>Conversion</td>
</tr>
<tr>
<td>Fe</td>
<td>Iron</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>FT</td>
<td>Fischer-Tropsch</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatograph</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>IS</td>
<td>Isomorphous substitution</td>
</tr>
<tr>
<td>MA</td>
<td>Mesoporous alumina</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>PSD</td>
<td>Pore size distribution</td>
</tr>
<tr>
<td>Ru</td>
<td>Ruthenium</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>WGS</td>
<td>Water-gas-shift</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Zr</td>
<td>Zirconium</td>
</tr>
</tbody>
</table>
Chapter 1 Introduction

1.1 Research Background and Motivation

Currently the volatility in oil price and dwindling petroleum reserves together with the rapidly growing global demand for liquid transport fuels have stimulated the utilisation of non-crude-oil carbon resources such as coal, natural gas, shale gas, as well as biological resources (such as biomass) for the production of liquid fuels and chemicals. However, it is still extremely daunting to achieve direct conversion of these alternative feedstocks into specific liquid fuel products or value-added chemicals. One of the most technically feasible ways for such transformation is to first produce synthesis gas (or syngas, CO + H$_2$) by gasification, and then convert the syngas into synthetic fuels or building-block chemicals (Figure 1-1) [1]. Generally, two types of products, namely hydrocarbons (e.g., gasoline, diesel and lower olefins) and oxygenates (e.g., methanol, ethanol and mixed higher alcohols), can be synthesised from the syngas contingent on the catalyst employed for the conversion process.

Figure 1-1 Conversion of non-petroleum carbon resources into liquid hydrocarbon fuels and chemicals via syngas (adapted from Ref. [1])

The transformation of syngas to hydrocarbons over metallic catalysts is the renowned Fischer-Tropsch synthesis (FT synthesis or FT), which was first reported by Franz Fischer and Hans Tropsch in 1923 [2]. The FT products can be either liquid fuels, like gasoline and diesel, or building-block chemicals such as light olefins. The syngas-based (or FT) diesel, which is largely n-alkanes of chain length 10–20 carbons, has superior merits over conventional petroleum-derived diesel, comprised of about 75% saturated hydrocarbons and 25% aromatic hydrocarbons. Firstly, FT fuels are of premium quality, being virtually free of sulphur, nitrogen, aromatics, and other contaminants typically found in petroleum-based products, thus making it more environmentally benign and can easily meet the increasingly stringent environmental requirements. Secondly, the Cetane number of an FT diesel is as high as 70-75, much higher than the market requirement of 45, and hence is conducive to reduce particulate emissions from
combustion in diesel engines. These combined features make the FT diesel deemed to be an ideal liquid automotive fuel [3].

Due to the sequential chain-growth mechanism involved in FT process [4], it is extremely difficult to obtain paraffin fractions with a specific carbon-chain range. FT products are always mixtures of a wide range, from light to very heavy, of hydrocarbons and some oxygenates, including light gases, naphtha and jet and diesel fuel fractions. As a consequence of the broad product spectrum, FT syncrudes produced by conventional FT catalysts entail a further refining stage before high-quality liquid fuels, such as gasoline and diesel fuel, can be obtained [4]. Yet, with respect to the conventional two-stage process, the direct generation of high-quality liquid fuels from syngas without refining stage would be more desirable in terms of energy consumption, capital and operating costs and could arguably give the FT technology a more competitive edge for hydrocarbon fuel production. Therefore, it is of paramount importance to develop novel selectivity-controllable FT catalysts, which can break the Anderson-Schulz-Flory (ASF) distribution law and tune the selectivity to target specific products, especially diesel.

Over the past decades, significant R&D efforts have been committed in this area but remaining barriers need to be overcome before the goal of direct production of clean fuels from syngas can be materialised [5].

In terms of the catalytic reaction of FT synthesis, most of the VIII group metals have appreciable activity in carbon monoxide hydrogenation but afford various products, such as hydrocarbons, acids and alcohols. Generally speaking, iron and cobalt metals are widely used as commercial FT catalysts for the long chain hydrocarbon production. Comparatively, the supported cobalt catalysts are particularly suitable for the FT synthesis in that they give high yield of long chain hydrocarbons, possess low activity for the water-gas-shift reaction and have relatively long active life time [3].

Recent reviews by Zhang et al [1, 6] identified that the utilisation of mesoporous materials with proper pore sizes can lead to middle distillate fuels with higher selectivity, compared to traditional non- or micro-porous counterparts. The pore size and structure (or texture), which can affect the reducibility and dispersion of active phase particles, the diffusions of reactants and products, as well as the probability of the secondary reactions, are among the key parameters influencing the product selectivity. Ohtsuka et al [7] reported an active Co/SBA-15 catalyst with a high selectivity of ca. 30% and high space time yields of 260-270 gC/kg catalyst/hr for C_{10}-C_{20} hydrocarbons as the main fraction of diesel fuel. Tang et al [8] further demonstrated that Co/SBA-15 catalysts exhibited higher C_{10}-C_{20} selectivity (ca. 40%) than the Co catalysts supported on other mesoporous materials or microporous materials. Liu et al [9] synthesised a series of mesoporous ZrO_2 samples with pore sizes ranging from 2.9 to 12.6 nm to support Co and applied them in FT synthesis. They found the catalyst with the largest pore size (12.6 nm)
could provide a high selectivity (ca. 32%) to the diesel fuel (C_{12–C_{18}}). Furthermore, Lesaint et al [10] discovered the C_{5+} selectivity was higher over the Co catalyst supported on mesoporous Al_{2}O_{3} with larger pores.

On the other hand, incorporation of promoters the catalysts has been verified as an effective way to modify the selectivity towards heavier hydrocarbons in the FT synthesis [xx]. Typical promoters employed with the Co-based catalysts are noble metals, transition metal oxides, such as ZrO_{2} and MnO_{x}, and some rare earth metal oxides (e.g. CeO_{2}) [1]. However, a traditional method for the incorporation of promoters is the post-synthesis wet impregnation, which usually results in uneven dispersion of the promoter species, greatly reducing surface area as well as with a non-uniform pore size distribution [11]. Recently, the one-pot synthesis of promoter modified FT catalysts through isomorphic substitution has shown a great superiority in circumventing these shortcomings, especially among the mesoporous silica supports [12]. However, so far there has been no report about the one-pot synthesis of promoter element modified mesoporous alumina and its application in FT process.

In this thesis work, the application of zirconium and cerium modified mesoporous alumina supported Co catalysts for the FT synthesis was explored for this purpose.

1.2 Overall Aims and Structure of the Thesis

The present study was aimed to increase the performance of supported Co catalyst in FT synthesis so as to achieve higher hydrocarbon selectivity in the range of diesel (C_{10–C_{20}}). Efforts were also committed to understanding the key process parameters affecting the diesel selectivity.

The thesis is composed of seven chapters. Each chapter involves its own aims and roles which are outlined below and also illustrated in the form of a Thesis Map as displayed in Figure 1-2.

Chapter 2 reviews the literature to establish the current status of knowledge, learn about the research methodologies and techniques from the literature and identify the specific research objectives. This Chapter starts with an overview of the fundamentals of the Fischer-Tropsch synthesis, which serves as a theoretical foundation for the development of highly selective FT catalysts. Then we discuss the challenge in the FT sphere and examine the recent research trends, especially with respect to the production of diesel-range oil, to identify the gaps for improvements – the leeway for further research and development. Chapter 3 depicts the research methodology, experimental set-up, and approach, analytical techniques, product analysis as well as data processing used in this thesis.
Chapter 4 studies the catalytic performance of zirconium-modified mesoporous alumina supported Co catalysts in the FT synthesis and the influence of different process parameters, including reaction temperature, pressure, space velocity, ratio of H₂/CO, on the activity and selectivity. Chapter 5 investigates the catalytic performance of cerium-modified mesoporous alumina supported Co catalysts in the FT synthesis as well as the effect of various process parameters on the activity and selectivity.

Chapter 6 gives a critical and objective evaluation of the results and findings from the present research, which naturally and logically leads to the final Chapter 7 that summaries the conclusions from this study and make recommendations for future research.
Chapter 1: Introduction
- Define the background and scope
- Establish the overall aims
- Thesis outline and structure

Chapter 2: Literature Review
- Review the current knowledge of FT catalysts for diesel production
- Identify knowledge gaps in the literature
- Establish the specific objectives of the thesis work
- Propose the research methodology, approach and techniques

Chapter 3: Methodology and Experimental Techniques
- Experimental set-up and procedure
- Catalyst preparation characterisation (XRD, TEM etc.)
- Catalytic activity screening and testing
- Products analysis (GC)
- Data analysis

Chapter 4: Zr-modified mesoporous alumina based Co catalysts
- Preparation, characterisation and testing of Zr-modified mesoporous alumina based Co catalysts with different Zr loadings
- Optimisation of operating parameters to achieve the optimal diesel selectivity, catalytic activity and stability
- Data analysis and error analysis

Chapter 5: Ce-modified mesoporous alumina based Co catalysts
- Preparation, characterisation and testing of Ce-modified mesoporous alumina based Co catalysts with different Ce loadings
- Optimisation of operating parameters to achieve the optimal diesel selectivity, catalytic activity and stability
- Data analysis and error analysis

Chapter 6: Evaluation and Practical Implications
- Evaluate the findings against the specific objectives, literature data and practical implications
- Identify new and significant findings
- Identify new gaps

Chapter 7: Conclusions and Recommendations
- Summarize new, significant findings as conclusions of the thesis work
- Make recommendations for future work based on new gaps

Figure 1-2 Thesis structure
1.3 References


Chapter 2 Literature Review

2.1 Introduction

Studies of highly selective Fischer-Tropsch (FT) catalysts for the production of the diesel range hydrocarbons require an understanding of the fundamentals of the FT synthesis and key factors affecting the selectivity of the FT catalysts. This chapter reviews various kinds of FT catalysts developed to improve the selectivity for the diesel range hydrocarbons with an emphasis on Co based catalysts.

This chapter provides an overview of the fundamentals of the FT synthesis, including an analysis of the types of typical catalysts studied, their performance and limitations. Next, FT catalysts with high diesel selectivity are discussed, which includes a summary of the performance of three kinds of FT catalysts. This review then describes some key research gaps pertaining to the highly selective FT catalysts for diesel production, and the scope and specific objectives of this study.

2.2 Fundamentals of Fischer-Tropsch Synthesis

2.2.1 Background of Fischer-Tropsch Synthesis

2.2.1.1 Chemistry of Fischer-Tropsch Synthesis

The FT process was invented in 1923 by Franz Fischer and Hans Tropsch, two German coal researchers [1]. They described FT synthesis using the following two chemical equations:

\[(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O\]  \hspace{1cm} (2-1)

\[2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O\]  \hspace{1cm} (2-2)

In practice, the chemistry of the FT synthesis is more complex and numerous reactions occur. Table 2-1 shows the major reactions involved in FT synthesis [2]. A characteristic feature of FT synthesis is its high exothermicity. The formation of 1 mole of -CH₂- is concomitant with release of 165 kJmol⁻¹ of heat.

The primary products of FT synthesis are linear olefins with terminal double bonds (70-80 mol %) and linear paraffins. The highly desired products are C₅ to C₂₀ hydrocarbons (naphta C₅-C₁₁, diesel C₁₃-C₂₀ and wax > C₂₀). The process aims to produce an
olefin/paraffin ratio higher than 1 to enable the α-olefin readsorption steps. Although the water-gas-shift (WGS) is considered to be an undesirable reaction in FT synthesis, this side reaction can be useful for lean hydrogen syngas feed as the WGS reaction produces hydrogen at the same time it produces carbon dioxide. Other undesirable reactions in FT synthesis are catalyst oxidation and carbide compound formation. Both of these side reactions contribute to catalyst deactivation. For example, catalyst oxidation enhances sintering of the catalyst particle.

Table 2-1  Major reactions involved in the FT synthesis [2]

<table>
<thead>
<tr>
<th>Type of reaction</th>
<th>Chemical equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main reactions</strong></td>
<td></td>
</tr>
<tr>
<td>1) Paraffins</td>
<td>((2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O)</td>
</tr>
<tr>
<td>2) Olefins</td>
<td>(2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O)</td>
</tr>
<tr>
<td>3) Water gas shift reaction</td>
<td>(H_2O + CO_2 \leftrightarrow CO + H_2)</td>
</tr>
<tr>
<td><strong>Side reactions</strong></td>
<td></td>
</tr>
<tr>
<td>4) Alcohols</td>
<td>(2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n - 1)H_2O)</td>
</tr>
<tr>
<td>5) Boudouard reaction</td>
<td>(2CO \rightarrow CO_2 + C)</td>
</tr>
<tr>
<td>6) Catalyst oxidation/reduction</td>
<td>(a) M_xO_y + yH_2 \leftrightarrow yH_2O + xM)</td>
</tr>
<tr>
<td></td>
<td>(b) M_xO_y + yCO \leftrightarrow yCO_2 + xM)</td>
</tr>
<tr>
<td>7) Bulk carbide formation</td>
<td>(xM + yC \leftrightarrow M_xC_y)</td>
</tr>
</tbody>
</table>

2.2.1.2 Reaction Mechanism of Fischer-Tropsch Synthesis

Although the reaction mechanism of the FT synthesis is quite complicated, it is now widely believed that this synthesis proceeds via a surface-catalysed polymerisation mechanism (Figure 2-1) [3-5].

![Figure 2-1](image)

Figure 2-1  Schematic representation of the FT synthesis reaction mechanism
In brief, CO undergoes dissociative or hydrogen-assisted dissociative chemisorption on the surface of active metal phases, such as Ru, Co, or Fe metal, or metal carbide nanoparticles. This forms CH$_x$ ($x = 0–3$) intermediates which act as monomers for polymerization. Coupling between CH$_x$ monomers leads to chain growth and provides C$_n$H$_{2n}$ intermediates. These C$_n$H$_{2n}$ intermediates can then undergo hydrogenation or dehydrogenation to yield olefins or paraffins as the final products.

### 2.2.1.3 Product Distribution in Fischer-Tropsch Synthesis

As a result of the aforementioned mechanism, the products of the FT synthesis typically follow the statistical Anderson–Schulz–Flory (ASF) law of distribution [6-8]. According to the ASF law, the molar fraction ($M_n$) of the hydrocarbon product with a carbon number of $n$ depends on the chain-growth probability ($\alpha$), which is a function of the rates of chain growth and chain termination, governed by the equation below:

$$M_n = (1 - \alpha)\alpha^n$$

This equation shows the product distribution is determined solely by the the value of $\alpha$. As shown in Figure 2-2, at low $\alpha$ values, lighter ($C_1–C_4$) hydrocarbons are expected with high selectivity. At high $\alpha$ values heavier ($C_{21+}$) hydrocarbons can be obtained with higher selectivity. However, the middle distillate products, which are usually the target products, do not have high selectivity. While the maximum selectivity for gasoline-range hydrocarbons ($C_5–C_{11}$) is approximately 45% ($\alpha = 0.76$), the maximum selectivity for diesel-range ($C_{12–C_{20}}$) hydrocarbons is only about 30% ($\alpha = 0.89$) [9].

![Figure 2-2](image)

Figure 2-2  Product selectivity in FT synthesis as a function of the chain growth probability ($\alpha$) (adapted from Ref. [9])
Due to their excellent CO or H₂ dissociation ability, all Group VIII metals display noticeable activity in the hydrogenation of CO to hydrocarbons. Of these active metals, Fe, Co and Ru are the most commonly used in the FT reaction [10-13]. A brief comparison of the characteristics of these three kinds of FT catalysts is given in Table 2-2. Among them, Ru possesses the highest intrinsic capacity for CO hydrogenation, and can render high molecular weight hydrocarbons at low temperature (<150 °C) and under higher partial pressures of water or other oxygenate-containing atmospheres [14, 15]. Ru is also capable of functioning efficiently in the absence of promoters, thus offering greater insight into the reaction mechanism. Yet, the high cost and limited availability of Ru retard its commercial application. In contrast, Fe and Co have been used in the industrialised FT synthesis [16, 17]. Relative to the cheaper Fe-based counterparts, Co-based catalysts exhibit higher activity and stability, higher selectivity to linear heavier hydrocarbons, and negligible effects of co-produced water [18-20]. However, Co FT catalysts can merely work under quite fixed reaction conditions to minimise CH₄ formation. Unlike Co-based catalysts, Fe FT catalysts are capable of operating at a broader range of temperatures, pressures as well as H₂/CO ratios without noticeably increasing CH₄ selectivity [21, 22]. Nonetheless, Fe catalysts are far more subject to the undesirable WGS reaction than their Co and Ru analogues, which results in low carbon utilisation [23].

The choice of a catalyst for FT synthesis depends on a number of factors such as the price of the active metal, the desired end products, and the carbon source for syngas production [24-26]. As Co catalysts have desirable stability, higher per pass conversion, and high linear hydrocarbon productivity, they represent the optimal choice for synthesis of long-chain hydrocarbons [27-29].

To increase exposure of the surface of the active phase, improve stability and mechanical strength, and facilitate mass and/or heat transfer, active metals are typically deposited onto porous supports as metal nanoparticles (NPs) rather than used directly in bulk phase [30]. A myriad of supports have been used for this purpose, including SiO₂, TiO₂, Al₂O₃, MgO, ZrO₂, activated carbon, carbon nanotubes, carbon fibres, zeolites, ordered mesoporous silicas, and ordered mesoporous carbons [31-42]. Of particular note are SiO₂ and Al₂O₃ which have been applied to industrial-scale FT processes.
Table 2-2  
Comparison of Fe, Co and Ru FT catalysts [19-21]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
</table>
| Ru       | • highest catalytic activity without the need of promotion  
          • low reaction temperature  
          • high resistance to deactivation  
          • low WGS reaction activity  
          • high selectivity to heavier paraffins | • High cost and limited supply |
| Fe       | • lowest prices and abundant reserves  
          • low methane selectivity  
          • flexibility in reaction pressure and temperature and as well as H₂/CO ratio (0.5–2.5) | • significant WGS reaction  
          • susceptibility to deactivation  
          • heavy reliance on promoters  
          • strong negative effect of co-produced water on the catalytic activity  
          • wide product spectrum, including olefins, aromatics, oxygenates and branched hydrocarbons |
| Co       | • moderate prices and availability  
          • not significant WGS reaction  
          • good resistance to deactivation  
          • insignificant effect of co-produced water on the catalytic activity  
          • high yields of linear long-chain hydrocarbons | • significant influence of reaction temperature and pressure on hydrocarbon selectivity  
          • relatively fixed H₂/CO ratio (~2)  
          • high levels of methane at high temperature |

2.2.1.5 Factors Influencing Product Selectivity in the Fischer-Tropsch Synthesis

Many factors can influence the catalytic behaviour of a FT catalyst, including the C₅⁺ selectivity. Some of major factors that can exert significant effects on product selectivity and CO conversion activity are shown in Figure 2-3.

In terms of the chemical state of the active phase, the current consensus is that metallic Ru and Co nanoparticles are the active phases for Ru- and Co-based catalysts. For Fe-based catalysts, the iron carbide phase is responsible for chain growth. For Ru- and Co-based catalysts, it is widely acknowledged that the preparation of catalysts containing
Ru\textsuperscript{0} or Co\textsuperscript{0} nanoparticles (with high reducibility and proper size) and keeping them in the metallic state during the reaction are very crucial for achieving a high C\textsubscript{5+} selectivity [43-45]. However, the strategy for how to prepare Fe-based catalysts with high C\textsubscript{5+} selectivity is far from clear [46]. This is due to the fact that the Fe-based catalysts undergo reconstruction at the initial reaction stage, and a mixture of various iron species (including Fe\textsubscript{3}O\textsubscript{4}, metallic Fe, and Fe carbides) are typically obtained at the steady state. Thus a large fraction of iron may not assist in the formation of C\textsubscript{5+} hydrocarbons and may even cause a reduction in the formation of these hydrocarbons.

![Figure 2-3](image-url)  

**Figure 2-3** Some major factors influencing product selectivity in the FT synthesis (artwork redrawn based on Ref. [1])

Apart from the chemical state, the size of the active phase is another crucial factor that determines the catalytic behaviour of FT catalysts, including C\textsubscript{5+} selectivity. A plethora of recent studies have established that the size of Ru\textsuperscript{0} and Co\textsuperscript{0} affects both the CO conversion activity and the product selectivity [47]. For many catalysts based on Co and Ru, the turnover frequency (TOF) for CO conversion and C\textsubscript{5+} selectivity increases with increasing particle size up to a critical point (6–10 nm, contingent on the catalyst and reaction conditions) after which there is no significant increase. Therefore, the preparation of catalysts containing larger Co or Ru particles favours C\textsubscript{5+} selectivity.

The choice of a proper support is also important for high FT performance (including C\textsubscript{5+} selectivity), and selection of a support that provides a balanced interaction between the
support and the active metal is particularly important. An interaction that is too weak may lead to a poor dispersion of the active metal, whereas an interaction that is too strong may cause a low degree of reduction of the active metal. Both are detrimental to the CO conversion activity and C$_{5+}$ selectivity [48].

**Table 2-3**  Effect of typical promoters on catalytic behaviour of Fe- and Co-based FT catalysts [48, 49]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Promoter</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-based</td>
<td>K$^+$ and alkali metal ions</td>
<td>increases the selectivity to C$_{5+}$ and the ratio of olefin to paraffin and decreases that to CH$_4$</td>
</tr>
<tr>
<td></td>
<td>Cu or Ru</td>
<td>increases the selectivity to C$_{5+}$ and reduces the carburisation of Fe species</td>
</tr>
<tr>
<td></td>
<td>MnO$_x$</td>
<td>enhances the dispersion of Fe species and the resistance to deactivation</td>
</tr>
<tr>
<td>Co-based</td>
<td>Noble metals like Ru, Pt, Re</td>
<td>increases selectivity to C$_{5+}$, and the reducibility and dispersion of Co and decreases selectivity to CH$_4$</td>
</tr>
<tr>
<td></td>
<td>MnO$_x$</td>
<td>increases the selectivity to C$_{5+}$ and the ratio of olefin to paraffin and decreases selectivity to CH$_4$</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$</td>
<td>increases the selectivity to C$_{5+}$, the Co reducibility and the olefin/paraffin ratio</td>
</tr>
<tr>
<td></td>
<td>Rare earth oxides such as La$_2$O$_3$ and CeO$_2$</td>
<td>increases the selectivity to C$_{5+}$ and the olefin/paraffin ratio</td>
</tr>
</tbody>
</table>

Besides, the size of the pores in the support is also a significant factor in FT catalytic behaviour. Pore size may affect the reducibility and the dispersion of active species, the diffusion of products and reactants, and the probability of secondary reactions through $\alpha$-olefin readsorption in a confined nanospace. These factors are all crucial in determining FT catalytic behaviour, especially product selectivity. Thus, elucidation of the effect of the pore size alone (such as the dimension of nanospaces inside which active metals are located) is quite difficult [49]. Many studies suggest that larger pore
sizes result in higher C$_{5+}$ selectivity as well as higher CO conversion activity. A few other studies suggest that there exits an optimum pore size.

Promoters also play a pivotal role in the FT synthesis, notably for Fe- and Co-based catalysts. The function of promoters is to enhance the activity or modify the selectivity and they achieve this in two ways - either by a structural effect that changes the structure of the active phase (such as the exposed crystalline plane or the dispersion of the active phase), or by an electronic effect, which modifies the electronic characters of the active phase through electron transfer or electronic interaction [50]. The effects of various promoters employed in Fe- and Co-based FT catalysts are summarised in Table 2-3.

**2.2.2 Challenges in the Fischer-Tropsch Synthesis**

Due to the escalating worldwide demand for liquid fuels and increasing environmental concerns, FT synthesis has received renewed interest in recent years. In addition to developments in the traditional gas-to-liquid (GTL) and coal-to-liquid (CTL) processes, the biomass-to-liquid (BTL) process using FT synthesis as the key technology has also been developed in the industrial realm recently [51]. Meanwhile, the development of new catalysts and novel reactor technologies has attracted substantial attention.

Yet, some challenges still exist in the development of catalysts for FT synthesis. From a fundamental perspective, the control of selectivity is one of the most formidable ones. Specifically, the development of new FT catalysts with high selectivity towards desired products, especially hydrocarbon fuels, remains a barrier yet to overcome. As mentioned before, the size and distribution of the hydrocarbon products of the reaction are generally governed by the ASF chain polymerization kinetics model [17]. Thus the hydrocarbon product distribution is quite wide for conventional FT catalysts, ranging from C$_1$ to C$_{80}$. As a result, FT syncrudes produced using conventional FT catalysts require a further refining stage before high-quality liquid fuels, such as gasoline and diesel fuel, can be produced. To obtain high selectivity of liquid fuels in the final products, it is essential to break the ASF distribution law, namely, to increase the selectivity for the C$_{5+}$ hydrocarbons while decreasing that for CH$_4$ and C$_2$–C$_4$ paraffins. Numerous recent studies have cast light on the understanding of the structure–performance relationships, which are beneficial for the rational design of efficient FT
catalysts with high C$_{5+}$ selectivity. However, it is still far from optimum and further work in this area is required.

### 2.2.3 Current Research and Development Trends

With respect to the conventional two-stage process (namely, FT synthesis followed by refining), the direct generation of high-quality liquid fuels from syngas without the refining stage would be more desirable. This would reduce energy consumption and operating costs and could give FT technology a more competitive edge for hydrocarbon fuel production. In particular, the transformation of small-scale, remote gas resources and scattered biomass resources without downstream hydro-treating processes under extreme process conditions would be of significant interest. The development of new FT catalysts with high selectivity for a specific range of hydrocarbons is the key to this one-stage process.

Among the syngas-based hydrocarbon fuels, FT diesel, which is largely n-alkanes of chain length 10-20 carbons, possesses superior advantages over conventional fossil-derived diesel, composed of about 75% saturated hydrocarbons (primarily paraffins including n-, iso-, and cyclo-paraffins) and 25% aromatic hydrocarbons (such as naphthalenes and alkylbenzenes). Firstly, the former is virtually contaminant (sulphur and nitrogen) free, thereby making it more environmentally benign and able to meet the increasingly stringent environmental regulations. Secondly, n-alkanes are much less prone to particulate formation upon combustion than are typical alicyclic and aromatic components in petroleum-based diesel and jet fuel. Moreover, n-alkanes in the C$_{10}$-C$_{20}$ range have far better diesel combustion quality as they have a relatively higher Cetane number (typically 70-75). These features, in combination with the fact that diesel engines are ~ 30% more efficient than gasoline engines, make the FT diesel deemed to be the ideal liquid automotive fuel. As a result, the development of FT catalysts for the selective production of diesel fuel is a strong focus in the current research of FT synthesis.

To increase the diesel selectivity, great efforts have been devoted to preparing catalysts with well-defined active phases, with new supports, or by optimising interactions between the support and the active phase [52, 53]. In terms of the choice of the active phase, Co is currently the focus of most studies, as it reportedly provides an optimum compromise between performance and cost for the synthesis of hydrocarbons from
syngas [54]. As for the support materials, interest in mesoporous materials are ever-increasing, as the nanopores of these supports can function as nanoreactors in which the readsorption of primary a-olefins can be enhanced and thus diesel selectivity can be increased [55]. Additionally, the addition of promoters has also been demonstrated to be an appealing and effective strategy to achieve higher diesel selectivity, as the promoter can modify the interaction between the support and the active phase and therefore the catalytic behaviour of the active phase [56].

2.3 Current Status of FT Catalysts for the Production of Diesel Range Hydrocarbons

Hitherto, the reports about direct conversion of syngas into diesel are not abundant. Only a paucity of FT catalysts based on Fe, Ru and Co with different supports and promoters have been designed, developed, synthesised and utilised for the FT process to break the ASF distribution law and tune the selectivity to diesel fuel (C$_{10}$–C$_{20}$).

2.3.1 Fe-based FT Catalysts

Wang et al [57] described the use of a zeolite faujasite support to determine the product distributions using supported Fe catalysts in the FT synthesis. To make a good comparison with other materials, the Fe catalysts were supported on microporous and mesoporous materials. Table 2-4 shows the FT product distributions over the Fe catalysts supported on various ordered microporous and mesoporous materials as well as SiO$_2$. As expected, most of these Fe-based catalysts showed low selectivity values of the C$_{10}$–C$_{20}$ hydrocarbons. But unexpectedly, the catalysts supported on MCM-41, MCM-48, Na-ZSM-5 and Na-BEA did not produce sufficient diesel range hydrocarbons. This study showed that using zeolite faujasite (NaX or NaY zeolite) as the support for Fe catalysts can significantly increase the C$_{10}$–C$_{20}$ hydrocarbon selectivity, in particular Li$^+$-exchanged zeolite Y (LiY) which can enhance the selectivity diesel range fuel to 26%.

Differences in the selectivity of these catalysts were explained in terms of catalyst structure. It is known that Na-ZSM-5 possesses a two-dimensional channel structure with cages at the crossing of the zigzag and the straight channels while the porous structure of zeolite mordenite can be viewed as a one-dimensional channel system with small pore diameters containing side pockets where a proportion of the ion-exchanged
cations are located. The channel system of both zeolites may restrict the diffusion of large and long-chain paraffin molecules. In contrast, zeolite beta (Fe/Na-BEA) possesses a three-dimensional channel structure with relatively larger pore diameters, but the Si/Al ratio of this zeolite is much higher than that of faujasite. This is undesirable as the lower acidity of the support is resulted and hence the re-adsorption of the intermediate olefines produced during the reaction and further chain growth would be suppressed. One distinct feature of faujasite (NaX and NaY) is its super-cage structure. The large voids are up to ca. 1.3 nm in diameter in the faujasite, with windows ca. 0.7 nm. It has been speculated that the peculiar structures might enhance the re-adsorption of reaction intermediates, increasing the probability of chain growth.

### Table 2-4 Catalystic performances of Fe catalysts for FT diesel production

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO conv.</th>
<th>CO₂</th>
<th>CH₄</th>
<th>C₂-C₄</th>
<th>C₅-C₉</th>
<th>C₁₀-C₂₀</th>
<th>C₂₁+</th>
<th>C₅+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/SiO₂&lt;sup&gt;a&lt;/sup&gt;</td>
<td>22.0</td>
<td>12.0</td>
<td>15.0</td>
<td>40.0</td>
<td>29.0</td>
<td>4.1</td>
<td>0.1</td>
<td>33.0</td>
</tr>
<tr>
<td>Fe/MCM-41&lt;sup&gt;a&lt;/sup&gt;</td>
<td>&lt;1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe/MCM-48&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.0</td>
<td>26.0</td>
<td>25.0</td>
<td>38.0</td>
<td>11.0</td>
<td>0</td>
<td>0</td>
<td>11.0</td>
</tr>
<tr>
<td>Fe/SBA-15&lt;sup&gt;a&lt;/sup&gt;</td>
<td>17.0</td>
<td>11.0</td>
<td>14.0</td>
<td>40.0</td>
<td>29.0</td>
<td>6.2</td>
<td>0.3</td>
<td>35.0</td>
</tr>
<tr>
<td>Fe/Na-ZSM-5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.0</td>
<td>19.0</td>
<td>14.0</td>
<td>48.0</td>
<td>19.0</td>
<td>0</td>
<td>0</td>
<td>19.0</td>
</tr>
<tr>
<td>Fe/Na-MOR&lt;sup&gt;a&lt;/sup&gt;</td>
<td>29.0</td>
<td>20.0</td>
<td>12.0</td>
<td>35.0</td>
<td>23.0</td>
<td>7.0</td>
<td>3.2</td>
<td>33</td>
</tr>
<tr>
<td>Fe/Na-BEA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5.8</td>
<td>24.0</td>
<td>16.0</td>
<td>46.0</td>
<td>14.0</td>
<td>0</td>
<td>0</td>
<td>14.0</td>
</tr>
<tr>
<td>Fe/NaX&lt;sup&gt;a&lt;/sup&gt;</td>
<td>48.0</td>
<td>30.0</td>
<td>5.6</td>
<td>18.0</td>
<td>24.0</td>
<td>18.0</td>
<td>5.1</td>
<td>47.0</td>
</tr>
<tr>
<td>Fe/NaY&lt;sup&gt;a&lt;/sup&gt;</td>
<td>49.0</td>
<td>21.0</td>
<td>7.8</td>
<td>23.0</td>
<td>23.0</td>
<td>17.0</td>
<td>8.9</td>
<td>48.0</td>
</tr>
<tr>
<td>Fe/LiY&lt;sup&gt;a&lt;/sup&gt;</td>
<td>40.0</td>
<td>8.6</td>
<td>6.7</td>
<td>16.0</td>
<td>27.0</td>
<td>26.0</td>
<td>16.0</td>
<td>69.0</td>
</tr>
<tr>
<td>Fe/Al₂O₃&lt;sup&gt;b&lt;/sup&gt;</td>
<td>21.9</td>
<td>27.0</td>
<td>11.2</td>
<td>14.3</td>
<td>48.1*</td>
<td>24.8#</td>
<td>1.6^</td>
<td>74.5</td>
</tr>
<tr>
<td>Fe-in-CNT&lt;sup&gt;c&lt;/sup&gt;</td>
<td>85.0</td>
<td>39.0</td>
<td>26.0</td>
<td>38.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>36.0</td>
</tr>
<tr>
<td>Fe-out-CNT&lt;sup&gt;c&lt;/sup&gt;</td>
<td>79.0</td>
<td>40.0</td>
<td>41.0</td>
<td>36.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>From Ref. [57]: 10 wt% Fe, T = 543 K, P = 2 MPa, H₂/CO = 2, GHSV = 3600 h⁻¹
<sup>b</sup>From Ref. [58]: 15 wt% Fe, T = 533 K, P = 1.5 MPa, H₂/CO = 0.67, GHSV = 1000 h⁻¹, * C₅–C₁₁, # C₁₁–C₁₉, ^ C₁₉
<sup>c</sup>From Ref. [59]: 12 wt% Fe, T = 543 K, P = 2 MPa, H₂/CO = 2, GHSV = 2000 cm³(STP)/(h·g), & data not available
<sup>d</sup>In percentage (%)
selectivity but an exceptionally high CO$_2$ and C$_2$–C$_4$ selectivity due to their vulnerability to the WGS reaction.

Clearly, it is still difficult for Fe FT catalysts to break the ASF law and achieve diesel selectivity higher than the theoretical value (35%). Thus Fe is not a desirable choice as the active metal for the design of catalysts with high diesel selectivity. Rather, it is more suitable for olefin production.

### 2.3.2 Ru-based FT Catalysts

Due to its exorbitant price and low availability, Ru is not an economically viable choice to be used directly as an active phase in a large scale. Thus, in most cases, Ru is used as a promoter while Ru based catalysts are typically used as model catalysts to provide fundamental insights into catalyst functioning and the reaction mechanisms. There are only a few, sporadic studies of Ru-based FT catalysts with controllable product distributions.

<table>
<thead>
<tr>
<th>Table 2-5</th>
<th>Catalytic performances of Ru catalysts for FT diesel production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst$^a$</td>
<td>CO conv. (%)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru/SiO$_2$</td>
<td>32.0</td>
</tr>
<tr>
<td>Ru/TiO$_2$</td>
<td>20.0</td>
</tr>
<tr>
<td>Ru/ZrO$_2$</td>
<td>22.0</td>
</tr>
<tr>
<td>Ru/MgO</td>
<td>3.0</td>
</tr>
<tr>
<td>Ru/NaY</td>
<td>23.0</td>
</tr>
<tr>
<td>Ru/HY</td>
<td>25.0</td>
</tr>
<tr>
<td>Ru/H-beta</td>
<td>24.0</td>
</tr>
<tr>
<td>Ru/AC</td>
<td>11.0</td>
</tr>
<tr>
<td>Ru/graphite</td>
<td>20.0</td>
</tr>
<tr>
<td>Ru/CNT</td>
<td>34.0</td>
</tr>
</tbody>
</table>

$^a$From Ref. [61]: H$_2$/CO =1:1, flow rate = 20 ml/min, P = 2.0 MPa, catalyst (0.50 g; 3.0 wt% Ru content), 533 K, and 10 h. AC: activated carbon; CNT: carbon nanotubes.

Recently, Xiong et al [60] compared the catalytic performances of Ru nanoparticles confined in the mesoporous channels of SBA-15 (Ru-in-SBA-15) and those located outside the mesopores of SBA-15 (Ru-out-SBA-15) They found that the confined Ru
nanoparticles exhibited significantly higher C\textsubscript{5+} (up to approximately 60%) and lower CH\textsubscript{4} selectivities than the Ru particles located outside the mesopores, although the confined Ru catalysts showed lower activity and higher CH\textsubscript{4} selectivity (over 20%). The authors of this study concluded that confinement of the Ru nanoparticles may have enhanced the repeated readsorption of \(\alpha\)-olefin intermediates, leading to the higher C\textsubscript{5+} selectivity.

Of particular interest is the study reported by Kang et al [61]. They carried out systematic investigations of Ru-catalysed FT synthesis using different supports. Table 2-5 summarises the catalytic performances of Ru catalysts on some typical supports for the conversion of syngas to hydrocarbons. In the cases where metal oxides were used as supports, the product distribution was typically wide, and C\textsubscript{1}–C\textsubscript{40} hydrocarbons were formed. Yet, they found that when CNTs were pretreated by nitric acid, the support could provide an outstanding selectivity to C\textsubscript{10}–C\textsubscript{20} hydrocarbons (60%), which is significantly higher than expected from the ASF distribution (maximum: 35 %). In comparison with the traditional SiO\textsubscript{2} support, the use of CNTs as a support for Ru nanoparticles considerably suppressed the selectivity to heavier hydrocarbons (C\textsubscript{21+}). The acid pretreatment for CNTs was found to be the key to obtaining high C\textsubscript{10}–C\textsubscript{20} selectivity; it led to the evolution of acidic functional groups, which may have catalysed the very mild hydrocracking of heavier hydrocarbons, thereby selectively producing diesel range hydrocarbons.

2.3.3 Co-based FT Catalysts

Co-based FT catalysts are particularly interesting from a commercial viewpoint due to their rather high activity (up to 60–70% CO conversion per single pass), selectivity and stability in the synthesis of linear hydrocarbons from CO/H\textsubscript{2} mixtures, resistance to attrition in slurry bubble column reactors and the relatively low negative effect of water on CO conversion.

Table 2-6 summarises the catalytic performances of Co on different supports as FT catalysts for diesel production. Notably, Co/ThO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} and Co/Ru/ThO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} prepared by Beuther et al [63, 64] provided a comparable C\textsubscript{9}–C\textsubscript{20} selectivity (62% and 57%, respectively) to the Ru/CNT catalyst of Kang et al [61]. The alumina support employed is either \(\gamma\)-alumina or \(\beta\)-alumina, or mixtures thereof, characterised as having low acidity, high surface area and high purity. It is believed that low acidity of the \(\gamma\)-
Al₂O₃ support used in the catalyst is required in order to enable the catalysts to produce high molecular weight hydrocarbon products in the diesel range through moderate hydro-cracking of the heavier wax produced. These high diesel selectivity cases suggest that the existence of moderate acidic sites on supports is crucial for high diesel selectivity.

In the meantime, different types of molecular sieves were utilised by Tang et al [62] as Co catalyst supports to study the effect of supports on the FT product distributions. They found zeolites favoured the production of C₅–C₉ hydrocarbons (gasoline fuel fraction) as a result of their relatively strong Brönsted acidity. Meanwhile, the mesoporous materials were also found to be promising for the production of C₁₀–C₂₀ hydrocarbons (diesel fraction) due to the space confinement effect of pores, which enhanced the re-adsorption of α-olefin intermediates produced during the reaction and the further moderate chain growth. Of the catalysts investigated, Co/beta and Co/SBA-15 exhibited the highest selectivities towards C₅–C₉ and C₁₀–C₂₀ hydrocarbons, respectively (Table 2-6).

Ohtsuka et al [65] also reported an active Co/SBA-15 catalyst where a good selectivity of ca. 30% and high space time yields of 260-270 gₜₜ/kgₜₜh for C₁₀–C₂₀ hydrocarbons as the main fraction of diesel fuel were achieved. These results indicate that compared to traditional non- or micro-porous counterparts, mesoporous materials, especially ordered ones, appear to be desirable FT catalyst supports in terms of tuning the selectivity towards diesel.

The size of mesopores also appear to have a strong effect on CO conversion and C₅⁺ selectivity, as shown by results of a study of Co/meso-ZrO₂ catalysts [66]. It can be seen from Table 2-6 that the catalyst with the largest pore size (12.6 nm) could provide the highest selectivity (ca. 32%) towards the diesel range hydrocarbons (C₁₂–C₁₈). Likewise, the C₅⁺ selectivity was higher over the Co catalyst supported on mesoporous Al₂O₃ with wider pores. This may be because the relatively larger pore size led to higher reducibility and larger metal particle size, resulting in higher C₅⁺ selectivity and higher CO conversion rates. Overall, key parameters influencing the product selectivity are (i) the pore size and structure (or texture), which may determine the reducibility and dispersion of metal particles, (ii) the diffusions of the reactants and products and (iii) the probability of the secondary reactions.
It is also worthwhile to point out that SiC may be also a promising support due to its higher thermal conductivity relative to traditional supports, which can favour fixed-bed heat dissipation and consequently temperature control. Osa et al. [67] demonstrated that a composition of 12.5 wt% Co with 2.0 wt% Ca promoter supported on SiC was optimum for diesel production, resulting in a 35.2% yield (Table 2-6).
From preceding discussion, it is evident that among the various catalysts investigated, the diesel selectivity was greatest for Ru, followed by Co and then Fe. Considering the price of these metals, Co-based catalysts are deemed to be the optimal choice for producing synthetic diesel fuels since they provide a good compromise between performance and cost.

Moreover, using solid-acid based bifunctional catalysts is known to be effective in tuning product distributions, particularly increasing selectivity to middle-distillate hydrocarbons, such as gasoline or diesel fuel. The bifunctional catalytic strategy is demonstrated in Figure 2-4. In short, the catalytic system consists of both the active metal (like Co and Ru nanoparticles) for the CO hydrogenation reaction (the primary reaction), over which heavier (C₅⁺) hydrocarbons can be produced, and the acid site for secondary reactions, including the hydrocracking and/or isomerization of heavier hydrocarbons to middle-distillate products. By manipulating the secondary reaction through altering the strength of acidity, high selectivity to C₅–C₁₁ (gasoline range) or C₁₀–C₂₀ (diesel range) hydrocarbons can be obtained.

![Figure 2-4](image)

**Figure 2-4** Schematic diagram of the bifunctional catalytic system strategy (adapted from Ref. [1])

### 2.4 Conclusions and Knowledge Gaps

Based on the aforementioned review of the vast volume of literature on the subject of FT synthesis and FT catalysts, the following conclusions can be drawn:

- FT synthesis is suitable for the diesel production but the development of catalysts with high diesel selectivity is still a formidable task. More efforts are needed in this sphere.
• Compared to Fe and Ru, Co based FT catalysts seem to be the optimal choice for higher hydrocarbon production as they provide a desirable compromise between performance and cost.

• The use of mesoporous materials is beneficial for the C\textsubscript{5+} selectivity owing to its space confinement effect of mesopores.

• The solid-acid based bifunctional catalyst system with moderate acidic sites on the support is an effective strategy to improve the FT diesel selectivity.

• \(\gamma\)-Alumina has been shown to be one of the best performing support candidates in terms of tuning the selectivity towards diesel fuels in the FT process because of its low acidity.

Since diesel range hydrocarbons are the target product of this work, Co based catalysts will be the focus of this thesis. Based on the idea of solid-acid based bifunctional catalysts, mesoporous alumina (MA) is proposed to be the support of choice. It features tunable mesoporosity in a wide range, high surface area, narrow pore size distributions, and therefore is expected to combine the benefits of mesoporosity and the acidic Al\(\textsubscript{2}\)O\(\textsubscript{3}\) support which are both favourable for the diesel selectivity. This support can also effectively circumvent the problems associated with traditional \(\gamma\)-Al\(\textsubscript{2}\)O\(\textsubscript{3}\) supported FT catalysts, such as low specific surface area (< 200 m\(^2\)/g), poorly controllable metal nanoparticles in terms of size and dispersion as well as ease of deactivation by pore plugging as a result of coke formation in disordered micropores. MA supported Ni and Co have been used in methane reforming reactions and presented exceptionally high activity and stability compared to traditional microporous \(\gamma\)-Al\(\textsubscript{2}\)O\(\textsubscript{3}\) supports. However, unlike its siliceous analogues, there has been little research directed towards the application of MA in the FT field, particularly MA modified by different promoters through in-situ sol-gel synthesis method, which has been proven to be superior to the conventional impregnation methods in terms of improving C\textsubscript{5+} selectivity.

2.5 Specific Objectives of the Present Research

The overall aim of the present study is to investigate the use of mesoporous alumina supported Co catalysts in the FT synthesis for diesel production. The specific objectives of this study are as follows:
• Develop a new method to synthesise Zr and Ce modified mesoporous alumina as a support.

• Evaluate the effect of promoter loading on the properties of the FT catalysts and their catalytic performance for the conversion of syngas to diesel range hydrocarbons.

• Explore the influence of reaction conditions (such as temperature, pressure and space velocity) on the performance of these catalysts in terms of diesel selectivity.

• Gain a better understanding of the catalysts using characterisation tests.
2.6 References


64. H. Beuther, C.L. Kibby, T.P. Kobylinski, R.B. Pannell, Catalyst for conversion of synthesis gas to diesel fuel and process for preparation of such catalyst, in, Google Patents, 1988.


Chapter 3 Methodology and Experimental Techniques

3.1 Introduction

In order to fulfil the research aims and objectives specified in Chapters 1 and 2, this thesis work utilised a series of complementary experimental and analytic techniques. This chapter outlines the research strategy and methodology and details the experimental procedures and the methods of data acquisition. The analytical techniques and data analysis used in this thesis work are described as well.

Section 3.2 introduces the experimental set-up and procedure used to obtain the original data of catalyst performance in the FT synthesis. Section 3.3 provides a detailed account of the catalyst preparation and characterisation techniques. These techniques qualitatively or quantitatively characterise the physical and chemical properties of the as-prepared catalysts. Section 3.4 describes the principles of product and data analysis which enables the comparison of performance of the various catalysts studied herein.

3.2 Experimental Set-up and Procedure

3.2.1 Experimental Set-up

The FT synthesis reaction was carried out in a single-pass, down-flow stainless-steel tubular fixed-bed reactor. A schematic of the experimental set-up is given in Figure 3-1. Syngas was supplied by a synthesis cylinder (BOC company) and its flow rate controlled by a mass flow controller (Brooks Instrument 5850, max. pressure: 100 bar). The syngas was preheated to the required experimental temperature in the reactor tube by means of an electric heater, which was regulated by a cascade temperature controller with one sliding thermocouple in the heater. This system allowed for an even temperature profile along the catalyst bed (±1 K). The reactor exit stream was allowed to pass through a trap containing ethyl acetate cooled with ice, in which liquid and solid hydrocarbon products were collected. The pressure of the reactor and the trap was controlled by a back pressure regulator (Swagelok 0–34.4 bar), which was placed next to the cool trap. The back pressure regulator reduced the pressure of the gaseous stream containing the gas phase products and unreacted feed to the atmospheric level. After that the gas stream was sampled and analysed online at a 2 h interval for composition. An Agilent 7890A gas chromatograph (GC) was used for this purpose. The liquid and
wax products collected in the cool trap were first added with CS$_2$ to ensure complete dissolution of the organic phase and then analysed for its chemical composition using another Agilent 7890A gas chromatograph equipped with one HP-5 column and an flame ionization detector (FID). Toluene was used as the GC internal standard for the quantification of the hydrocarbon products.

![Figure 3-1](image)

**Figure 3-1**  Schematic diagram of the experiment set-up with a fixed-bed reactor

### 3.2.2 Experimental Procedure

In a typical reaction run, ~ 0.4 g of a pelletized and sieved catalyst (pellet size ~1 mm) was loaded into the middle section of the vertically located quartz tube (with internal diameter of 10 mm and 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 of the furnace. Prior to the catalytic reaction experimentation the catalyst was reduced in situ at atmospheric pressure by increasing the temperature at a heating rate of 2 K/min up to 623 K and maintained at this temperature for 10 h while a flow of pure hydrogen (45 mL/min) was passed through the reactor. After this reduction step the temperature was lowered to 423 K under the flow of N$_2$ and then the reactant gas mixture (in a H$_2$:CO:Ar volume ratio of 6:3:1, Ar was also used as the internal standard) was introduced at a certain total flow rate (H$_2$/CO = 2), and the reactor pressure was slowly increased up to 20 bar. Then, the temperature in the catalyst bed was increased from 423–493 K at a controlled heating rate of 1 K/min in order to avoid instability of the system induced by the highly exothermic FT synthesis reaction. Once the reaction
A temperature of 493 K was achieved (TOS = 0), the reaction was allowed to proceed over a period of 20–24 h to ensure stabilisation of the catalyst activity.

3.3 Supports and Catalysts

This thesis work focused on the mesoporous alumina supported Co FT catalysts promoted with Zr and Ce, respectively. The mesoporous alumina supports were synthesised through a sol-gel self-assembly process in the presence of a soft template while the preparation of the catalyst following a classic wet impregnation procedure. Meanwhile, essential characterisations were also performed, which included nitrogen (N$_2$) adsorption–desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) techniques.

3.3.1 Support and Catalyst Preparation

Mesoporous alumina supports were synthesized via a sol-gel method [1]. The supports were composite metal oxides with a formula of $x$ mol% M–$y$ mol% AlO$_{3/2}$ (M refers to the added modifying metals (Zr, Ce), $x$ mol% = $\frac{nM}{nM + nAl} \times 100\%$, $x + y = 100$, denoted as MA-$x$M(100-$x$)Al in the following text). Typically, 36 mL (2 mol) of hot water (85 °C) was quickly added to 4.08 g (20 mmol) of aluminium isopropoxide in a reaction flask. The hydrolysis ratio, $h = [\text{H}_2\text{O}] / [\text{Al}]$ was 100. After 15 min of vigorous stirring, the white precipitate was peptized by adding 0.097 ml nitric acid (HNO$_3$, 70%, $[\text{HNO}_3]/[\text{Al}] = 0.07$) and the temperature of the flask was increased to 85 °C for 4 h to produce a transparent sol. The reaction flask was kept uncovered in the first 1 h to allow the evaporation of isopropanol formed during the hydrolysis. After 4 h, the promoter precursor (cerium nitrate hexahydrate or zirconium oxonitrate) and the Pluronic F127 template were then added to the sol and the mixture was gently stirred for 24 h at room temperature. The sol was then dried in air in an oven at 70 °C for 48 h to create the xerogel and was calcined in air at 700 °C for 3 h. The resulting MA sample was ground using a pestle and mortar into a fine powder.

The catalysts used in this thesis were supported cobalt catalysts with 10 wt% Co. The 10Co/MA-$x$M(100-$x$)Al catalysts were prepared by wetness impregnation to give a cobalt loading of 10 wt% [2]. 1.95 g cobalt nitrate (Co(NO$_3$)$_3$$\cdot$6H$_2$O) was dissolved in 10 ml of ethanol and stirred until a clear solution was obtained. A solution of cobalt salt was slowly added into 2 g of as-synthesised MA support powder and vigorously stirred
at room temperature until sample paste was formed. The sample paste was then dried at 110 °C overnight and calcined in air at 300 °C for 4 h, respectively. To make a comparison, commercial alumina obtained from Sigma-Aldrich was also used as a support to prepare a catalyst using the method described above.

### 3.3.2 Support and Catalyst Characterisation

To elucidate the difference in the catalytic performance between different as-prepared catalysts, several analytical techniques were employed in the thesis, including N₂ adsorption–desorption, powder X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). These techniques were used to characterise the catalysts for the following physical and chemical properties: surface area, pore volume and size, crystal phase, particle morphology, binding energy and reduction temperature. XRD, TEM were performed at the Centre for Microscopy, Characterisation and Analysis, UWA. XPS was conducted at Changchun Institute of Applied Chemistry of the Chinese Academy of Sciences. The other analyses were done in the Centre for Energy, UWA.

#### 3.3.2.1 N₂ Adsorption–Desorption

N₂ physisorption was employed to determine the surface-area determination and pore volume and pore size distribution (PSD) of the MA supports and calcined catalysts [3]. Prior to a measurement, the samples were degassed under vacuum at 200 °C overnight to remove moisture and other absorbed species. The N₂ adsorption-desorption isotherms were measured using a Tristar 3020 volumetric analyser (Micromeritics Co. Ltd). The specific surface area was calculated from the adsorption data using the Brumauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.30 [3]. The PSD was derived from desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) calculations. The pore volume \( V_p \) shows the BJH desorption cumulative volume of pores between 17 Å and 3000 Å. The average pore diameter \( D_a \) indicates the average pore diameter by BET while the diameter of pore size \( D_p \) was defined as the peak value of the PSD curve derived from desorption branch of the isotherm using the BJH calculation method.
3.3.2.2 Powder X-ray Diffraction (XRD)

To determine the crystal phase of as-prepared MA supports and the active phase of cobalt, a powder X-ray diffraction analyser (Empyrean, PANalytical, Cu-Kα radiation at 40 kV, 40 mA) was used to perform wide angle x-ray scattering (WAXS) from 10° to 80° [4]. Microscope glass slides were used as supports.

3.3.2.3 Transmission Electron Microscopy (TEM)

In order to ascertain the dispersion of active phases on the catalysts and their particle size, transmission electron micrographs (TEM) were obtained using a JEM-2100 JEOL electron microscope equipped with LaB6 filament and operating at 120 kV [5]. Samples were gently ground, dispersed in ethanol by moderate sonication and then deposited on a Cu grid (200 mesh).

3.3.2.4 X-ray Photoelectron Spectroscopy (XPS)

The surface composition of the catalysts was determined by X-ray photoelectron spectroscopy (XPS) using a Thermo ESCALAB 250 spectrometer with a monochromatised Al Kα source (1486.6 eV) at constant analyser pass energy of 20 eV [6]. The binding energy was estimated to be accurate within 0.1 eV. All binding energies (BEs) were corrected by reference to the C1s (284.6 eV) peak of the contamination carbon used as the internal standard. The Co2p binding energy of the core level was determined by computer fitting of the measured spectra. The pressure of the analysis chamber was maintained at $5 \times 10^{-10}$ mbar.

3.4 Product Analysis and Data Processing

This section describes the analysis of the composition of the FT products using GCs equipped with different columns and detectors. Meanwhile, how the catalytic performance data was obtained and processed using mass balance equations is also outlined in this section.

3.4.1 Product Analysis

The total product stream was split into two phases: an oil and wax phase from the high pressure cool trap), and a low pressure gaseous phase.
The gaseous phase was analysed for CO, H₂, N₂, CO₂, linear paraffins C₁–C₁₀, and α-olefins C₂–C₅ using an Agilent 7980A gas chromatograph (GC) [7]. The GC was equipped with two series of sampling loops and sample valves. Two samples were taken simultaneously and each was injected into a parallel column. The CH₄, H₂, CO, CO₂, and N₂ components were separated from the hydrocarbon products on a Hayesep T packed column (support: HayeSep T; support size: 80/100 mesh; length/OD: 1.5m×1/8”) and then further separated on a Hayesep Q packed column (support: HayeSep Q; support size: 80/100 mesh; length/OD: 1.5m×1/8”) and a Ms 5A capped column. The components were finally analysed using a TCD. At the same time the hydrocarbon products in the other sample loop were separated on a Gas Pro packed column (support: Porapak Q; support size: 80/100 mesh; length/OD: 2m×1/8”) and analysed using an FID. He (BOC 99.99%) was used as carrier gas for both detectors.

The initial temperature of the GC oven was maintained at 40 °C for 7 min, after which it was increased to 200 °C at the rate of 3 °C/min. Once it had reached 200 °C, this temperature was maintained for 31 min. The total online analysis time was 60 min. During this 60 min period, all the components of interest were eluted.

The analysis of the oil and wax products was carried out using an off-line Agilent 7980A GC with a HP-5 capillary column and an FID [8]. For the analysis of these condensed phases, a mass composition was directly obtained from the GC peak area percentages, as the mass response factors were ~ 1. Peak identification was performed using an injection of pure components. The initial temperature of the GC oven (30 °C) was maintained for 8 min, after which it was increased to 250 °C at the rate of 10 °C/min. Once it had reached 250 °C, this temperature was maintained for 40 min. The total online analysis time was 60 min.

3.4.2 Data Processing

The configuration of the experimental set-up used in this study (Figure 3-1) enabled the inlet volumetric flowrate to be set, from which the outlet flow rate was calculated [9]. Ar was used in the reactor feed as the internal standard. As it was an inert gas during the FT reaction, Ar was present only in the feed stream and in the reactor outlet gas stream. The Ar balance across the reactor was therefore expressed as:

\[ F_{\text{in}} \times X_{\text{Ar,in}} = F_{\text{out}} \times X_{\text{Ar,out}} \]  

(3-1)
where: $F_{\text{in}}$ = total molar flowrate [mol/min] of the reactor feed;

$F_{\text{out}}$ = total molar flowrate [mol/min] of the reactor outlet gas stream;

$X_{\text{Ar, in}}$ = molar fraction of argon in the reactor feed;

$X_{\text{Ar, out}}$ = molar fraction of argon in the reactor outlet gas stream.

The rate of CO conversion can be calculated as follows:

$$
\frac{F_{\text{CO, out}} - F_{\text{CO, in}}}{m_{\text{cat}}}
$$

where: $F_{\text{CO, in}}$ = total molar flowrate [mol/min] of CO in the reactor feed;

$F_{\text{CO, out}}$ = total molar flowrate [mol/min] of CO in the outlet gas stream;

$m_{\text{cat}}$ = mass [gram] of catalyst;

$r_{\text{CO}}$ = rate of CO conversion [mol/min/g$\text{cat}$].

Substituting expressions (3-3) and (3-4) into expression (3-2) and after expressing $F_{\text{in}}$ as a function of $F_{\text{out}}$ using equation (3-1), the rate of CO consumption was expressed as:

$$
\frac{F_{\text{out}} \times (X_{\text{CO, out}} - X_{\text{CO, in}} \times \frac{X_{\text{Ar, in}}}{X_{\text{Ar, out}}})}{m_{\text{cat}}}
$$

In this thesis work, Equation (3-6) as given below, was used to calculate the rate of CO conversion directly, as $X_{\text{CO, in}}$ and $X_{\text{Ar, in}}$ were known from the premixed gas composition in the cylinder and $X_{\text{CO, out}}$ and $X_{\text{Ar, out}}$ were derived from the reactor outlet gas analysis. $F_{\text{out}}$ was also calculated from the total gas volumetric flow rate at the reactor exit by assuming the ideal gas law.

The CO conversion was calculated as follows:
The rate of formation of a gas product \( \theta_i \) was calculated as follows:

\[
Y_{CO} = \frac{[X_{CO, in} - X_{CO, out} \times X_{Ar, out} \times X_{Ar, in}]}{X_{CO, in}}
\]  

(3-6)

The rate of formation of a gas product \( \theta_i \) was calculated as follows:

\[
r_{\theta_i} = \frac{F_{out} \times X_{\theta_i, in}}{m_{cat}}
\]  

(3-7)

where \( r_{\theta_i} \) is the rate in mole/min/g_cat and \( X_{\theta_i} \) the molar fraction of product \( \theta_i \) in the reactor outlet gas.

The carbon balance was checked as follows:

\[
[nC]_{gas, product} + [nC]_{liquid, product} + [nC]_{wax, product} = r_{CO} \times t \times m_{CO}
\]  

(3-8)

where \( nC \) represents the total number of moles of carbon contained in a product fraction (gas, liquid or wax) at the end of the mass balance period, \( t \).

The error in the carbon balance was calculated as:

\[
\text{error} = \frac{[r_{CO} \times t \times m_{CO} - [nC]_{gas, product} - [nC]_{liquid, product} - [nC]_{wax, product}]}{r_{CO} \times t \times m_{CO}}
\]  

(3-9)

The carbon balance was considered satisfactory when an error was < 5%.

The product selectivity was calculated on the moles of carbon basis, as follows:

\[
\text{Sel}(\theta) = \frac{[nC]_\theta}{r_{CO} \times t \times m_{CO}}
\]  

(3-10)

where \( \text{Sel}(\theta) \) represents the selectivity of product \( \theta \) and \( [nC]_\theta \) represents the number of moles of carbon contained in the product \( \theta \).

3.4.3 Error Analysis for Experimental Data

Since a large number of data in the thesis were experimentally obtained, imbedded uncertainties for each analysis have been tackled. Table 3-1 shows the errors in the experimental data and the number of samples corresponding to each analysis. In most cases, uncertainties are calculated using pooled standard deviations [9]. Note that the pooled standard deviation is the average spread of all data points about their group mean, not the overall mean. It is a weighted average of each data group's standard deviation. As such, the weighting gives a larger group a proportionally greater effect on the overall estimate. It is inappropriate to use the pooled standard deviation to compare the data and errors in different data groups.
Consider a series of analyses, and each series with \( B \) measurements. This yields to the data set \( x_{ij} \) with \( A \times B \) members, where \( i = 1, 2, \ldots B \) and \( j = 1, 2, \ldots A \). The mean of each series is defined by

\[
\bar{x}_j = \frac{1}{B} \sum_{i=1}^{B} x_{ij}
\]

where \( x_{ij} \) = single experimental data; 
\( \bar{x}_j \) = mean value for each series.

The pooled standard deviation of \( x \) is defined by

\[
SD_x = \sqrt{\frac{1}{A (B-1)} \sum_{j=1}^{A} \sum_{i=1}^{B} (x_{ij} - \bar{x}_j)^2}
\]

with degree of freedom, \( \nu = A \times (B - 1) \).

The Student t-values are found from the \( t_{(95\%, \nu)} \) distribution table for 95% of confidence interval and degree of freedom \( \nu \) [9]. For the present thesis, uncertainties are summarised in Table 3-1 in the form of \( \pm SD_x \cdot t_{(95\%, \nu)} \).

**Table 3-1**  The error of the experimental data

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Number of sample (A)</th>
<th>Number of analysis per sample (B)</th>
<th>Standard deviation (SD(_x))</th>
<th>Student ( t_{(95%, \nu)} )</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 ) physisorption (BET surface area)</td>
<td>25</td>
<td>2</td>
<td>3.5</td>
<td>2.04</td>
<td>( \pm 7 \text{ m}^2/\text{g} )</td>
</tr>
<tr>
<td>( \text{N}_2 ) physisorption (pore volume)</td>
<td>25</td>
<td>2</td>
<td>0.01</td>
<td>2.04</td>
<td>( \pm 0.02 \text{ cm}^3/\text{g} )</td>
</tr>
<tr>
<td>( \text{N}_2 ) physisorption (pore size)</td>
<td>25</td>
<td>2</td>
<td>0.15</td>
<td>2.04</td>
<td>( \pm 0.3 \text{ nm} )</td>
</tr>
<tr>
<td>XRD (diffraction degree)</td>
<td>25</td>
<td>2</td>
<td>0.25</td>
<td>1.97</td>
<td>( \pm 0.05^\circ )</td>
</tr>
<tr>
<td>TEM</td>
<td>14</td>
<td>6 images</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>XPS (BE of Co 2p level)</td>
<td>14</td>
<td>2</td>
<td>0.004</td>
<td>1.98</td>
<td>( \pm 0.02 \text{ eV} )</td>
</tr>
<tr>
<td>Activity (CO conversion rate)</td>
<td>38</td>
<td>3</td>
<td>2.5</td>
<td>2.01</td>
<td>( \pm 5% )</td>
</tr>
<tr>
<td>Hydrocarbon selectivities</td>
<td>38</td>
<td>3</td>
<td>1.1</td>
<td>2.01</td>
<td>( \pm 2% )</td>
</tr>
<tr>
<td>Mass balance for carbon</td>
<td>38</td>
<td>3</td>
<td>2.0</td>
<td>2.01</td>
<td>( \pm 4% )</td>
</tr>
</tbody>
</table>
3.5 References


Chapter 4 Zr-modified Mesoporous Alumina Supported Co Catalysts in Fischer-Tropsch Synthesis

4.1 Introduction

Fischer–Tropsch (FT) synthesis is an attractive process for the production of high-quality liquid fuels from syngas, which can be derived from the gasification and/or reforming of coal, biomass, and natural gas [1]. The cobalt based catalysts are very appealing for the FT synthesis, as they have high activity and high selectivity towards linear hydrocarbons, low activity for the water gas shift (WGS) reaction and acceptable prices [2]. An effective support for the Co catalysts in FT synthesis is alumina owing to its excellent texture, satisfactory Co dispersions and superb attrition resistance. Recently, mesoporous alumina (MA) has garnered considerable attention as a catalyst support with large surface area and porosity enabling the high dispersion of a great number of catalytically active species [3].

One major issue associated with the alumina supported Co catalysts, however, is that they show limited reducibility as a result of the strong interaction between the cobalt species and the alumina support. The reducibility of cobalt based catalysts can be enhanced to some degree by promotion with a metal or metal oxide such as Ru, Pt, ZrO₂ [4]. To date, a plethora of studies have revolved around zirconia as a promoter for the supported cobalt catalyst. Zr-promoted Co catalysts have been reported to enhance the catalytic activity and C₅⁺ selectivity for the FT synthesis compared with the nonpromoted counterparts. Ali et al. [5] studied Zr-promoted Co/SiO₂ catalysts and proposed that the promotion of Zr possibly formed an active interface with Co, which improved the activity by facilitating CO dissociation. Xiong et al. [6] reported that the Zr addition could increase the cobalt cluster size and inhibit the formation of CoAl₂O₄, thus improving the activity and C₅⁺ selectivity of Co/Al₂O₃ catalysts. Ma et al. [7] studied the effect of pore size of alumina support and found that Zr primarily enhanced Co dispersion for the wide pore catalysts while it chiefly improved Co reduction for the narrow pore catalysts.

The effect of different promoter incorporation methods on the catalytic performance in the FT synthesis reactions has also been systematically investigated. Liu et al. [8] studied the introduction of zirconium in SBA-15 using four methods, namely wet
impregnation, coprecipitation, isomorphic substitution (IS) and chemical grafting. They found that when IS was used to prepare zirconium modified SBA-15 as supports, the cobalt catalysts showed higher activity than the one prepared by incipient wetness impregnation, but lower activity than those prepared by grafting. Following this, Tao et al. [9] investigated a range of cobalt catalysts supported on the isomorphically Zr-substituted mesoporous SBA-15 with different Zr/Si ratios to elucidate the effect of Zr content. It was found that the catalyst with a Zr/Si ratio of 1/20 showed the best performance in terms of activity and C$_5$ selectivity. However, the incorporation of metal on MA supported cobalt catalysts for FT synthesis, especially by the superior IS method, has not been explored in depth.

In the present work, a series of Co/MA catalysts with isomorphically substituted zirconium were synthesised and characterised. Their catalytic performance during FT synthesis was tested in a fixed bed reactor. The effect of zirconium concentration on the structure of the mesoporous alumina supports was assessed along with the activity and selectivity of the cobalt catalysts. Besides, the catalyst with a Zr/(Zr + Al) atomic ratio of 5% was tested under different process conditions in order to optimise activity and selectivity.

### 4.2 Experimental

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td><strong>Table 4-1</strong></td>
<td>A list of the as-prepared supports and catalysts</td>
</tr>
<tr>
<td><strong>Support</strong></td>
<td><strong>Catalyst</strong></td>
</tr>
<tr>
<td>Commercial alumina (Com-A)</td>
<td>10Co/Com-A</td>
</tr>
<tr>
<td>Mesoporous alumina (MA)</td>
<td>10Co/MA</td>
</tr>
<tr>
<td>MA-1Zr99Al</td>
<td>10Co/1ZrMA-(i)</td>
</tr>
<tr>
<td>MA-2Zr98Al</td>
<td>10Co/2ZrMA-(s)</td>
</tr>
<tr>
<td>MA-5Zr95Al</td>
<td>10Co/5ZrMA-(s)</td>
</tr>
<tr>
<td>MA-10Zr90Al</td>
<td>10Co/10ZrMA-(s)</td>
</tr>
<tr>
<td>MA-15Zr85Al</td>
<td>10Co/15ZrMA-(s)</td>
</tr>
</tbody>
</table>

Using the method described in Chapter 3, six MA supports and eight catalysts were synthesised, as shown in Table 4-1. For simplicity, the commercial alumina and pure mesoporous alumina supports are denoted as Com-A and MA, respectively, while Zr
modified MA supports are denoted as MA-\(x\)Zr(100-\(x\))Al (\(x\) denotes the \(Zr/(Zr + Al)\) molar ratio). In these catalysts, 10Co represents 10 wt% Co content. Additionally, (i) indicates that Zr was added using the post-impregnation method while (s) indicates that Zr was introduced using the isomorphic substitution method.

### 4.3 Results and Discussion

#### 4.3.1 Characterisation

##### 4.3.1.1 \(N_2\) Adsorption–Desorption

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area(^a) (m(^2)/g)</th>
<th>Pore Volume (V_p)^(b) (cm(^3)/g)</th>
<th>Pore Diameter (D_p)^(c) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Com-Al</td>
<td>150.0</td>
<td>0.91</td>
<td>-</td>
</tr>
<tr>
<td>MA</td>
<td>268.9</td>
<td>1.48</td>
<td>13.3</td>
</tr>
<tr>
<td>MA-1Zr99Al</td>
<td>236.6</td>
<td>1.26</td>
<td>13.0</td>
</tr>
<tr>
<td>MA-2Zr98Al</td>
<td>220.2</td>
<td>1.15</td>
<td>12.4</td>
</tr>
<tr>
<td>MA-5Zr95Al</td>
<td>206.3</td>
<td>1.09</td>
<td>12.0</td>
</tr>
<tr>
<td>MA-10Zr90Al</td>
<td>193.4</td>
<td>1.02</td>
<td>11.4</td>
</tr>
<tr>
<td>MA-15Zr85Al</td>
<td>180.5</td>
<td>0.97</td>
<td>10.8</td>
</tr>
<tr>
<td>10Co/Com-A</td>
<td>80.1</td>
<td>0.72</td>
<td>-</td>
</tr>
<tr>
<td>10Co/MA</td>
<td>238.4</td>
<td>1.29</td>
<td>10.8</td>
</tr>
<tr>
<td>10Co/1ZrMA-(s)</td>
<td>220.6</td>
<td>1.17</td>
<td>10.3</td>
</tr>
<tr>
<td>10Co/2ZrMA-(s)</td>
<td>202.2</td>
<td>1.02</td>
<td>10.0</td>
</tr>
<tr>
<td>10Co/5ZrMA-(s)</td>
<td>193.3</td>
<td>0.93</td>
<td>10.1</td>
</tr>
<tr>
<td>10Co/5ZrMA-(i)</td>
<td>179.4</td>
<td>0.84</td>
<td>7.5</td>
</tr>
<tr>
<td>10Co/10ZrMA-(s)</td>
<td>173.2</td>
<td>0.82</td>
<td>7.4</td>
</tr>
<tr>
<td>10Co/15ZrMA-(s)</td>
<td>161.3</td>
<td>0.77</td>
<td>7.2</td>
</tr>
</tbody>
</table>

\(^a\) BET surface area measured in the relative pressure range of 0.05–0.30
\(^b\) The BJH desorption cumulative volume of pores between 17 Å and 3000 Å width
\(^c\) The peak positions of the distribution curves by BJH
The $\text{N}_2$ adsorption–desorption isotherms of the supports are shown in Figure 4-1 (a). For the supports, except Com-A, the nitrogen adsorption–desorption isotherms were Type IV with an obvious H1 hysteresis loop at high relative pressure, which is typical of mesoporous materials [10, 11]. However, as the increase of the Zr/(Zr + Al) molar ratio increased, the isotherms became less regular, suggesting that the mesoporous structure of alumina was partially destroyed [12]. All the supports except Com-A also presented quite narrow pore size distributions (PSDs), with the centre of the curves falling in the mesopore range (2–50 nm) in Figure 4-1 (b). For Com-A, the BET surface
area, pore volume ($V_p$) and average pore diameter ($D_p$) was smaller than its mesoporous counterparts and these values decreased with increasing Zr/(Zr + Al) atomic ratio (Table 4-2). The BET surface area and pore volume decreased markedly when the Zr/(Zr + Al) atomic ratio was over 5%, indicating that the mesoporous structure was partially collapsed during the synthesis and subsequent calcination process due to the high content of Zr. Moreover, the pore size reduced gradually as the Zr/(Zr + Al) atomic ratio increased, this also suggests single ZrO$_2$ particles were formed outside the meso-structure blocking the mesoporous channels.

**Figure 4-2** Nitrogen adsorption–desorption isotherms (a) and BJH pore size distribution (b) of catalysts
The N₂ adsorption–desorption isotherms of the catalysts are shown in Figure 4-2 (a). Obviously, the isotherms of the MA supported catalysts still showed the H1 hysteresis loop, indicating they retained a mesoporous structure. But the isotherms were much less regular, suggesting the mesoporosity decreased as a result of the deposition of Co onto the surface of supports. This is in line with the results from Figure 4-2 (b), in which the PDS curves broadened after Co loading. As expected, the BET surface area, Vₚ and Dₚ of all the catalysts were smaller than the corresponding values of their supports (Table 4-2). The BET surface area, Vₚ and Dₚ of 10Co/5ZrAl-(s) were larger than those of 10Co/5ZrAl-(i), showing that the mesoporous structure of alumina was better preserved when the sample was prepared by isomorphic substitution.

4.3.1.2 Powder X-ray Diffraction (XRD)

The XRD patterns of the supports are shown in Figure 4-3 (a). All the supports showed a group of diffraction peaks, assigned to γ-alumina (JCPDS Card No. 10-0425). It is worthwhile to note that for supports with a Zr/(Zr + Al) atomic ratio lower than 5%, the characteristic peaks of zirconium compounds were not observed, suggesting that zirconium was well dispersed in the alumina matrix [13]. When the Zr/(Zr + Al) atomic ratio was higher than 5%, the characteristic peaks belonging to the tetragonal ZrO₂ phase were observed [14] and the peak intensity of the tetragonal ZrO₂ phase increased with the increase of Zr/(Zr + Al) ratio, indicating that isolated particles of tetragonal ZrO₂ appeared on the surface of the catalysts. This could explain the aforementioned decrease in the surface area and pore size as observed in Table 4-2.

The XRD patterns of the catalysts are shown in Figure 4-3 (b). The diffraction peaks at 45.6° and 66.6° were due to the alumina support, while other peaks were reasonably ascribed to the spinel phases of Co₃O₄ and the different crystal phases of Co₃O₄–Al₂O₃ species including CoAl₂O₄ [15]. Peaks for the tetragonal ZrO₂ phase were not observed, possibly because they were masked by other relatively strong peaks.
The transmission electron micrographs of the catalysts are shown in Figure 4-4. It can be seen that, different from the Com-A supported Co catalyst, all MA supported Co samples showed wormhole-like appearance of pores, with any obvious pore arrangements. There was no significant difference in morphology between the MA and Zr-modified MA supported catalysts. However, as the Zr/(Zr + Al) atomic ratio increased, the agglomeration of Co species became more pronounced.
Figure 4-4  TEM images of catalysts: 10Co/Com-A (a), 10Co/MA (b), 10Co/1ZrMA - (s) (c), 10Co/2ZrMA-(s) (d), 10Co/5ZrMA-(s) (e), 10Co/5ZrMA-(i) (f), 10Co/10ZrMA-(s) (g), 10Co/15ZrMA-(s) (h)
4.3.1.4 X-ray Photoelectron Spectroscopy (XPS)

XPS was used to investigate the surface composition of catalysts. The XPS data are shown in Table 4-3 and Figure 4-5. The 10Co/Com-A catalyst showed the highest binding energy (BE) for Co 2p_{3/2} (781.78 eV) while 10Co/5ZrMA-(s) had the lowest (780.42 eV). The Co 2p_{3/2} BEs of the MA supported catalysts noticeably decreased with increasing Zr/(Zr + Al) atomic ratio but remained in the region of 780.42 eV for 10Co/5ZrMA-(s) and 781.04 eV for 10Co/MA. This suggests that the main phase on the catalysts surface was Co_3O_4, in agreement with the XRD results. The BE for 10Co/Com-A was higher than that of pure Co_3O_4 (BE = 780.3 eV), indicating that the cobalt–alumina phase was formed on the catalyst surface. Similar results have been reported by Xiong et al. [6].

![XPS spectra of the Co 2p level for catalysts](image)

Figure 4-5  XPS spectra of the Co 2p level for catalysts

Notably, a feature in our XPS spectra of the Co 2p regions for catalysts was the shift to lower BE value of Co 2p_{3/2} by the introduction of zirconium, but still higher than that of pure Co_3O_4. It is well-known that metallic Co has the lowest BE of all cobalt chemical states [16]. The binding energies of the Co 2p_{3/2} electrons rise from Co^0 to Co^{2+} in a predictable fashion. Yet, Co_3O_4 possesses a lower BE than CoO. However, we observed that the Co 2p_{3/2} BE matched neither Co_3O_4 nor CoO, and with increasing Zr content the BE for Co 2p_{3/2} shifted to pure Co_3O_4. This suggests that the addition of Zr inhibited the formation of cobalt surface phase; therefore, the strong interaction between the cobalt species and the alumina support was possibly suppressed [6, 7]. For the catalysts that
had high Zr contents (10Co/10ZrMA-(s) and 10Co/15ZrMA-(s)) or were prepared by post-impregnation (10Co/5ZrMA-(i)), the Co 2p\textsubscript{3/2} peak shifted toward relatively higher energies, suggesting the interaction between cobalt species and supports had increased.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co 2p\textsubscript{3/2} BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Co/Com-A</td>
<td>781.45</td>
</tr>
<tr>
<td>10Co/MA</td>
<td>781.04</td>
</tr>
<tr>
<td>10Co/1ZrMA-(s)</td>
<td>780.97</td>
</tr>
<tr>
<td>10Co/2ZrMA-(s)</td>
<td>780.86</td>
</tr>
<tr>
<td>10Co/5ZrMA-(s)</td>
<td>780.52</td>
</tr>
<tr>
<td>10Co/5ZrMA-(i)</td>
<td>780.83</td>
</tr>
<tr>
<td>10Co/10ZrMA-(s)</td>
<td>780.66</td>
</tr>
<tr>
<td>10Co/15ZrMA-(s)</td>
<td>780.77</td>
</tr>
</tbody>
</table>

4.3.2 Fischer-Tropsch Synthesis

4.3.2.1 Effect of Zr promotion

The results of FT synthesis activity and product selectivity of the catalysts are summarised in Table 4-4. In terms of activity the following trends are obvious: (1) The CO conversion of 10Co/Com-A was the lowest among catalysts under the same conditions; (2) With the increase of Zr content from 0 to 5%, the CO conversion increased, but decreased with further increase in the Zr/(Zr + Al) ratio from 5% to 15%; (3) At the same Zr level, the CO conversion of the 10Co/5ZrMA-(s) prepared by isomorphic substitution was higher than that of 10Co/5ZrMA-(i) prepared by post-impregnation.

It has been proved that the catalytic activity of Co catalysts for FT synthesis depended on the reducibility [17]. In theory, the activity of reduced cobalt catalysts should be influenced by the concentration of surface metal cobalt sites [17]. In this study, when Zr\textsuperscript{4+} ions were introduced into the alumina framework of the MA supported Co catalysts, they retained relatively high surface area and large pore volume and hence the probability of Zr\textsuperscript{4+} ions contacting Co\textsubscript{3}O\textsubscript{4} particles was high. Furthermore, with increasing Zr content, the density of surface cobalt and the extent of reduction of Co increased, more accessible cobalt active surface sites were formed, and thus the CO
conversion increased. However, when the Zr/(Zr + Al) atomic ratio increased from 10% to 15%, the mesostructure was destroyed, giving rise to a decrease in surface area and pore volume as well as the formation of strong interaction of the cobalt species with the supports, therefore a decrease in the degree of reduction of cobalt. Thus, CO conversion fell. The low activity of 10Co/Com-A can be attributed to the lower surface area, pore volume and decrease in reducibility of the cobalt species in the catalysts. At the same content of Zr, 10Co/5ZrMA-(s) showed higher activity than 10Co/5ZrMA-(i), perhaps due to higher reducibility of cobalt species in the catalysts.

Regarding to product selectivity, 10Co/Com-A gave the highest methane selectivity and the lowest diesel (C_{10–C_{20}}) selectivity (Table 4-4). For MA supported catalysts, by the addition of Zr, methane selectivity decreased from 15.6% to 7.5%, and then increased to 13.7% while diesel selectivity increased from 29.5% to 34.6% and after that fell to 31.0%. When 10Co/5ZrMA-(s) and 10Co/5ZrMA-(i) are compared, the former showed lower methane selectivity and higher diesel selectivity than the latter.

Table 4-4 Performance of the as-synthesised catalysts in FT synthesis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO conv. (%) a</th>
<th>C_1</th>
<th>C_{2–C_{4}}</th>
<th>C_{5–C_{9}}</th>
<th>C_{10–C_{20}}</th>
<th>C_{21+}</th>
<th>α b</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Co/Com-A</td>
<td>20.4</td>
<td>25.2</td>
<td>23.5</td>
<td>22.3</td>
<td>23.6</td>
<td>5.4</td>
<td>0.67</td>
</tr>
<tr>
<td>10Co/MA</td>
<td>25.6</td>
<td>15.6</td>
<td>20.1</td>
<td>27.3</td>
<td>29.5</td>
<td>7.5</td>
<td>0.71</td>
</tr>
<tr>
<td>10Co/1ZrMA-(s)</td>
<td>27.5</td>
<td>11.6</td>
<td>18.1</td>
<td>29.4</td>
<td>32.3</td>
<td>8.6</td>
<td>0.75</td>
</tr>
<tr>
<td>10Co/2ZrMA-(s)</td>
<td>35.4</td>
<td>9.1</td>
<td>15.2</td>
<td>30.7</td>
<td>33.4</td>
<td>11.6</td>
<td>0.79</td>
</tr>
<tr>
<td>10Co/5ZrMA-(s)</td>
<td>38.9</td>
<td>7.7</td>
<td>11.0</td>
<td>31.7</td>
<td>34.6</td>
<td>15.0</td>
<td>0.80</td>
</tr>
<tr>
<td>10Co/5ZrMA-(i)</td>
<td>26.8</td>
<td>14.4</td>
<td>18.7</td>
<td>28.2</td>
<td>30.7</td>
<td>8.0</td>
<td>0.72</td>
</tr>
<tr>
<td>10Co/10ZrMA-(s)</td>
<td>29.7</td>
<td>10.3</td>
<td>16.1</td>
<td>30.1</td>
<td>32.8</td>
<td>10.7</td>
<td>0.74</td>
</tr>
<tr>
<td>10Co/15ZrMA-(s)</td>
<td>28.3</td>
<td>13.7</td>
<td>18.2</td>
<td>28.8</td>
<td>31.0</td>
<td>8.3</td>
<td>0.78</td>
</tr>
</tbody>
</table>

a Reaction conditions: 493 K, 2 MPa, H_2/CO = 2, GHSV = 4.5 NL g^{-1} h^{-1}.

b Chain-growth probability (α) obtained from the ASF plot in the C_{8–C_{14}} hydrocarbons range.

High methane selectivity was usually reported for catalysts having low cobalt reducibility and surface area [18]. This resulted in the formation of unreduced cobalt oxides which catalysed the WGS reaction. As discussed above, the 10Co/Com-A exhibited the strongest interaction of the cobalt species with the supports and the smallest surface area, which would result in the lowest reducibility of cobalt species. By
contrast, when Zr was added, the interaction of the cobalt species with the supports was initially suppressed, but after the Zr/(Zr + Al) atomic ratio was increased to 5% further addition of Zr resulted in a decrease in the suppression effect and the degree of reduction of cobalt. Additionally, the higher diesel selectivity of all MA supported samples than the Com-A supported sample could be also attributed to the space confinement effect of mesopores, which enhanced the re-adsorption of the α-olefin intermediates produced during the reaction and further moderate chain growth [19].

Since 10Co/5ZrMA-(s) showed the best performance in terms of catalytic activity and the selectivity of methane and diesel, it would be used a model catalyst in the following experiments to optimise the process variables, including temperature, pressure, space velocity and feed composition (H₂/CO ratio).

4.3.2.2 Effect of Temperature

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO conv. (%) a</th>
<th>Product distribution (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁</td>
<td>C₂–C₄</td>
</tr>
<tr>
<td>483</td>
<td>31.2</td>
<td>7.1</td>
<td>19.9</td>
</tr>
<tr>
<td>493</td>
<td>38.9</td>
<td>7.7</td>
<td>11.0</td>
</tr>
<tr>
<td>503</td>
<td>47.4</td>
<td>9.2</td>
<td>7.5</td>
</tr>
<tr>
<td>513</td>
<td>60.7</td>
<td>15.6</td>
<td>9.4</td>
</tr>
<tr>
<td>523</td>
<td>78.8</td>
<td>19.1</td>
<td>14.9</td>
</tr>
</tbody>
</table>

a Reaction conditions: 2 MPa, H₂/CO = 2, GHSV = 4.5 NL g⁻¹ h⁻¹.

The effect of temperature on FT synthesis activity and product selectivity of 10Co/5ZrMA-(s) are presented in Table 4-5. It can be seen that the CO conversion increased from 31.2% to 78.8% as the reaction temperature increased to 523 K. This was consistent with the previous reports that increasing temperature increases FT rate [20, 21]. The methane selectivity also increased noticeably with increasing the temperature. In contrast, the diesel selectivity initially increased, and then decreased as the temperature increased above 503 K. At lower temperatures the reaction proceeded quite slowly and the chain growth reaction was hard to be initiated, thus selectivity for methane and heavier hydrocarbons was relatively low [20]. When the temperature increased, the chain growth reaction accelerated, as a result the selectivity to heavier
hydrocarbons, including diesel, improved. However, the desorption of intermediate species was also accelerated at these temperatures, reducing the possibility of the polymerisation of intermediate species into long-chain hydrocarbons and decreasing diesel selectivity [20]. As the catalyst showed the best diesel selectivity and acceptable CO conversion at 503 K, this temperature was used in the following optimisation steps.

**4.3.2.3 Effect of Pressure**

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>CO conv. (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Product distribution (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;–C&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>1.0</td>
<td>42.9</td>
<td>13.4</td>
<td>20.1</td>
</tr>
<tr>
<td>2.0</td>
<td>47.4</td>
<td>9.2</td>
<td>7.5</td>
</tr>
<tr>
<td>3.0</td>
<td>49.1</td>
<td>9.0</td>
<td>6.1</td>
</tr>
<tr>
<td>4.0</td>
<td>50.2</td>
<td>8.2</td>
<td>5.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 503 K, H<sub>2</sub>/CO = 2, GHSV = 4.5 NL g<sup>−1</sup> h<sup>−1</sup>.

The performance of the 10Co/5ZrMA-(s) catalyst at different pressures in FT synthesis is outlined in Table 4-6. As expected, the CO conversion followed an increasing trend as the pressure increased. The methane selectivity gradually decreased with the increase of the pressure whereas the diesel selectivity increased. By 3.0 MPa, however, the diesel selectivity plateaued. These results can be explained by the volume-reducing nature of the FT reaction [22]. When the pressure initially increased, it promoted the conversion of gaseous feedstocks (CO and H<sub>2</sub>) into liquid and solid heavier hydrocarbons (C<sub>5</sub>–C<sub>21+</sub> hydrocarbons), which resulted in the reduction of the overall volume of the reaction system. But when the pressure reached 3.0 MPa, the catalytically active sites would be covered by excessive heavier hydrocarbons that do not diffuse easily, thus retarding further conversion of syngas into heavier hydrocarbons [22]. As the 10Co/5ZrMA-(s) catalyst could achieve high CO conversion and desirable diesel selectivity at 3.0 MPa, this pressure was used in the subsequent optimisation steps.
4.3.2.4 Effect of Space Velocity

The effect of space velocity on FT synthesis activity and product selectivity of 10Co/5ZrMA-(s) are presented in Table 4-7. It can be seen that the CO conversion decreased considerably with the increase of space velocity. The methane selectivity increased dramatically from 7.9% to 24.2% when the space velocity rose from 3.0 NL g⁻¹ h⁻¹ to 7.5 NL g⁻¹ h⁻¹. By contrast, diesel selectivity decreased with increasing the space velocity. When the space velocity was increased, the contact time of the Co active phases with the syngas was reduced. As a result, the syngas had fewer opportunities to be converted and the extent of secondary reactions of intermediate species to form long-chain hydrocarbons was much lower [23]. It should also be noted that when the space velocity was below 4.5 NL g⁻¹ h⁻¹, the methane and diesel selectivity did not change markedly. At this low space velocity, mass transfer was inhibited and further chain growth was suppressed [24]. Since the catalyst exhibited the highest diesel selectivity and CO conversion at 3.0 NL g⁻¹ h⁻¹, this space velocity was utilised for further optimisation of reaction conditions.

**Table 4-7** Performance of the 10Co/5ZrMA-(s) catalyst at different space velocities in FT synthesis

<table>
<thead>
<tr>
<th>Space velocities (NL g⁻¹ h⁻¹)</th>
<th>CO conv. (%)ᵃ</th>
<th>Product distribution (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0ᵇ</td>
<td>55.3</td>
<td>8.0 5.3 33.1 36.6 17.0 0.87</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>49.1</td>
<td>9.0 6.1 32.5 36.1 16.3 0.86</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>38.1</td>
<td>18.5 14.2 27.6 30.4 10.3 0.75</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>27.5</td>
<td>24.2 17.6 22.3 25.6 5.3 0.62</td>
<td></td>
</tr>
</tbody>
</table>

ᵃReaction conditions: 503 K, 3.0 MPa, H₂/CO = 2.
ᵇThis space velocity was achieved by doubling the amount of the catalyst to 0.8 g.

4.3.2.5 Effect of H₂/CO ratio

The performance of the 10Co/5ZrMA-(s) catalyst at different H₂/CO ratios in FT synthesis is summarised in Table 4-8. It is obvious that the CO conversion decreased with decreasing the H₂/CO ratio. Besides, reducing the hydrogen content in the feed also resulted in lower methane selectivity and higher diesel selectivity. This was owing to intensification of the polymerisation reactions when the hydrogen content was low.
Interestingly, the hydrocarbon selectivities were reasonably similar at H₂/CO ratios of 2.0 and 1.6, but deviated significantly when the ratio of was 1.2.

Table 4-8  Performance of the 10Co/5ZrMA-(s) catalyst at different H₂/CO ratios in FT synthesis

<table>
<thead>
<tr>
<th>H₂/CO ratio</th>
<th>CO conv. (%) a</th>
<th>Product distribution (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁</td>
<td>C₂–C₄</td>
</tr>
<tr>
<td>1.2</td>
<td>38.6</td>
<td>6.4</td>
<td>4.4</td>
</tr>
<tr>
<td>1.6</td>
<td>47.2</td>
<td>7.5</td>
<td>5.0</td>
</tr>
<tr>
<td>2.0</td>
<td>55.3</td>
<td>8.0</td>
<td>5.3</td>
</tr>
</tbody>
</table>

a Reaction conditions: 503 K, 3.0 MPa, GHSV = 3.0 NL g⁻¹ h⁻¹.

4.4 Conclusions

Zr isomorphic substitution of MA did not affect the structure of the parent MA support at lower zirconium contents. However, when the Zr/(Zr + Al) ratio reached 5%, there was partial collapse of the mesostructured. By introducing lower levels of Zr, the strong interaction of Co species with the alumina supports was suppressed, which facilitated the reduction of cobalt oxides. At higher Zr contents, the surface area and pore volume decreased, and the strong interaction between cobalt and supports led to decreased reduction in cobalt reducibility. Consequently the catalytic activity and products selectivity of the catalysts were affected.

All the MA supported catalysts showed better catalytic performance than the Com-A supported sample without mesoporous structure. Among the MA supported catalysts, 10Co/5ZrMA-(s) exhibited the highest activity and diesel selectivity as well as the lowest methane selectivity. Compared to wetness impregnation method, isomorphic substitution method was better in terms of retaining the integrity of the mesoporous structure, improving the cobalt reducibility and promoting catalytic performance.

Preliminary optimisation tests suggested that 10Co/5ZrMA-(s) showed superior methane and diesel selectivity at 503 K, 3.0 MPa, 3.0 NL g⁻¹ h⁻¹ and a H₂/CO ratio of 1.2.
4.5 References


Chapter 5 Ce-modified Mesoporous Alumina Supported Co Catalysts in Fischer-Tropsch Synthesis

5.1 Introduction

As discussed in Chapter 2, CeO$_2$ has also been proved to be a desirable promoter for cobalt based FT catalysts [1]. The effect of CeO$_2$ on product selectivity is complicated and depends on the catalyst preparation technique. An appropriate preparation method may result in higher selectivity to middle distillates. Ernst et al. [2] found the introduction of CeO$_2$ (4.5–38.2 wt%) into 25 wt% Co/SiO$_2$ could change the product selectivity, while CO conversion remained relatively unchanged. Specifically, in the presence of CeO$_2$ promoter the selectivity towards C$_5$-C$_{13}$ became higher (ca. 33% at its highest) while the selectivity towards C$_{22+}$ (wax) fell. However, the selectivity to CH$_4$ and C$_2$–C$_4$ increased markedly. It was suggested that the presence of CeO$_2$ accelerated the hydrogenation ability. But Shen et al. [3, 4] reported very different promoting effects of CeO$_2$ in CeO$_x$–Co/SiO$_2$ (10.5–15 wt% Co; Ce/Co=0.2–0.6) catalysts prepared by co-impregnation method. The addition of CeO$_2$ to Co/SiO$_2$ was found to increase CO conversion and the selectivity to heavier hydrocarbons. The presence of CeO$_2$ reduced the selectivity to gasoline (C$_5$–C$_{10}$) fraction and increased the selectivities to middle distillates (C$_{11}$–C$_{16}$) and C$_{16+}$. The addition of CeO$_2$ was shown to slightly inhibit the reducibility of cobalt species but improve Co dispersion. Meanwhile, the modification by CeO$_2$ also accelerated the dissociation of CO on the catalyst surface and enhanced the concentration of active intermediates for chain growth [4].

In light of these contradictory reports, more studies are needed to determine the promoting mechanism of CeO$_2$. To our knowledge, currently there have been no reports describing the introduction of CeO$_2$ into MA supported Co catalysts, especially by the isomorphic substitution method.

In this chapter a series of Co/MA catalysts with isomorphically substituted cerium were also synthesised and characterised. Their catalytic performance in FT synthesis was tested in a fixed bed reactor to systematically investigate the effect of different cerium contents on the structure of the mesoporous alumina supports as well as the activity and selectivity of the cobalt catalysts. In order to optimise the catalytic performance, the
catalyst with a Ce/(Ce + Al) atomic ratio of 5% was tested under different process conditions.

**5.2 Experimental**

**Table 5-1** A list of the as-prepared supports and catalysts

<table>
<thead>
<tr>
<th>Support</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesoporous alumina (MA)</td>
<td>10Co/MA</td>
</tr>
<tr>
<td>MA-1Ce99Al</td>
<td>10Co/2CeMA-(i)</td>
</tr>
<tr>
<td>MA-2Ce98Al</td>
<td>10Co/1CeMA-(s)</td>
</tr>
<tr>
<td>MA-5Ce95Al</td>
<td>10Co/2CeMA-(s)</td>
</tr>
<tr>
<td>MA-10Ce85Al</td>
<td>10Co/5CeMA-(s)</td>
</tr>
<tr>
<td>MA-10Ce85Al</td>
<td>10Co/10CeMA-(s)</td>
</tr>
</tbody>
</table>

Utilising the synthesis procedures described in Chapter 3, five MA supports and six catalysts were prepared, as shown in Table 5-1. Similar to Zr-modified samples, pure mesoporous alumina supports are denoted as MA while Ce modified MA supports are denoted as MA-xCe(100-x)Al (x denotes the Ce/(Ce + Al) molar ratio). In these catalysts, 10Co represents 10 wt% Co content. In addition, (i) indicates that Ce was added by post-impregnation method while (s) indicates that Ce was introduced by isomorphic substitution method.

**5.3 Results and Discussion**

**5.3.1 Characterisation**

**5.3.1.1 N2 Adsorption–Desorption**

The N2 adsorption–desorption isotherms of the supports are presented in Figure 5-1 (a). The N2 adsorption–desorption isotherms of all supports belonged to Type IV and showed an evident H1 hysteresis loop at higher relative pressure, characteristic of mesoporous materials [5, 6]. However, with the increase of the Ce/(Ce + Al) molar ratio, the isotherms became less regular, indicating that the mesoporous structure of alumina was partially collapsed. Pore size distributions (PSDs) of the supports in Figure 5-1 (b) broadened gradually with increasing the Ce/(Ce + Al) ratio, but the centre of the curves still fell in the mesoporous range. As shown in Table 5-2, the BET surface area and Vp
decreased with increasing Ce/(Ce + Al) atomic ratio whereas $D_p$ increased. The BET surface area and pore volume decreased noticeably when Ce/(Ce + Al) atomic ratio was higher than 5%, suggesting the partial collapse of mesoporous structure during the synthesis process.

### Table 5-2  Adsorption parameters of supports and catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area(^a) (m(^2)/g)</th>
<th>Pore Volume $V_p$(^b) (cm(^3)/g)</th>
<th>Pore Diameter $D_p$(^c) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>268.9</td>
<td>1.48</td>
<td>13.3</td>
</tr>
<tr>
<td>MA-1Ce99Al</td>
<td>253.6</td>
<td>1.39</td>
<td>14.1</td>
</tr>
<tr>
<td>MA-2Ce98Al</td>
<td>234.7</td>
<td>1.28</td>
<td>14.4</td>
</tr>
<tr>
<td>MA-5Ce95Al</td>
<td>213.3</td>
<td>1.11</td>
<td>15.5</td>
</tr>
<tr>
<td>MA-10Ce90Al</td>
<td>197.4</td>
<td>1.04</td>
<td>17.8</td>
</tr>
<tr>
<td>10Co/MA</td>
<td>238.4</td>
<td>1.29</td>
<td>10.8</td>
</tr>
<tr>
<td>10Co/1CeMA-(s)</td>
<td>226.6</td>
<td>1.20</td>
<td>15.2</td>
</tr>
<tr>
<td>10Co/2CeMA-(s)</td>
<td>210.5</td>
<td>1.09</td>
<td>15.4</td>
</tr>
<tr>
<td>10Co/2CeMA-(i)</td>
<td>198.1</td>
<td>0.96</td>
<td>24.7</td>
</tr>
<tr>
<td>10Co/5CeMA-(s)</td>
<td>181.4</td>
<td>0.87</td>
<td>18.8</td>
</tr>
<tr>
<td>10Co/10CeMA-(s)</td>
<td>175.8</td>
<td>0.84</td>
<td>28.6</td>
</tr>
</tbody>
</table>

\(^a\)BET surface area measured in the relative pressure range of 0.05–0.30
\(^b\)The BJH desorption cumulative volume of pores between 17 Å and 3000 Å width
\(^c\)The peak positions of the distribution curves by BJH

The $N_2$ adsorption–desorption isotherms of the catalysts are shown in Figure 5-2 (a). It is evident that the isotherms of the MA supported catalysts still showed the H1 hysteresis loop, indicating the mesoporous structure was preserved. However, the isotherms were far less regular after the loading of Co, suggestive of the decrease of mesoporosity [7]. This is in agreement with the results from Figure 5-2 (b), in which the PDS curves became considerably more broadened upon the deposition of Co. As expected, the BET surface area and $V_p$ of all the catalysts decreased in comparison with the equivalent figures for their supports (Table 5-2). Notably, the BET surface area, $V_p$ and $D_p$ of 10Co/2CeAl-(s) were larger than those of 10Co/2CeAl-(i), suggesting that the mesoporous structure of alumina was better retained when the sample was synthesised by isomorphic substitution.
Figure 5-1  Nitrogen adsorption–desorption isotherms (a) and BJH pore size distribution (b) of supports
Figure 5-2  Nitrogen adsorption–desorption isotherms (a) and BJH pore size distribution (b) of catalysts
5.3.1.2 Powder X-ray Diffraction (XRD)

![XRD Patterns](image)

**Figure 5-3** Powder XRD patterns of supports (a) and catalysts (b)

The XRD patterns of the supports are shown in Figure 5-3 (a). All the supports exhibited a group of characteristic diffraction peaks, attributed to γ-alumina (JCPDS Card No. 10-0425). It should be noted that for supports when the Ce/(Ce + Al) atomic ratio reached 2%, the characteristic peaks corresponding to the fluorite CeO$_2$ phase (JCPDS 34-0394) were observed and the peak intensity of the fluorite CeO$_2$ phase increased with increasing Ce/(Ce + Al) ratio. This suggests that isolated particles of fluorite CeO$_2$ appeared on the surface of the catalysts [8, 9], which perhaps explained the falling trend of the surface area and pore volume observed in Table 5-2.
The XRD patterns of the catalysts are presented in Figure 5-3 (b). The diffraction peaks at 45.6° and 66.7° were due to the alumina support [10]. The diffraction peaks at 2θ of 19.1°, 31.3°, 36.9°, 45.1°, 59.4° and 65.4° indicated that cobalt species were primarily in the form of spinel Co₃O₄ on the catalysts [11]. The characteristic peaks of the fluorite CeO₂ phase were noticeably observed, especially at Ce/(Ce + Al) atomic ratio ≥ 5%.

5.3.1.3 Transmission Electron Microscopy (TEM)

![TEM images of catalysts](image)

**Figure 5-4** TEM images of catalysts: 10Co/MA (a), 10Co/1CeMA-(s) (b), 10Co/2CeMA-(s) (c), 10Co/2CeMA-(i) (d), 10Co/5CeMA-(s) (e), 10Co/10CeMA-(s) (f)
The transmission electron micrographs of the catalysts are shown in Figure 5-4. All the samples exhibited wormhole-like appearance of pores without the presence of any obvious pore arrangements. No significant difference in morphology was found between the MA and Ce-modified MA catalysts. Notably, the addition of Ce improved the Co dispersion but when Ce/(Ce + Al) atomic ratio was above 5% the agglomeration of Co species became apparent and thus the Co dispersion decreased. Besides, the agglomeration of Co species over 10Co/2CeMA-(i) (Figure 5-4 (e)) was much worse than over 10Co/2CeMA-(i) (Figure 5-4 (d)), which suggested isomorphic substitution method could result in better dispersion of active phase and promoter than post-impregnation method.

5.3.1.4 X-ray Photoelectron Spectroscopy (XPS)

The XPS data are shown in Table 5-3 and Figure 5-5. The Co 2p3/2 BE for 10Co/MA was higher than that of pure Co3O4 (BE = 780.3 eV), suggesting that the cobalt–alumina phase was formed on the catalyst surface [12, 13]. It is also obvious that the Co 2p3/2 BEs of the MA supported catalysts increased with increasing Ce/(Ce + Al) atomic ratio. According to the analysis in the previous chapter, this suggests that the introduction of Ce did not inhibit the strong interaction between Co species and alumina support and the formation of cobalt–alumina phase; rather, it induced stronger interaction. As a result, the extent of reduction of Co species would decrease. Similar results of the inhibiting effect of Ce on the reducibility of Co were reported by Shen et al. [3, 4].
Moreover, the Co 2p$_{3/2}$ BE for 10Co/2CeMA-(s) was much lower than that of 10Co/2CeMA-(i), suggesting that isomorphic substitution was preferable over post-impregnation in terms of reducing the inhibiting effect of Ce on Co reducibility.

Table 5-3  Co 2p$_{3/2}$ binding energy (BE) of different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co 2p$_{3/2}$ BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Co/MA</td>
<td>781.04</td>
</tr>
<tr>
<td>10Co/1CeMA-(s)</td>
<td>781.20</td>
</tr>
<tr>
<td>10Co/2CeMA-(s)</td>
<td>781.36</td>
</tr>
<tr>
<td>10Co/2CeMA-(i)</td>
<td>781.58</td>
</tr>
<tr>
<td>10Co/5CeMA-(s)</td>
<td>781.40</td>
</tr>
<tr>
<td>10Co/10CeMA-(s)</td>
<td>781.63</td>
</tr>
</tbody>
</table>

5.3.2 Fischer-Tropsch Synthesis

5.3.2.1 Effect of Ce promotion

Table 5-4  Performance of the as-synthesised catalysts in FT synthesis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO conv. (%)$^a$</th>
<th>Product distribution (wt%)</th>
<th>$\alpha$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C$_1$</td>
<td>C$_2$–C$_4$</td>
</tr>
<tr>
<td>10Co/MA</td>
<td>25.6</td>
<td>15.6</td>
<td>20.1</td>
</tr>
<tr>
<td>10Co/1CeMA-(s)</td>
<td>27.1</td>
<td>12.1</td>
<td>18.8</td>
</tr>
<tr>
<td>10Co/2CeMA-(s)</td>
<td>37.4</td>
<td>8.9</td>
<td>11.8</td>
</tr>
<tr>
<td>10Co/2CeMA-(i)</td>
<td>29.7</td>
<td>13.2</td>
<td>19.4</td>
</tr>
<tr>
<td>10Co/5CeMA-(s)</td>
<td>31.9</td>
<td>18.5</td>
<td>24.3</td>
</tr>
<tr>
<td>10Co/10CeMA-(s)</td>
<td>28.3</td>
<td>23.6</td>
<td>25.0</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 493 K, 2 MPa, H$_2$/CO = 2, GHSV = 4.5 NL g$^{-1}$ h$^{-1}$.

$^b$ Chain-growth probability ($\alpha$) obtained from the ASF plot in the C$_8$–C$_{14}$ hydrocarbons range.

The results of FT synthesis activity and product selectivity of the catalysts are outlined in Table 5-4. In terms of activity the following trends could be observed: (1) The CO conversion of Ce modified samples was higher than that of the unmodified counterpart under the same conditions; (2) As the Ce content increased from 0 to 2%, the CO conversion increased, and then decreased with further increase in the Ce/(Ce + Al) ratio; (3) At the same content of Ce, the CO conversion of the 10Co/2CeMA-(s)
prepared by isomorphic substitution was higher than that of 10Co/2CeMA-(i) prepared by post-impregnation.

The catalytic activity of Co catalysts for FT synthesis depended on the density of surface metal cobalt sites, which is correlated with its dispersion and reducibility [14, 15]. When Ce$^{4+}$ ions were introduced into the alumina framework of the MA supported catalysts, Co dispersion was improved and more accessible cobalt active surface sites were generated, therefore the CO conversion increased. However, at the same time the Co reducibility was inhibited by the addition of Ce, which resulted in a decrease in surface metallic Co particles. On the other hand, at higher Ce contents the mesostructure was partially destroyed, leading to a decrease in surface area and pore volume. Therefore the density of surface metal cobalt sites decreased at higher Ce contents and CO conversion fell. 10Co/2CeMA-(s) showed higher activity compared to 10Co/2CeMA-(i), perhaps due to higher dispersion of cobalt species in the catalysts.

As shown in Table 5-4, by the addition of Ce, methane selectivity initially decreased from 15.6% to 8.9%, and then dramatically increased to 23.6% on further increasing the Co content. By contrast, diesel selectivity first increased from 29.5% to 33.8% and then significantly fell to 25.1%. It should be noted that when the Ce/(Ce + Al) was over 5%, diesel selectivity was even lower than that of pure MA supported Co catalyst while the methane selectivity was much higher. This suggests only a slight amount of Ce addition was beneficial for the diesel production. Similar results were reported for another rare earth oxide promoter La$_2$O$_3$ [16-18]. When 10Co/2CeMA-(s) and 10Co/2CeMA-(i) are compared, the former showed lower methane selectivity and higher diesel selectivity.

Previous studies showed that the modification by CeO$_2$ could facilitate the dissociation of CO on catalyst surface and enhance the concentration of active intermediates for chain growth, which resulted in an increase in the selectivity for long-chain hydrocarbons [3, 4].

As 10Co/2CeMA-(s) showed the best performance in terms of catalytic activity and the selectivity of methane and diesel, it would be employed a model catalyst in the following experiments to optimise the process conditions, such as temperature, pressure, space velocity and feed composition (H$_2$/CO ratio).
5.3.2.2 Effect of Temperature

The effect of temperature on the FT synthesis activity and product selectivity of 10Co/2CeMA-(s) is presented in Table 5-5. The CO conversion increased from 30.7% to 77.3% with the rise of temperature, in accord with the result of Zr-modified samples in the previous chapter. As expected, the methane selectivity increased noticeably from 8.3% to 20.3% with increasing the temperature. But the diesel selectivity first increased as the temperature increased from 483 K to 503 K, and then decreased when further increasing the temperature. This suggests the Ce-modified catalyst also showed the best performance at 503 K in terms of product selectivity. As the catalyst showed the highest diesel selectivity and acceptable CO conversion at 503 K, this temperature would be applied in the following optimisation steps.

Table 5-5 Performance of the 10Co/2CeMA-(s) catalyst at different temperatures in FT synthesis

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CO conv. (%)</th>
<th>Product distribution (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁</td>
<td>C₂–C₄</td>
</tr>
<tr>
<td>483</td>
<td>30.7</td>
<td>8.3</td>
<td>20.7</td>
</tr>
<tr>
<td>493</td>
<td>37.4</td>
<td>8.9</td>
<td>11.8</td>
</tr>
<tr>
<td>503</td>
<td>46.9</td>
<td>10.4</td>
<td>8.3</td>
</tr>
<tr>
<td>513</td>
<td>59.2</td>
<td>16.8</td>
<td>10.2</td>
</tr>
<tr>
<td>523</td>
<td>77.3</td>
<td>20.3</td>
<td>15.7</td>
</tr>
</tbody>
</table>

*a Reaction conditions: 2 MPa, H₂/CO = 2, GHSV = 4.5 NL g⁻¹ h⁻¹.

5.3.2.3 Effect of Pressure

The performance of the 10Co/2CeMA-(s) catalyst at different pressures in FT synthesis is summarised in Table 5-6. Obviously, with the increase of the pressure the CO conversion increased from 42.1% to 49.7% but the extent of increase was much smaller at higher pressures. As expected, the methane selectivity gradually decreased with increasing the pressure whereas the diesel selectivity increased from 29.0% to 35.5%. However, by 3.0 MPa the effect of the pressure on the diesel selectivity was almost negligible and diesel selectivity reached a plateau as observed in the previous chapter. As the high CO conversion and desirable diesel selectivity for the 10Co/2CeMA-(s)
catalyst were obtained at 3.0 MPa, this pressure was applied in the subsequent optimisation process.

Table 5-6 Performance of the 10Co/2CeMA-(s) catalyst at different pressures in FT synthesis

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>CO conv. (%) a</th>
<th>Product distribution (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C1</td>
<td>C2–C4</td>
</tr>
<tr>
<td>1.0</td>
<td>42.1</td>
<td>14.6</td>
<td>20.9</td>
</tr>
<tr>
<td>2.0</td>
<td>46.9</td>
<td>10.4</td>
<td>8.3</td>
</tr>
<tr>
<td>3.0</td>
<td>48.5</td>
<td>10.2</td>
<td>6.9</td>
</tr>
<tr>
<td>4.0</td>
<td>49.7</td>
<td>9.4</td>
<td>6.2</td>
</tr>
</tbody>
</table>

a Reaction conditions: 503 K, H2/CO = 2, GHSV = 4.5 NL g⁻¹ h⁻¹.

5.3.2.4 Effect of Space Velocity

Table 5-7 Performance of the 10Co/2CeMA-(s) catalyst at different space velocities in FT synthesis

<table>
<thead>
<tr>
<th>Space velocities (NL g⁻¹ h⁻¹)</th>
<th>CO conv. (%) a</th>
<th>Product distribution (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C1</td>
<td>C2–C4</td>
</tr>
<tr>
<td>3.0 b</td>
<td>54.6</td>
<td>9.2</td>
<td>6.1</td>
</tr>
<tr>
<td>4.5</td>
<td>48.5</td>
<td>10.2</td>
<td>6.9</td>
</tr>
<tr>
<td>6.0</td>
<td>37.3</td>
<td>19.7</td>
<td>15.1</td>
</tr>
<tr>
<td>7.5</td>
<td>26.3</td>
<td>25.4</td>
<td>18.4</td>
</tr>
</tbody>
</table>

a Reaction conditions: 503 K, 3.0 MPa, H2/CO = 2.

b This space velocity was achieved by doubling the amount of the catalyst to 0.8 g.

The effect of space velocity on the FT synthesis activity and product selectivity of 10Co/2CeMA-(s) is shown in Table 5-7. The CO conversion decreased considerably with the increase of space velocity. The methane selectivity increased markedly from 9.2% to 25.4% when the space velocity rose from 3.0 NL g⁻¹ h⁻¹ to 7.5 NL g⁻¹ h⁻¹. By contrast, the diesel selectivity decreased with increasing the space velocity. It is worthwhile to note that when the space velocity reached 4.5 NL g⁻¹ h⁻¹, further reducing it only resulted in minor changes in the methane and diesel selectivity. The explanation is the same as that described in the previous chapter. Since the catalyst exhibited the
highest diesel selectivity and CO conversion at 3.0 NL g⁻¹ h⁻¹, this space velocity was used in the following study.

5.3.2.5 Effect of H₂/CO ratio

The performance of 10Co/2CeMA-(s) catalyst at different H₂/CO ratios in FT synthesis is presented in Table 5-8. Clearly, the CO conversion decreased with the decrease of H₂/CO ratio, which is in line with the previous result of the Zr-modified sample. Additionally, when the H₂/CO ratio decreased methane selectivity decreased gradually from 9.2% to 7.6% whereas diesel selectivity increased slightly from 35.8% to 36.6%. These results were in line with the previous results of the Zr-modified sample. Similarly, the methane and diesel selectivities were quite close at H₂/CO ratios of 2.0 and 1.6, but greatly departed from those at the ratio of 1.2.

Table 5-8 Performance of the 10Co/2CeMA-(s) catalyst at different H₂/CO ratios in FT synthesis

<table>
<thead>
<tr>
<th>H₂/CO ratio</th>
<th>CO conv. (%)¹</th>
<th>Product distribution (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁</td>
<td>C₂–C₄</td>
</tr>
<tr>
<td>1.2</td>
<td>35.2</td>
<td>7.6</td>
<td>5.2</td>
</tr>
<tr>
<td>1.6</td>
<td>46.7</td>
<td>8.7</td>
<td>5.8</td>
</tr>
<tr>
<td>2.0</td>
<td>54.6</td>
<td>9.2</td>
<td>6.1</td>
</tr>
</tbody>
</table>

¹Reaction conditions: 503 K, 3.0 MPa, GHSV = 3.0 NL g⁻¹ h⁻¹.

5.4 Conclusions

The introduction of Ce into MA did not obviously change the structure of the MA support when the Ce content was low, but resulted in partial collapse of the mesostructure when the Ce content was high. The modification of Ce improved the Co dispersion of the catalysts while inhibited the reducibility of Co species. As a result, the catalytic activity and product selectivity of the catalysts were affected.

Among the MA supported catalysts studied, 10Co/2CeMA-(s) exhibited the highest activity and diesel selectivity as well as the lowest methane selectivity. Compared to wetness impregnation, the isomorphic substitution was superior in preparing catalysts with better catalytic performance.
Preliminary screening tests of process conditions showed that 10Co/2CeMA-(s) exhibited the best performance in terms of methane and diesel selectivity under this process conditions at 503 K, 3.0 MPa, 3.0 NL g$^{-1}$ h$^{-1}$, and a H$_2$/CO ratio of 1.2.
5.5 References


Chapter 6 Evaluation and Practical Implications

6.1 Introduction

In the present chapter, the results and findings from the two preceding chapters are integrated and evaluated against the objectives presented in Chapter 2 and their potential implications are also assessed. In order to evaluate the present study, the results from the present work are compared with the previous literature data as described in Chapter 2. Additionally, new gaps are found, which leads to recommendations for future research.

6.2 Performance of Zr- and Ce-modified Mesoporous Alumina Supported Co Catalysts in Fischer-Tropsch Synthesis

As shown in Chapter 4, the results of the FT synthesis tests confirmed that the Co catalysts supported on mesoporous alumina could provide higher diesel selectivity and CO conversion than those on conventional Al₂O₃ owing to the enhanced Co site density and the space confinement effect of the mesopores. Some literature studies have already demonstrated that the use of mesoporous materials with proper pore sizes can produce middle distillate fuels with higher selectivity [1-3]. This finding has further confirmed that mesoporous materials are promising as FT catalyst supports in tuning the product selectivity.

Besides, in both studies the promoted catalysts prepared by isomorphic substitution showed better performance than those prepared by post-impregnation in terms of FT activity and the selectivity of diesel and methane. So far there is only a paucity of reports about FT catalysts prepared by isomorphic substitution [4-6]. Consistent with the previous results, this work further demonstrated the superiority of this method relative to conventional post-impregnation method and its potential use in the future catalyst preparation and modification.

Table 6-1 compares the results from the present studies and those from the open literature on the catalytic performances of Co catalysts for FT diesel production. It should be pointed out that only those catalysts with over 30% diesel selectivity (C₁₀–C₂₀) were chosen to be shown in this table. It can be seen that under the same conditions
10Co/5ZrMA-(s) showed slightly better performance than 10Co/2CeMA-(s) in terms of both activity and product selectivity. Their diesel selectivity data (37.4% and 36.6%) are comparable to most Co catalysts supported on other mesoporous materials (meso-ZrO₂, MCM-41, SBA-1 etc.), but are relatively much lower than those of the three best performing catalysts reported to date (around 60%)—Co/Ru/ThO₂/Al₂O₃, Co/ThO₂/Al₂O₃ and Ru/CNT. This shows the great potential of MA supported Co catalysts in the FT diesel production; however, there is still much room for improvement to achieve higher diesel selectivity.

Table 6-1  Comparisons between the present experimental results and literature data on the catalytic performances of Co catalysts for FT diesel production

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO conv. (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₁–C₄</td>
</tr>
<tr>
<td>Co/MCM-41 a</td>
<td>86.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Co/Cab-O-Sil a</td>
<td>41.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Co/meso-ZrO₂-12.6 b</td>
<td>86.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Co/Na-mordenite a</td>
<td>43.0</td>
<td>35.0</td>
</tr>
<tr>
<td>12.5Co–2Ca/SiC c</td>
<td>59.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Co/SBA-1 a</td>
<td>61.0</td>
<td>26.0</td>
</tr>
<tr>
<td>Co/SBA-15 a</td>
<td>92.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Co/Ru/ThO₂/Al₂O₃ d</td>
<td>70.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Ru/CNT e</td>
<td>34.0</td>
<td>17.4</td>
</tr>
<tr>
<td>Co/ThO₂/Al₂O₃ f</td>
<td>24.0</td>
<td>9.0</td>
</tr>
<tr>
<td>10Co/5ZrMA-(s) g</td>
<td>38.6</td>
<td>10.8</td>
</tr>
<tr>
<td>10Co/2CeMA-(s) g</td>
<td>35.2</td>
<td>12.8</td>
</tr>
</tbody>
</table>

a From Ref. [1]: Co content was 5.0 wt% except for Co/Cab-O-Sil (2.0 wt%); reaction conditions: T = 523 K, P = 2 MPa, H₂/CO = 2, flow rate = 20 ml/min
b From Ref. [2]: Co content was 10 wt%; the numbers in the formula represent the pore size (nm) of meso-ZrO₂ reaction conditions: T = 503 K, P = 2 MPa, H₂/CO = 2, GHSV = 1000 h⁻¹, * C₅–C₁₁, # C₁₂–C₁₈, ^ C₁₉+
c From Ref. [7]: reaction conditions: T = 523 K, P = 2.0 MPa, H₂/CO = 2, GHSV = 6000 h⁻¹
d From Ref. [8]: Co content was 15 wt%; reaction conditions: T = 468 K, P = 1 MPa, H₂/CO = 1, flow rate = 10 ml/min, * C₅–C₈, # C₉–C₂₀
e From Ref. [9]: reaction conditions: H₂/CO =1:1, flow rate = 20 ml/min, P = 2.0 MPa, catalyst (0.50 g; 3.0 wt% Ru content), 533 K, and 10 h
f From Ref. [10]: Co content was 21.9 wt%; reaction conditions: T = 448 K, P = 1 MPa, H₂/CO = 1, flow rate = 9 ml/min, * C₅–C₈, # C₉–C₂₀
From the present studies: Co content was 10 wt%; reaction conditions: T = 503 K, P = 3.0 MPa, H\textsubscript{2}/CO = 1.2, GSHV = 3.0 NL g\textsuperscript{-1} h\textsuperscript{-1}

The studies of the catalytic performance of Zr- and Ce-modified MA supported Co FT catalysts have shown that the modification of Zr and Ce within a certain content could improve the activity and selectivity to heavier hydrocarbons. But their working mechanisms are different. The introduction of Zr could suppress the strong interaction of Co species with the alumina supports and thus facilitate the reduction of cobalt oxides. In contrast, the addition of Ce would improve the Co dispersion of the catalysts but inhibit the reducibility of Co species. The results from the current research have important implications in the understanding of working mechanisms of ZrO\textsubscript{2} and in particular CeO\textsubscript{2} promoters. There are some contradictory reports about CeO\textsubscript{2} promoter in the previous literature [11-13]. And the results from this research are in line with those of Shen et al. [12-13] and further proved the beneficial effect of Ce.

The present studies also showed that the main process parameters that could greatly influence the catalytic behaviour of Co FT catalysts. An increasing temperature would result in an increased FT activity and a shift of the selectivity towards shorter hydrocarbons. By contrast, an increase in total pressure led to a shift to heavier hydrocarbons but also a rise in activity. The higher contact time (lower space velocity) would give rise to an increase of heavier products, a reduced selectivity to methane and a higher activity. An increase of the H\textsubscript{2}/CO ratio resulted in an increased activity, and the selectivity would instead be shifted to lower molecular weight hydrocarbons. These results highlight the importance of choosing proper process conditions in order to achieve higher diesel selectivity.

So far, the evaluation of the catalytic performance of these MA supported Co catalysts has focused on the short term test and did not study the stability of the catalysts over the long run. It has been reported that factors such as sintering, metal–support solid state reactions and surface carbon formation can considerably deactivate Co FT catalysts with time on stream [14]. Thus, stability is also a significant factor when considering put a catalyst into practical use. In future, the studies should be extended to investigate the long-term stability of these catalysts, especially the effect of coke deposition on the stability.

Additionally, the loading content of Co was fixed at 10 wt% in the current study. But some studies have shown that the loading amount of Co had a significant effect on the
performance of Co catalysts in FT synthesis [15]. In order to further optimise the composition of the catalysts, it should be worthwhile to investigate the performance of different catalysts with varying Co loading amounts.

Although the addition of Zr and Ce and were shown to be able to improve the activity and diesel selectivity of MA supported Co catalysts, the performance of these catalysts was far from desirable for practical use and further modification seems to be entailed. It is well-known that the industrialised Co FT catalysts were typically composed of four elements—support, cobalt, oxide promoter and noble metal promoter [16]. In the current catalyst system, no noble metal promoter (such as, Ru, Pd, Pt) was employed, but they have been proven to have beneficial promoting effects, including inhibiting the formation of cobalt-support mixed compounds, suppressing the deactivation of cobalt FT catalysts and tuning the product selectivity towards heavier hydrocarbons [17]. Therefore, a systematic study of the effect of noble metal promoters on the performance of MA supported Co catalysts is highly recommended.

The lack of evaluation of the catalysts over long periods of time on stream due to time limit is also a major gap in the current study. It is important to learn about the performance of these catalysts over a long run time especially their stability before they can be considered for practical applications. And hence further research of the long-term stability is required on this particular area.

6.3 Overall Evaluation and Implications

The overall aim to investigate MA supported Co catalysts in FT synthesis has been achieved. The findings from the present research work are highlighted below:

- Better understanding of the promoting mechanism of Zr and Ce in the MA supported Co catalysts for FT synthesis.

- Systematic studies of the effects of different process conditions on the performance of MA supported Co FT catalysts.

- Understanding of the effects of different promoter introduction methods on the performance of Co FT catalysts.

These findings have a variety of implications in the practical utilisation of MA supported Co catalysts in FT synthesis. Gaining insights into the promoting mechanisms
and the effects of process conditions and preparation methods offers more confidence to use this catalyst system and possibly enable the modification of the existing catalysts and the development of novel catalysts. Though there has been a deeper understanding of the catalytic behaviours of MA supported Co catalysts through this research work, the study in this field is anything but perfect and complete and thus there is still room for improvements in further research.
6.4 References


Chapter 7 Conclusions and Recommendations

7.1 Introduction

The current research has enhanced the status of understanding of the use of Zr and Ce modified MAs as supports for Co catalysts in FT synthesis. The conclusions and previous evaluations of the present study, have also led to the recommendations for future research in this sphere.

7.2 Conclusions

7.2.1 Zr-modified Mesoporous Alumina Supported Co Catalysts in Fischer-Tropsch Synthesis

The mesoporous alumina supported Co catalysts showed better catalytic performance than the non-mesoporous commercial alumina supported sample, which was attributed to the space confinement effect of mesopores.

The introduction of Zr into MA by isomorphic substitution did not affect the structure of the parent MA support at lower zirconium contents. It could also suppress the interaction of Co species with the alumina supports, leading to the increase of Co metal active sites and the reducibility of cobalt oxides. As a result, the use of Zr promoter improved the FT activity and diesel selectivity while suppressed the methane selectivity. But at higher contents (over 5%), this promotion effect would be reduced due to the collapse of the mesostructure.

It was also found that the Zr promoted catalyst prepared by isomorphic substitution was superior to the one prepared by post-impregnation in terms of catalytic performance.

The main process parameters including temperature, pressure, space velocity and feed composition were demonstrated to greatly influence the catalytic behaviour. An increasing temperature resulted in a continually increased FT rate but a shift of the selectivity towards heavier hydrocarbons initially and then to shorter hydrocarbons. On the contrary, an increase in total pressure would give rise to a shift to heavier hydrocarbons and also an increase of conversion. The lower space velocity (higher contact time) would lead to a higher CO conversion, improved heavier products and a
reduced selectivity towards methane. This could be explained by a higher extent of secondary reactions. With the increase of the H₂/CO ratio, the FT activity was enhanced and the selectivity would instead be shifted to lower molecular weight hydrocarbons.

7.2.2 Ce-modified Mesoporous Alumina Supported Co Catalysts in Fischer-Tropsch Synthesis

The incorporation of Ce into MA did not bring about an obvious change to the structure of the MA support at lower Ce contents. By the promotion of Ce, the Co dispersion of the catalysts was enhanced while the reduction of Co species was inhibited. As a result, only a very slight amount of Ce addition (no more than 2%) could be conducive to the performance of the Ce-modified catalysts. The excessive addition would instead result in a decrease in activity and diesel selectivity as well as an increase in methane selectivity.

In comparison with the Zr-modified MA supported Co catalysts, Ce-promoted counterparts showed relatively lower catalytic performance in FT synthesis in terms of activity and diesel selectivity under the same process conditions.

It was proved again that the promoted catalyst prepared by isomorphic substitution was better than the one prepared by post-impregnation with the former showing higher catalytic activity and diesel selectivity but lower methane selectivity.

7.3 Recommendations for Future Work

Even though the overall objectives of the present study have been achieved, new gaps are also identified based on the conclusions and evaluations of the present study, which forms the recommendations for future studies.

In this thesis work, the loading amount of Co was fixed at 10 wt%. Future work can be done to explore and evaluate the effect of Co loading on the performance of these catalysts so that an optimal Co loading can be identified.

Furthermore, it was previously revealed that Co catalysts were prone to deactivation during the long-term run. And surface carbon formation was one of the main factors affecting the stability of Co catalysts. Thus, future studies are also recommended to
investigate the influence of coke deposition on the performance of MA supported Co catalysts over a long run to verify their stability.

In the present study, only one kind of promoter was added. But the typical chemical composition of conventional patented Co-based FT catalysts involves support, cobalt, oxide promoter and noble metal promoter. Because of their higher hydrogenation activity relative to cobalt, noble metal promoters (such as Pt, Pd, Ru and Re) have been proved to effectively delay the formation of cobalt-support mixed compounds, inhibit the deactivation of cobalt FT catalysts and shift the product selectivity towards heavier hydrocarbons. Therefore, it is also suggested that more research should be conducted to understand the effect of noble metal promoters in this catalyst system. As such, further improvement can be made on the performance of the MA supported Co FT catalysts.