1 **Relating Coke Formation and Characteristics to Deactivation of ZSM-5**

2 **Zeolite in Methanol to Gasoline Conversion**

3
4 Zhijian Wan*, Gang (Kevin) Li, Chuanfu Wang, Hong Yang and Dongke Zhang
5 Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway,
6 Crawley, WA 6009, Australia

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27 * Corresponding author: Dr Zhijian Wan

28 Email: zhijian.wan@uwa.edu.au

29 Phone: +61 8 6488 5528

30 Fax: +61 8 6488 7622

Abstract

Two ZSM-5 catalysts, differing only in their crystal size, viz, nanocrystal at ~ 100 nm and microcrystal at 13 μm , respectively, were synthesised and tested in methanol to gasoline (MTG) conversion, with a focus on the formation and characteristics of coke deposits. Over time periods when methanol conversion decreased to 50%, herein termed as the *service lifespan* of the catalyst, the nanocrystal catalyst incurred 31.1 wt% coke deposition, while the microcrystal counterpart had 14.1 wt% coke. The nanocrystal catalyst showed a service lifespan almost seven times longer than the microcrystal catalyst. The difference in the catalytic service lifespans was examined in terms of the rate of formation of *internal* coke and structural properties of *external* coke, as determined using nitrogen physisorption, TGA and TEM. It was found that the internal coke was quickly formed in the microcrystal catalyst leading to rapid coverage of the active sites and blockage of the pores, resulting in fast deactivation. In contrast, coke formed preferentially on the external surface in the case of the nanocrystal catalyst. This external coke was of porous graphitic structures, and thus was not detrimental to the catalytic performance. The coke fouled nanocrystal catalyst was regenerated and the activity of the regenerated catalyst was evaluated under the same reaction conditions. An increase in catalytic service lifespan compared to the pristine nanocrystal catalyst was observed, due to the effect of decreased Al concentration on the catalytic performance.

Keywords: catalyst coking; deactivation; methanol to gasoline; percolation theory; ZSM-5 zeolite

1. Introduction

The formation of coke over acidic zeolite catalysts in hydrocarbon processing, such as methanol to gasoline (MTG) conversion, is one of the main causes of the catalyst deactivation; thus, understanding the coke formation mechanisms and characteristics is of paramount importance for the development of robust catalysts and the improvement of process efficiency and economics [1, 2].

Coking involves complex mechanisms. The formation of coke requires not only the chemical reactions but also the retention of coke molecules in the microporous channels and/or on the external surface of the catalyst. Coke formation is also affected by various factors such as the nature of catalyst (the type of catalyst, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and acidity, and crystal size, etc.) and process conditions. Reaction temperature significantly affects coke composition [3-6]. Previous studies revealed that coke formed at low temperatures is generally non-polyaromatic in nature, whereas at temperatures above 350 °C, the retained coke compounds become more carbonaceous and heavy, ultimately dominated by polyaromatics [3, 4].

In terms of the effect of catalyst properties, crystal size which directly affects molecular diffusion path can be very significant to the coke formation. In the case of ZSM-5 zeolite, the crystalline aluminosilicate has three-dimensional microporous channels with openings of ~0.55 nm in diameter [7, 8]. This channel system renders the passage of gasoline components. However, it causes restricted diffusion for large aromatics which would be trapped in the channels, undergo condensation, hydrogen transfer and elimination reactions, and subsequently form coke [9, 10]. Correspondingly, many catalyst development efforts have been devoted to mitigating the diffusion limitations [11, 12].

Reduction of crystal sizes into the nanometre range and creation of mesopores have been considered effective to enhance the mass transfer within the catalyst and hence an improved catalytic performance [13]. Extensive studies have been reported on the improvement of

activity and service lifespan of ZSM-5 catalysts with nano and hierarchical structures compared to their microcrystal counterparts in various reactions [12, 14-19]. For example, Fu and co-workers [19] reported an extension of catalytic service lifespan by 58 h and a doubled gasoline yield using 30–60 nm ZSM-5 nanocrystals against 2 μ m microcrystals in MTG reaction. Such enhanced performance was often explained as reduced coking potential in catalyst particles with shortened diffusion paths as a result of smaller crystal size and higher external surface areas [12, 14]. However, in fact, nanocrystal ZSM-5 was found to bear much more coke (e.g. as high as 6 times more) [19] than the microcrystals by the end of their service lifespan. The reason for the high coke tolerance but superior catalytic performance for the nanocrystal ZSM-5 catalyst still requires further mechanistic understanding, considering both external and internal coke could be responsible for the catalyst deactivation [5-8, 20].

In this study, the formation and characteristics of internal and external coke, and their subsequent impact on the catalytic activity and service lifespan of two ZSM-5 catalysts in MTG under the same operation conditions were investigated. These two ZSM-5 zeolites differed only in crystal size, namely, ~100 nm nanocrystals and ~13 μ m microcrystals but were of the same type with similar structural properties and amounts of active sites, allowing for an effort to peek into the relationship between coke formation behaviour and deactivation of catalysts with different length of diffusion paths. The coke and spent catalysts were subjected to various analysis and characterisation. The rate of formation of internal coke and structural properties of external coke were determined, enabling an in-depth understanding of the mechanism that the nanocrystal ZSM-5 catalyst displayed superior service lifespan while retaining high catalytic activity despite the greater deposition of coke. Furthermore, regeneration of the coke fouled nanocrystal ZSM-5 catalyst was performed at 550 °C in air for 4 h and the activity of the regenerated sample was also evaluated and compared to that of the virgin nanocrystal catalyst.

2. Experimental

2.1 Synthesis of nanocrystal and microcrystal ZSM-5 catalysts

The catalyst synthesis reagents were purchased from Sigma–Aldrich and used as supplied without any modification. Sodium aluminate (NaAlO_2 , anhydrous, analytic reagent) and tetraethyl orthosilicate (TEOS, $\geq 99.0\%$) provided the alumina and silica sources, respectively. Tetrapropylammonium hydroxide (TPAOH, 1.0 M aqueous solution) was used as the structure directing agent.

A nanocrystal ZSM-5 catalyst was prepared using a hydrothermal synthesis method from a sol-gel solution with a molar composition of 1 Na_2O : 1 Al_2O_3 : 50 SiO_2 : 12.5 TPAOH: 578.5 H_2O . In brief, TEOS (6.4 g) was added drop-wise to a clear aqueous solution of NaAlO_2 (0.1 g) in 1.0 M TPAOH (8.0 g). The mixture was stirred at ambient temperature to form a sol-gel solution gradually, followed by a further 0.5 h stirring before being transferred to an 80 °C oil bath for 1 h. After cooling natural to ambient temperature and another 20 h of stirring for aging, the solution was hydrothermally treated in a Teflon-lined autoclave at 180 °C for 48 h. The solid product was washed three times by resuspending the sample in deionised water and collected by centrifugation.

The microcrystal ZSM-5 sample was synthesised by modifying the aforementioned method. Briefly, 20 g (instead of 8 g) of 1.0 M TPAOH aqueous solution was used and the hydrothermal synthesis was carried out for 72 h (instead of 48 h).

In both cases, the structure directing agent (TPAOH) was removed by calcination in air at 550 °C for 5 h. The resultant white powder was ion exchanged twice with NH_4^+ (1.0 g of zeolite in 10 mL of 1.0 M NH_4NO_3 solution at 50 °C for 24 h) and finally calcined at 500 °C for 5 h to produce the protonated ZSM-5 catalyst, denoted as H-ZSM-5.

2.2 Characterisation

The crystal structures of the synthesised catalysts were analysed using powder X-ray diffraction (XRD) (PANalytical Empyrean X-ray diffractometer equipped with a Cu K α ($\lambda=1.54439$ Å) radiation source at 40 kV and 40 mA). The SiO₂/Al₂O₃ ratios of the samples were determined from the bulk composition results of the samples using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Thermo Scientific iCAP 6500 Duo ICP-AES). Microscopic morphologies were obtained using a scanning electron microscopy (SEM) (FEI Verios XHR at 10 kV) and a transmission electron microscopy (TEM) (JEOL 2100 at 120kV). The high angle annular dark field scanning transmission electron microscopy image and energy dispersive X-ray spectroscopy elemental maps (HAADF STEM-EDS) of the spent nanocrystal ZSM-5 sample were also obtained using a Titan G2 80-200 TEM at 200 kV. The HAADF STEM-EDS analysis was not applied to the microcrystal ZSM-5 sample as its crystal size was too large to offer quality images and useful information.

In-situ temperature programmed ammonia adsorption/desorption (NH₃-TPA/TPD) was conducted using a Quantachrome ChemBET PULSAR TPR/TPD. Specifically, the sample (~0.1 g) was heated from room temperature to 500 °C at a rate of 10 °C min⁻¹ in a helium (He) flow (high purity, 15 mL min⁻¹) for 60 min and then cooled down to 120 °C. NH₃ adsorption was then performed by flushing the sample with a 5 v/v% NH₃/He mixture (15 mL min⁻¹) for 40 min. The sample was again purged with He (15 mL min⁻¹) for 40 min to remove the physisorbed NH₃. At a heating rate of 10 °C min⁻¹, the sample was heated to 650 °C to allow the desorption of NH₃ absorbed on the acid sites. The NH₃ desorbed was recorded every 5 s using a thermal conductivity detector (TCD).

Nitrogen adsorption/desorption isotherms at -196 °C were obtained using a Micromeritics Tristar II instrument. Before each measurement, the sample was degassed under vacuum at 200 °C for 12 h. The Brunauer-Emmett-Teller (BET) equation was applied to calculate the

specific surface area using the adsorption data in the range of $p/p_0=0.05-0.2$ [21, 22]. The t-plot method was used to calculate the external surface area, micropore area and micropore volume using the adsorption data in the range of $p/p_0=0.2-0.5$ [22]. The total pore volume was determined from the amount of nitrogen adsorbed at $p/p_0=0.995$.

2.3 Catalytic MTG reaction test

The performance of the catalyst in MTG was conducted using a high pressure fixed-bed reactor. Powder catalysts were pelletised, crushed and sieved into a size fraction of 1–1.5 mm in diameter. 0.24 g of a sieved catalyst was loaded into the middle of a quartz lined stainless steel reactor of 7 mm in internal diameter. The reactor was placed in a vertical furnace and aligned to ensure the catalyst was sitting at the centre of the isothermal zone. Before the MTG reaction, the catalyst was activated at 375 °C for 2 h in a high purity nitrogen flow rate (44 mL min⁻¹). Liquid methanol (Sigma-Aldrich, HPLC grade, 99.9%) at a flow rate of 0.01 mL min⁻¹ was vaporised at 375 °C in an electric preheater and introduced into the reactor using a high purity nitrogen carrier gas at a flow rate of 44 mL min⁻¹, giving a 10% (v/v) methanol in the nitrogen mixture. The reaction was performed under a set of constant reaction conditions of 375 °C, 1 MPa and weight hourly space velocity (WHSV) 2 h⁻¹. The reaction experiment was terminated when methanol conversion decreased to 50%, the duration of which was defined as the service lifespan of the catalyst (denoted as $t_{1/2}$).

The downstream manifolds of the reaction system were maintained at 180 °C to avoid any product condensation in the exit stream. The product composition was analysed online at 1 h intervals using an Agilent 7890A gas chromatograph (GC), to quantify the product selectivity and calculate the methanol conversion as a function of time on stream [16, 18, 23]. The GC was equipped with two capillary columns, VF-1 ms and PoraBOND Q, connected to a thermal conductivity detector (TCD) for composition analysis of light hydrocarbons (C₁–C₄), and three capillary columns, CP Ms 5A, CP-Sil 8 CB and PoraBOND Q, connected to a flame

ionisation detector (FID) for composition analysis of C₅₊ liquid fractions (aliphatics and aromatics) as well as unreacted methanol.

2.4 Coke Analysis

The total amount of coke formed in the spent catalyst was determined using a SDT600 TGA (TA Instrument). The measurements were first conducted in a nitrogen atmosphere to vaporise absorbed organic volatiles at elevated temperatures, followed by oxidation in air to burn off the remaining hard coke. In a typical TGA run, with high purity nitrogen at a flow rate of 100 mL min⁻¹, about 10 mg of the spent sample was placed in an alumina crucible and heated to 105 °C at a heating rate of 20 °C min⁻¹ and maintained for 15 min to remove any surface moisture. The sample was further heated to 550 °C at a heating rate of 10 °C min⁻¹ and kept for 15 min. The gas atmosphere was then switched to air with a flow rate of 100 mL min⁻¹, and the sample was held for 40 min to allow for complete coke oxidation. The mass loss in nitrogen above 105 °C but below 550 °C was ascribed to the removal of volatile species absorbed on the catalyst. The mass loss in the air was associated with oxidation of the hard coke.

The chemical composition, molecular structure and morphology of the coke were studied using gas chromatography mass spectrometry (GC–MS), ¹H and ¹³C nuclear magnetic resonance (NMR) and high-resolution TEM (HRTEM), respectively. Coke was extracted from the fouled catalyst by dissolving the spent catalyst in a solution of sodium hydroxide (NaOH) and ethanol (EtOH), a schematic of the procedures for coke extraction is shown in the Supporting Information Figure S1. Briefly, 0.2 g of a spent catalyst, 1.5 g of NaOH and 15mL of EtOH were mixed in a sealed Teflon-lined autoclave, and the resulting mixture was kept at 100 °C for 24 h. After cooling to room temperature, the solution was transferred to a polypropylene beaker and heated to 80 °C in an oil bath until EtOH was fully evaporated. The resulting solid was soaked with deionized water and then dichloromethane (DCM), and

subsequently filtered to give a black solid (insoluble coke) which was collected and dried for TEM imaging analysis. The filtrate was transferred to a separating funnel and extracted twice using DCM solvent. The recovered DCM phase was concentrated and subsequently analysed using a GC–MS and ^1H and ^{13}C NMR to detect possible solute (soluble coke). The amount of internal and external coke was respectively quantified following a method reported in the literature [4, 24]. Briefly, assuming that the decrease in micropore volume of the spent catalyst sample compared with that of the virgin catalyst is attributed to the deposition of internal coke, thus the amount of internal coke can be calculated by referring the coke density to 1.22 g cm^{-3} of a coal having a H/C ratio of 0.8 [4, 24]. The amount of external coke can then be calculated by subtracting the internal coke from the total coke content determined from the TGA analysis. In this study, the volatile species were considered as coke as they also contributed to the reduction in micropore volume, although it was difficult to tell if they were deposited on the external or internal surfaces. The total coke content comprised the amount of volatiles and hard coke.

3. Results and Discussion

3.1. General characteristics of the catalysts

The crystal structures of the nanocrystal and microcrystal ZSM-5 samples were verified by the powder XRD patterns. As shown in Figure 1a, both samples exhibited diffraction patterns consistent with and corresponding to the reference standard of a highly crystalline ZSM-5 zeolite [25]. The nanocrystal ZSM-5 sample was also shown to have slightly less resolved peaks than the microcrystal ZSM-5 in the $22.5 - 25^\circ 2\theta$ angle range. This can be understood according to the Scherrer equation that nanosized crystals would show broad peaks in a diffraction pattern [26, 27].

The morphologies of the two ZSM-5 samples are illustrated by representative SEM and TEM images in Figure 1(b–e). The nanocrystal ZSM-5 displayed clean and segregated particles consisting of single crystals with uniform sizes of ~100 nm (Figure 1b and c). The microcrystal ZSM-5 consisted of twined crystals with an average size of ~13 μm (Figure 1d). It must be noted that these crystals incurred some physical cracking or rupture, being partially crushed during the pelletisation, thus producing irregular particles but remaining basically similar crystal size (Figure 1e).

The NH_3 –TPD profiles of the fresh nanocrystal and microcrystal ZSM-5 are shown in Figure 1f. Both samples had two distinct desorption peaks. The one at 150–320 $^\circ\text{C}$ is categorised as the low temperature peak (LT–peak) attributed to the desorption of weakly bound NH_3 , and the peak area is considered to correspond to the density of weak acid sites. Similarly, the one at 320–550 $^\circ\text{C}$ is known as the high temperature peak (HT–peak) resulting from the desorption of strongly bound NH_3 , with its area corresponding to the density of strong acid sites [28–30]. The nanocrystal ZSM-5 had a lower peak area at the LT–peak but a greater peak area at HT–peak than those of the microcrystal ZSM-5. The overall peak area is very similar for both samples, indicating they had comparable amounts of total acid sites, in good agreement with their almost identical $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio as determined by the ICP–AES results, being 47 and 51 for the fresh nanocrystal and microcrystal ZSM-5 samples, respectively.

The nitrogen physisorption isotherms of the fresh ZSM-5 samples are shown in Figure 1g. The nanocrystal ZSM-5 showed type–IV isotherms with a steep nitrogen uptake and hysteresis loops at high relative pressures ($p/p_0 > 0.9$), indicating the existence of mesopores in the structure which can be attributed to the intercrystal voids between nanosized crystals. The microcrystal ZSM-5 had type–I isotherms, indicating it was a solely microporous material. The two samples also had almost the same steep uptakes in the low relative pressure region ($p/p_0 < 0.01$), indicative of high microporosity, suggesting that both ZSM-5 samples had

virtually the same intact microporous framework with high crystallinity. As further evidenced by the pore characteristics summarised in Table 1, the two ZSM-5 samples had very similar micropore areas and volumes typical of highly crystalline ZSM-5 zeolites. The nanocrystal ZSM-5 had doubled external surface areas and total pore volumes compared to the microcrystal ZSM-5 as a result of its nanosize.

3.2. Catalytic performance in MTG

The performance of the two catalysts in MTG was evaluated in a fixed bed reactor under identical reaction conditions of temperature 375 °C, pressure 1 MPa, and WHSV 2 h⁻¹. This set of reaction condition is similar to that applied for the commercial MTG process [31, 32].

The results of methanol conversion as a function of time on stream for the two catalysts are compared in Figure 2a. The nanocrystal ZSM-5 showed $t_{1/2}$ of 270 h, almost seven times longer than that of its microcrystal counterpart at 40 h. ZSM-5 catalysts with smaller particle sizes have been known to have improved catalytic service lifespan in MTG due to shortened diffusion path [15, 33] for easier transport of hydrocarbons in/out of the intra-crystal micropore channels and thus less chance for coke formation and deposition. Similarly, as observed in this study, the enhanced catalytic service lifespan may be logically assigned to the obvious difference in crystal size between the two catalysts, considering that both had similar structural properties and active site density. However, this is seemingly superficial and inadequate. An interesting question arises as to if and how this stark discrepancy in catalytic service lifespan can be explained by the coking behaviour on the nanocrystal and microcrystal catalysts, since coking is the main cause of the deactivation of ZSM-5 catalyst in MTG.

The product selectivity, for the nanocrystal and microcrystal ZSM-5 catalysts respectively, is shown in Figure 2b and 2c. The product selectivity over the nanocrystal ZSM-5 catalyst remained relatively steady over time on stream until about 200 h after which a small decrease in the selectivity of the aromatics fraction as well as the C₁–C₄ fraction and a noticeable

increase in the C₅₊ aliphatics fraction were evident. Significant changes in the product selectivity occurred when the methanol conversion was dramatically decreased, indicating a great loss of the catalyst activity. This can be understood as the catalytic acidity is gradually reduced due to increasing coverage of active sites by the coke formed over time on stream. Such a result is consistent with our earlier study on the effect of SiO₂/Al₂O₃ ratio on the product selectivity for the nanocrystal ZSM-5 catalyst in MTG [34]. A similar phenomenon was also observed for the microcrystal catalyst. However, it should be noted that the product of the nanocrystal ZSM-5 catalyst was dominated by aromatics while the C₁–C₄ fraction was the main product of the microcrystal catalyst. This discrepancy can be explained by their vast difference in the crystal size. Limited by the long diffusion paths of the microcrystal catalyst, the intermediates would more easily undergo further reactions such as dealkylation and condensation, leading to a higher C₁–C₄ product selectivity and faster formation and deposition of internal coke. In contrast, the nanocrystal catalyst with short diffusion paths afforded a greater chance for the aromatics to escape from the internal pores without incurring significant coking [35].

3.3 Coke formation and characteristics

To understand the mechanism of deactivation of these two catalysts due to coking, a detailed analysis of coke characteristics was performed to not only quantify the total amount of coke formed, but also understand the nature and locations of coke formed within the catalyst structure.

3.3.1 Internal and external coke

The total amounts of coke formed during the MTG reaction for both catalysts were determined from the TGA curves shown in Figure 3a. The total mass losses were 23.7 and 12.6 wt% for the spent nanocrystal and microcrystal catalysts, respectively. It corresponds to 31.1 wt% of coke formed on the virgin nanocrystal catalyst during the reaction. In other

words, 1 g of the fresh nanocrystal catalyst incurred 0.31 g of coke deposition by the time when the methanol conversion decreased to 50%. Similarly, 14.4 wt% of coke formed on fresh microcrystal catalyst.

The amounts of internal and external coke were determined by combining the nitrogen physisorption and TGA results. The micropore volume of the spent catalyst was estimated from the nitrogen physisorption data. The adsorption/desorption isotherms for the two spent catalysts are shown in Figure 3 b and c, respectively, together with those for their virgin samples. Comparing to the fresh samples, both spent catalysts showed significantly reduced adsorption capability in the low relative pressure region. This was indicative of a substantial reduction in micropore volume, suggesting that the micropore channels for the two spent samples were largely occupied by coke. As summarised in Table 1, the nanocrystal catalyst showed a $0.07 \text{ cm}^3 \text{ g}^{-1}$ reduction in the micropore volume. The content of internal coke deposited was thereby determined to be 9 wt% of the virgin nanocrystal catalyst, and external coke 22.1 wt%. Similarly, the loading of the internal and external coke for the microcrystal catalyst was determined to be 10 wt% and 4.4 wt%, respectively. These results are summarised in Figure 3d. Clearly, nanocrystal ZSM-5 catalyst incurred more external coke formation whilst microcrystal ZSM-5 incurred predominantly internal coke. Despite a five-fold loading of external coke on the former compared with the latter, interestingly, both catalysts accumulated almost the same amount of internal coke at $t_{1/2}$. This phenomenon is discussed in detail in later sessions.

The differences in coke formation for the two catalysts were also reflected by the changes in their morphologies before and after use. Figure 4 shows the SEM and TEM images of the spent nanocrystal and microcrystal catalysts. In contrast to segregated particles of single crystal (Figure 1b and c), the spent nanocrystal catalyst showed agglomerates of crystals 'glued' together by amorphous substances on the external surface of the crystals (Figure 4a

and b). These substances were further examined and a typical HAADF STEM image and associated EDS elemental mapping of the spent sample are shown in Figure 5. The elemental distribution of carbon is shown in Figure 5b presenting a mapping area identical to the samples observed in the STEM. In particular, some areas of the map show highly concentrated carbons (highlighted in Figure 5b) but no trace of Si and Al as shown in Figure 5c and d. This observation is consistent with the SEM characteristics of coke deposited on the external surface of the catalyst. Since the possibility of residual carbon from the ZSM-5 synthesis process can be ruled out due to thorough calcination of the catalyst at 550 °C for 5 h prior to each use, it can be confirmed that this carbon was the coke formed during the MTG reaction and a significant fraction was external coke when nanocrystal ZSM-5 catalyst was used. Unlike the case of nanocrystal catalyst, the spent microcrystal catalyst displayed morphology almost identical to that of the pelletised fresh sample (Figure 4c) with little evidence of visible coke on the external surface (Figure 4d), confirming that much less external coke was formed on the microcrystal catalyst.

The stark difference in coke formation, distribution and characteristics between the two catalysts may be explained in terms of their different crystal sizes. The diffusion paths of the nanocrystal catalyst were greatly shortened owing to its nanosized crystals, leading to markedly enhanced mass diffusion [33, 36, 37]. Coke precursors (e.g. aromatic fragments) initially formed in the micropore channels could readily migrate to the external surface, either dissipating into the reacting stream or resulting in predominantly external coke (~1.5 times more than the internal coke). In the case of the microcrystal catalyst, the migration of coke precursors was sluggish due to substantially longer diffusion path in the microcrystal ZSM-5 (~130 times longer than the nanocrystal calculated based on their crystal sizes). The coke precursors would further undergo condensation and polymerisation reactions and ultimately

be trapped in the micropore channels, leading to 56% less external coke than internal coke for the microcrystal catalyst.

3.3.2 Coke characteristics

Studying coke composition and properties requires the materials to be separated from the spent zeolite catalyst and extracted commonly using DCM. Therefore, the aluminosilicate of the spent catalyst needs to be completely dissolved, normally through leaching by hydrofluoric acid (HF) aqueous solution [4, 24]. However, HF is a notorious highly corrosive chemical and the handling of HF must follow a series of stringent requirements which is not adaptable for most chemical engineering laboratories. In this study, a greener and safer method using a NaOH/EtOH solution was developed to successfully dissolve the catalyst without adversely altering the chemical properties of the coke.

The coke extracted using DCM (soluble coke) was subsequently subjected to GC–MS and ^1H and ^{13}C NMR analysis (shown in supporting information, Figure S2 and Figure S3). A molecule of $\text{C}_{14}\text{H}_{12}$ was identified by referencing the NIST standard database for GC–MS. Unfortunately, the overall data obtained were insignificant due to the extremely low concentration of soluble coke despite that the solution was concentrated to above the minimal volume required for the GC and NMR analyses. Such a negligible solute content is indicative of only a trace amount of soluble coke formed during the reaction. Indeed, coke would tend to be more carbonaceous due to aging under such long reaction time and high temperatures, ultimately promoting the formation of more hard coke (insoluble coke). This claim is also echoed in the TGA curve (Figure 3a), in which the mass loss of the spent catalysts under a nitrogen atmosphere (before combustion) was very low, particularly below 300 °C (less than 1 wt%), indicating that little volatile species associated with soluble coke was formed in the spent nanocrystal sample.

Coke insoluble in DCM, or insoluble coke, was collected by filtering the NaOH/EtOH solution, dried and analysed using TEM. As shown in Figure 6, the insoluble coke appeared in a form of randomly entangled chains of ~ 11 nm in width. The “chain” structure was further confirmed by the high-resolution TEM (HRTEM) image in Figure 6 d in which clear lattice fringes with ~ 0.33 nm spacing was evident, indicating the existence of localised graphitic structures in the coke. It is worth noting that during TEM imaging of the spent nanocrystal catalyst, the crystals were often found to be heavily encapsulated by coke, and some of the coke casings were found to be isolated but still remained the contour shape of the crystals, as shown in Figure 7. Moreover, the thickness of the external coke directly peeled off the ZSM-5 nanocrystal was found to be similar to the width of the insoluble coke isolated after the NaOH/EtOH digestion of the zeolites, as evident in Figure 6. The morphology of insoluble coke observed was thus likely to have been produced following the mechanism as schematically illustrated in Figure 8. Firstly, coke layers wrapping or partially wrapping the crystals were formed during MTG. After the removal of zeolites, coke was segregated as a suspension in the NaOH/EtOH solution. During the subsequent filtration, internal coke was highly likely to have collapsed due to its very thin structure (maximum ~0.55 nm); external coke separated was randomly stacked together and a transmissive view would resemble that illustrated in Figure 6.

3.4 Relating coke formation and characteristics to catalyst deactivation

The catalyst is deactivated by coke formation that leads to progressive pore blockage, coverage and subsequent loss of active sites [1, 6, 38, 39]. Coke is composed of large aromatics formed as a by-product at the active sites by reactions parallel to the main MTG reaction. Since reactions predominantly take place in micropore channels of ZSM-5 zeolite where the majority of active sites are located [40], the deposition of coke in the channels (internal coke) can lead to direct coverage of the active sites and obstruction of diffusion thus

imposing detrimental effect on the durability of the catalyst. Furthermore, the formation of coke on the external surface (external coke) of the catalyst may lead to plugging of pore mouth if the coke is non-porous and impermissible for gas molecules involved. This would prevent the reactant from accessing the active sites, adversely affecting the catalyst performance. Therefore, it infers that the rate of formation of internal coke and structural properties of external coke hold the key to explaining the different deactivation behaviour of the two catalysts.

In this study, the two catalysts had very similar internal coke content at $t_{1/2}$ even though the $t_{1/2}$ for the nanocrystal ZSM-5 was 7 times longer than that of the microcrystal ZSM-5, which could also be understood as when the accumulation of internal coke reached about 10 wt%, both ZSM-5 catalysts would lose 50% of its activity. However, taking the reaction duration into account, it took 270 h for the nanocrystal catalyst to form the same amount of internal coke, while it was merely 40 h for the microcrystal catalyst. The averaged formation rates of internal coke for the nanocrystal and microcrystal catalyst were thus calculated to be $1.4 \times 10^{-3} \text{ g g}^{-1} \text{ h}^{-1}$ and $1.0 \times 10^{-2} \text{ g g}^{-1} \text{ h}^{-1}$, respectively, one order of magnitude in difference. Clearly, the nanocrystal catalyst showed a tremendously slow formation of internal coke, and consequently, much slower coverage of active sites and blockage of channels, leading to a much longer catalytic service lifespan.

On the other hand, the nanocrystal catalyst showed a great longevity even with a significant amount of external coke deposited (~1.5 times higher than the internal coke). This implies that the formation of external coke has much less impact on the catalyst activity than normally anticipated, provided that the coke has a porous structure permissible to diffusion of the reactants and products. As mentioned before, whether external coke is harmful to the catalyst performance or not really depends on its pore structure. The coke isolated by digesting the spent catalyst was thus analysed using nitrogen physisorption, from which typical type-V

isotherms are evident as shown in Figure 9. The hysteresis loop at relative pressures $p/p_0 > 0.6$ was indicative of the existence of mesopores in the coke sample, which was further confirmed by the pore size distribution (Figure 9 inset) showing appreciable fraction of mesopores ranging from ~3 nm to 10 nm. It should be noted that the coverage of external coke on the spent nanocrystal ZSM-5 was non-uniform, incomplete, and sometimes loose (Figure 7a, b and d), and the external coke tended to form aggregates of flakes (Figure 4b), providing various pores and channels. The porous nature of the external coke was also evidenced by the increased external surface area (by $41 \text{ m}^2 \text{ g}^{-1}$) on the coke fouled nanocrystal ZSM-5 compared to the fresh catalyst. These pores allowed the surface of the catalyst to remain accessible to MTG reactants and products in spite of a heavy deposit of external coke. It was therefore ascertained that the external coke was less harmful to the catalyst performance.

It should be noted that the methanol conversion over the nanocrystal ZSM-5 showed a steep decrease after being sustained at ~ 98% for approximately 200 h (Figure 2). This might imply a sudden change in the pore network of the catalyst that impedes the accessibility of active sites and the diffusion of reactant and products. ZSM-5 zeolite is known to have a three-dimensional interconnected porous network. Since coke is accumulated over time [41], such deposit inside the ZSM-5 crystals may change the interconnectivity of the network thus affecting the pore accessibility. It is anticipated that the entire pore network gradually loses the diffusion paths for hydrocarbon molecules with increasing time on stream and eventually becomes non-through at the end of catalytic service lifespan. However, as evidenced by the present experimental data, the transition of catalyst deactivation was rather abrupt well before the micropores were fully blocked in the spent ZSM-5 catalysts. This phenomenon may be explained by the percolation theory [42-44]

The percolation theory hypothesises that when the fraction of blocked pore volume approaches a threshold, the remaining pores are no longer accessible, and diffusion through

the pore network is terminated. A percolation probability, P , is used to describe the probable fraction of through pores inside the network, and thus can be related to the accessibility of the pore network [45, 46]. Hence, P decreases with increasing number of blocked pores, and becomes zero at the percolation threshold. In the case of ZSM-5 zeolite in MTG, as internal coke causes the pore blockage, the accessibility of the pore network or P decreases with increasing internal coke formation, and becomes zero when the internal coke accumulates to a certain amount, by means of reaching the percolation threshold. This could lead to a dramatic loss of the catalyst activity, causing the aforementioned sudden drop in methanol conversion. The present study found the nanocrystal ZSM-5 catalysts lost 58% of its initial micropore volume at the time of sharp decrease in methanol conversion, and surprisingly similar, 64% in microcrystal ZSM-5, indicating a percolation threshold of around 0.58 ~ 0.64, in line with the value (0.64) predicted by the dynamic Monte Carlo simulation for the MFI type topology [47].

3.5 *Catalytic performance of the regenerated nanocrystal catalyst*

In industrial practice, coke fouled ZSM-5 catalysts are subjected to regeneration to remove the coke by combustion in air (500-600 °C) [20, 48, 49]. However, the activity of the catalyst cannot be fully restored [20, 50]. Such degradation is believed to be mainly due to the loss of Al by hydrolysis during the reaction and regeneration.

In this study, the spent nanocrystal ZSM-5 sample was regenerated and the characteristics and activity of the regenerated catalyst were also examined again. The regeneration of the deactivated catalyst was carried out at 550 °C in air for 4 h. Figure 10 shows the general characteristics of the regenerated catalyst. After oxidising the coke off the spent catalyst in air, the morphology of the regenerated catalyst (Figure 10a and b) was basically identical to that of the fresh catalyst. In addition, the regenerated catalyst also showed very similar adsorption/desorption isotherms (Figure 10c) as the fresh one, suggesting no noticeable damage occurred during the reaction and regeneration of the nanocrystal catalyst. However, a

decrease in the total amount of acid sites was evident by the NH_3 -TPD profiles for the regenerated catalyst shown in Figure 10d, as compared to that of the fresh one. This is in agreement with an increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio determined from the ICP-AES analysis (the spent sample had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 61), revealing an approximately 30% Al loss after one reaction and regeneration cycle.

The rejuvenated catalyst was subsequently tested under the same reaction conditions. The methanol conversion as a function of time on stream is shown in Figure 11. The regenerated catalyst showed a similar trend in methanol conversion to that of the fresh catalyst. However, instead of incurring an activity loss, the regenerated catalyst exhibited an increase of the catalytic service lifespan $t_{1/2}$ to 300 h. This may be understood in terms of the effect of Al concentration on the performance of the catalyst.

It is well documented in the literature [11, 51] that the Al concentration (commonly represented as Si/Al or $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) of a ZSM-5 catalyst plays a pivotal role in determining its catalytic performance. The protonated H-ZSM-5 possesses strong acidity that enables it to have high catalytic activity suitable for wide applications in heterogeneous catalysis [52]. The acid strength is determined by the number of acid sites which is proportional to the Al concentration in the catalyst. Generally, the higher the Al concentration, the stronger the acidity and thus, the higher activity the catalyst has. However, since coke formation is also a function of the acidity, coke formation increases with increasing acid strength and concentration. The high concentration of Al would also increase the coke formation rate leading to faster catalyst deactivation [1, 53]. A catalyst with a low Al concentration can extend its life time but may sacrifice its catalytic activity. A suitable range of Al concentration is thus essential for desired catalytic service lifespan while also preserving the high activity. Our recent study showed a nanocrystal ZSM-5 catalyst with a

499 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 217 had the best performance among those with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios
500 between 23–411 [34].

501 The regenerated catalyst showed a moderate decrease in the total amount of acid sites,
502 resulting in an enhanced catalytic service lifespan. More importantly, the activity of the
503 regenerated nanocrystal ZSM-5 in present work was not compromised, as it was still
504 sufficient to sustain a 98% MeOH conversion in the MTG process. However, as the loss of Al
505 was irreversible, it is believed that the catalyst would eventually lose its activity for effective
506 MTG when the Al level drops below a certain threshold after many repeated cycles, thereafter
507 due for replenishment.

508

4. Conclusions

This study demonstrated two coke formation and deposition mechanisms and the relationship between the formation and characteristics of the coke and the deactivation of the catalyst in ZSM-5 zeolite catalysed MTG reaction. The nanocrystal ZSM-5 (crystal size of ~ 100 nm) was shown to have more than doubled coke content but surprisingly sustained a catalytic service lifespan seven times longer than its microcrystal counterpart (~ 13 μm). The total amount of coke formed thus was not a good indication of the catalyst service lifespan.

An insight into the coking behaviour was revealed in that it was the formation rate of internal coke that directly determined the catalytic service lifespan while the formation of external coke had little impact on the catalyst performance. The improved service lifespan of the nanocrystal ZSM-5 catalyst was attributed to the slow accumulation of internal coke as a result of the short diffusion paths, which allowed coke precursors to readily migrate to the outer surface to dispose or form external coke. The external coke found mainly on the surface of nanocrystal catalyst was porous and thus less detrimental to the catalyst activity.

The loss of Al during the reaction and regeneration could also lead to an increase in the catalytic performance depending on the optimal Al range. The Al concentration of the nanocrystal ZSM-5 catalyst was reduced by 30% after the first reaction and regeneration cycle. However, the regenerated catalyst had a longer service lifespan than the virgin ZSM-5 catalyst. This finding implies that starting the MTG process with a nanocrystal ZSM-5 having higher Al content may significantly extend the overall cyclic service lifespan of the catalyst without the catalytic performance being compromised.

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References

- [1] M.D. Argyle, C.H. Bartholomew, *Catalysts*, 5 (2015) 145-269.
- [2] M. Guisnet, F.R. Ribeiro, *Deactivation and regeneration of zeolite catalysts*, World Scientific, London, 2011.
- [3] H. Schulz, K. Lau, M. Claeys, *Appl. Catal. A*. 132 (1995) 29-40.
- [4] M. Guisnet, P. Magnoux, *Appl. Catal. A*. 212 (2001) 83-96.
- [5] M. Guisnet, L. Costa, F.R. Ribeiro, *J. Mol. Catal. A: Chem.* 305 (2009) 69-83.
- [6] S. Muller, Y. Liu, M. Vishnuvarthan, X.Y. Sun, A.C. van Veen, G.L. Haller, M. Sanchez-Sanchez, J.A. Lercher, *J. Catal.* 325 (2015) 48-59.
- [7] G.T. Kokotailo, S.L. Lawton, D.H. Olson, W.M. Meier, *Nature*. 272 (1978) 437-438.
- [8] S. Teketel, W. Skistad, S. Benard, U. Olsbye, K.P. Lillerud, P. Beato, S. Svelle, *ACS Catal.* 2 (2012) 26-37.
- [9] D.X. Liu, A. Bhan, M. Tsapatsis, S. Al Hashimi, *ACS Catal.* 1 (2011) 7-17.
- [10] X. Sun, S. Mueller, Y. Liu, H. Shi, G.L. Haller, M. Sanchez-Sanchez, A.C. van Veen, J.A. Lercher, *J. Catal.* 317 (2014) 185-197.
- [11] A. Primo, H. Garcia, *Chem. Soc. Rev.* 43 (2014) 7548-7561.
- [12] J. Kim, M. Choi, R. Ryoo, *J. Catal.* 269 (2010) 219-228.
- [13] N.L. Michels, S. Mitchell, J. Perez-Ramirez, *ACS Catal.* 4 (2014) 2409-2417.
- [14] M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, *Nature*. 461 (2009) 246-249.
- [15] S.K. Saxena, N. Viswanadham, A.H. Al-Muhtaseb, *J. Ind. Eng. Chem.* 20 (2014) 2876-2882.
- [16] Z.J. Wan, W. Wu, W. Chen, H. Yang, D.K. Zhang, *Ind. Eng. Chem. Res.* 53 (2014) 19471-19478.
- [17] J.A. Zhou, Z.L. Hua, Z.C. Liu, W. Wu, Y. Zhu, J.L. Shi, *ACS Catal.* 1 (2011) 287-291.

564 [18] Z. Di, C. Yang, X. Jiao, J. Li, J. Wu, D. Zhang, *Fuel*. 104 (2013) 878-881.

565 [19] T. Fu, H. Zhou, Z. Li, *Catal. Lett.* 146 (2016) 1973-1983.

566 [20] F. Schmidt, C. Hoffmann, F. Giordanino, S. Bordiga, P. Simon, W. Carrillo-Cabrera, S.

567 Kaskel, J. *Catal.* 307 (2013) 238-245.

568 [21] J.J.C. Groen, L.A.A. Peffer, J. Perez-Ramirez, *Micropor. Mesopor. Mat.* 60 (2003) 1-17.

569 [22] S. Lowell, *Characterization of porous solids and powders: surface area, pore size and*

570 *density*, Springer, 2004.

571 [23] K. Kim, R. Ryoo, H.D. Jang, M. Choi, J. *Catal.* 288 (2012) 115-123.

572 [24] D.M. Bibby, N.B. Milestone, J.E. Patterson, L.P. Aldridge, J. *Catal.* 97 (1986) 493-502.

573 [25] M.M. Treacy, J.B. Higgins, R. von Ballmoos, I.Z. Association, S. Commission,

574 *Collection of simulated XRD powder patterns for zeolites*, Elsevier, New York, 1996.

575 [26] D.P. Serrano, J. Aguado, J.M. Escola, J.M. Rodriguez, A. Peral, J. *Catal.* 276 (2010) 152-

576 160.

577 [27] J.K. Reddy, K. Motokura, T.-r. Koyama, A. Miyaji, T. Baba, J. *Catal.* 289 (2012) 53-61.

578 [28] F. Lónyi, J. Valyon, *Micropor. Mesopor. Mat.* 47 (2001) 293-301.

579 [29] L. Rodríguez-González, F. Hermes, M. Bertmer, E. Rodríguez-Castellón, A. Jiménez-

580 López, U. Simon, *Appl. Catal. A.* 328 (2007) 174-182.

581 [30] L. Rodríguez-González, E. Rodríguez-Castellón, A. Jiménez-López, U. Simon, *Solid*

582 *State Ionics*. 179 (2008) 1968-1973.

583 [31] D.M. Bibby, R.F. Howe, G.D. Mclellan, *Appl. Catal. A.* 93 (1992) 1-34.

584 [32] F.J. Keil, *Micropor. Mesopor. Mat.* 29 (1999) 49-66.

585 [33] A.A. Rownaghi, F. Rezaei, J. Hedlund, *Catal. Commun.* 14 (2011) 37-41.

586 [34] Z. Wan, W. Wu, G.K. Li, C. Wang, H. Yang, D. Zhang, *Appl. Catal. A.* 523 (2016) 312-

587 320.

588 [35] Z. Wan, C. Wang, H. Yang, D. Zhang, 41st Chemeca 2013: Challenging Tomorrow,
 589 Brisbane, Qld, (2013) 885-889.

590 [36] A.A. Rownaghi, J. Hedlund, Ind. Eng. Chem. Res. 50 (2011) 11872-11878.

591 [37] A.A. Rownaghi, F. Rezaei, J. Hedlund, Micropor. Mesopor. Mat. 151 (2012) 26-33.

592 [38] E.C. Nordvang, E. Borodina, J. Ruiz-Martínez, R. Fehrmann, B.M. Weckhuysen, Chem.
 593 Eur. J. 21 (2015) 17324-17335.

594 [39] J.E. Schmidt, J.D. Poplawsky, B. Mazumder, Ö. Attila, D. Fu, D.A. de Winter, F. Meirer,
 595 S.R. Bare, B.M. Weckhuysen, Angew. Chem. Int. Ed. 55 (2016) 11173-11177.

596 [40] P.L. Benito, A.G. Gayubo, A.T. Aguayo, M. Olazar, J. Bilbao, Ind. Eng. Chem. Res. 35
 597 (1996) 3991-3998.

598 [41] Y. Song, Y. Xu, Y. Suzuki, H. Nakagome, Z.-G. Zhang, Appl. Catal. A. 482 (2014) 387-
 599 396.

600 [42] T.V.W. Janssens, J. Catal. 264 (2009) 130-137.

601 [43] A. Izadbakhsh, F. Khorasheh, Chem. Eng. Sci. 66 (2011) 6199-6208.

602 [44] M.D.P. Sørensen, Chem. Eng. Sci. 106 (2014) 126-135.

603 [45] A.O.E. Beyne, G.F. Froment, Chem. Eng. Sci. 48 (1993) 503-511.

604 [46] D. Chen, H.P. Rebo, A. Holmen, Chem. Eng. Sci. 54 (1999) 3465-3473.

605 [47] B.B.L. Trout, A.K. Chakraborty, A.T. Bell, Chem. Eng. Sci. 52 (1997) 2265-2276.

606 [48] A. deLucas, P. Canizares, A. Duran, A. Carrero, Appl. Catal. A. 156 (1997) 299-317.

607 [49] S.J. Jong, A.R. Pradhan, J.F. Wu, T.C. Tsai, S.B. Liu, J. Catal. 174 (1998) 210-218.

608 [50] A.G. Gayubo, A.T. Aguayo, M. Castilla, M. Olazar, J. Bilbao, Chem. Eng. Sci. 56 (2001)
 609 5059-5071.

610 [51] A. Corma, J. Catal. 216 (2003) 298-312.

611 [52] H. Zhang, Z. Hu, L. Huang, H. Zhang, K. Song, L. Wang, Z. Shi, J. Ma, Y. Zhuang, W.
 612 Shen, ACS Catal. 5 (2015) 2548-2558.

613 [53] S. Inagaki, S. Shinoda, Y. Kaneko, K. Takechi, R. Komatsu, Y. Tsuboi, H. Yamazaki,
614 J.N. Kondo, Y. Kubota, ACS Catal. 3 (2012) 74-78.

615

616 **Figure Captions**

617 Figure 1 General characteristics of fresh catalysts: (a) XRD patterns; (b) SEM images and
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619 microcrystal ZSM-5 before and after pelletising; (f) NH_3 -TPD profiles, and (g)
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621 hollow ones for desorption

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624 conditions of 375 °C, 1 MPa and WHSV 2 h⁻¹

625 Figure 3 Determination of coke deposited on the *internal* and *external* surfaces of the spent
626 nanocrystal and microcrystal ZSM-5 catalysts: (a) TGA curves; (b) and (c)
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628 counterparts, and (d) amounts of *internal* and *external* coke for the two spent
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636 Figure 6 Typical TEM images of insoluble coke separated from the spent nanocrystal
637 ZSM-5 catalyst (a–c), and HRTEM image (d) showing the existence of localised
638 graphitic structures

639 Figure 7 Typical TEM images of the spent nanocrystal ZSM-5 catalyst (a) highlighting the
640 encapsulation (b and c) and the exfoliation (d) of the *external* coke on the ZSM-5
641 crystals while retaining the original shape

642 Figure 8 Schematic of isolation and collection of coke formed on spent nanocrystal ZSM-5
643 catalyst

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List of Tables

Table 1 Nitrogen physisorption characteristics of the nanocrystal and microcrystal ZSM-5 catalysts

Sample	S_{BET} (m^2g^{-1})	t-Plot S_{Micro} (m^2g^{-1})	t-Plot S_{Exter} (m^2g^{-1})	V_{Total} (cm^3g^{-1})	t-Plot V_{Micro} (cm^3g^{-1})
Fresh nanocrystal ZSM-5	420	304	116	0.33	0.12
Spent nanocrystal ZSM-5	248	101	147	0.23	0.05
Fresh microcrystal ZSM-5	352	302	50	0.17	0.11
Spent microcrystal ZSM-5	99	75	24	0.05	0.03

Note: S_{BET} for BET surface area, calculated using the BET method; t-Plot S_{Micro} for micropore area, determined using the t-plot method; t-plot S_{Exter} for external surface area, calculated by subtracting the micropore area from the BET area; V_{Total} for total pore volume, determined from the adsorbed amount at $p/p_0=0.995$; and t-plot V_{Micro} for micropore volume, calculated using the t-plot method.

720 Figure S1

722 **Figure S1** A schematic of the procedure for coke extraction using an EtOH/NaOH solution

723 Figure S2

724

725 **Figure S2** GC–MS spectrum of the soluble coke extracted using dichloromethane. The first
726 peak is likely to be associated with $C_{14}H_{12}$ according to the NIST standard
727 reference database [Standard Reference Data Program, National Institute of
728 Standards and Technology, Gaithersburg, MD. Standard Reference Database IA.
729 Internet address: <http://www.nist.gov/srd/nist1a.htm>]. The second peak has been
730 identified to be from plasticizer contamination and thus ignored.

731 Figure S3

732

733 **Figure S3** ^1H and ^{13}C NMR signals for the soluble coke extracted using dichloromethane.

734

735 The NMR spectroscopic analysis was performed using a Varian 400 NMR

736 spectrometer operating at 399.86 MHz for the ^1H mode and 100.55 MHz for the

737 ^{13}C mode. Deuterated chloroform (CDCl_3) was used as the solvent. The spectra

738 were referenced to the residual chloroform (CHCl_3) resonance at 7.26 ppm for ^1H

739 NMR spectroscopy and 77.16 ppm for ^{13}C NMR spectroscopy. In addition,

740 chromium acetylacetonate [$\text{Cr}(\text{acac})_3$] was added to the solution at a concentration

741