



Feature Article

Relating coke formation and characteristics to deactivation of ZSM-5 zeolite in methanol to gasoline conversion



Zhijian Wan*, Gang Kevin Li, Chuanfu Wang, Hong Yang, Dongke Zhang

Centre for Energy (M473), The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

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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.

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, SiO₂/Al₂O₃ 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 μm 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

* Corresponding author.

E-mail address: zhijian.wan@uwa.edu.au (Z. Wan).

[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 μm 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 re-suspending 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 $\text{Cu K}\alpha$ ($\lambda = 1.54439 \text{ \AA}$) radiation source at 40 kV and 40 mA). The $\text{SiO}_2/\text{Al}_2\text{O}_3$ 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 120 kV). 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 (NH_3 -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 $10^\circ\text{C min}^{-1}$ in a helium (He) flow (high purity, 15 mL min^{-1}) for 60 min and then cooled down to 120°C . NH_3 adsorption was then performed by flushing the sample with a 5 v/v% NH_3/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 NH_3 . At a heating rate of $10^\circ\text{C min}^{-1}$, the sample was heated to 650°C to allow the desorption of NH_3 adsorbed on the acid sites. The NH_3 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 (C_1 – C_4), 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 C_5+ liquid fractions (aliphatics and aromatics) as well as unreacted methanol.

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