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Influence of crystal size on the catalytic performance of H-ZSM-5 and Zn/H-ZSM-5 in the conversion of methanol to aromatics



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ABSTRACT

H-ZSM-5 zeolites with a uniform crystal size from 0.25 to 2 µm were obtained by adding colloidal silicalite-1 seed in the synthesis gel; with H-ZSM-5 as the support, Zn/H-ZSM-5 was prepared by incipient wet impregnation. The influence of crystal size on the state of Zn species and its relation to the catalytic performance of Zn/H-ZSM-5 in the conversion of methanol to aromatics (MTA) was then investigated. The results illustrated that the state of Zn species and catalytic performance of Zn/H-ZSM-5 are closely related to the crystal size, though the crystal size has little influence on the overall acidity. There exist mainly two types of zinc species, viz., ZnO and ZnOH⁺; Zn/H-ZSM-5 with smaller crystal size is provided with more ZnOH⁺ species. The selectivity to aromatics and catalyst stability can be improved greatly by using small crystal Zn/H-ZSM-5. A good linear correlation is observed between the amount of ZnOH⁺ species and the selectivity to aromatics, suggesting that ZnOH⁺ species plays an important role in enhancing the dehydrogenation of alkanes and aromatization of alkenes to aromatics. As a result, small crystal Zn/H-ZSM-5 with large portion of ZnOH⁺ species exhibits high selectivity to aromatics and long lifetime in MTA.

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1. Introduction

The conversion of methanol to aromatics (MTA) over acidic zeolite catalysts is now considered as an important non-petroleum route to get valuable chemicals [1–7], where methanol can be easily produced via syngas from various carbon resources such as coal, natural gas, and biomass. H-ZSM-5 is one of most effective zeolite catalysts in MTA [5–7]; however, its catalytic performance is influenced by many factors such as the Si/Al ratio, crystal size, morphology and promoters.

It has been proved that the crystal size of a zeolite has a remarkable influence on its catalytic performance in methanol conversion and alkylation reactions [8–11]. In contrast to large crystallites, nano-crystal H-ZSM-5 zeolite showed long catalytic lifetime and high selectivity to C_{5+} hydrocarbons and aromatics in the conversion of methanol to hydrocarbons (MTH) [12,13]. Jang and co-workers found that SAPO-34 and ZSM-5 with a moderate size of 200–500 nm exhibited excellent catalytic performance in MTH [8], whereas extremely small

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nanocrystallites (<150 nm) led to low methanol conversion and rapid deactivation. To improve the performance of a zeolite catalyst in MTA, it is then necessary to regulate the crystal size and understand the size-related catalytic behavior [14,15]. A great deal of effort has been made to the controllable synthesis of ZSM-5 zeolite, such as confined space synthesis [16,17], low-temperature crystallization [18] and seed-induction synthesis [12,19–22]; among them, the seed-induction synthesis proved to be quite effective in finely tuning the zeolite crystal size.

Modification of zeolites by adding proper promoters is also an effective approach to enhance their catalytic performance. For MTA over H-ZSM-5, the selectivity to aromatics can be boosted by modifying with various metal species such as Zn [23–28], Ag [29], Ga [30–35], Sn [36] and La [37]. Among these metal elements, zinc is most attractive owing to its low cost and high effectiveness in promoting the aromatization of methanol and light alkanes. By introducing Zn cations into ZSM-5 through ion-exchange, Ono and co-workers found that the yield of aromatic hydrocarbons for MTH over Zn-H-ZSM-5 reached 67.4%, much higher than the value of 40.3% over the parent H-ZSM-5 [23]; moreover, the yield of aromatic hydrocarbons increased with the increase of ion-exchange degree. Ni and co-workers also reported that the nano-sized H[Zn,Al]-ZSM-5 zeolite obtained from direct synthesis showed high selectivity to BTX (benzene, toluene and xylene) and good stability in MTA [2]. Wang and co-workers synthesized mesoporous Zn-ZSM-5 for MTA by one-step desilication and reassembly and found that the selectivity to BTX increased gradually with the increase of zinc content [24]; moreover, the mesoporous Zn-ZSM-5 showed a longer catalytic lifetime than H-ZSM-5. Ma and co-workers prepared a nano-sized ZSM-5 with a short b-axis and fully open straight channels [25]; after modification with zinc, its catalytic performance in MTA was greatly enhanced and very high selectivity to aromatics (>90%) was then achieved over the nano-sized Zn/ZSM-5.

Although the enhancement of selectivity to aromatics in MTA by adding Zn has been well proved, the state and location of Zn species in the Zn modified ZSM-5 are still highly controversial. By using CO as a probe molecule, Berndt and co-workers proposed that ZnOH⁺ was present in Zn/ZSM-5 and its catalytic activity was related to the content of ZnOH⁺ [38]. On the contrary, Biscardi and co-workers thought that the ZnOH⁺ species was unstable [39]; it reacted further with acidic OH groups, forming active Zn species bridged by oxygen $(0^{-}-Zn^{2+}-0^{-})$. Similarly, by measuring pyridine adsorption on Zn modified ZSM-5, Yakerson and co-workers [40] observed that one Zn²⁺ cation replaced two protons and interacted with two Al sites. El-Malki and co-workers found that the structure of Zn species in Zn/ZSM-5 was related to the Si/Al ratio [41]; Zn was stable in cationic exchange positions, either compensating the charge of two Alcentered tetrahedra or being ligated to one internal silanol or OH group. In the previous work [42], we observed that the nature of zinc species and subsequent catalytic performance of Zn/ZSM-5 in MTA were significantly influenced by the preparation method for introducing zinc. As the effects of crystal size and Zn promoter were investigated independently in most cases up to now, the influence of crystal size on distribution of Zn species and its relation to the catalytic performance of Zn/H-ZSM-5 in MTA were still unclear.

In this work, therefore, H-ZSM-5 zeolites with a uniform crystal size from 0.25 to 2 μ m were obtained by adding colloidal silicalite-1 seed in the synthesis gel; with H-ZSM-5 as the support, Zn/H-ZSM-5 was prepared by incipient wet impregnation. The influence of crystal size on the distribution of Zn species and its relation to the catalytic performance of H-ZSM-5 and Zn/H-ZSM-5 in MTA was then investigated.

2. Experimental

2.1. Catalyst preparation

Silicalite-1 seed was prepared following the procedures described by Xu and co-workers [43]. Na-ZSM-5 with a designed Si/Al molar ratio of 40 was then synthesized from sodium hydroxide, silica sol (40 wt.% SiO₂, 0.4 wt.% Na₂O), sodium aluminate (Al₂O₃ \geq 41.0 wt.%), tetrapropylammonium hydroxide (TPAOH, 48.7 wt.% in aqueous solution), with the molar composition of SiO₂:0.011Al₂O₃:0.02Na₂O:0.15TPAOH:30H₂O. To control the crystal size, a desired amount of colloidal silicalite-1 seed was added to the synthesis gel. The crystallization was conducted at 170 °C for 40 h in a Teflon-lined stainless steel autoclave under rotation (20 r/min). The solid product was recovered by centrifugation and washed with de-ionized water repeatedly until the mother liquid showed a pH value of 7-8, followed by drying at 110 °C overnight and calcination at 550 °C for 10 h in air. The ZSM-5 zeolite in hydrogen form (H-ZSM-5) was obtained through ion-exchange with aqueous NH₄NO₃ solution and Zn/H-ZSM-5 containing 5 wt.% Zn was obtained by impregnating the parent H-ZSM-5 zeolites in $Zn(NO_3)_2$ solution [42].

For the brevity of description, the ZSM-5 zeolites with different crystal sizes in this work are denoted by Z-*s*, where *s* represents the average crystal diameter in μ m. Particularly, H-ZSM-5 and Zn/H-ZSM-5 zeolites with an average crystal diameter of *s* are then referred to HZ-s and Zn/HZ-s, respectively.

2.2. Catalyst characterization

The actual contents of Si, Al and Zn elements were determined by inductively coupled plasma-atomic emission spectrum (ICP-AES) and the morphology and size of various zeolites were measured by field emission scanning electron microscope (FE-SEM), as reported previously [42,43]. Similarly, the X-ray powder diffraction (XRD, to determine the crystal phases and relative crystallinity), nitrogen adsorption/desorption (to measure the textural properties), temperature-programmed desorption of NH₃ (NH₃-TPD, to get the overall acidity by acid strength), Fourier transform infrared spectra and infrared spectra for pyridine adsorption (FT-IR and Py-IR, to determine the acidity by acid type [44]), as well as the diffuse reflectance ultraviolet-visible spectrum (UV-vis DRS), Zn $2p_{3/2}$ X-ray photoelectron spectroscopy (XPS) and in situ Zn K-edge X-ray absorption spectroscopy (XAS, to determine the state of Zn species in Zn/H-ZSM-5) were performed by following the similar procedures with the same apparatus as described previously [42,43].

The thermogravimetric (TG/DTA) curves of spent zeolites after MTA reactions were acquired on a Rigaku Thermo plus Evo TG 8120 instrument by heating in air, to determine the coke amount deposited.

2.3. Catalytic tests and analytic procedures

The MTA reaction was performed at 390 °C and 0.5 MPa in a fixedbed microreactor (a stainless steel tube with an inner diameter of 10 mm). Prior to the reaction, 1.5 g of zeolite catalyst (20–40 mesh) was first pretreated at reaction temperature for 8 h in a nitrogen flow; after that, methanol was pumped into the reactor with a liquid weight hourly space velocity (WHSV) of 3.2 h⁻¹. The gaseous and liquid (including organic and aqueous phases) products were separated with a cold trap and then analyzed with three sets of gas chromatographs (GC), following the similar procedures described previously [42].

3. Results and discussion

3.1. Textural properties

By adding the colloid silicalite-1 seeds in the synthesis gel, the crystal size of ZSM-5 zeolite can be finely tuned, through epitaxially growing ZSM-5 crystals around the seeds [20]. A uniform crystal size from 0.25 to 2 μ m has been attained through adjusting the amount of silicalite-1 seeds, as shown by the SEM images in Fig. 1. Obviously, the crystal size decreases with the increase of the amount of silicalite-1 seeds added in the synthesis gel. The ZSM-5 zeolites with average crystal sizes of about 2, 1, 0.5 and 0.25 μ m are obtained by adding 0.004, 0.04, 0.2 and 2 wt.% silicalite-1 seeds in the synthesis gel, respectively. Uniform morphology of cross type with smooth crystal surface is achieved when the crystal size is >0.5 μ m, whereas the small crystal HZ-0.25 zeolite is an aggregate of smaller crystals (0.05–0.1 μ m). Fig. 1 also illustrates that the introduction of zinc species by impregnation has little influence on the crystal size and the morphology of the parent H-ZSM-5 zeolites.

Fig. 2 shows the XRD patterns of the H-ZSM-5 and Zn/H-ZSM-5 zeolites with various crystal sizes. All these zeolites exhibit typical diffraction peaks of MFI structure, suggesting that the alteration in crystal size and loading of Zn by impregnation have little impact on the parent structure of ZSM-5. No distinct peaks for ZnO are observed, suggesting that the Zn species are highly dispersed in the parent H-ZSM-5. In comparison with the parent H-ZSM-5, as given in Table 1, the relative crystallinity of Zn/H-ZSM-5 is slightly decreased, which is probably attributed to the high X-ray absorption coefficient of impregnated metal species [37,45].

Table 1 also lists the composition and textural properties of the H-ZSM-5 and Zn/H-ZSM-5 zeolites. The Si/Al ratio of H-ZSM-5 or Zn/H-ZSM-5 increases slightly with the decrease of the crystal size, as smaller crystallites are prepared with more silicalite-1 seeds of high silicon

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