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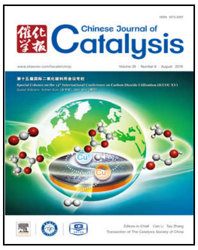

Article

External surface modification of as-made ZSM-5 and their catalytic performance in the methanol to propylene reaction

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ABSTRACT

Post-synthetic treatment of high-silica as-made ZSM-5 with organic template in the micropores was explored to reduce/remove the external surface acid density of ZSM-5. It is found that Na_2H_2EDTA treatment can selectively remove the surface Al atoms, but generates new acid sites (likely silanol nests) on the external surface. H_3PO_4 treatment is unable to remove surface Al atoms, while small amount of P is left on the external surface, which effectively decreases the acid density. The catalytic performance of the resultant materials is evaluated in the methanol conversion reaction. H_3PO_4 treatment can effectively improve both the catalytic lifetime and the stability of propene selectivity. This occurs due to a combination of the increased tolerance to the external coke deposition and the depressed coking rate (reduced side reactions). Na_2H_2EDTA treatment only prolongs the catalytic lifetime, resulting from the improved tolerance to the external coke deposition. Under the optimized H_3PO_4 treatment condition, the resultant ZSM-5 gives a catalytic lifetime of about 1.5 times longer than the precursor. Moreover, the propene selectivity is improved, showing a slight increasing trend until the deactivation.

1. Introduction

With the depletion of oil resource, the methanol to propene (MTP) process provides an alternative route to produce propene beyond the conventional steam cracking of naphtha and fluid catalytic cracking process [1–4]. The MTP reaction has aroused significant interest in both the academic and industrial fields since it was originally developed by Lurgi company [1]. It has been recognized that the methanol conversion over zeolite catalysts is a typical acid catalyzed process and coke deposition is the main cause of the catalyst deactivation [5–8]. ZSM-5 zeolite, with a 3D interconnected pore system composed of 10-membered rings, is currently the most effective catalyst, which has found application in the industrial fixed bed MTP

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process.

Due to the space limitation in the micropores of ZSM-5 (0.51 nm × 0.55 nm, 0.53 nm × 0.56 nm), the coke deposition in the crystal interior can be greatly avoided during the MTP reaction. And the deactivation on ZSM-5 is closely related to the external surface acidity [9]. Therefore, attempts have been made to reduce the external surface acidity of ZSM-5, aiming to retard the coke deposition rate and improve the catalytic stability. The strategies developed to passivate the external surface acid sites of zeolites can be mainly classified as macromolecule deposition [10–19], synthesis of zeolites with core-shell structure [20–23], metal or non-metal modification [24–28] and so on.

The macromolecules reported for the passivation/modification of external surface acid sites of zeolites include bulky organophosphorus compounds [10,11], bulky nitrogen compounds [12] and various siloxane [14–19]. Losch et al. [29] once investigated the effect of surface passivation of nano-sized ZSM-5 on the methanol conversion reaction by a chemical liquid deposition (CLD) technique using tetraethylorthosilicate. The resultant catalyst exhibited an enhanced selectivity to lower olefins, but a significant decrease in the stability, which was due to the partial blocking of micropores (the coking process exclusively occurred within the pores and fastened the catalyst deactivation). Phosphorus modification of HZSM-5 zeolite by wet impregnation has long been known to decrease aromatic formation and improve catalytic stability in methanol conversion chemistry [26,30,31]. Impregnation of HZSM-5 with phosphoric acid leads to the hydrolysis of framework Al and the condensation of Brønsted acid sites with POH groups, resulting in higher framework Si/Al ratio and the decrease of strong acid sites [31,32]. However, phosphoric acid can deposit both in the inner pore and external surface of ZSM-5 due to its smaller size. Recently, Liu et al. [24] reported an effective method to prepare P-modified H-ZSM-5 with the preferential covering of the external surface acid sites by adding ethanol during the impregnation. This occurred because bulky organic phosphates were likely formed from the reaction of phosphoric acid and ethanol, which deposited on the external surface of HZSM-5 crystals. The obtained material gave high *p*-xylene selectivity along with a relatively high catalytic activity in toluene disproportionation reaction.

Zeolites with core-shell structure are generally synthesized by epitaxial growth of inert shell outside zeolite core. In principle, the degree of surface coverage and shell thickness are the key factors influencing the catalytic performance. Luo et al. [33] successfully synthesized ZSM-5@S-1 material, which gave comparable propene selectivity with the ZSM-5 precursor and a prolonged lifetime from 74 to 139 h in the MTP reaction. The change in lifetime should result from the reduced number of external acid sites and the attenuated occurrence of side reactions. Yin et al. [34] also demonstrated that the coverage of surface acid sites as a result of contiguous silicalite-1 coating was the reason for the high stability and selectivity of ZSM-5 in CH_3Br conversion reaction.

Recently, selective dealumination methods were reported to remove the external surface acid sites of ZSM-5. Inagaki et al. [35] found that post-synthetic HNO_3 treatment of ZSM-5 zeolite synthesized in the absence of organic structure-directing agent can selectively remove framework Al on the external surface, producing a unique ZSM-5 zeolite catalyst that has very few acid sites on its external surface. The treated ZSM-5 showed high resistance to coke formation during the cracking of hexane or other paraffin molecules.

In this contribution, a facile post-synthetic treatment method was developed to remove/modify the external surface acidity of ZSM-5 by utilizing as-made ZSM-5 containing organic structure directing agent (OSDA) as the precursor. The existence of OSDA in the as-made ZSM-5 crystals may effectively block the channels and confine the modification on the crystal exterior without altering the internal acidity and integrity of the crystals. Two common reagents, Na_2H_2EDTA and H_3PO_4, herein were explored for the post-synthetic treatment. It is mentioned that large molecule EDTA, as a powerful chelating agent, has been widely used for the dealumination of Y zeolite [36]. But its use for the dealumination of ZSM-5 is quite rare. The variations of structure integrity, surface acid density and catalytic performance of the modified ZSM-5 were investigated. Moreover, the H_3PO_4 concentration was optimized to further prolong the lifetime in the MTP reaction.

2. Experimental

2.1. Materials

The chemical reagents used in synthesis and modification of ZSM-5 zeolites include: tetraethyl orthosilicate (TEOS, Tianjin Kemiou Chemical Reagent Co), aluminium iso-propoxide ($Al(OPri)_3$, Sinopharm Chemical Reagent Co.), tetrapropylammonium hydroxide (TPAOH, 10 wt% Tianjin Jingrun Chemical Co), urea (Tianjin Damao Chemical Co), ethylenediamine tetraacetic acid disodium salt (Na_2H_2EDTA, Tianda Chemical Reagent Co. Ltd.), phosphoric acid (85.0 wt%, Sichuan Xianfeng Chemical Co.).

2.2. Synthesis and modification of ZSM-5 zeolites

The synthesis of ZSM-5 zeolite was according to the reported literature [37]. The gel molar composition was $300SiO_2:1Al_2O_3:90TPAOH:6000H_2O:450urea$. Detained synthesis procedure was carried out as follows: 104.2 g TEOS was added dropwise into 210.5 g TPAOH solution under stirring. After 12 h, 0.681 g $Al(OPri)_3$ was added into the mixture and stirred for 12h. After further addition of 45.0 g urea and stirred for 1 h, the resulting mixture was transferred into an autoclave. The crystallization was carried out at 180 °C for 48 h under tumbling 60 r/min. The as-made sample was centrifuged, washed with distilled water, dried at 120 °C overnight.

Typical post-synthetic modification treatment process with H_3PO_4 solution was as follows: 1.5 g as-made sample was added to 20.0 mL solution (1 mol/L) in a Teflon-lined stainless steel autoclave. After treatment at 90 °C for 12 h under tumbling 60 r/min, the slurry was filtered, washed with distilled water for three times until pH=7. All products were dried at 120 °C overnight and calcined at 550 °C for 8 h to remove the organic tem-