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Fabrication of a nano-sized ZSM-5 zeolite with intercrystalline mesopores for conversion of methanol to gasoline

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ABSTRACT

Carbon deposition during methanol to hydrocarbons leads to the quick deactivation of ZSM-5 catalyst and it is one of the major problems for this technology. Decreasing the crystal size or introducing mesopores into ZSM-5 zeolites can improve its diffusion property and decrease the coke formation. In this paper, nano-sized ZSM-5 zeolite with intercrystalline mesopores combining the mesoporous and nano-sized structure was fabricated. For comparison, the mesoporous ZSM-5 and nano-sized ZSM-5 were also prepared. These catalyst samples were characterized by XRD, BET, NH_3-TPD, TEM, Py-IR and TG techniques and used on the conversion of methanol to gasoline in a fixed-bed reactor at $T = 405$ °C, WHSV = 4.74 h^{-1} and $P = 1.0$ MPa. It was found that the external surface area of the nano-sized ZSM-5 zeolite with intercrystalline mesopores reached 104 m^2/g, larger than that of mesoporous ZSM-5 (66 m^2/g) and nano-sized ZSM-5 (76 m^2/g). Catalytic lifetime of the nano-sized ZSM-5 zeolite with intercrystalline mesopores was 93 h, which was only longer than that of mesoporous ZSM-5 (86 h), but shorter than that of nano-sized ZSM-5 (104 h). Strong acidity promoted the coke formation and thus decreased the catalytic lifetime of the nano-sized ZSM-5 zeolite with intercrystalline mesopores though it presented large external surface that could improve the diffusion property. The special zeolite catalyst was further dealuminated to decrease the strong acidity. After this, its coke formation rate was slowed and catalytic lifetime was prolonged to 106 h because of the large external surface area and decreased weak acidity. This special structural zeolite is a potential catalyst for methanol to gasoline reaction.

1. Introduction

As a result of the increasing global demand on the transport fuel and the adverse effects of fluctuating energy price, searching for alternatives to crude oil has become one of the most important issues in current society [1,2]. This situation is more crucial for the country whose petroleum consumption strongly depends on the importation. Among possible alternatives, methanol to gasoline (MTG) technology is currently gaining more and more attentions because feedstock methanol is readily produced from synthesis gas through gasification of coal, biomass, wastes or steaming reforming of natural gas, and the obtained methanol can be catalytically converted to high octane gasoline [3,4]. For this technology, ZSM-5 zeolite has been proved to be the major catalyst that can complete above conversion, due to its well-defined micropores, large surface area, strong acidity and high hydrothermal stability [5]. However, it is the well-defined micropores that seriously restrict the diffusion of bulk molecules, which slows down the diffusion of the coke precursors from micropores to the external surface. These coke precursors could polymerize within the micropores to form coke and then lead to the rapid catalyst deactivation due to the coverage on strong acid sites and blocking of micropores [6–9]. Coke deposition of ZSM-5 has been deemed as one key problem to be solved for MTG technology.

Generally, two most promising strategies are being investigated to solve this problem. One is to decrease the crystal size of ZSM-5 zeolite, which has been recognized as an important way to improve the catalytic performance in methanol to hydrocarbon (MTH) reactions. Rownaghi and Hedlund [10] found that nano ZSM-5 with crystal size of 120 nm realized a complete conversion of methanol at the first 10 h of the reaction, while the conversion of methanol on micrometer ZSM-5 was only 65% and decreased quickly to 60% after only 5 h of reaction. Firoozi et al. [11] investigated the effects of crystal size of ZSM-5 on the methanol to propene performance and found that during 200 h reaction of testing, methanol conversion on nano-sized ZSM-5 was always higher than that on micro-sized ZSM-5. The high catalytic activity and long lifetime of the small sized ZSM-5 were attributed to its decreased diffusion length and more available acid sites. However, the synthesis of nano-sized ZSM-5 is far from industrial production due to long crystallization

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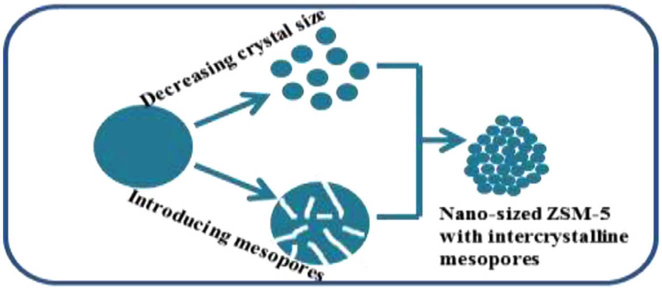

Fig. 1. Schematic diagram of nano-sized ZSM-5 with intercrystalline mesopores.

time, low yield and large consumption of expensive organic directing agents (ODA), which could increase the manufacturing costs and cause air pollution during the process of removing templates. In addition, the separation using high-speed centrifugation and the low crystallinity of nano-sized ZSM-5 also restrict its application on a large scale. Currently, the search of simple and economical preparation methods for nano-sized ZSM-5 is still a key issue for its practical application.

Another approach to solve the coke problem is to fabricate mesopores on ZSM-5. Alkaline desilication is a simple and efficient means. These mesopores are mainly produced inside the ZSM-5 crystal and their positive influence on the catalytic performance has been evidenced in MTH reaction. Fathi et al. [12] studied the effects of alkaline types ($CaCO_3$, Na_2CO_3 and NaOH) on mesopores formation and found that desilicated ZSM-5 by Na_2CO_3 solution showed greater improvement in catalytic lifetime and the yield of gasoline hydrocarbons. The effects of the concentration of NaOH solution on the pore structure of ZSM-5 and its MTG performance was also investigated by Bjørgen et al. [13]. It was found that the catalytic lifetime of the sample treated by 0.05 M alkaline solution was prolonged from 35 to 75 h at the conditions of 370 °C and WHSV = 8 h^{-1}. Enhanced catalytic performance and coke-resistance have also been observed for mesoporous ZSM-5 obtained by NaOH post-treatment in methane aromatization reaction and the beneficial effects were attributed to the formation of mesopores and improved mass transfer efficiency [14]. However, it is known that the extraction of Si during desilication process is ruled by the framework Al [15]. The presence of framework Al in ZSM-5 zeolite prevents the Si from being extracted. The nonuniform distribution of framework Al induces excessive Si extraction in the interior of crystal during desilication process and results in large voids or even broken crystal pieces, which is not beneficial to the enhancement of diffusion property. Also, the extraction of Si during desilication process causes a waste of synthetic raw material and results in a low yield of treated products.

Salt-aided seed-induced route has been recently proposed to synthesize nano-sized ZSM-5 with intercrystalline mesopores. With the aid of seeds, the crystallization process was fast and the yield of products could reach 85%. Interestingly, the gel-rich system with Na^+, K^+, Br^- and SO_4^{2-} ions causes the salting out of aluminosilicates, which results in abundant intercrystalline mesopores by the assembly of adjacent nanocrystallines [16,17]. The in situ formation of mesopores replaces the desilication process and avoids the waste of synthetic raw material. The difficulty of separation of nano-sized ZSM-5 after crystallization is also solved due to the aggregated structure formed by stacking of the nano-sized crystallites. The most important thing is that nano-sized ZSM-5 with intercrystalline mesoporous structure possesses the advantages of both mesoporous ZSM-5 and nano-sized ZSM-5 (as shown in Fig. 1). Moreover, the intercrystalline mesoporous ZSM-5 has rich strong acid sites, although it is composed of a large number of nanocrystallines, which usually presents weak acidity due to the framework defects [18].

In view of the significant influence of mesopore and crystal size of ZSM-5 on the catalytic performance, nano-sized ZSM-5 with intercrystalline mesopores are expected to display an excellent activity in MTG reactions. However, there has not been any research about the application of nano-sized ZSM-5 with intercrystalline mesopores on MTG reaction, and the influence mechanism of the composite structure formed with nano-size crystals and mesopores on the catalytic activity remains unclear. In this work, nano-sized ZSM-5 with intercrystalline mesopores was prepared by salt-aided seed-induced route. In comparison, nano-sized ZSM-5 and mesoporous ZSM-5 were also prepared. The catalytic performance of the above catalysts on MTG reaction was studied. Concerning the strong acidity of nano-sized ZSM-5 with intercrystalline mesopores would accelerate the formation of coke species and shorten the catalytic lifetime, it was dealuminated to reduce the acidity to increase the longevity. Based on this research, we expect to find a new ZSM-5 catalyst with good MTG performance.

2. Experimental

2.1. Catalyst preparation

ZSM-5 catalyst with average crystal size of 500 nm was synthesized from a clear solution according to the procedure reported by Mochizuki et al. [19]. The molar composition of the starting gel was 1 SiO_2:0.017 Al_2O_3:0.25 TPAOH:0.05 Na_2O:60 H_2O. Firstly, required tetraethyl orthosilicate (TEOS, 98 wt%), tetrapropylammonium hydroxide (TPAOH, 25 wt%) and water were mixed under stirring at 80 °C for 24 h. Then, the solution containing water, $Al(NO_3)_3$•$9H_2O$ and NaOH was added to the above clear mixture. The prepared gel was transferred to a 300 mL Teflon lined steel autoclave and crystallized at 170 °C for 24 h. The products were then recovered by centrifugation, washed with deionized water and dried at 120 °C overnight. Thereafter, Na-ZSM-5 sample was obtained by calcination at 550 °C for 6 h to remove TPA^+ species. H-form zeolite was prepared by ion-exchanged with 0.8 M NH_4NO_3 (20 mL/g-sample) for 3 × 8 h at 80 °C followed by calcination at 550 °C for 6 h. The obtained sample is designated as Z5-500. Nano-sized ZSM-5 with average crystal size of 70 nm was also synthesized by the similar process and the molar composition of the starting gel was 1 SiO_2:0.017 Al_2O_3:0.25 TPAOH:0.05 Na_2O:8.3 H_2O. The obtained sample is designated as Z5-70.

ZSM-5 with intracrystalline mesopores was prepared by mixed alkaline treatment (TPAOH and NaOH) of Z5-500. During the process, the use of TPA^+ could protect the Si extraction and avoid the formation of large pores or hollow structure caused by the excessive desilication. Typically, the desilication process of Z5-500 was carried out in a 0.2 M mixed alkaline solution (the mole ratio of $TPA^+/OH^- = 0.25$) solution (15 mL/g-zeolite) under vigorous stirring at 50 °C for 2 h then cooled in ice water immediately, followed by filtration and washing with de-ionized water until neutral. The solid products were dried overnight at 120 °C and then calcinated at 550 °C for 6 h. H-form zeolite was obtained by ion-exchanged with 0.8 M NH_4NO_3 (20 mL/g-zeolite) for 3 × 8 h at 80 °C followed by calcination at 550 °C for 6 h. The obtained sample is designated as Z5-500-Si.

Nano-sized ZSM-5 with intercrystalline mesopores was synthesized by the "salt-aided seed-induced route" [16,17]. For the typical synthesis process, a starting aluminosilicate gel with the molar ratio of 1 SiO_2:0.017 Al_2O_3:0.15 Na_2O:0.1 TPABr:0.3 KF:30 H_2O was prepared. The procedure was simply described as follows: the solution of NaOH, $Al_2(SO_4)_3$•$9H_2O$, KF and TPABr were mixed well under vigorous stirring, then colloidal silica was added dropwise by plunger pump. Thereafter, the colloidal solution of silicate-1

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