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The Effect of Mesoporous Increasing On Activity High Silica HZSM-5 Zeolite in the Methanol Conversion to Olefins

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Abstract

In this paper, the effect of mesoporous increasing on activity high silica ZSM-5zeolite in methanol conversion to olefins investigated. Therefore, for forming the mesoporous, desiliction method with Sodium Hydroxide, tetrapropylammonium hydroxide and cetyltrimethylammonium bromide materials are used. The samples were characterized by XRD, FESEM, N_2 Adsorption/Desorption and NH_3-TPD techniques. The XRD results indicated that using Tetrapropylammonium hydroxide in desilication process by Sodium Hydroxide (in meso pore Na-TPA sample) caused high crystallinity preservation for Ref-ZSM-5 zeolite. FESEM images for this sample showed cracks and small holes on the surface of crystals. The N_2 Adsorption/Desorption results confirmed an increase in the meso pore volume and meso surface area in Na-TPA sample compare to Ref-ZSM-5 zeolite. These new mesoporous, with increasing access to active sites in framework, caused improvement on the catalytic performance. Performing the reactor test on catalyst in same reaction condition showed that this catalyst with methanol conversion higher than 90% in 41 days had acceptable stability. During this time, average of propylene selectivity, total olefins selectivity and propylene to ethylene ratio were 43%, 76% and 6% respectively. While the desilicated sample with Sodium Hydroxide and cetyltrimethylammonium bromide showed complete change from Ref-ZSM-5zeolite to mesoporous Al-MCM-41molecular sieves. This molecular sieves with completely mesoporous structure and, acid sites with low strength did not show activity in the methanol to olefin reaction.

Keywords: HZSM-5 Zeolite, Methanol Conversion to Olefins, Desilication, Sodium Hydroxide, Cetyltrimethylammonium Bromide.

Introduction

Olefins (mostly ethylene and propylene) are important raw materials in petrochemical industry. Methanol to olefins (MTO) conversion due to availability of methanol has attracted attentions. The high silica HZSM-5 zeolite is a very promising candidate as a catalyst for the MTO reaction [1]. In recent years, desilication of HZSM-5 zeolite in alkaline solutions (typically NaOH) has been proven to be effective method to introduce mesoporosity in its structures [2]. Temperature of 65°C, time of 30 min and 0.2 M alkaline solutions have been identified as optimal condition in desilication process [8]. This treatment depends on molar Si/Al molar ratio. So that, application of desilication by an aqueous NaOH solution is limited to zeolites with a Si/Al ratio in the range of 25–50 [3]. Recently, the desilication of high-silica HZSM-5 has attracted much attentions. However, the major drawback of this treatment is uncontrolled silicon extraction, resulting in loss of a significant part of the zeolite structure. To overcome this problem, the addition of a pore-directing agent such as tetraalkylammonium cations (tetrapropyl ammonium hydroxide) along with NaOH has been proposed [4]. Another approach involves desilication by mixture of NaOH and CTAB. Cetyltrimethylammonium bromide (CTAB) is a long-chain alkylammonium surfactant. CTAB is much less expensive than tetraalkylammonium cations and the overall operation of this strategy is much easier. Furthermore, in comparison with desilication of HZSM-5 in alkaline solutions, the aluminosilicate species in the filtrate can be utilized, and this process can reduce the production of Al- and Si-containing waste [5]. However, the concentration of alkaline solution is important [6].

In this study, we have investigated the influence of desilication (with combinations of NaOH and TPAOH solution and NaOH and CTAB solution) on the mesoporosity of a high silica HZSM-5 zeolite and their catalytic performance in MTO reaction. For comparison, a conventional microporous HZSM-5 have been synthesized and employed.

Methodology

High silica HZSM-5zeolite was synthesized by hydrothermal method in stirring stainless-steel Teflon-lined autoclave. The detail synthesis was the same as the one that was reported previously by our research group [1]. This sample named as Ref-ZSM-5 Silicic acid, sodium aluminate, tetrapropyl ammonium bromide, ammonium nitrate, sodium hydroxide, sulfuric acid, tetrapropyl ammonium hydroxide (TPAOH) and cetyltrimethyl ammonium bromide (CTAB) were the catalyst precursors which were purchased from Merck Company.

Desilication of Ref-ZSM-5sample by mixture of NaOH and TPAOH were performed in following conditions: concentration of alkaline solution equal 0.2 M, temperature °65C, time 0.5 hour, TPAOH/(NaOH + TPAOH) molar ratios equal 0.2. After desilicating, the zeolite suspension was cooled down immediately using an ice water bath, and filtered. The filtration cake was washed with deionized water until a neutral pH value was obtained and finally dried and calcined. This sample named as Na-TPA. For desilication of reference HZSM-5 sample by mixture of NaOH and CTAB, firstly, HZSM-5powder was mixed with 1.0 mol/L NaOH solution at 80°C for 1 h. Then 0.2 mol/L CTAB solution was added into the above solution. The pH of the suspension was then adjusted to 10.5 by adding H_2SO_4 Then,

the slurry was transferred into a Teflon-lined stainless steel autoclave and heated at °110C for 24 h Eventually, the sample was filtrated, washed, dried and calcined. This sample named as Na-CTA. The samples were characterized by XRD, FESEM, Brunauer–Emmett–Teller (BET) and NH_3-TPD analysis. The catalytic performances of the reference and desilicated HZSM-5 catalysts were evaluated in a continuous-flow fixed-bed reactor under the same operation conditions (T = 460°C, P = 1 atm, and WHSV = 1.44 h^{-1}).

Discussion and Results

In Figure 1, X-ray diffraction patterns of the zeolites are shown. Na-TPA zeolite same as Ref-ZSM-5 sample showed typical XRD pattern of MFI-structure of ZSM-5. Characteristic diffraction peaks of ZSM-5 orthorhombic structure (JCPDS: 44-0003) (2θ = 7.8, 8.7, 23.1, 23.8 and 24.3) were detected for both zeolites [7]. As can be seen from Fig. 1, the intrinsic MFI structure was preserved and that no additional phase was formed during desilication of Na-TPA sample under the experimental conditions. However, XRD pattern of Na-CTA sample presents a strong (100) diffraction peak (2θ=2.4°) with two small (110) and (200) diffraction peaks (respectively (2θ=4.1° and 4.7°). The occurrence of prominent peaks at 2θ ranging between 2 and 5° is indicative of mesoporous Al-MCM-41 structure [6, 8].

Conclusions

In high silica HZSM-5 zeolite desilication, concentration of alkaline solution is an important factor. The N_2 Adsorption/Desorption results (not shown here) confirmed an increase in the meso pore volume and meso surface area in Na-TPA sample in comparison with Ref-ZSM-5 zeolite. While the desilicated sample with sodium hydroxide and cetyltrimethylammonium bromide showed complete change from Ref-ZSM-5 zeolite to mesoporous Al-MCM-41 molecular sieves.

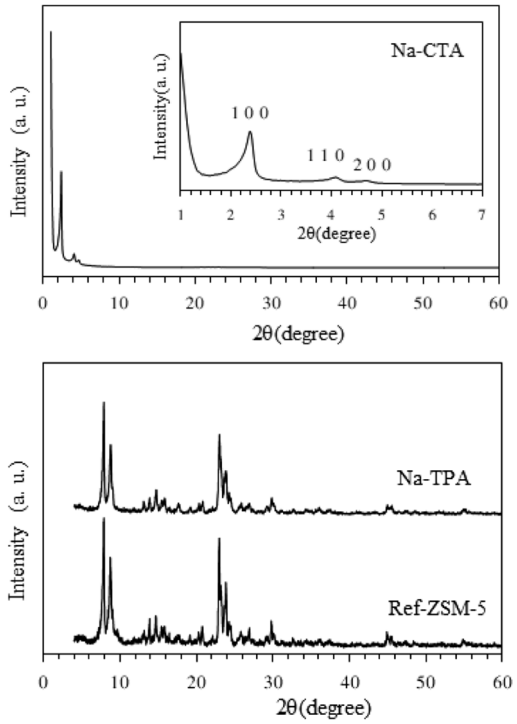

Fig. 1: XRD patterns of the reference and desilicated HZSM-5 samples.

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