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Short Communication

Spatial confinement effects of cage-type SAPO molecular sieves on product distribution and coke formation in methanol-to-olefin reaction

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ABSTRACT

Three kinds of 8-membered ring silicoaluminophosphate (SAPO) molecular sieves with different cage structures, SAPO-34, SAPO-18 and SAPO-35, were employed in methanol-to-olefin (MTO) reaction. The main products over SAPO-34 and SAPO-18 were propene and butenes, whereas ethene and propene especially ethene were predominantly generated over SAPO-35. Coke species formation greatly depended on reaction temperature and varied systematically with cage size. The differences in production distribution and generated coke species in the MTO reaction suggest great spatial confinement effects imposed by cage structure of SAPO catalysts.

1. Introduction

The application of coal-to-olefin technology opens a new era for the production of light olefins, the backbone feedstock of petrochemical industry, from non-oil resources. Methanol-to-olefin (MTO) process has been proved to be completely successful in China [1]. Extremely high selectivity of light olefins has been obtained using a silicoaluminophosphate molecular sieve SAPO-34 with 8-membered ring pore opening and CHA supercages [2].

The mechanism of MTO reaction over microporous solid acid catalysts was extensively reported in several reviews published recently [1,3–5]. The hydrocarbon pool (HP) mechanism, supported by experimental and theoretical results [6–11], has been widely accepted. According to this mechanism with methanol conversion to hydrocarbon in an indirect way, methanol is continuously added on the "HP species" retained in the catalyst and light olefins are split off from these species. Polymethylbenzenes [6,7] and polymethylnaphthalenes [12,13] have been proposed to be the main HP species over SAPO-34. These observations indicate that the occurrence of MTO reaction following the HP mechanism requires wide space as the catalytic environment for the accommodation of bulky intermediates [10]. Recently, Bhawe and coworkers studied effect of cage size on the MTO reaction over LEV, CHA and AFX type zeolite with eight-membered ring, and they found that selectivity to ethene decreases as the cage size increases [14]. Using a first-principle kinetic study, Wispelaere and co-workers found a low-barrier path for olefin formation based on the side-chain mechanism during the MTO conversion over SAPO-34 [15].

According to the HP mechanism, MTO reaction goes through an induction period, during which HP species are formed and the fresh catalysts are transformed into working catalysts [16,17]. The further growth and aging of these active intermediates to confined coke species like polycyclic aromatics might cause the catalyst deactivation [13]. In our recent study, a new kind of non-aromatic hydrocarbon residues was found as deactivating species during the MTO reaction at low reaction temperature [18]. At reaction temperature of 300–325 °C, diamondoid hydrocarbons especially methyl-substituted adamantanes were generated as retained compounds in the nanocages of SAPO-34 and resulted in rapid deactivation [18]. Formation and accommodation of aromatics or adamantane hydrocarbons as the confined coke species, demonstrate that cage structure may provide catalytic environment for the generation of retained hydrocarbons with multiple rings.

In this contribution, three kinds of 8-membered ring cage-type SAPO molecular sieves, SAPO-34, SAPO-18 and SAPO-35, with similar physicochemical properties and close medium-strong acidity, were prepared and applied in the MTO reaction at various reaction temperatures. Based on the comparative studies, spatial confinement effects of cage structures on the production distribution and coke formation were highlighted.

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2. Experimental

2.1. Synthesis

Detailed procedure was described in Supplementary data.

2.2. Characterization

The characterization of SAPO-34, SAPO-18 and SAPO-35 using multiple techniques, including X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM), N_2 adsorption and 2-^{13}C-acetone adsorption experiment, was described in detail in Supplementary data.

2.3. Catalytic test

Methanol conversion was performed in a fixed-bed quartz tubular reactor at atmospheric pressure. A catalyst sample of 100 mg was loaded into the reactor and the reactions were carried out at 300 °C, 350 °C and 400 °C. The methanol was fed by passing helium through a saturation evaporator with a WHSV of 2.0 h^{-1}. The reaction products were analyzed by on-line gas chromatography (Agilent GC 7890A) equipped with a HP-PLOT Q capillary column and a FID detector.

2.4. Confined organics analysis

Organic species trapped in the cages of the SAPO molecular sieves during the reaction were analyzed following the procedures as described in the literature [19]. The spent catalysts were dissolved in 20% hydrofluoric acid solution. The organic phase was extracted by dichloromethane (CH_2Cl_2), and then analyzed using an Agilent 7890A/5975C GC/MSD.

3. Results and discussion

3.1. Textural structure of silicoaluminophosphate catalysts

SAPO-34, SAPO-18 and SAPO-35 are three kinds of silicoaluminophosphate molecular sieve with 8-membered ring pore openings and different cage structures (Fig. 1). SAPO-34 possesses large CHA cages which are made up of 12 four-membered rings, 2 six-membered rings, and 6 eight-membered rings, and these cages are interconnected to six adjacent cages by 8-membered rings with pore opening of 3.8 × 3.8 Å in diameter and cage dimension of 1.27 nm × 0.94 nm. The pear-like supercages of SAPO-18 with cage dimension of 1.27 nm × 1.16 nm are also made up of analogous rings to SAPO-34, and the window dimension of AEI cages in SAPO-18 is very close to that of CHA cages in SAPO-34. The LEV cages in SAPO-35 are built from 9 four-membered rings, 5 six-membered rings, and 3 eight-membered rings, and 8-membered ring pore has a free diameter of 3.8 × 4.8 Å. Even with the window a bit of bigger than that of SAPO-34 and SAPO-18, the LEV cages in SAPO-35 with cage dimension of 0.73 nm × 0.63 nm are significantly smaller than the CHA and AEI cages.

3.2. Characterization of silicoaluminophosphate catalysts

The powder XRD patterns of calcined SAPO-34, SAPO-18 and SAPO-35 samples are shown in Fig. S1. Silicon content, crystallize size, morphology and BET surface area of prepared SAPO catalysts are shown in Table 1. The scanning electron microscope (SEM) images are shown in Fig. S2, which show that subtle differences exist in morphology and crystal size between as-synthesized samples. 2-^{13}C-acetone adsorption experiment showed that three SAPO catalysts have close medium-strong acidity.

For the effect of acidity variation with the chemical composition of the three SAPO catalysts, strong acid strength and higher acid site density will lead to more rapid catalyst deactivation due to the severe hydrogen transfer reaction [1]. In the present work, 2-^{13}C-acetone adsorption NMR experiment indicates that three SAPO catalysts employed in this study have similar moderate acid strength. XRF characterization (Table S2) shows that average Si atoms per cage in SAPO-34, SAPO-18 and SAPO-35 are 0.74, 0.70 and 1.55 separately, so acid site density is approximately close for SAPO-34 and SAPO-18, while this value is relatively higher for SAPO-35 owing to its high Si content. Recently, E. Sastre and co-workers [20] also found that MTO reaction over SAPO-34 catalysts with different silicon contents exhibits similar product distribution. Moreover, acidity amount was not considered to be the main cause of the selectivity to light olefins in the MTO reaction over cage-type small-pore molecular sieves [21].

In some previous literatures regarding MTO reaction performed over the catalysts with different crystal sizes, the selectivity to different olefins was observed to be not relevant to the crystal size of SAPO-34 [22]. G. Seo and co-workers [23] found that product compositions of MTO reactions over three SAPO-34 catalysts with different crystallite sizes were essentially the same, indicating that the mechanism of MTO reaction through polymethylbenzenes as reactive intermediates was not affected by the crystallite size of the SAPO-34 catalysts. Therefore, spatial confinement effects of the three SAPO catalysts with different cage structures may play a more important role in the product distribution.

Our recent work [24] studied the confined coke formation in the MTO reaction over the SAPO-34 catalysts with different crystal sizes, ranging from 20 nm to 8000 nm. It was found that nanosized catalysts exhibited the longest catalyst lifetime and lowest coking rate in MTO reactions, and it is worthy to note that for both of the two SAPO-34 catalysts in micrometer scale (1 μm and 8 μm), the coke species and coke amount after deactivation are very similar [24]. In the present study, the SEM images of three SAPO catalysts showed that the crystallite sizes of SAPO-34, SAPO-18 and SAPO-35 are 4–6 μm, 0.5–1 μm and 2–4 μm separately (Table 1). The subtle difference in crystallite size of three SAPO catalysts indicates that the differences in product distribution

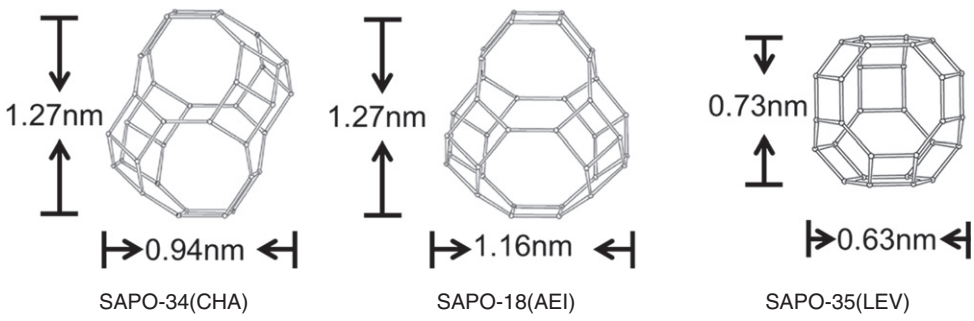

Fig. 1. Cage structure of SAPO-34, SAPO-18 and SAPO-35.