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Synthesis of hierarchical MeAPO-5 molecular sieves – Catalysts for the oxidation of hydrocarbons with efficient mass transport

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ABSTRACT

Hierarchical molecular sieves possess the characters of both microporous molecular sieves and meso- and/or macro-porous materials, and have potential application in adsorption and separation of macromolecules and diffusion limited catalytic reactions. In this work, hierarchical MeAPO-5 (MeAPO-5-meso, Me = Co, Mn, Fe, Mg and Ti) molecular sieves were synthesized directly using glucose as mesopore template. The synthesized MeAPO-5-meso molecular sieves were characterized by X-ray diffraction, X-ray fluorescence, N_2 physisorption, thermogravimetric analysis and scanning electron microscopy. It was proved that mesopores with the pore size distribution of 5–30 nm were introduced to MeAPO-5-meso. The improvement effect of the introduced mesopores on the catalytic performance of MeAPO-5-meso (Me = Mn, Fe and Co) was investigated in the oxidation of various hydrocarbons with different molecular dimensions including cyclohexene, ethylbenzene, indan, tetralin, diphenylenemethane and fluorene. For comparison, these oxidation reactions were also performed over the ordinary MeAPO-5. The results indicated that mesopores benefited the diffusion of the reactants and the products, so the conversion of the reactants was improved while the selectivity of the products was slightly improved or maintained at higher conversion. In addition, the promotion effect is dependent on the dimension of the substrates with respect to the micropore size of molecular sieves.

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1. Introduction

Zeolites are widely used in adsorption, separation, and heterogeneous catalysis fields due to their uniform, small pore size, high internal surface area, flexible frameworks, and controlled chemistry [1]. The well-defined micropores endow zeolites with molecular sieve effect, so, as heterogeneous catalysts, the shape-selective catalysis can occur on the basis of the complete exclusion, or on the strongly hindered diffusion, of certain reactants, intermediates, or products in the zeolite micropores [2,3]. However, from another point of view, the sole presence of micropores also imposes diffusion limitations on the reactions involving reactants or products whose size is comparable to the diameter of micropore. In these cases, mass transport to and from the active sites located within the micropores is slow, which limits the performance of the zeolite catalysts [4]. To circumvent the diffusion limitations imposed by the zeolite micropores, several strategies have been developed. One possibility is the synthesis of zeolites/zeotypes containing meso- and/or macropores. Numerous methods for preparing hierarchical zeolites have been reported in the literatures, and the templating approach is one of the most effective methods. In a typical procedure, a mesopore template, such as carbon particles [5,6], carbon nanotube [7], mesoporous carbon [8,9], carbon derived from sucrose [10], starch gel [11], polyurethane foams [12], and polymer [13], is mixed with a zeolite precursor mixture after which a hydrothermal treatment is carried out to grow the crystals. In the following calcination step, the templates are removed resulting in meso- and/or macropores in the zeolite crystals.

Aluminophosphate molecular sieves (AlPO-*n*) have attracted much interest since the discovery of this class of microporous materials in the early 1980s [14], and AlPO-5 with AFI structure is one of the most frequently studied members of this family. Mesopores can also be generated in aluminophosphate molecular sieves like that in zeolites. For example, mesoporous AlPO-5 has been synthesized in fluoride media using carbon as mesopore template by Christensen et al. [15]. Recently, our group reported the synthesis of hierarchical AlPO-5 (AlPO-5-meso) using glucose as mesopore template. It was disclosed that glucose was incorporated into AlPO-5-meso through the interaction with the surface negative charges. After crystallization, the glucose embedded in the

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crystals was removed by combustion, and then the AlPO-5-meso molecular sieves were obtained [16]. However, the neutral framework of AlPO-5 limits its applications as catalyst. Contrarily, metal ions doped AlPO-5 materials are promising catalysts for a variety of heterogeneously catalyzed reactions [17–22]. To the best of our knowledge, only a few reports studied the synthesis of hierarchical metal ions doped AlPO-5 [23–25]. Here, we report the synthesis of hierarchical MeAPO-5 (MeAPO-5-meso, Me = Co, Mn, Fe, Mg and Ti) using glucose as mesopore template, and study the promotion effect of the introduced mesopores on the catalytic performance of MeAPO-5-meso molecular sieves. The selective oxidation of various hydrocarbons with different molecular dimensions (MDs) including cyclohexene, ethylbenzene, indan, tetralin, diphenylenemethane and diphenylmethane were investigated using MeAPO-5-meso (Me = Mn, Fe and Co) as catalyst and molecular oxygen as oxidant.

2. Experimental section

2.1. Materials

Pseudoboehmite (78.4 wt.% Al_2O_3), phosphoric acid (85 wt.%), triethylamine (TEA, 99%), anhydrous magnesium(II) sulfate (99%), cobalt(II) acetate tetrahydrate (99%), tetrabutyl titanate(IV) (99%), ferric(III) chloride hexahydrate (99%), and manganese(II) acetate tetrahydrate (99%) were obtained from commercial sources without further purification. Glucose (AR) was used as the template to generate mesopores.

Pseudoboehmite treated with KOH was prepared as described elsewhere [16]. Typically, twenty gram of pseudoboehmite was dispersed in 50 mL of ethanol solution of KOH (0.1 mol L^{-1}) under refluxing condition and the mixture was stirred for 2 h. Then the solid was filtrated and washed with ethanol until the filtrate was neutral. Finally, it was dried at room temperature for 48 h.

2.2. Synthesis of MeAPO-5-meso

MeAPO-5-meso was prepared with the following molar composition: 0.1 Me:1.0 Al_2O_3:1.0 P_2O_5:1.55 TEA:50 H_2O:0.13 Glucose. In a typical synthesis, the calculated amount of pseudoboehmite treated with KOH was added to the deionized water in a plastic beaker under stirring, followed by the addition of glucose. And then phosphoric acid was added into the solution. After stirring for 1 h, the addition of metal salt solution was carried out. TEA was added dropwise after stirring for 20 h. And the obtained mixture was stirred for another 1 h. Finally, the obtained gel was transferred into a stainless-steel autoclave lined with polytetrafluorethylene and crystallized statically at 453 K for 48 h. After the hydrothermal process, the MeAPO-5-meso products were filtered, washed with deionized water, dried at 393 K for 12 h, and finally calcined at 823 K in air for 24 h. AlPO-5-meso was prepared by the similar method without addition of metal salt solution.

For preparation of ordinary MeAPO-5 (Me = Mn, Fe and Co), the pseudoboehmite was directly used as aluminum source and glucose was absent. The gel composition and the other synthesis conditions are same as those of MeAPO-5-meso.

2.3. Characterization

Powder X-ray diffraction (XRD) was performed on a Panalytical X'pert PRO instrument with Cu Kα (λ = 0.15418 nm) radiation. The crystallinities of the samples were calculated according to the intensity of the peaks at 2θ of 7.5°, 12.9°, 15.0°, 19.8°, 21.0° and 22.5°. Tube voltage and tube current are 40 kV and 40 mA, respectively. The chemical compositions of all the samples were analyzed by a Philips Margix X-ray fluorescence (XRF) spectrometer. The adsorption/desorption isotherms were measured with a Quantachrome Autosorb using N_2 as adsorbate at 77 K. Samples were outgassed at 423 K for 1.5 h prior to measurements. Total surface area was calculated according to Barrett-Emmet-Taller (BET) method, and pore size distributions were calculated from the desorption branch of the isotherm based on Barret-Joyner-Halenda (BJH) method. Thermogravimetric analysis (TG) was performed on a NETZSCH STA 409 PC thermal analyzer under air atmosphere. The morphology of the samples was examined by scanning electron microscopy (SEM) with an FEI Quanta 200F.

2.4. General procedure for catalytic oxidation of hydrocarbons

The oxidation of hydrocarbons was performed in an 80 mL autoclave reactor equipped with a magnetic stirrer, thermocouple, automatic temperature controller and a pressure gauge. After the addition of desired amount of reactants and catalysts, the autoclave was sealed. The atmosphere over the mixture was replaced with O_2 for three times. Then the reactor was heated to the desired temperature with stirring. Subsequently, the pressure of O_2 was charged to 0.5 MPa and kept constant during the reaction through feeding O_2. When the reaction was finished, the reactor was cooled down to the ambient temperature. The products of the oxidation were analyzed by gas chromatography equipped with a flame ionization detector. And the contents of the products were determined by the area normalization method.

3. Results and discussion

3.1. Characterization

The XRD patterns of AlPO-5-meso, MeAPO-5-meso and ordinary AlPO-5 are shown in Fig. 1. All the samples were in the AFI structure [26], and no peaks from other crystalline phase were observed. The value of d_{100} (listed in Table 1) for FeAPO-5-meso, CoAPO-5-meso, MgAPO-5-meso, MnAPO-5-meso and TiAPO-5-meso was 11.87, 11.83, 11.84, 11.83 and 11.80 Å, respectively. These values were slightly bigger than that of AlPO-5-meso (11.77 Å). Accordingly, the values of the cell parameter a_o of FeAPO-5-meso (13.71 Å), CoAPO-5-meso (13.66 Å), MgAPO-5-meso (13.67 Å), MnAPO-5-meso (13.66 Å) and TiAPO-5-meso (13.63 Å) were bigger than that of AlPO-5-meso (13.59 Å). Because the ionic

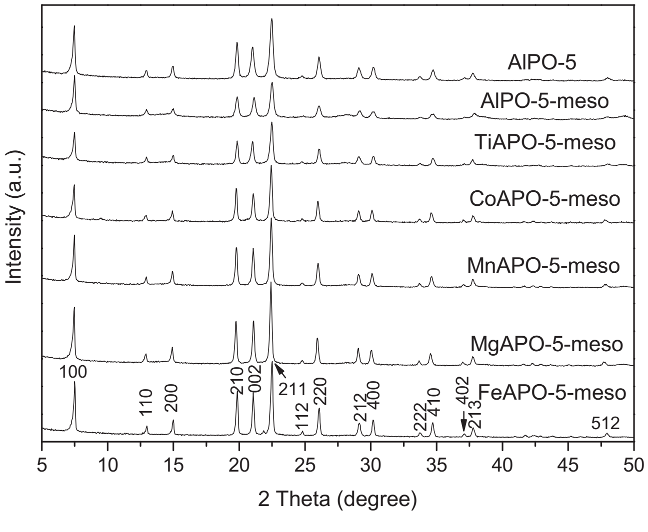

Fig. 1. XRD patterns of AlPO-5-meso, MeAPO-5-meso and ordinary AlPO-5.

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