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Synthesis of hierarchical porous silicalite-1 and its catalytic performance in Beckmann rearrangement

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ABSTRACT

Hierarchical porous silicalite-1 with micropores and mesopores was successfully synthesized via dry gel conversion route using tetrapropylammonium hydroxide (TPAOH) and polyvinyl alcohol (PVA) as microporous and mesoporous templates, respectively. The obtained hierarchical porous silicalite-1 was characterized by X-ray diffraction (XRD), nitrogen adsorption and desorption, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The characteristics of the samples are comparable with conventional silicalite-1. The influence of the PVA on the hierarchical porous properties of the samples was investigated. The hierarchical porous silicalite-1 showed higher activity and selectivity than conventional silicalite-1 in vapor phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam under reaction condition.

1. Introduction

Microporous zeolites with uniform pore size, adjustable acidity, and excellent stability are widely used in petrochemical industry as catalysts and catalyst supports [1–3]. However, the relative small pore size of the microporous zeolites (pore diameter <1.5 nm) results in slow diffusion of reactants and products from the active sites of the microporous zeolites, which restricting their further applications [4]. Several different approaches have been proposed to overcome the drawback of the zeolite limitation. These approaches consist of synthesizing nanosized zeolites [5,6] and synthesizing mesoporous materials with ordered pore (2 nm < pore diameter < 50 nm) [7–10]. However, the synthesis process of nanosized zeolite is difficult to handle and the mesoporous materials have low acidity and hydrothermal stability, which preventing their further applications.

In recent decade, a variety of methods for synthesizing hierarchical porous zeolites with both micropores and mesopores have been reported such as post treatment methods [11–15] and templating methods (carbon, mesoscale cationic polymers and organosilane) [16–28]. These hierarchical porous zeolite catalysts exhibit excellent catalytic performances for many reactions [29–39]. However, those methods have some disadvantages because they were complicated or those mesoporous templates were expensive and difficult to obtain. So we need simple methods and low-cost mesoporous templates to synthesize hierarchical porous zeolites.

Silicalite-1 is an MFI-type zeolite with special 10-ring channel structure and no aluminum. It is well known that silicalite-1 has been widely used in gas separation [40], catalysis [41,42] and fine chemical industry [43]. It is one of the catalysts for industrialization that vapor phase Beckmann rearrangement of cyclohexanone oxime to caprolactam. ε-Caprolactam is an important industrial chemical applied for the production of Nylon 6 fibers and resins. The reaction was performed in the presence of concentrated sulfuric acid as a homogeneous catalyst. Environmental reason was indeed the basis of the research for the production of ε-Caprolactam via a clean heterogeneous process. Zeolites, especially silicalite-1 were found with high activity and selectivity in Beckmann rearrangement of cyclohexanone oxime to caprolactam [44–47]. In view of cost and usefulness, hierarchical porous silicalite-1 obtained from cheap raw materials and easy synthesis method is very important. It is possible to improve the mass transfer by introducing hierarchical porous into the silicalite-1 zeolite.

The mesopore generation effect by the polyvinyl alcohol (PVA) in an aqueous-phase synthesis was reported [48]. In this work, we used tetrapropylammonium hydroxide (TPAOH) as microporous template and PVA which is simple and common as mesoporous template for synthesis of hierarchical porous silicalite-1 by using dry gel conversion route. Vapor phase Beckmann rearrangement of cyclohexanone oxime over hierarchical porous silicalite-1 was tested.

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2. Experimental

2.1. Synthesis

All the reagents including NaOH, tetrapropylammonium hydroxide (TPAOH, 25 wt%), tetraethyl orthosilicate (TEOS) and polyvinyl alcohol (PVA) were purchased from Sinopharm Chemical Reagent Company (China) and used as received without further purification or treatment.

The precursor sol with silicalite-1 primary and secondary building units was prepared by mixing 0.1 g NaOH, 10 ml of TPAOH solution (25 wt%), 9 ml of tetraethyl orthosilicate (TEOS) with 25 ml of H_2O under stirring for 3 h. The mixture was then aged at 90 °C for 20 h, giving a clear sol. At 90 °C, 0.8 g of polyvinyl alcohol (PVA) and 50 ml H_2O added with stirring until a clear solution was obtained. Then the clear sol obtained above was added into this clear solution. After a while, the solution became viscous and turned into gel. This gel was dried in the oven at 90 °C over night in order to evaporate the H_2O. The obtained dry gel was transferred into autoclave for crystallization at 140 °C for 96 h. The product was collected by filtration, washing with distilled water, drying in air and calcination at 550 °C for 5 h.

For comparison, dry gel conversion silicalite-1 was synthesized according to the above procedure in the absence of PVA and conventional silicalite-1 was synthesized according to a procedure described in the literature [44].

2.2. Characterizations

X-ray diffraction (XRD) patterns were obtained with a Siemens D5005 diffractometer using CuKα radiation. The isotherms of nitrogen were measured at 77 K using a Micromeritics ASAP 2010 system. The samples were outgassed for 10 h at 300 °C before the measurements. The pore-size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model. Scanning electron microscopy (SEM) experiments were performed on Hitachi S-4000 electron microscopes. Transmission electron microscopy (TEM) experiment was performed on a JEM 3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The Fourier transform infrared (FT-IR) spectra were recorded on Nicolet Impact 400 FT-IR spectrometer. Samples were pressed into self-supported wafers that were placed into a cell with BaF2 window. The wafers were heated at 300 °C for 3 h. After the samples were cooled to room temperature, the IR spectrum was recorded with 80 scans and 4 cm^{-1} resolution.

The vapor phase Beckmann rearrangement reaction of cyclohexanone oxime to ε-caprolactam was run in continuous-flow microreactor at atmospheric pressure. The catalyst (0.5 g, 20–40 mesh size) was loaded in the reactor and subjected to activation in a nitrogen stream at 350 °C for 1 h. Then, the catalyst was regulated to 300 °C for 4 h. First a solution of cyclohexanone oxime in toluene (5 wt%) was injected using a syringe pump under a nitrogen flow (30 ml/min). The weight hourly space velocity (WHSV) was 5 h^{-1}. The product collected at an ice-water trap was analyzed by gas chromatography (Shimadzu GC-17A) equipped with a FID detector.

3. Result and discussion

3.1. Catalyst characterization

The XRD pattern of hierarchical porous silicalite-1 (Fig. 1) indicated that highly crystallized silicalite-1 formed without any impurities. The obtained sample exhibits the characteristic diffraction peaks occurred at 2θ of 8.0°, 8.8°, 23.2°, 23.9°, and 24.5°, which are exclusively indexed with MFI structure [49]. It is indicated that the sample crystallized in the presence of PVA also show good crystallinity.

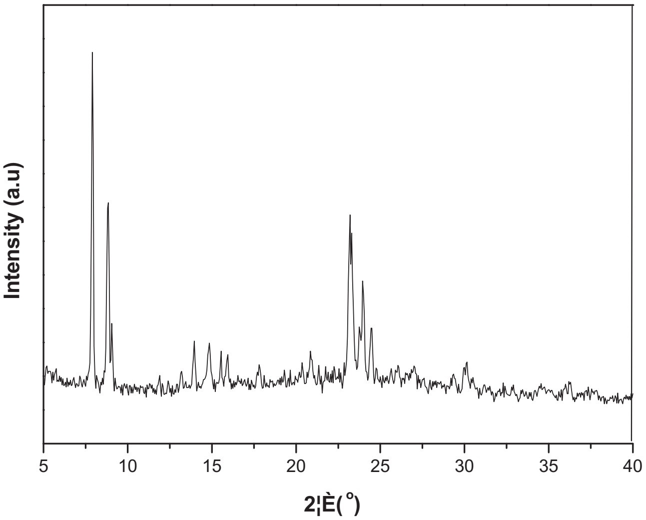

Fig. 1. XRD pattern of calcined hierarchical porous silicalite-1.

Fig. 2a shows the nitrogen adsorption and desorption isotherm of the hierarchical porous silicalite-1. The isotherms of sample show adsorption step and a hysteresis loop in the range of $P/P_0 > 0.6$, corresponding to capillary condensation of adsorbate at the mesoporous structures. A steep increase in adsorption volume of the sample occurs at relative pressure $P/P_0 < 0.05$ indicating the presence of micropores. It is noted that, in Fig. 2b, a wide BJH pore size distribution ranged 5–20 nm could be observed, confirming the presence of hierarchical mesopores [14,21]. These results indicate that the hierarchical porous silicalite-1 sample contains mesopores, which may be important for mass transport [2,4]. The presence of additional mesopores in this sample is a consequence of the removal of PVA. Table 1 summaries the BET surface areas, micropore volume, mesopore volume of three samples. It is noted that mesopore volume of hierarchical porous silicalite-1 (0.19 $cm^3\ g^{-1}$) is much bigger than that of conventional silicalite-1 (0.04 $cm^3\ g^{-1}$) and dry gel conversion silicalite-1 (0.05 $cm^3\ g^{-1}$). These results indicated mesoporosity in sample is generated by adding PVA in the synthesis.

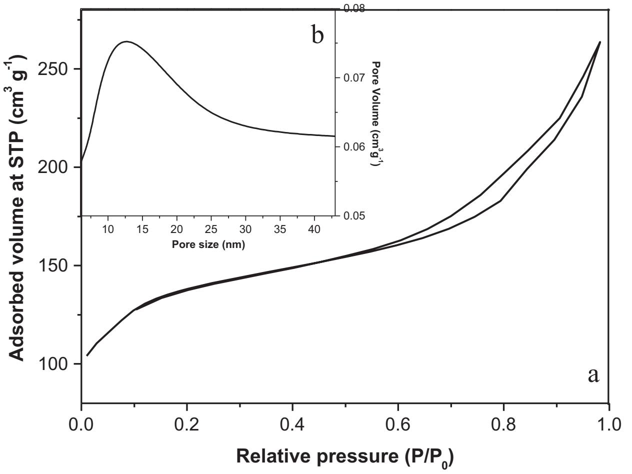

Fig. 2. N_2 isotherm (a) and pore size distribution (b) of calcined hierarchical porous silicalite-1.