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Synthesis and characterization of mesoporous ZSM-12 by using carbon particles

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Abstract

The generation of mesoporosity in 1-dimensional zeolite ZSM-12 was explored by using carbon black as template for the expected mesoporosity during synthesis. After the carbon particles were burned off, intracrystalline mesopore networks were formed. For relatively high C/Si and H_2O/Si ratios, there is higher opportunity to generate mesoporosity. All the samples were characterized by X-ray diffraction, nitrogen physisorption, SEM, ICP and FT-IR. Mesoporous ZSM-12 samples with nominal Si/Al ratios of 40, 60, 75, 100 in the gel, were successfully synthesized. The mesopore volumes were in the range of 0.15–0.19 cm^3/g and the mesopores distributed in the range of 10–50 nm were determined by nitrogen physisorption. The STPD and FT-IR results revealed that these mesoporous ZSM-12 samples possess the same number of acid sites as regularly synthesized ZSM-12 samples for comparable Si/Al ratios. For the synthesis gel containing the same Si/Al ratios, Si/Al ratios were almost the same in both the mesoporous and conventional ZSM-12 products, which indicated that the carbon black involved in the synthesis did not affect the crystallization efficiency of aluminum during the nucleation. The conversion of *n*-tridecane and 1,3-dimethylcyclohexane were chosen as test reactions. The mesoporous ZSM-12 samples ("Swiss Cheese" like) are found to exhibit higher activity compared to conventional ones especially under high WHSVs. The enhanced activity we observed can be attributed to the introduction of the mesopores in the zeolite crystals, which decreases the intracrystalline mass transfer limitations. Moreover, the mesoporous samples promoted the production of longer and more branched products than the case of the traditional samples since the former ones favor to a higher extent the outwards diffusion of the products.

Keywords: Mesoporous Zeolites; ZSM-12; Carbon Black; Template; Synthesis

1. Introduction

Zeolite and zeolite-like materials have been extensively used in industry for adsorption, separation and catalysis. Due to their inherent acidity and hydrothermal stability, a large number of chemical reactions in refinery and petrochemical processing are catalyzed by zeolites, which often exhibit exceptional characteristics in terms of activity and selectivity [1]. However, the catalytic performance of zeolites can be seriously limited due to their microporous channel structure which restricts accessibility of the reactants to the interior regions of the zeolite crystals. Much effort has been devoted to circumvent this problem. One strategy is to increase the pore size of the material. For instance, the synthesis of M41S family materials, which was first reported 10 about years ago, is one of such accomplishments [2,3]. The silica based mesoporous M41S materials offer excellent flexibility to tune the pore size in the range of 1.5–20 nm, high surface area and pore volume. Nevertheless, M41S materials exhibit relatively lower stability and acidity due to the amorphous nature of their structure compared to zeolites [4]. Another strategy is to decrease the crystal size of zeolites. Several methods which allow the synthesis of nanosized zeolite crystals have been reported recently [5–7]. Nevertheless, decreasing the zeolite particles into nanometer range, results sometimes in difficulties to handle the zeolite crystals. Another elegant

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approach to introduce the mesopores into the zeolite crystals is achieved by applying the post-treatment procedures such as dealumination [8] or desilication [9], which cause sometimes partial collapse of the zeolite crystals [10].

Recently, introducing intracrystalline mesopores into the zeolites is realized by using carbon material as template during the zeolite crystallization [11,12]. This strategy consists of impregnating a carbon source namely, carbon black [12] with a zeolite precursor solution which promotes the nucleation of the zeolite crystals around the carbon material. In this manner, the zeolite crystals grow and partially encapsulate the carbon. During the subsequent calcination, the carbon is burned off, which results in the generation of intracrystalline mesopores. Compared to other strategies, this method possesses several advantages. First of all, it is a general method for introducing mesopores into zeolite crystals regardless of their structure and can be used in principle for any zeolite to form a "Swiss cheese" like network of meso- and even macropores. Moreover, one can form mesoporosity without utilizing dealumination that may decrease significantly the zeolite's acidic nature and crystallinity.

In this paper, we report the preparation of mesoporous ZSM-12 with different Si/Al ratio for the first time. ZSM-12 is a high silica zeolite with unidimensional 12-membered ring channel system and pore openings of 5.7×6.1 Å [13]. The acidic form of ZSM-12 has demonstrated to possess better selectivity in the hydroisomerization of *n*-C7 over other zeolites [14]. However, due to its unidimensional channel, the intracrystalline diffusion is highly limited in ZSM-12. By using carbon as template, meso- and even macropores are generated after carbon is burned off. All the samples synthesized with carbon were highly crystalline based on the XRD results. The synthesized materials possessed a secondary pore size distribution ranging from 10 to 50 nm. Conversion of tridecane and 1,3-dimethylcyclohexane were chosen as a model test. The mesoporous ZSM-12 exhibited better conversion compared with conventional ZSM-12 of comparable Si/Al ratios, which offers proof for enhanced mass transfer in these mesoporous ZSM-12.

2. Experimental

2.1. XRD

XRD was employed to identify the synthesized zeolite and its crystallinity. The XRD patterns were recorded with a Siemens powder X-ray diffractometer using CuKα radiation. The 2θ values chosen were from 5° to 40° with stepwise 0.1°/s.

2.2. Nitrogen physisorption

Nitrogen adsorption and desorption measurements were performed at liquid nitrogen temperature on a Micromeritics ASAP 2010. The samples were degassed in vacuum at 200 °C for 4 h prior to measurement. Micropore volumes and external surface areas were determined using *t*-plot analysis [15]. Pore size distribution was calculated from the adsorption isotherm according to the method developed by Barret et al. [16].

2.3. SEM

Scanning electron microscopy was done on selected samples to determine the crystallite size and morphology using a Hitachi S-4000 field emission SEM. The calcined samples were placed on a carbon film and Pt was deposited onto the samples for 20 min to attain adequate conductivity.

2.4. Acidity characterization

The number of acid sites was characterized by STPD. Catalyst (50 mg) was loaded in a quartz reactor. After dried at 500 °C for 2 h in a flow of helium, the sample was cooled down to 150 °C and exposed to a mixture of NH_3 and helium for 1 h. Then, pure helium was purged for 2 h in order to remove the physisorbed NH_3. Finally, the sample was heated in helium flow of 30 ml/min at a rate of 10°/min up to 600 °C. The ammonia concentration was recorded by the TCD.

FT-IR was performed to check the presence of extra-framework Al. FT-IR measurements were performed by using a Bio-Rad FTS-40 spectrometer equipped with a high temperature flow cell having CaF_2 windows. After purging with helium at 500 °C, the sample was cooled down to 150 °C and pyridine was adsorbed until saturation was achieved. The sample was then purged with helium for 1 h under 200 °C and the spectrum was collected.

2.5. Synthesis of mesoporous ZSM-12

For the synthesis experiments, tetraethylammonium hydroxide (Fluka, 40 wt.% in water) was used as the template, LUDOX HS-40 colloidal silica (40 wt.%, DuPont) was used as the silica source and sodium aluminum oxide (Alfa Aesar, Technical grade) was the aluminum source. Carbon black particles (BP-2000) having an average particle diameter of 12 nm obtained from Cabot Corporation were used as inert matrices. The carbon black was dried at 150 °C for 10 h prior to use. Distilled water was used throughout the work.

Mesoporous ZSM-12 samples with different Si/Al ratios were synthesized during the work. The preparation of the gel for one of our batches is described below as an example. TEAOH solution (10.8 ml) was mixed with 6.8 ml of distilled water and 0.144 g of sodium aluminum oxide and stirred till the solid dissolved. Then, 4.6 g carbon black was impregnated to incipient wetness with the above solution and stirred vigorously. Then, 14.8 ml Ludox and 44 ml H_2O were added to the mixture. The gel was transferred into a 120 ml capacity Teflon-lined stainless steel autoclave