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Preparation, characterization of MCM-56 and catalytic activity in one-step synthesis of MIBK from acetone

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Abstract

High crystalline MCM-56 was synthesized by dynamic method hydrothermally, and it was used as supports to prepare Pd/MCM-56 catalysts by ion-exchange method. The materials were characterized by means of N_2 adsorption, XRD, TEM, TPD. We found that as-made MCM-56 was made of very thin MWW-type layers with only one unit cell along the c direction. One-step synthesis of methyl isobutyl ketone from acetone was investigated over Pd/MCM-56. A conversion of 33.5% and a selectivity of 81.2% to MIBK were achieved. A stable MIBK yield was also obtained as well, maintaining 72 h of time on stream.

Keywords: Pd/MCM-56; Acetone; Methyl isobutyl ketone; One-step synthesis

1. Introduction

In recent years, many modifications in the synthesis procedure and catalytic applications of MCM-22 have been published [1–4], while little is reported about the properties of MCM-56, especially the catalytic applications. Fung [4] first reported the synthesis of MCM-56. As MCM-56 and MCM-22 all share the MWW structure [5], MCM-56 exhibited some similarities with MCM-22, including the sinusoidal network channel and a large number of 12 MR cups exposed to the crystal exterior [6]. MCM-56 can be thermally treated without affecting its layered structure, while the structure of as-made MCM-22 changed markedly after calcinations. Large supercages with an inner diameter of approximately 0.71 nm and a height of 1.82 nm appear in calcined MCM-22 [7]. The most interesting feature of MCM-56 in comparison with MCM-22 is that the former adsorbs larger amounts of bulky molecule and shows a much faster adsorption rate than MCM-22. The unusual porous network and unique property of MCM-56 suggests its potential use as support and catalysts [7].

Methyl isobutyl ketone (MIBK) is widely used in the fields of solvent and protective coating systems. It has been commercially produced by a conventional three-step process: (i) aldol condensation of acetone to diacetone alcohol (DAA) over basic catalysts; (ii) acid-catalyzed DAA dehydration to mesityl oxide (MO); and (iii) selective hydrogenation of MO to MIBK [8]. The first two steps are usually limited by equilibrium, and the third one may produce a relatively large amount of side-products. High costs and corrosive problem also exists in the process. Those drawbacks strongly induce the studies for a one-step process using a catalyst with condensation, dehydration and hydrogenation functions.

Several papers have been reported on one-step synthesis of MIBK in liquid phase at 10–100 atm., including

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palladium supported on KOH–Al_2O_3, MgO–SiO_2, cation exchange resins [9], Ce, Hf and Ta oxides-carbon [10], $Zr_3(PO_4)_2$ [11], Nb_2O_5 [12]. 90% selectivity to MIBK was achieved in these reports. Recently, several catalytic systems on one-step synthesis in gas phase have been published, including Pd/KH-ZSM-5 [13], Pd/SAPO-34 [14], Pd/calcined hydrotalcite [15], Ni/MgO [16], Ni/ALPON [17], Pt/HZSM-5 [18] and Co/MgO [19]. The selectivity to MIBK is about 60–80%, which is much slower than that in liquid phase. Thus, finding a new catalyst with high selectivity to MIBK in gas reaction is priority concern.

In this paper, we first used MCM-56 as supports for the synthesis of MIBK from acetone. We presented the preparation and characterization of MCM-56 and Pd/MCM-56, as well as their catalytic properties for MIBK synthesis. The catalytic activity of Pd/MCM-22 was also studied for comparison.

2. Experimental

2.1. Zeolite synthesis

MCM-56 was prepared as described in literature [6]. A typical synthesis procedure is as follows: 4.56 g of $NaAlO_2$ and 20 mL HMI were first dissolved in 80 mL of H_2O, then 120 g of silica was slowly added to the solution under vigorously stirring and was maintained for 30 min, leading to a composition of SiO_2:0.04Al_2O_3:0.12NaOH:0.35HMI:18.9H_2O. The slurry was then introduced into a stainless-steel autoclave, rotated at 45 rpm, and heated at 140 °C for 36 h. NaMCM-56 obtained after synthesis was washed with deionized water, dried at 120 °C for 12 h and calcined at 550 °C for 6 h. Synthesized NaMCM-56 was dissolved in 1 M NH_4NO_3 solution at room temperature for 30 h. HMCM-56 obtained after ion-exchange was dried at 120 °C for 5 h and calcined at 550 °C for 3 h. The Pd/HMCM-56 catalysts were prepared by the ion-exchanged method, using aqueous solution of palladium nitrate. Ion-exchanged was carried out in a rotator-evaporator at 180 °C for 48 h. The synthesized Pd/MCM-56 catalysts were dried at 120 °C for 5 h and calcined at 450 °C for 5 h.

The synthesis of MCM-22 was described in [20]. Pd/MCM-22 was prepared by the same principle as Pd/MCM-56.

2.2. Catalyst characterization

The textural properties of the samples were obtained in an ASAP 2020 apparatus.

Temperature-programmed desorption of NH_3 (TPD-NH_3) was carried out with a self-designed apparatus.

X-ray diffraction (XRD) patterns were recorded using a Shimadzu XRD-6000 diffractometer operated 40 kV and 30 mA and using Cu Kα radiation ($\lambda = 0.1542$ nm).

Transmission electron microscopy (TEM) of the samples was performed on Hitachi H-8100 apparatus operating at 200 kV.

The average particle size of Pd was calculated from the dispersion of Pd measured by H_2 chemisorption method as described by Spenadel and Boudart [21].

2.3. Catalytic activity test

The reactions were carried out in a fixed bed tubular reactor using 0.5 g catalyst at high pressure. Before reaction, the catalysts were reduced "in situ" in flowing hydrogen at 400 °C for 3 h and then cooled down to the reaction temperature. The stream of gas mixture was introduced at a constant rate into the upper zone of the reactor, which was packed with SiO_2 pellets maintaining the reaction temperature for preheating and vaporization. The products were analyzed by on-line gas chromatography (Shimadzu GC-14B).

3. Result and discussion

3.1. Characterization

The XRD pattern of the as-made and the calcined MCM-56 are shown in Fig. 1, respectively. Compared with the literature, the line positions and relative intensities of the peaks are in good agreement with those published for MCM-56 zeolite [6,7]. It can be concluded that as-made MCM-56 is of high crystalline phase. The peak widths between 7–10° and 20–25° indicate that MCM-56 is composed of thin layers that extend in the *a* and *b* directions while short in the *c*-direction [6].

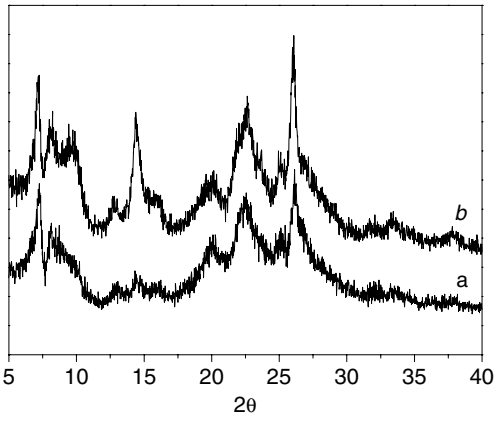

Fig. 1. XRD pattern of: (a) as-made MCM-56 and (b) calcined MCM-56.