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The synthesis of Mo/H-MCM-36 catalyst and its catalytic behavior in methane non-oxidative aromatization

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Abstract

MCM-36 was synthesized by swelling and pillaring the layered MCM-22 precursor and its physical and acidic properties were characterized by XRD, TEM, BET and IR spectroscopy of d_3-acetonitrile adsorption. Mo/H-MCM-36 catalyst was prepared with MoO_3 and H-MCM-36, and its catalytic behavior in methane non-oxidative aromatization was studied comparing with Mo/H-MCM-22 catalyst. It was found that in the initial period of reaction Mo/H-MCM-36 exhibited a relative high conversion of CH_4 and selectivity of CO. Then it showed a low conversion of CH_4 and high formation rate of coke. We supposed that the different pore structure, acidity and Mo dispersion of the two catalysts were responsible for their different catalytic behaviors.

Keywords: Mo/H-MCM-36; Pore structure; Acid sites; Supercage; 12-Ring pocket; Methane

1. Introduction

The direct catalytic conversion of methane to aromatics in the absence of oxygen over Mo/HZSM-5 catalysts has received much attention since it was first reported in 1993 [1]. Recently, researches found that Mo supported catalysts on MCM-22 or MCM-49 zeolites showed higher catalytic activities than Mo/HZSM-5 catalyst [2–5], and it was suggested that the special structure of MCM-22 should be responsible for the high activities. Typically, both MCM-22 and MCM-49 [6–8] are MWW topology structural layer zeolites comprised of three different independent pore systems, one is defined by 10-ring two-dimensional sinusoidal channels. The second consists of large supercages with inner free dimensions of $7.1 \times 7.1 \times 18.2$ Å, which is accessible through 10-membered rings. The third is 12-ring pockets located on external surface. Up to now, there is not yet a suitable method to distinguish the respective role of these three pore systems in non-oxidative aromatization of methane. We have attempted to modify the external surface of MCM-49 by reacting with large molecular organic silica $[SiO(CH_4)_2]_4$ in order to understand the role of external 12-ring pockets [9], and concluded that the external acid sites (especially Brønsted acid sites) promoted the formation of naphthalene and larger hydrocarbons. In recent years, a new layered molecular sieve MCM-36 was obtained by introducing silica (Al_2O_3, MgO, BaO) pillar into the MCM-22 precursor [11–13], and the material was shown to present sinusoidal channel, external surface pockets and mesoporous channel containing 12-ring pockets. In this study, silica pillared MCM-36 was synthesized by swelling the MCM-22 precursor, thus the supercage in MCM-22 was disintegrated to two separated 12-ring pockets to form MCM-36. MoO_3/HMCM-36 catalyst was prepared

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and its catalytic properties in methane non-oxidative aromatization were studied in order to explain the respective role of supercages and 12-ring pockets. This work might provide a feasible method to further study the role of sinusoidal channels.

2. Experimental

2.1. Dynamic synthesis of MCM-22

The nanosize MCM-22 zeolite with Si/Al = 25 was synthesized by a hydrothermal procedure using hexamethyleneimine (HMI) as the template and silica gel as the silica source [10]. The original slurry was obtained by stirring the mixture of certain amounts of sodium aluminate, silica gel, HMI and water. After being crystallized at 443 K with rotating rate of 60 rpm for 3 days, the resulting solids (MCM-22 precursor) were filtrated, washed and dried.

2.2. Synthesis of MCM-36

The MCM-36 was synthesized according to the method reported in [11]. The swollen sample was obtained by continuous stirring the mixture of MCM-22 precursor, cetyltrimethylammonium chloride solution and tetrapropylammonium hydroxide with a relative weight ratio of 1:4:1.2, first at 373 K for 68 h and then at room temperature for 4 h. After being filtered, washed with a small amount of water and dried, the solid was mixed with tetraethylorthosilicate with a weight ratio of 1:5. The mixture was stirred at 363 K for 25 h in a nitrogen atmosphere, and then filtered and dried overnight. The resulting solid was finally hydrolyzed in water with a 1:10 ratio of solid powder and water at 413 K for 6 h, then filtered and dried overnight.

2.3. Synthesis of H-MCM-22 and H-MCM-36

The occluded organic of zeolites was removed by heating at 723 K for 3 h under a continuous flow of nitrogen before a flow of air at 813 K for 6 h to obtain the calcined samples. H-MCM-22 and H-MCM-36 were prepared by three times repeated ion exchange of the calcined samples with an aqueous solution of 1 mol/l ammonium nitrate and calcination in air at 773 K for 3 h.

2.4. Synthesis of Mo/H-MCM-22 and Mo/H-MCM-36

Mo loaded zeolite catalysts were prepared by mixing MoO_3 and H-MCM-22 or H-MCM-36 with a Mo content of 6 wt.% and calcination in air at 773 K for 3 h. The two catalysts prepared using H-MCM-22 and H-MCM-36 are designated as Mo22 and Mo36, respectively.

2.5. Catalysts characterization and catalytic test

XRD patterns were obtained on Shimadzu XRD-6000 spectrometer using Cu Kα radiation at room temperature with instrumental settings of 40 kV and 30 mA. The morphology of the zeolites was observed by Hitachi H-8100 transmission electron microscopy. The specific surface area and volume of pores from nitrogen absorption isotherms were received on an apparatus ASAP 2020 after pretreating the samples under vacuum at 623 K overnight. The chemical compositions of zeolite were reported by a Perkin–Elmer Plasma/1000 Emission Spectrometer. The acidity of H-MCM-22 and H-MCM-36 was determined after the adsorption of d_3-acetonitrile followed by IR spectroscopy using a Nicolet Impact 410 FTIR spectrometer. d_3-Acetonitrile is used as a small and sensitive probe molecule to detect the presence of both Brønsted and Lewis sites [14,15]. Zeolite samples were pressed in the form of self-supported wafers, fixed in a quartz holder and then introduced into an infrared cell with NaCl windows. d_3-Acetonitrile was pretreated by freeze-pump-thaw cycles. Before adsorption of d_3-acetonitrile, the zeolites were treated in situ by evacuation at 623 K in 10^{-3} Pa. Adsorption was carried out at 298 K for 20 min, followed by an evacuation at the same temperature. And the IR profiles were deconvoluted using a Gaussian curve-fitting method.

Catalytic tests were carried out under atmospheric pressure in a continuous flow fixed bed quartz reactor of 1 cm ID, which was charged with 0.5 g of catalyst (40–60 meshes). The feed gas mixture of 92.5% CH_4 and 7.5% N_2 was introduced into reactor at 1500 ml/g h through a mass flow controller and the temperature was raised to 973 K for reaction within 50 min. An on-line gas chromatograph (GC-17A) was used, equipped with a 6 m × 3 mm HayeSep D80/100 column to analyze H_2, N_2, CO, C_2H_4, C_2H_6 by on-line TCD and a CBP1-M50-025 (Shimadazu) quartz capillary to analyze condensable aromatics such as benzene, toluene, naphthalene by on-line FID. The methane conversion and the product selectivity were calculated on a carbon number base using N_2 as inner reference.

The amount of the coke during the reaction was analyzed by a thermal analysis. TGA and DTA were performed using a Shimadzu DTG-60. The reacted samples were heated from 303 to 1073 K at a rate of 10 K/min under a flow of dry air.

3. Results and discussion

The powder X-ray diffraction patterns of synthesized MCM-22 precursor and MCM-36 are shown in Fig. 1. The XRD patterns of MCM-36 display an intensive low angle peak at 2θ between 1° and 2°, which corresponds to a d-spacing larger than 5 nm. The d-spacing includes the c-parameter of the unit cell of MCM-22