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Dealumination of HMCM-22 by various methods and its application in one-step synthesis of dimethyl ether from syngas

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Abstract

A series of MCM-22 zeolites were prepared by hydrothermal synthesis and subsequent dealumination by oxalic/citric acid leaching and steaming. The structural and acidic properties of the prepared samples were characterized by methods of XRD, ICP-AES, ^{27}Al MAS NMR, pyridine-adsorbed IR and NH_3-TPD. The results indicated that the sample treated by oxalic acid (MCM-22O) has the lowest aluminum content while the samples treated by steam have little change of the aluminum content. Unusually, sample MCM-22O possessed the strongest acidity among the dealuminated samples in spite of its lowest content of aluminum. It may be due to its least content of extraframework aluminum, which may lead to the weakening of acidity. Additionally, the prepared zeolites were mixed with a methanol synthesis catalyst and then applied in the process of syngas to dimethyl ether. Citric acid treated sample performed best with the least generation of byproducts, which have been well related to its structural and acidic properties.

Keywords: MCM-22 zeolite; Dealumination; Acidity; Methanol dehydration; Dimethyl ether; One-step synthesis; Syngas

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1. Introduction

MCM-22 is a relatively new zeolite, first prepared by Rubin et al. in 1990 [1]. The structure of MCM-22 (coded as MWW) consists of two independent pore systems. One is composed of the two-dimensional sinusoidal channels with 10-ring (10MR) pore openings and the other is the interlayer supercages with 12-ring (12MR) openings. Because of its unique pore structure, zeolite MCM-22 combines the behavior of both the 10MR and 12MR porous systems, making it some unusual catalytic properties. Thus, much attention has been paid to its catalytic performances in many reactions such as isomerization [2–7], disproportionation [8–11], alkylation [3,12–15], cracking [3,16–18], methane aromatization [19–21], etherification [22] and some other reactions [23,24]. Besides these catalytic applications, the synthesis and characterization of zeolite MCM-22 have also been reported constantly [25–30]. However, only a few works have been reported about the dealumination of zeolite MCM-22 and its influences on the zeolitic acidity. The hydrothermal treatment was the most frequently employed method among them [5,8,31,32]. Besides, there was also other works focusing on the dealumination of MCM-22 by oxalic acid [33].

Dimethyl ether (DME) is a potential fuel for diesel engine because of its lower NO_x emission, near-zero smoke production and even lesser engine noise compared with conventional diesel oil [34]. And the syngas to DME (STD) process is presently one of the most favorable techniques for DME production. Catalysts for the STD process are usually composed of a methanol synthesis catalyst and a solid acid catalyst for methanol dehydration, while the

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most common solid acids applied in STD process are γ-Al_2O_3 and HZSM-5. Very recently, we have made efforts on the application of MCM-22 zeolite in the STD process [35], and found that the high-silica MCM-22 had a good performance in the STD test.

In this study, various methods were adopted for dealumination of MCM-22 in order to discover their influences on aluminum localization and acidity of HMCM-22 zeolite. Since the acidity of zeolites is dependent on their aluminum contents and distributions, the HMCM-22 samples prepared by different methods should possess various acid properties because of their dissimilar degree of dealumination. Upon that, XRD, ICP-AES, ^{27}Al MAS NMR, pyridine-IR and NH_3-TPD (temperature programmed desorption) were employed to characterize the physical and chemical properties of the parent and treated HMCM-22 samples and the data collected were compared and related. In addition, these prepared HMCM-22 samples were employed in the STD process as dehydration catalysts. The correlation between acidic and catalytic properties was discussed and some interesting conclusions have been made.

2. Experimental

2.1. Preparation of HMCM-22 zeolite

The parent MCM-22 zeolite was prepared by mixing hexamethylenimine (HMI), $Al(NO_3)_3 \cdot 9H_2O$, sodium hydroxide and deionized water together and then mixed with silica sol (40.0 wt.% SiO_2, 0.103 wt.% Al_2O_3) under stirring. The final composition of the gel was 5NaOH:2Al$(NO_3)_3$:25SiO_2:1000H_2O:12.5HMI. After being aged for 1 h under continuous stirring at room temperature, the mixture was transferred into a Teflon lined autoclave and then heated to 150 °C for 7 days under magnetic stirring. The product was finally recovered by filtration, washing, drying and calcination in flowing air at 600 °C for 4 h. To obtain H-form MCM-22 (HMCM-22), the product after calcination was then ion exchanged with 1 mol/l ammonium nitrate solution at 85 °C for 1 h and repeated twice. The obtained product was finally calcined in flowing air at 550 °C for 4 h.

2.2. Methods of dealumination

MCM-22 zeolite prepared above was employed as the parent material (MCM-22P) for the following dealumination procedures. Steaming and acid (oxalic and citric acids) extracting were the dealuminating methods applied in this paper. For steaming, the treatment was carried out in a quartz tube heated by an electric furnace. The samples were heated to 600 °C at 10 °C min^{-1} and maintained at this temperature for 4 h in a flow of steam–air mixture, which was composed of 12 ml min^{-1} g^{-1} of water and 100 ml min^{-1} g^{-1} of air. The steamed HMCM-22 sample was named MCM-22S. And for acid leaching, the zeolite was treated with a 0.5 mol/l oxalic or citric acid solution at 85 °C under reflux for 24 h. The ratio of liquid to solid was 20 ml/g. After that, the solid product was filtrated, dried and calcined at 550 °C for 4 h. The final product was named as MCM-22O or MCM-22C for the oxalic or citric acid treated sample, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-II X-ray diffractometer with Ni-filtered CuK_α radiation, with a scan speed of 8°/min and a scan range of 5–50° at 30 kV and 20 mA.

The SiO_2/Al_2O_3 ratio of the product was measured by an inductively coupled plasma atomic emission spectroscopy method (ICP-AES, BAIRD: PS-6) after the digestion of the sample with HF solution.

^{27}Al magic angle spining nuclear magnetic resonance (^{27}Al MAS NMR) spectra of the parent and dealuminated zeolites were obtained on a DSX 300 spectrometer (Bruker) at the flip angle of 10° with 0.31 μs excitation pulses, a spinning speed of 12 kHz and a recycle delay of 0.2 s. The ^{27}Al chemical shifts were referenced to the external $Al(H_2O)_6^{3+}$ in saturated aluminum chloride solution. Before packed into the NMR MAS rotors, all the samples were equilibrated in the saturated water vapor of an NH_4Cl solution. The Al_{EFW}/Al_{FW} ratio of each sample expressed the ratio of extraframework Al to framework Al and was defined to equal to the integrated area ratio of peaks at 0 ppm and at 55 ppm.

Fourier-transform infrared (FT-IR) spectra and pyridine-adsorbed FT-IR (pyridine-IR) spectra were measured on a NEXUS 470 IR spectrometer. The self-supported zeolitic wafers were degassed in a vacuum (0.66 Pa) at 300 °C for 4 h, and then exposed to the vapor of pyridine after cooling down to room temperature. The pyridine-IR spectra were then recorded at several temperatures after vacuumizing for 15 min. The absorption data of Lewis acid sites were calculated from the peak area per milligram sample at 1450 cm^{-1} while those of Brønsted acid sites were from that at 1547 cm^{-1}.

Temperature programmed desorption of ammonia (NH_3-TPD) was also applied for the determination of acid properties of the parent and treated samples. For this mensuration, about 0.10 g of the pelletized sample was in situ activated in the reactor at 600 °C in flowing helium gas for 40 min. After cooling down to room temperature, ammonia gas was introduced into the reactor for a certain time to assure a saturated adsorption on the sample. The physisorbed ammonia was desorbed in a helium gas flow at 150 °C for about 1 h. After that, the sample was heated from 150 to 600 °C at 10 °C/min and maintained at 600 °C for 30 min in a flow of helium gas, and the effluent gas was first analyzed by an online gas chromatograph with a TCD detector and then absorbed by a dilute sulfuric acid solution followed by a titration step to determine the amount of ammonia.