

DIRECT SYNTHESIS OF HIGH-SILICA MORDENITE WITH SMALL CRYSTAL SIZE

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INTRODUCTION

Mordenite is a zeolite with an ideal composition of $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}\cdot n\text{H}_2\text{O}$ and a structure refined in the Cmc₂m space group[1]. The micropore system of mordenite consists of two pore channels; an elliptical pore channel (6.7×7.0Å) which runs parallel to the c-axis, and another pore channel which runs parallel to the b-axis (2.6×5.7Å) [2]. Due to its good thermal stability and acid property, mordenite has been used as catalysts for many important reactions such as hydroisomerization, alkylation, reforming, etc[3,4]. High-silica MOR zeolite is preferred in these reactions, which is usually prepared through removal of aluminum from the zeolite framework by treatment with steam and/or acid. However, the dealuminated MOR zeolite is known to be less thermally stable than the directly synthesized high-silica MOR zeolite [5]. Smaller crystals of zeolites have larger surface areas and less diffusion limitations compared to zeolites with larger crystals [6]. In the present work, mordenite with high silica to alumina ratio(15-35) and small crystal size has been prepared directly by surface-wetting method. The catalytic performance is evaluated in isomerization of C5/C6 hydrocarbon.

EXPERIMENTAL

Synthesis mixtures were prepared with the following reagents: commercial solid silica gel, pseudoboehmite, sodium hydroxide, aqueous tetraethylammonium hydroxide (TEAOH), and distilled water. The gel was homogenized by stirring, and transferred to a stainless-steel autoclave for crystallization. A two-stage crystallization procedure was employed [7].

The crystalline phases of the solid products were analyzed by powder X-ray diffraction (XRD) using a D/MAX-11A diffractometer (CuK radiation). Crystal morphologies were observed by transmission electron microscopy (TEM) using a JEM-2000FXII microscope. The SiO₂/Al₂O₃ ratio in the samples was determined by ²⁹Si and ²⁷Al MAS NMR spectra on a Bruker DRX-400 spectrometer. Surface area and total pore volume were obtained from low temperature N₂ adsorption experiments using a Micromeritics ASAP2400 instrument.

The catalytic tests were carried out in a microreactor system consisting of a stainless-steel tube reactor, equipped with a flow controller and heated by an electrical heater. The isomerization of C5/C6 hydrocarbon was then studied under the following conditions: temperature 533 K; pressure 1.6 MPa; WHSV=1.0 h⁻¹; H₂/hydrocarbon=2:1(mol). The gas flow rate was such as to exclude the effect of external diffusion. During each run, products were collected every 4 h until the reaction reached a pseudo-stable state. Products were analyzed by GC.

RESULTS AND DISCUSSION

The direct synthesis of high-silica MOR zeolite was carried out by different parameters, such as dissolution of solid silica, crystallization temperature and time, and SiO₂/Al₂O₃ ratio (15-35). The influences of all these parameters on crystallinity and crystal size of mordenite were studied. The results show that the source of silica has strong influence on the crystallization rate of mordenite. If uncalcined silica was used as silica source, mordenite crystals with 0.75×0.45μm in size were obtained when crystallization time reached 72h. When using calcined silica as silica source, crystallization time must be increased to 84h in order to get the same crystallinity, and larger crystals(1.5×0.75μm) of mordenite were obtained. The dissolution of amorphous

silica particles was found to be the rate-limiting step in the synthesis of mordenite. Unlike calcined silica, uncalcined silica has good solubility in the preparation system, so there is more availability of nutrients to start the nucleation and growth of zeolite crystals, causing high crystallization rate and smaller crystal size.

Partial isomorphous substitution of silicon by other tetrahedron forming elements has influence on crystal size. The crystal size of mordenite was decreased from $0.75 \times 0.45 \mu\text{m}$ to 150-200nm when decreasing SAR of the starting gel from 25 to 15. This result has been previously explained in literature by applying Lowenstein's rule [8]. Aluminate ions in solution react only with silicate groups on the growing crystal surface, while silicate ions in solution react with either silicate or aluminate surface groups. The presence of aluminum is associated with the formation of smaller crystals.

The crystal size of zeolite is a function of the ratio between the nucleation rate and the rate of crystal growth [9]. The synthesis of mordenite with small crystal size requires a high rate of nucleation and a low rate of crystal growth. From the above results, it can be easily controlled by choosing the source of silica and changing SAR. According to the literature [10], the size of crystals can be also controlled by crystallization time and temperature. When reducing the temperature and the time, smaller crystals could be obtained. But under low temperature the rate of crystallization is also decreased and a great deal of amorphous material will also be present.

Mordenite directly synthesized by surface-wetting method with high SAR($\text{SiO}_2/\text{Al}_2\text{O}_3=25$) and small crystal size($0.2 \times 0.4 \mu\text{m}$) shows good catalytic property in isomerization of C5/C6 hydrocarbon comparing the commercially mordenite catalysts.

CONCLUSION

High-silica mordenite($\text{SiO}_2/\text{Al}_2\text{O}_3=15-35$) with small crystal size has been directly prepared by surface-wetting method. The crystal size can be modified by the source of silica and SAR. When used as catalyst in isomerization of C5/C6 hydrocarbon, it shows good catalytic property in comparison with the commercially mordenite catalysts.

ACKNOWLEDGEMENT

This work was supported by the State Key Basic Research Projects scheme (2006CB202502). We thank Professor Xiuping Zhang for the catalytic evaluation, Nanguai Huang for XRD, Heping Zhang for N₂ adsorption measurement and Jin Zhang for TEM measurements.

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