Title	高シリカモルデナイトの直接水熱合成とその特性
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Citation	
Issue Date	2005-09
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/2182
Rights	
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Direct Hydrothermal Synthesis and Characteristics of High-silica Mordenite

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In this thesis, the highly crystalline and pure MOR zeolite with a Si/Al ratio of ca. 34 was successfully prepared using seed crystals, NaF and NH_4NO_3, this Si/Al ratio is the highest value among the literature. In addition, the relationship between the thermal stability and Si/Al ratio was first clear. Moreover, the Al distribution of the high-silica MOR zeolite was also apparently using CD_3CN and benzene molecules as adsorption probe. The main results are described as follows.

In the presence of TEAOH and fluoride ions, $Al(NO_3)_3$ was the best aluminum sources, and the highly crystalline MOR zeolites with a Si/Al ratio of approximately 30 were successfully prepared. The addition of NaF as a fluoride source into the synthesis gel depressed the nucleation of BEA zeolite, and enhanced the crystal growth of MOR zeolite. The BET surface area and the micropore volume of the MOR zeolite synthesized with NaF were smaller than those without NaF probably due to NaF present in zeolite crystals. The high-silica MOR zeolites synthesized with NaF had rectangular parallelepiped and rice grain-like crystals with the length of 10-15 μm. There was a good relationship between the thermal stability and bulk Si/Al ratio of MOR zeolite obtained without NaF, and the NaF remaining in zeolite crystals reduced considerably it's thermal stability. In addition, the MOR zeolite synthesized with NaF was very poorer in framework defects as compared with sample obtained without NaF as indicated by IR and ^{29}Si MAS NMR techniques.

When the seed crystals with a Si/Al ratio of 15 synthesized without NaF were employed, the highly crystalline MOR zeolite with a Si/Al ratio of approximately 30 was successfully prepared. It's morphology was leaf-like with the crystal length of ≈ 7.5 μm. The BET surface area and the micropore volume of the obtained MOR were larger than those obtained using NaF, and were similar to those of commercial available zeolite. The MOR zeolite synthesized with the addition of seed crystals had a high thermal stability.

The addition of NH_4NO_3 restrains the formation of quartz and enhances the crystallization of high-silica MOR zeolite. The MOR zeolites synthesized with NH_4NO_3 had square parallelepiped crystals with ≈ 12 μm in length. From the FT-IR and ^{29}Si CP MAS NMR spectra of these MOR zeolites, it was found that a fewer concentration of internal silanol groups exists in the MOR zeolite obtained with NH_4NO_3 than that obtained without NH_4NO_3, indicating that the addition of NH_4NO_3 is also efficient for reducing defect sites in a similar manner as NaF addition. The considerably increase in the micropore surface area, the external surface area and the micropore volume were observed for the MOR zeolite synthesized with NH_4NO_3 as compared with those without NH_4NO_3. Taking into account that the high-silica MOR zeolite synthesized with NH_4NO_3 has fewer defect sites, the increase in the micropore surface area and the micropore volume seem to be attributable to the high crystallinity. The MOR zeolite synthesized with NH_4NO_3 also showed high thermal stability. Finally, we tried to synthesize the high-silica MOR with the further Si/Al ratio by adding NH_4NO_3, NaF and seed crystals. When the alkali source NaOH was not subdivided into two solutions, the pure MOR zeolite could not be obtained. However, NaOH was subdivided into two parts to prepare two solutions, under well-optimized conditions, the highly crystalline and high purity MOR with a Si/Al ratio of ≈ 34 was successfully obtained. This is the highest value among the Si/Al ratios reported so far. The MOR zeolite seems to be composed of an aggregation of ≈ 1.2 μm long and ≈ 1.0 μm wide plate crystals.

As acetonitrile is a base molecule and is small enough to penetrate the side pockets of MOR zeolite, it reacts easily with acidic hydroxyl groups (Si(OH)Al) located inside. Therefore, it is possible to evaluate the localization of the two different hydroxyl groups present in the main channels and the side pockets of MOR zeolite, namely the Al distribution. The peak at 2300 cm^{-1} indicates the interaction of CD_3CN with the hydroxyl groups in the main channels, whereas the peak at 2314 cm^{-1} to the interaction of CD_3CN with the hydroxyl groups in the side pockets. It was found from CD_3CN and benzene adsorption experiments that the Al distributions in high-silica MOR zeolites are strongly dependent upon the Si/Al ratio. The proportion of Al atoms in the main channels relatively decreased with an increase in the Si/Al ratio of MOR zeolite. However, there is no difference in the Al distribution in the MOR zeolites synthesized with TEAOH when NaF was employed as mineralizer.

In this thesis, I have established various synthesis methods of high-silica MOR zeolite, and succeeded in synthesizing the high-silica MOR zeolite with the highest Si/Al ratio of ≈ 34. I have also found that the adsorption ability of high-silica MOR zeolite to benzene increased with an increase in the Si/Al ratio. Therefore, the high-silica MOR zeolite can be expected to act as the high effective adsorbent of harmful gas containing alkanes and aromatic organic compounds. In addition, the high-silica MOR zeolite can be also expected to play the catalysis at the high temperature such as hydrocracking, hydroisomerization, alkylation, reforming and dewaxing due to that high thermal stability clarified in this thesis.