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Preparation and Characterization of Single Crystals of MAPO-43 Molecular Sieve

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Abstract: Large single crystals of MAPO-43 molecular sieve have been synthesized hydrothermally using dimethylamine as the template. The typical molar composition of the starting mixture was $1.0P_2O_5 : 0.54Al_2O_3 : 0.8MgO : 8.5CH_3NHCH_3 : 0.68HF : 180H_2O$. The sample was characterized by XRD, TGA, DTA and IR.

Keywords: MAPO-43 single crystal, dimethylamine, hydrothermal synthesis.

The discovery of one, two and three-dimensional aluminophosphates [1,2,3] has stimulated the synthesis of phosphate compounds with various metals as counter ions or as heteroatoms. Because of their potential application as catalysts, adsorbents, sensors and electrodes[4-10], zeolitic aluminophosphates with heteroatoms have attracted much attention. In 1989, Pluth *et al.* reported the synthesis and structure of MAPO-43 molecular sieve[11], but there were defects in the crystals and the as-synthesized sample was not pure MAPO-43 phase. It contained MAPO-11 and MAPO-46 besides the MAPO-43 phase[12]. Here we describe the synthesis of pure MAPO-43 single crystals by varying the organic templates and the molar ratios of the mixed reactants.

Experimental

The MAPO-43 compound was synthesized hydrothermally by treating a gel with an empirical molar composition of $P_2O_5 : 0.54Al_2O_3 : 0.8MgO : 8.5CH_3NHCH_3 : 0.68HF : 180H_2O$. The reaction mixture was vigorously stirred for 4 hours until homogeneous, sealed in a Teflon-lined stainless steel autoclave and heated at 180°C for 2~3 days under autogenous pressure. The resulting single crystals were collected by filtration, washed with distilled water, and dried at ambient temperature.

Results and Discussion

The powder XRD pattern of the sample is shown in **Figure 1**. By comparison of this pattern with the standard one[11], we conclude that the as-synthesized material is

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well-crystallized MAPO-43 without impurities.

Figure 2 shows the IR spectrum of the as-synthesized MAPO-43. The absorption bands at 3433 and 1637 cm^{-1} can be assigned to the O–H vibrating modes, while the bands at 1070 and 500 cm^{-1} are attributed to the tetrahedron stretching modes in a zeolite. The other bands are due to the absorptions of dimethylamine.

Figure 1 The XRD pattern of MAPO-43

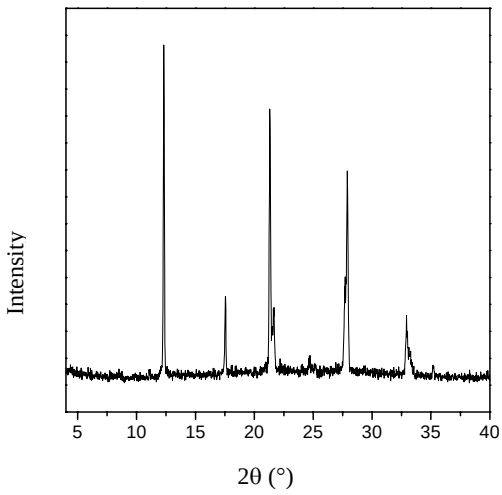
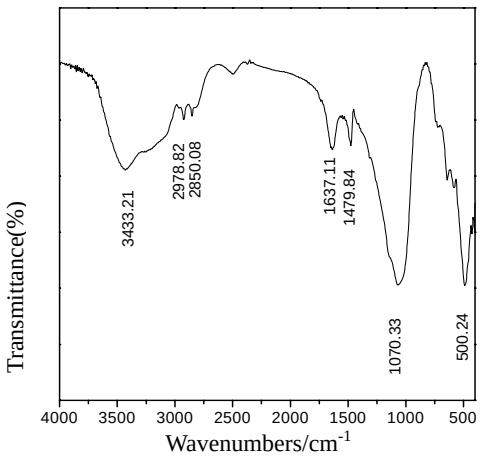
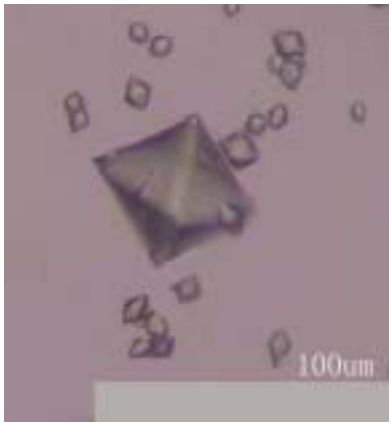


Figure 2 The IR spectra of MAPO-43



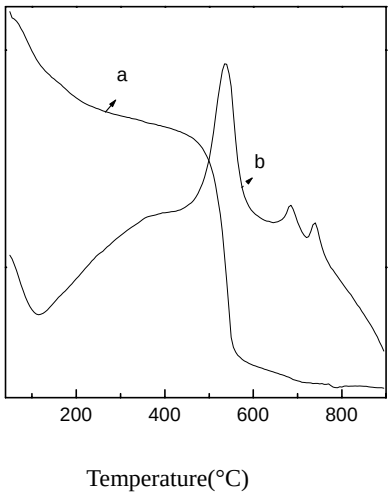
The optical microscope image of MAPO-43 crystals is shown in **Figure 3**. We can clearly see that the crystal shape is octahedral and the maximum crystal size reaches 60 um. During the preparation of the crystal, we changed the molar ratios of the mixed reactants, especially the content of dimethylamine, and we found that the molar ratio given in this paper was optimal.

Figure 3 The optical microscope image of MAPO-43 crystals



In order to investigate the thermal properties of MAPO-43, TG-DTA analyses were carried out from 30 to 900°C. The analysis results are displayed in **Figure 4**. The TG curve shows two major weight losses. The first loss can be attributed to the removal of the water in the zeolite, while the latter arises from the decomposition of the template. The DTA curve exhibits three exothermic effects at 470, 680 and 740°C. The peak at 470°C corresponds to the decomposition of the template, and the last two peaks may be due to phase transformations.

Figure 4 Curves of TGA (a) and DTA (b) for MAPO-43



The template is very important for the crystal growth of MAPO-43. It not only acts as structure-directing agent but also adjusts the pH value. The fluoride anions play an important role as well in synthesizing the crystals. The presence of fluoride ions improves the mineralization as well as the solubility of aluminum. Without fluoride ions,

no crystals of MAPO-43 have been obtained from our reaction systems.

Acknowledgments

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