On the role of OSDA and hetero-seed in the synthesis of zeolite: synergistic directing effect and mechanism insight

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Abstract: Aluminogermanosilicate IWR zeolite was prepared in the presence of both choline hydroxide and Beta zeolite, which acted as organic structure-directing agent (OSDA) and hetero-seed, respectively. A series of solid products obtained after crystallization of IWR zeolite for different periods were characterized by multiple techniques to disclose the growth procedure. The synergistic directing effect between OSDA and hetero-seed and mechanism thereof were presented for the first time. This new concept makes a contribution to the understanding of zeolite crystallization and sheds light on the discovery of novel zeolites.

Keywords: OSDA, Hetero-seed, Synergistic directing effect.

1. Introduction

Zeolites are widely used in in catalysis, ion exchange, gas adsorption and separation. These materials are prepared from mixtures of silica, alumina (or oxides of boron, germanium, etc.), a solvent (usually water), a structure-directing agent, a mineralizing agent and in some cases, zeolite seed[1]. Organic structure-directing agent (OSDA) plays a significant role in the preparation of high-silica zeolite. Zeolite seed was added into the synthesis gel in the very beginning to accelerate the zeolite crystallization process, reduce the crystal size and improve the purity of crystal product. In 2008, Xiao and his coworkers reported the first fast synthesis of Beta zeolite in the absence of any OSDA[2]. After that, a series of zeolites, including ZSM-12、ZSM-22、MCM-68、VPI-8 were prepared *via* the so-called OSDA-free seed-assisted approach, where the zeolite seeds directed the crystallization of zeolite crystals. Therefore, the zeolite seeds in the seed-directed synthesis routes are reasonably considered to be a third type of SDA. Zeolite seed possesses distinct framework structure from target zeolite is termed as hetero-seed, while that is of the same framework structure with target zeolite is called homo-seed. It has been proved that OSDA and homo-seed can work synergistically in directing the crystallization of zeolite[3, 4]. However, the relationship between OSDA and hetero-seed has been ignored all the time. In this contribution, we disclose a synergistic directing effect between choline hydroxide and Beta zeolite in the synthesis of IWR zeolite[5] for the first time. The crystallization process was studied to reveal the mechanism for this unprecedented route.

2. Experimental

The synthesis of IWR zeolite was achieved by heating the initial gel with a molar composition of 0.5 Choline : SiO_2 : 0.5 GeO_2 : 0~0.02 Al_2O_3 : 5 H_2O at 443 K for 7 days. Zeolite Beta was used as Al-source and seed. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO diffractometer. UV Raman spectra were collected on a Raman spectrograph from Horiba Jobin-Yvon.

3. Results and discussion

The influence of OSDA and seed on the products was studied. Several kinds of OSDAs such as TMAOH, TEAOH, choline hydroxide together with different zeolite seeds and/or Al-source including aluminum isopropoxide, zeolite Beta, ZSM-5, MCM-22, mordenite, USY were used in the synthesis. It turned out that IWR zeolite could only be obtained when both choline hydroxide and Beta zeolite were present in the initial gel. In another word, Beta zeolite as well as choline hydroxide played a directing role in the synthesis of IWR zeolite. We proposed that these two "directing agents" worked in a synergistic way. A series of solid products obtained after crystallization of IWR zeolite for different periods were characterized

by XRD and UV Raman techniques, as shown in Fig. 1 and Fig. 2. The diffraction peaks of zeolite Beta diminished as the increasing of the crystallization period and disappeared after 48 h. The diffraction peaks related to CDO zeolite emerged at 12 h and disappeared at 120 h, suggesting this material was an intermediated phase. The growth of IWR zeolite started at 12 h and completed after 168 h. The UV Raman spectrum of zeolite Beta shows bands at 468, 428, 398 and 345 cm^{-1}. The former two bands are assigned to the bending mode of the characteristic 4-membered rings (4MR), while the band at 398 and 345 cm^{-1} are ascribed to 5 MR and 6 MR, respectively. 4MR, 5MR and 6MR are also the building units in the framework of IWR zeolite and the corresponding bands in the UV Raman spectrum are at 460, 398 and 345 cm^{-1}, respectively. 4MR and 6MR are not the building units of CDO zeolite framework, and consequently there is only a broad band at 443 cm^{-1} assigned to 5MR in the spectrum of CDO zeolite. During the crystallization procedure, the band at 428 cm^{-1}, which can only be found in the spectrum of zeolite Beta disappeared after 48 h, indicating the thorough dissolution of zeolite seed, which was in consistence with the XRD results. The band at 468 cm^{-1} shifted to 460 cm^{-1} after a period of 12 h, suggesting the appearance of CDO and IWR zeolite. The intensity of the bands at 398 and 345 cm^{-1} displayed a tendency of declining at the beginning and then rising up, arising from the degradation of Beta followed by the growth of IWR zeolite. In a summary, both the XRD and UV Raman spectra results demonstrated the degradation of the zeolite seed, the evolution of the intermediate CDO zeolite phase and the growth of IWR zeolite.

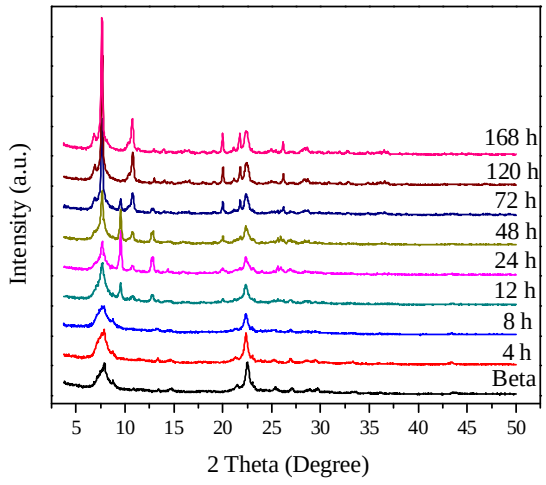

Fig. 1 XRD patterns for a series of solid products obtained after crystallization of IWR zeolite for different periods.

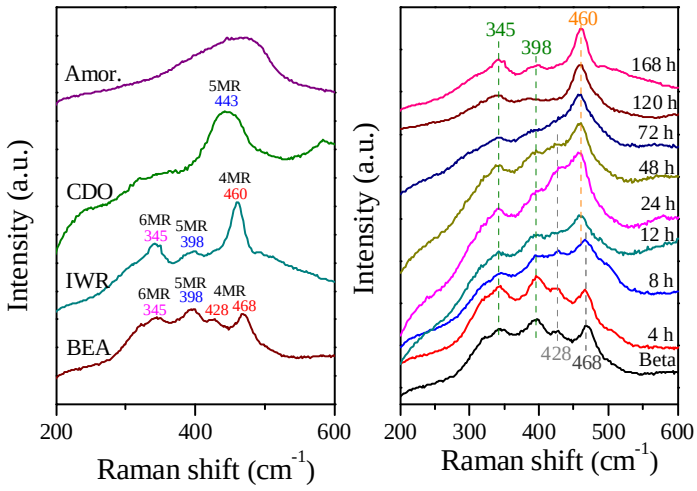

Fig. 2 UV Raman spectra of zeolite materials with different topologies (left) and a series of solid products obtained after crystallization of IWR zeolite for different periods (right).

4. Conclusions

IWR zeolite was prepared by utilizing the synergistic directing effect between choline hydroxide and Beta zeolite. By detecting the crystallization process, one can conclude that zeolite seed gradually degraded and IWR zeolite was transformed from an intermediate CDO zeolite phase. Since the framework structure of the product zeolite is different from that of seed zeolite, this new route provides an opportunity to synthesize novel zeolites.

References

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