Combinatorial synthesis of SAPO-34 *via* vapor-phase transport

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By applying a combinatorial method, SAPO-34 was successfully synthesized *via* vapor-phase transport technique, and the synthesis factors were systematically examined.

Combinatorial method is a very efficient way to systematically evaluate and produce both inorganic and organic materials, but its application to the synthesis of zeolites and their aluminophosphate counterparts is limited, however. Akporiaye and co-workers[1] first designed a multi-autoclave suitable for the combinatorial hydrothermal synthesis of microporous zeolites. Maier and co-workers[2] modified the multi-autoclave so that the microgram-scale hydrothermal synthesis of TS-1 could be conducted in an array format on a Si wafer, which allowed automated X-ray diffractometry. Later on, Bein and co-workers[3] developed a new methodology based on automatic dispensing reagents into autoclave blocks, followed by synthesis, isolation, and automatic structure analysis without any manipulation of individual samples. They applied this new method to the synthesis of aluminophosphate molecular sieves. Following the combinatorial strategy, Xu and co-workers[4] hydrothermally synthesized new zinc phosphates with interesting framework architectures. On the other hand, Gavalas and his co-workers[5] parallel synthesized zeolite ZSM-5 films with different compositions using a 21-well reactor. All the above reports dealt with the hydrothermal synthesis of zeolites and aluminophosphate molecular sieves, but these can also be synthesized by the so-called vapor-phase transport (VPT) method. Various molecular sieves, such as ZSM-5,[6] ZSM-35,[7] ZSM-11,[8] mordenite,[8] ZnAPO-34,[9] AlPO4-5, AlPO4-11, SAPO-5 and SAPO-11[10,11] had been synthesized by this technique. The novel combinatorial method has not been used for the synthesis of zeolitic materials by the VPT technique, however.

In this paper, we present the first application of the combinatorial method to the synthesis of SAPO-34, a silicon-substituted aluminophosphate molecular sieve, by the VPT method. A multiwell reactor suitable for the combinatorial VPT synthesis was designed, as shown in Fig. 1. The reactor is composed of two Teflon blocks with a diameter of 38 mm, containing 12 holes (4 mm diameter) or 9 holes (6 mm diameter) to contain the dry gels with different compositions. The depth of the holes in the bottom block (6 mm thickness) is 3 mm, while the holes in the upper block (1.5 mm thickness) are open at both ends. The diameters and the patterns of the holes on both blocks are exactly the same so that the two blocks can match each other very well to form the reactor. Some other small holes were drilled through the blocks to facilitate passing of the vapor from the bottom. For use, the two blocks were put together with the

Fig. 1 Schematic of the Teflon multiwell reactor.

holes matched exactly and the holes were filled with dry gels. The reactor was installed into a Teflon liner of a conventional autoclave above the liquid phase, which was previously charged into the bottom of the liner. Under such circumstance, the dry gels with different compositions could be crystallized in an identical vapor atmosphere. After reaction, the reactor was taken out. It was observed that the flat dry gel surfaces became concave after the VPT reaction, which rendered them unsuitable for the following characterization. In order to make a flat surface, the upper block was carefully removed and the products converted from the dry gels were exposed from the holes of the bottom block. A glass slide was used to carefully press the exposed products into the holes so that a flat surface could be formed. In this case, the bottom block with products in the holes was ready for X-ray diffraction (XRD) and scanning electron microscopy (SEM) characterization. The XRD analysis was conducted following the procedure used by Gavalas *et al*.[5] A conventional powder XRD diffractometer (Bruker D8 Advance) was used, and all holes but one were covered at a time with a lead foil.

The dry gels were prepared by mixing appropriate molar ratios of aluminium isopropoxide, phosphoric acid and silica gel with deionized water, respectively. The gels were heated to 353–373 K under stirring to form dry gels.

In this study, the effect of P_2O_5/Al_2O_3 and SiO_2/Al_2O_3 on the VPT synthesis of SAPO-34 was examined at a fixed water molar ratio to alumina of 150. Various volatile organic amines, including triethylamine (TEA), diisopropylamine (DiPA), di-propylamine (DPA), isopropylamine (iPA), morphiline (MOR), n-buylamine (n-BA), ethylamine (EA), and cyclohexylamine (CHA) were used as liquid phase, respectively. Some of the results are listed in Fig. 2. In Fig. 2, each of the figures is the result of two combinatorial VPT syntheses with the synthesis having 12 samples in the multiwell reactor. The experiments were mostly conducted at 443 K, but some were also carried out at 473 K.

Fig. 2a shows the results of two combinatorial VPT syntheses using TEA at 443 K for 36 h. All the samples were examined by XRD. We can see that no crystals were produced when P_2O_5/Al_2O_3 was 0.31. SAPO-34 was synthesized with SiO_2/Al_2O_3 of 0.5, 1.0 and 1.2 when P_2O_5/Al_2O_3 was 0.63. When P_2O_5/Al_2O_3 was 0.94, SAPO-34 was made with SiO_2/Al_2O_3 of 0.5 and 0.75. As P_2O_5/Al_2O_3 was increased to 1.25, the synthesis range of SiO_2/Al_2O_3 increased from 0.25 to 1.5 with a 0.25 increment. In other two combinatorial syntheses, the synthesis time was prolonged to 48 h. The results (Fig. 2b) show that the SAPO-34 synthesis range was broader with longer synthesis time, indicating that longer synthesis time favored the production of SAPO-34 at the above synthesis condition. In addition, the same combinatorial VPT synthesis was also conducted at 473 K for 36 h. The results (Fig. 2c) show that SAPO-34 was produced in much narrower range, a mixture of SAPO-34 and SAPO-5 was detected when P_2O_5/Al_2O_3 was 0.94 and SiO_2/Al_2O_3 was 0.25, 1, 1.25 and 1.5, when P_2O_5/Al_2O_3 was increased to 1.25, SAPO-5 could be synthesized. Therefore, higher synthesis temperature tended to form SAPO-5.

Other sets of combinatorial syntheses were conducted with DiPA as liquid phase at 443 k for 48 h (Fig. 2d). It can be seen
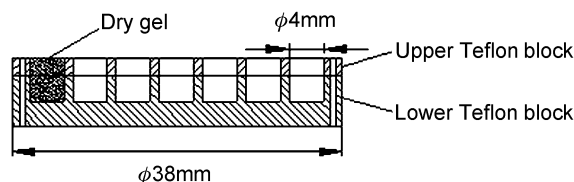
that SAPO-34 was, in most cases, synthesized when P_2O_5/Al_2O_3 was 0.63 and 0.94. Higher P_2O_5/Al_2O_3 ratios produced a mix of SAPO-5 and SAPO-34 or impure SAPO-11. When DPA was used as liquid phase, a very narrow composition range was detected for the synthesis of SAPO-34 with the synthesis conducted at 473 K for 24 h (Fig. 2e). However, when MOR was used as liquid phase, SAPO-34 was synthesized at 473 K for 24 h with a very wide composition range of P_2O_5/Al_2O_3 from 0.63 to 1.25 and SiO_2/Al_2O_3 from 0.25 to 1.5. When the iPA was used, impure SAPO-34 was produced. Other volatile organic amines, such as CHA, n-BA and EA produced crystals showing XRD patterns for which we could not find a match in the XRD database provided by Bruker. From Fig. 2, it was very clear that only amorphous products were produced in all SiO_2/Al_2O_3 ranges when P_2O_5/Al_2O_3 was 0.31, no matter what volatile organic amines were applied.

Some of SAPO-34 powders were taken out from the multiwells and were characterized by thermal analysis (Thermogravimetry (TG) and Differential Scanning Calorimeter (DSC), NETZSCH, STA409) and Fourier Transform Infrared Spectra (FTIR, Thermo Nicolet Corporation, NEXUS). TG results clearly showed a weight loss above 673 K, indicating the residue of the amines in the micropores of SAPO-34 (Fig. 3) and at the same time, DSC also proved that the amines were thermally decomposed and driven off above 673 K. FTIR spectra also showed the characteristic peaks of SAPO-34[12] at 635, 530, 480 cm^{-1} (Fig. 4). The above characterization elucidated that SAPO-34 could be synthesized by the VPT method with several volatile organic amines.

We designed a multiwell reactor, which is suitable for the combinatorial VPT synthesis of zeolites and zeolite-like
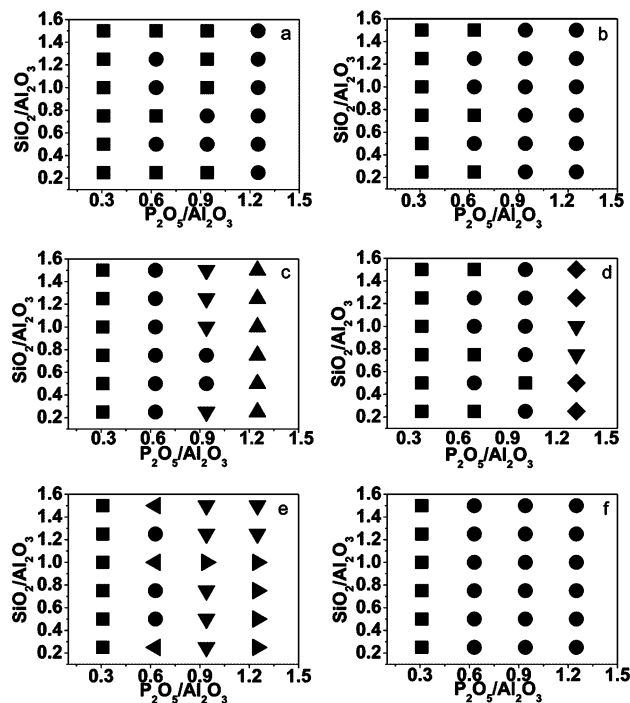

Fig. 3 TG and DSC curves of SAPO-34 with $P_2O_5/Al_2O_3 = 0.63$ and $SiO_2/Al_2O_3 = 1$ (dotted line) and 0.5 (solid line) at 443 K for 48 h with TEA.

Fig. 4 IR Spectra of samples of SAPO-34 with $P_2O_5/Al_2O_3 = 0.63$ and $SiO_2/Al_2O_3 = 1$ (a) and 0.5 (b) at 443 K for 48 h with TEA.

materials. With this new methodology, the synthesis factors for SAPO-34 molecular sieve by VPT technique could be quickly and effectively examined. Like hydrothermal synthesis of SAPO-34, which can also be synthesized with various amines and in a broad composition range by VPT. Combinatorial VPT synthesis provides a rapid and efficient way for the synthesis and evaluation of zeolites and zeolite-like materials.

Fig. 2 Combinatorial VPT synthesis results at 443 K for 36 h (a) and 48 h (b), at 473 K for 36 h with TEA (c); at 443 K for 48 h with DiPA (d); at 473 K for 24 h with DPA (e) and MOR (f). SAPO-34 (●); amorphous (■); mix of SAPO-5 and SAPO-34 (▼); SAPO-5 (▲); impure SAPO-11 (◆); impure SAPO-5 (▶); unidentified (◀),
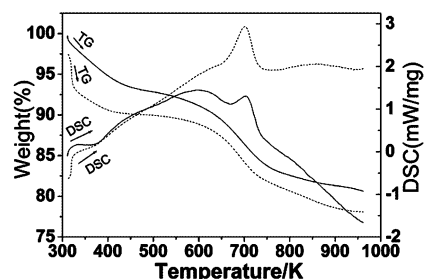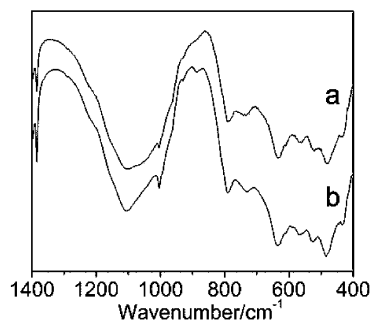
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