Hydrothermal synthesis of pure ZSM-22 under mild conditions

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Successful hydrothermal synthesis of pure ZSM-22 devoid of impurities is achieved under mild conditions of 433 K and horizontal stirring at 20 revolutions per minute (rpm) using Teflon-coated bar magnets to enhance gel mixing.

Zeolites are microporous crystalline materials that play important roles in catalysis, ion exchange, and adsorption sciences, and the molecular-sieving properties of zeolites are exploited in many applications.[1] ZSM-22 is a high-silica zeolite that is isostructural with theta-1, having a TON structural type.[2–4] The unique features of ZSM-22, unidimensional channels with medium-sized pores of *ca.* 0.45 × 0.55 nm constituting 10-membered rings, provide special shape-selective properties that have specific importance in skeletal isomerization of normal alkanes through the use of Pt-supported ZSM-22.[5–10] To achieve high catalytic activity for such reactions, small particle size is one of the key parameters of zeolite-based molecular sieves.[8]

The synthesis of pure zeolite materials is important for certain reactions and applications, and the synthesis of pure ZSM-22 has remained a challenge. Even the patent (US Pat. 4 902 406) filed for the synthesis of this zeolite reports the inclusion of impurities.[2,3,11–17] The synthesis of zeolites is usually carried out under hydrothermal conditions. For ZSM-22, high-speed mixing of the synthesis gel during the hydrothermal synthesis process is required in order to prevent cocrystallization of commonly incurred impurities of ZSM-5 and cristobalite.[11,18] Stirring at speeds of up to 400 rpm have been recommended,[11,18] as static synthesis or slow stirring produces ZSM-5 zeolite or a mixture of ZSM-5 and ZSM-22. Hydrothermal synthesis at 400 rpm requires a vertically stirred autoclave, which introduces the problem of inhomogeneous product distribution, inevitably concentrating some amount of the sample on the walls of the container. This inhomogeneous product distribution also leads to the formation of impurities.

In the present study, the synthesis of pure zeolite under milder conditions is investigated by evaluating the use of an autoclave in which the synthesis vessels are rotated horizontally. In such a horizontal system, the product remains homogenous, and a rotation speed of just 20 rpm is generally sufficient, to avoid poor mixing due to centrifugal force. The incubation conditions of the synthesis gel of ZSM-22, which control the crystallization of the zeolite,[19] are fine-tuned, and the use of Teflon-lined bar magnets is examined as a means to enhance mixing.

Following the procedure of Kuhl,[18] a typical hydrothermal synthesis of pure ZSM-22 was performed using starting materials of SiO_2 and Al_2O_3 at a ratio of 90 : 1. In a Teflon beaker, 1.0 g of KOH (Kanto Chemicals) was dissolved in 4.55 g of deionized water, to which an aqueous solution of 0.44 g $Al_2(SO_4)_3 \cdot 16H_2O$ (Wako) prepared in 4.55 g of deionized water was added, resulting in a clear solution upon thorough mixing. Among the various structure-directing agents (SDAs) that have been used for the synthesis of TON-type zeolites,[3] 1,8-diaminooctane (Wako) was used as the SDA in the present study. Separately, 2.6 g of 1,8-diaminooctane was dissolved in 18.2 g of deionized water and added into the Teflon beaker under constant stirring using a motor-driven stirrer. The mixture was then stirred for a further 30 min to obtain a clear solution. Colloidal silica (30 wt% SiO_2; Sigma-Aldrich) was used as a silica source. 11.9 g of the colloidal silica mixed with 6.74 g of deionized water was also added under stirring. The final reaction mixture was stirred for 90 min to yield the synthesis gel.

A range of hydrothermal synthesis conditions were examined in order to identify the conditions most suitable for the preparation of pure ZSM-22 in the present configuration. As stirring at 20 rpm is alone insufficient to ensure adequate mixing of thicker gels, Teflon-coated bar magnets were tested as a means of enhancing the mixing action. After incubation of the synthesis gel at 298 K for 24 h, hydrothermal synthesis was carried out under three different conditions: at 400 rpm using the conventional vertical apparatus (100 mL capacity), and at 20 rpm using the horizontal system (50 mL) capacity with and without the Teflon-coated bar magnets as gel mixing enhancers. All the vessels were Teflon-lined, and the 50 mL vessels were sealed in steel bombs. The temperature was raised to 433 K in all experiments at a ramp of 0.5 K min^{-1}, and the maximum temperature was maintained for 72 h. On ceasing the reaction, the product was quenched in cold water, diluted with deionized water, and allowed to settle. The solid phase was then separated by filtration, washed with deionized water, and dried for 12 h in an oven at 353 K.

X-Ray diffraction (XRD) patterns were recorded on a Rigaku Multiflex diffractometer using Cu Kα radiation. The positions of the most significant X-ray diffraction lines for the ZSM-22 synthesized in this study are in accordance with previous reports,[11,18] confirming that the product consists of ZSM-22.

Fig. 1 shows XRD patterns for the product obtained by stirring at 400 rpm in the vertical apparatus. The patterns indicate the presence of cristobalite and ZSM-5 as impurities, similar to the findings of other researchers.[2,3,11–18] During the synthesis of ZSM-22 in the vertically stirred autoclave, some of the product was observed to become stuck to the walls of the Teflon liner. Both the

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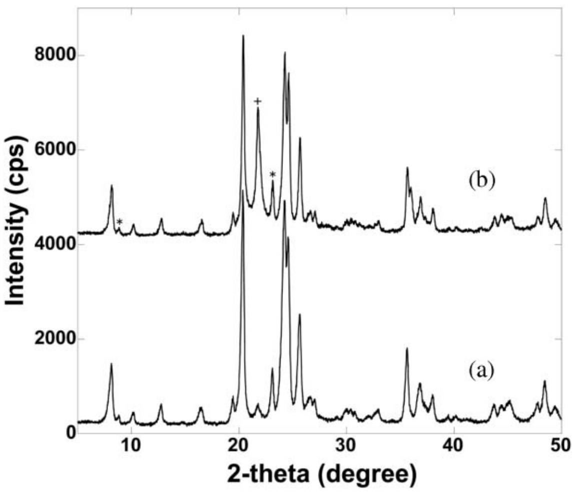

Fig. 1 XRD patterns of ZSM-22 synthesized at 400 rpm: (a) main product, (b) material stuck to the walls of the Teflon liner. * (ZSM-5) and + (cristobalite) denote impurities.

main product and the sample stuck to the walls exhibited XRD lines assignable to ZSM-22 and impurities, although the material stuck to the walls appears to contain a higher concentration of impurities, especially cristobalite (Fig. 1). This result suggests that impurities in the main product may be derived from the material stuck to the walls of the Teflon liner.

Fig. 2 shows the XRD results for the two ZSM-22 samples synthesized at 20 rpm in the horizontal apparatus. The XRD pattern of the product synthesized without the Teflon-coated bar magnets is poorly crystallized ZSM-22, while the product synthesized using the Teflon-coated bar magnets appears to have been fully crystallized, yielding a phase-pure ZSM-22 without the peaks attributable to cristobalite or ZSM-5. The unit cell parameters obtained for the phase-pure ZSM-22 were $a = 13.86$ Å, $b = 17.41$ Å, and $c = 5.04$ Å. The XRD peak intensities of ZSM-22 synthesized without mixing enhancers is *ca.* 15% of that of the phase-pure ZSM-22. During the preparation of the synthesis gel, it was observed that the final gel became hazier over time, accompanied by an increase in the viscosity. Therefore, the viscosity of the gel is likely to have increased over the 24 h incubation period. It is thus apparent that homogeneous mixing of the synthesis gel during the hydrothermal synthesis is important in order to ensure the yield of a phase-pure ZSM-22. The present preparation method of enhanced gel mixing in a horizontally rotating autoclave at low rotation speed therefore achieves the synthesis of phase-pure ZSM-22 without the severe conditions of hydrothermal synthesis at 400 rpm and the poor mixing and impurity formation in the vertically stirred autoclave.

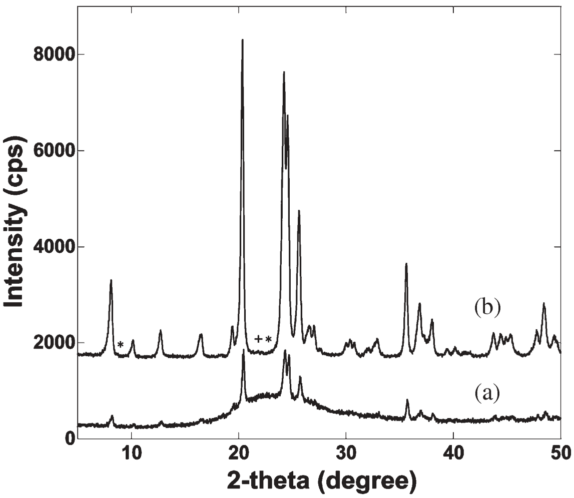

Fig. 2 XRD patterns of ZSM-22 synthesized at 20 rpm (a) without and (b) with enhanced mixing by Teflon-coated bar magnets. * (ZSM-5) and + (cristobalite) indicate the positions for the impurities.

Although the present preparation procedure starts with the same conditions as employed in previous synthesis,[18] the present product is free of the impurity peaks at 21.5° and 23.5° in the XRD pattern observed in the preceding study. Comparison of all the XRD lines in the 2θ range of 8–30° with another previously reported data (Table 1)[11] indicates that the reference data for 100% ZSM-22 includes cristobalite and ZSM-5 as impurities, whereas the present ZSM-22 product synthesized at 20 rpm with enhanced gel mixing is 100% phase-pure according to the XRD pattern. Many studies have reported on the synthesis of ZSM-22 using a range of SDAs and hydrothermal synthesis conditions, usually involving vigorous stirring.[2,3,11–18] However, even under such severe conditions, pure ZSM-22 was not obtained, but with numerous XRD lines attributable to impurities.[2,3,11–18] Certain other syntheses performed at higher temperature and without incubation have achieved comparatively pure ZSM-22.[20,21]

Table 1 Comparison of crystallographic data for ZSM-22

2θ/°		Intensity ratio (I/I_o)	
US patent[11]	This study	US patent[11]	This study
8.17	8.22	32	28
8.90	—	1[a]	—
10.17	10.24	8	9
12.76	12.80	11	13
16.35	16.40	4	4
16.58	16.60	8	9
18.40	—	1[b]	—
19.45	19.52	11	10
19.80	19.90	3	3
20.40	20.44	100	100
21.85	—	1[b]	—
22.18	22.19	1	1
23.10	—	3[a]	—
23.30	—	3[a]	—
24.27	24.34	77	78
24.65	24.66	70	72
25.72	25.72	43	43
26.38	26.46	4	4
26.64	26.70	5	5
27.06	27.16	8	8
27.68	27.74	1	1

[a] ZSM-5. [b] Cristobalite.

The crystallinity and morphology of the present product was examined by scanning and transmission electron microscopy (SEM and TEM). Fig. 3 shows a SEM image recorded using a Keyence model VE 9800 instrument. The sample can be seen to consist of needle-shaped crystals, typical of ZSM-22. These ZSM-22 particles are shorter (*ca.* 1 μm) than those reported for previous syntheses under more severe conditions (2–5 μm).[3,13,15] Yunfeng *et al.*, who has also reported the synthesis of pure

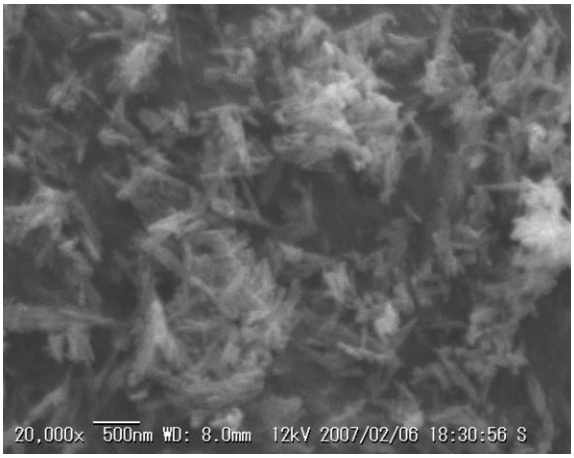

Fig. 3 SEM image of ZSM-22.

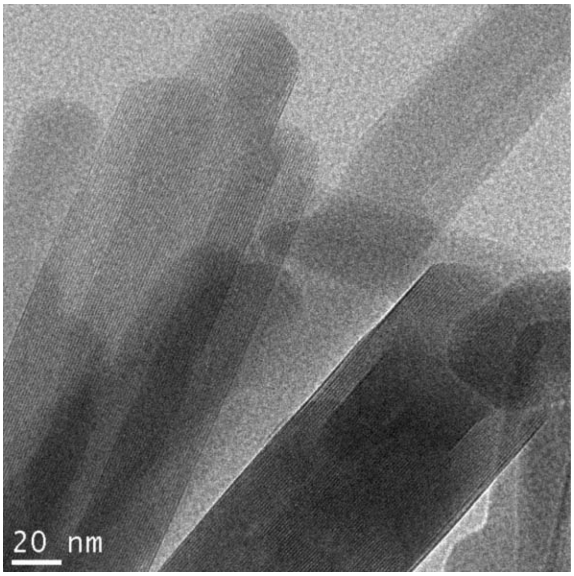

Fig. 4 TEM image of ZSM-22.

ZSM-22, obtained a material with a particle size of up to 5 μm, which is too large for use as an effective catalyst.[20] A TEM image taken using a Field Emission Industry Tecnai F 30 instrument operated at 300 kV (Fig. 4) confirms the needle-shaped morphology and uniform crystallinity of the ZSM-22.

The chemical composition of the present pure ZSM-22 was determined by electron probe microanalysis (EPMA) using a Shimadzu EPMA-1610 instrument operated at 15 kV. A final product with a composition characterized by a SiO_2/Al_2O_3 ratio of 80 was obtained from a starting gel with a corresponding ratio of 90.

In summary, the synthesis of pure ZSM-22 was successfully achieved under mild hydrothermal conditions through the use of an autoclave in which the gel is rotated horizontally at low rotation speed (20 rpm). To obtain pure ZSM-22 under these conditions, mixing must be enhanced by the use of Teflon-coated magnetic stirrers. The obtained product is purer and finer than achievable by previous methods and the original patented method, which involve high rotation speeds. This is a simple but important approach to the improvement of the synthesis of pure ZSM-22 that can be applied to the syntheses of other materials to gain high purity of the product under mild conditions.

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