

Transformation of ZSM-5 Zeolite to ZSM-11 Zeolite under High Pressure

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The irreversible direct transformation of ZSM-5 zeolite to ZSM-11 zeolite under high pressure is observed and characterized by means of X-ray powder diffraction, thermogravimetric analysis and differential thermal analysis.

Zeolites are complex aluminosilicates with three-dimensional framework structures enclosing cavities occupied by ions and water molecules. From the thermodynamic point of view, zeolites are members of unstable phases. With changes of pressure or temperature, a particular zeolite may be transformed into another zeolite or an inorganic salt. The effect of temperature on the stability of zeolites has been widely studied, but there has been little work on the effect of pressure.

In this communication, we report for the first time the effect of pressure on the stability of a zeolite. For simplicity we chose to study the all-silicon ZSM-5 zeolite, which has the simple formula $\text{Si}_{96}\text{O}_{192}\cdot 16\text{H}_2\text{O}$. We have found that ZSM-5 is directly transformed into ZSM-11 zeolite and that this transformation is irreversible.

The ZSM-5 zeolite was synthesized under hydrothermal methods using tetrapropylammonium bromide as templating agent. Before the high-pressure experiments, ZSM-5 was heated to 200 °C to remove the adsorbed water and water of crystallization. The anhydrous ZSM-5 was then subjected to a pressure of 4.0 GPa for 15 min and the pressure was then released.

X-Ray powder diffraction (XRD) studies were performed using a Rigaku 12 kW copper rotating-anode X-ray diffractometer with a graphite monochromator. Silica was used as an internal standard, and cell parameters were refined by least squares. Thermogravimetric-differential thermal analysis (TG-DTA) curves were obtained using a Rigaku CN 8097E thermal analyser at a heating rate of 10 °C min⁻¹ in air.

The X-ray powder diffraction pattern of ZSM-5 zeolite is shown in Fig. 1. Comparison with the XRD data of Jablonski *et al.*² and Barlocher³ shows that the sample used in this paper is pure ZSM-5 zeolite without ZSM-11 intergrowths. The X-ray powder diffraction pattern of ZSM-5 following high-pressure treatment at room temperature is shown in Fig. 2.

The relative heights of the (10,0,0) and (0,10,0) peaks in the 2θ range of 44–46° are suggested by Jablonski *et al.*² as being characteristic of the extent of intergrowth of ZSM-11 in ZSM-5.² For the pure ZSM-11 sample, the (10,0,0) peak has a relative intensity of 21% and there is no (0,10,0) peak, whereas for the pure ZSM-5 sample, the (10,0,0) peak has a relative intensity similar to that of the pure ZSM-11 but the (0,10,0) peak has nearly the same intensity as the (10,0,0) peak. For ZSM-5 zeolite, any reductions in the relative height of the (0,10,0) peak can be regarded as evidence of ZSM-11 intergrowths and can be used to estimate the extent of the intergrowth. In our work, the (0,10,0) peak of ZSM-5 disappears completely after high-pressure treatment. Therefore, treatment of ZSM-5 zeolite under high pressure causes its complete transformation into ZSM-11 zeolite, in a process which is irreversible.

Further convincing evidence for the transformation of ZSM-5 to ZSM-11 zeolite under high pressure is provided by the TG-DTA results of the two samples. TG-DTA curves of

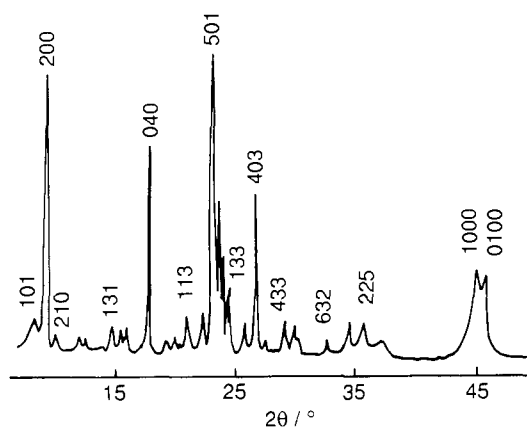


Fig. 1 X-Ray powder diffraction pattern of ZSM-5

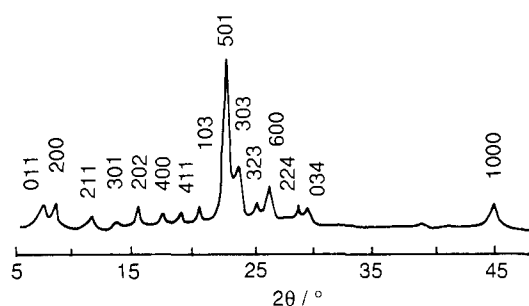


Fig. 2 X-Ray powder diffraction pattern of ZSM-11

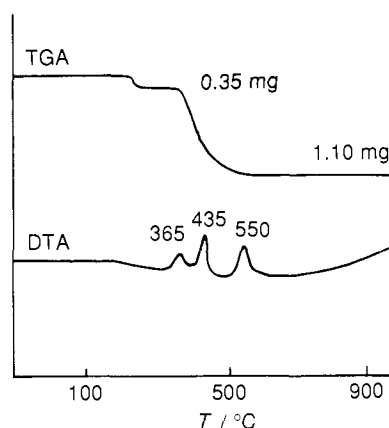


Fig. 3 TG-DTA curves for ZSM-5

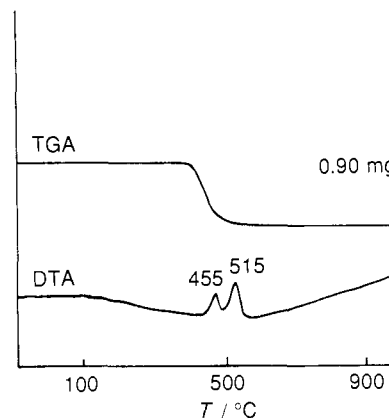


Fig. 4 TG-DTA curves for ZSM-11

ZSM-5 zeolite and ZSM-5 zeolite following high-pressure treatment are given in Figs. 3 and 4. The presence of different exothermic peaks for the two samples confirms that the two species have different channel structures. The initial ZSM-5 sample shows three exothermic peaks: at 365, 435 and 550 °C, and weight changes occur at 365 and 435 °C.

The foregoing results can be explained by escape of the organic templating agents in different ways. Because there are two sets of channels in ZSM-5 zeolite:⁴ one straight and the other S-shaped, the temperature at which the templating agents escape from the different cavities will be different. We think that the templating agents escape from the straight channels at 365 °C and from the S channels at 435 °C. At 550 °C, the organic components escaping from cavities are burned. For the pressure-treated sample, there are two exothermic peaks at 455 and 515 °C and changes in weight occur at 455 °C. Under high pressure ZSM-5 is transformed into ZSM-11 zeolite which has only one type of channels: the straight channels. Thus, with increase in temperature, the organic templating agents escape from the cavities only at 455 °C and burn at 515 °C.

Further high-pressure experiments indicate that ZSM-11 zeolite is stable up to a pressure of 8.0 GPa.

In conclusion, we have confirmed that the direct transformation of ZSM-5 to ZSM-11 zeolite by skeletal rearrangement occurs under high pressure, showing that pressure can markedly change the structure of zeolites at room temperature.

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References

- 1 D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974, p. 4.
 - 2 G. A. Jablonski, L. B. Sand and J. A. Gard, *Zeolites*, 1986, **6**, 396.
 - 3 C. Barlocher, *Collection of Simulated XRD Powder Patterns for Zeolites*, ed. R. von Ballmoos, Butterworth Scientific Ltd, 1984, p. 74.
 - 4 G. T. Kokotailo, P. Chu and S. L. Lawton, *Nature*, 1978, **275**, 14.
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