

## Synthesis of Cancrinite in a Butane-1,3-diol Systems

Chunhui Liu, Shougui Li, Kungang Tu and Ruren Xu\*

*Laboratory of Inorganic Hydrothermal Synthesis, Department of Chemistry, Jilin University, Changchun, P.R. China*

Cancrinite, a low-silica zeolite synthesized in a non-aqueous butane-1,3-diol system, can adsorb water, hexane or cyclohexane, unlike the cancrinite synthesized in aqueous media.

---

The synthesis of zeolites in organic non-aqueous systems is important for the formation of novel structures or compositions, or special characteristics. Since Bibby and Dale<sup>1</sup> prepared silica-sodalite in ethylene glycol or propanol solvents, several high-silica zeolites or aluminophosphates with known or novel structures<sup>2-5</sup> have been synthesized in organic non-aqueous media. Here, we report the synthesis of cancri-

nite, a low-silica zeolite, in a butane-1,3-diol non-aqueous systems.

A typical synthesis was as follows: appropriate amounts of NaOH were added to calculated amounts of butane-1,3-diol. The mixture was stirred until homogeneous, and then calculated amounts of fused silica and aluminium isopropylate were added to the mixture with stirring for 1 h. Crystallization

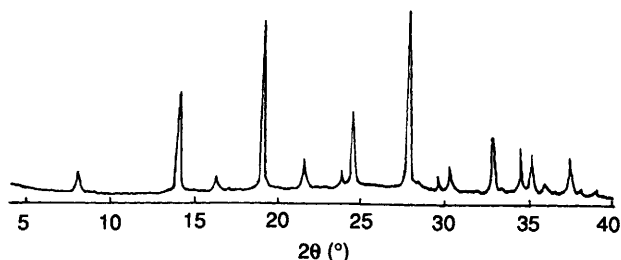


Fig. 1 XRD pattern of cancrinite synthesized in the 5.12 Na<sub>2</sub>O : 3.72 SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : 62.2 butane-1,3-diol system

Table 1 Synthesis conditions and crystallization products<sup>a</sup>

No.	Gel composition (mol ratio)		Product <sup>b</sup>	Crystallinity (%)
	Na <sub>2</sub> O	SiO <sub>2</sub>		
1	2.79	4.95	CAN + ANA	—
2	3.25	4.95	CAN	68
3	5.12	4.95	CAN	83
4	6.53	4.95	CAN	100
5	7.93	4.95	CAN	69
6	9.30	4.95	SOD	—
7	5.12	1.67	CAN	95
8	5.12	2.20	CAN	97
9	5.12	3.72	CAN	100
10	5.12	5.00	CAN	59
11	5.12	6.20	CAN	37
12	5.12	8.68	CAN	28
13	5.12	11.16	CAN + ANA	—

<sup>a</sup> For all gels in Table 1 mol ratios for Al<sub>2</sub>O<sub>3</sub> and butane-1,3-diol are 1 : 62.2; *T* = 180 °C and *t* = 25 d. <sup>b</sup> CAN; cancrinite; ANA; analcite; SOD; sodalite.

of the reaction mixture was carried out in a stainless steel autoclave at 180 °C for 25 days. The crystallization products were filtered, washed with acetone and water, and dried at ambient temperature. The X-ray powder diffraction (XRD) pattern of the cancrinite product is given in Fig. 1; the peak positions are similar to the XRD pattern of the cancrinite prepared in aqueous media, but different in intensities. The XRD pattern of the cancrinite product was indexed based on hexagonal symmetry with the TREOR program, and unit cell parameters of *a* = 12.767 and *c* = 5.178 Å were obtained.

The synthesis conditions and crystallization products are summarized in Table 1. Narrow ranges of SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> ratios are necessary to obtain the pure phase of cancrinite and the crystallinity is strongly dependent on alkaline content. On fixing the ratio of SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> at 4.95 and increasing the ratio of Na<sub>2</sub>O : Al<sub>2</sub>O<sub>3</sub> from 3.25 to 6.53, the crystallinity of cancrinite increases from 68 to 100%. But, excess alkaline content results in a decrease of crystallinity of cancrinite and/or formation of impurity; thus, the optimal alkaline content is important for synthesis of cancrinite. The ratio of SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> also affects the crystallization. High SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> ratios, more than 8.68, lead to formation of analcite, and low SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> ratios, less than 1.67, lead to decrease of crystallinity of the cancrinite. The crystallization kinetics studies on the cancrinite at 180 and 200 °C showed that an increase of crystallization temperature results in a decrease of induction period and an increase in the crystallization rate.

The cancrinite sample No. 9 was calcined at 500 °C for 1 h to remove the organic molecules. Brunauer–Emmett–Teller adsorption experiments on this calcined sample showed that it has type I adsorption isotherms<sup>6</sup> (Fig. 2) and indicated that the adsorption amounts of water, hexane and cyclohexane are 13.7, 9.5 and 9.2 % m/m respectively. This is quite different from the natural mineral, or that synthesized in aqueous media, which do not have adsorption characteristics since

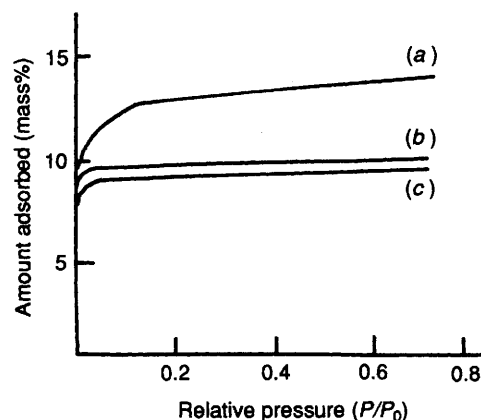


Fig. 2 Adsorption isotherm curves of cancrinite sample No. 9: (a) water; (b) hexane; (c) cyclohexane

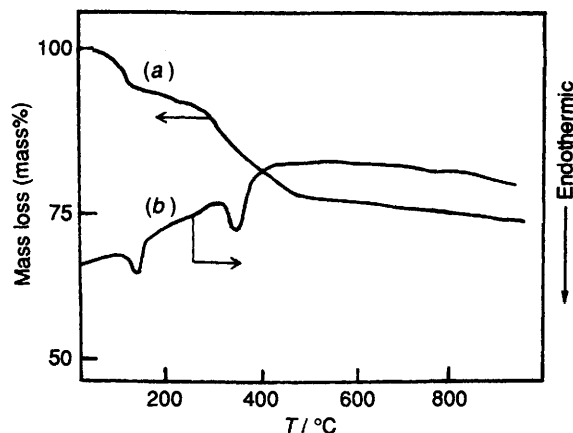


Fig. 3 Thermal gravimetry (a) and DTA (b) for cancrinite sample No. 9

their channels are blocked by intercalated salt or stacking faults.<sup>7</sup>

The cancrinite sample No. 9 has also been subjected to thermal analysis on a Perkin-Elmer differential thermal analysis (DTA) instrument in a flow of N<sub>2</sub> at a rate of 10 °C min<sup>-1</sup> (Fig. 3). Thermogravimetric analysis of sample No. 9 indicated that % m/m losses of 7.5 % m/m from 30 to 220 °C and 15.0 % m/m from 220 to 560 °C were observed, respectively. The mass loss below 220 °C corresponds to the amount of water adsorbed on the surface of the sample and the mass loss from 220 to 560 °C to the amount of organic molecules adsorbed by the cancrinite. The existence of the organic molecules in the cancrinite is also confirmed by the IR spectra, in which there are strong C–H absorptions (asymmetric and symmetric deformation vibrations) at 1465 and 1380 cm<sup>-1</sup>. The DTA showed that the structure of the cancrinite is stable up to 900 °C.

We thank the National Natural Science Foundation of China for financial support.

Received, 3rd June 1993; Com. 3/03159D

## References

- D. M. Bibby and M. P. Dale, *Nature (London)*, 1985, **317**, 157.
- Q. Huo, S. Feng and R. Xu, *J. Chem. Soc., Chem. Commun.*, 1988, 1486.
- W. Xu, J. Li and G. Liu, *Zeolites*, 1990, **10**, 753.
- Q. Huo and R. Xu, *J. Chem. Soc., Chem. Commun.*, 1990, 783.
- Q. Huo, R. Xu, S. Li, Z. Ma, J. M. Thomas, R. H. Jones and A. M. Chippindale, *J. Chem. Soc., Chem. Commun.*, 1992, 875.
- D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, Wiley, London, 1973.
- R. M. Barrer, J. F. Cole and H. Villiger, *J. Chem. Soc. (A)*, 1970, **9**, 1523.