

SYNTHESIS AND CHARACTERIZATION OF NOVEL INORGANIC MICROPOROUS BERYLLOPHOSPHATES*

Long YU^a and Wenqin PANG^b

^a Department of Chemistry, Liaoning University, Shenyang, 110036, China

^b Department of Chemistry, Jilin University, Changchun, 130021, China

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Five new types of microporous beryllorphosphates were hydrothermally synthesized using $\text{BeO}-\text{P}_2\text{O}_5-\text{R}-\text{MCl}$ (or MCl_2)- H_2O , R being cyclohexylamine (CHA), pyrrolidine, 1-butylamine or triethylamine, M alkali or alkali earth cation. X-Ray diffraction patterns (XRD), infrared (IR), TG-DT and elemental analyses show that the crystalline beryllorphosphates have novel, unique framework structures, composed from basic units of tetrahedral PO_4 and BeO_4 . These materials exhibit zeolite-like adsorption and ion-exchange properties. Factors affecting the product crystallization (as e.g. pH), type of cation and composition of reaction mixture are discussed.

Zeolite molecular sieves play an important role in industrial catalysis, ion-exchange and gas adsorption processes. Since the synthesis of AlPO_4 molecular sieves, many new types of crystalline inorganic materials with zeolite-like properties have been prepared (SAPO , MeAPO , MeAPSO , ElAPSO)^{1,2}. Zeolites containing T atoms other than Al and/or Si, such as M-ZSM-5 (M = B, Be, Ti etc.), have been intensively studied. These heteroatoms change substantially the zeolite properties which is reflected in the catalytic activity. A large number of these zeolite-like materials has been synthesized, however, those containing Be and P, which are able to form stable tetrahedral frameworks, have been less intensively studied³⁻¹¹.

In the present paper, we report on the synthesis and characterization of five novel types of microporous beryllorphosphates which we have denoted $\text{BePO}_4-\text{CJ}_n$ ($n = 8-12$).

EXPERIMENTAL

Preparation of $\text{BePO}_4-\text{CJ}_{8-12}$: Beryllium oxides and phosphoric acid were dissolved in water and mixed in the Be/P ratio equal to 1. The alkali or alkali earth chlorides and organic amines were then added (see Table I); pH was kept equal to 6 by the addition of HCl. The mixture was

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stirred until homogeneous, sealed in a teflon-lined autoclave and heated at 150°C for 7–14 days under autogeneous pressure. The crystalline products were separated from the amorphous phase by ultrasonic wave, washed with water and dried under air atmosphere at 100°C.

Instruments employed for the material characterization were: A Rigaku D/MAX-III X-ray diffractometer (CuK α radiation, 30 mA, 40 kV, 8°/min, $2\theta = 4, 40^\circ$), a Nicolet DX-FT/IR spectrometer, a P-240C element analyser, a TAS-100 thermobalance (Ar, 50 ml min $^{-1}$) and a Cahn 2000 vacuum electrobalance.

RESULTS AND DISCUSSION

Synthesis

The batch composition of the initial hydrogels and conditions of the crystallization are listed in Tables I and II. It follows that the composition of the initial reactants

TABLE I

Recommended composition of initial mixture for BePO $_4$ —CJ $_{8-12}$ synthesis (mol)

BePO $_4$ —CJ $_n$	BeO	P $_2$ O $_5$	MCl (MCl $_2$)	H $_2$ O	Template
—CJ $_8$	1.0	0.5	1.7–2.1 Ba $^{2+}$	70–100	1.4–1.9 CHA
—CJ $_9$	1.0	0.5	1.7–2.1 Sr $^{2+}$	90–100	1.5–2.1 CHA
—CJ $_{10}$	1.0	0.5	1.8–2.4 Na $^+$	80–100	1.2–2.3 pyrrolidine
—CJ $_{11}$	1.0	0.5	2.0–2.2 Ca $^{2+}$	60–100	1.6–2.2 pyrrolidine
—CJ $_{12}$	1.0	0.5	2.0 K $^+$ + 0.4 NH $_4^+$	100	1.1–1.45 triethylamine

TABLE II

Crystallization conditions for the synthesis of BePO $_4$ —CJ $_{8-12}$ and composition of products

BePO $_4$ —CJ $_n$	Time days	Temperature °C	pH	Chemical composition of products, mol
—CJ $_8$	5	150	5.7	Ba $_{0.49}$ BePO $_{4.0}$ ·0.93 H $_2$ O
—CJ $_9$	8–10	150	5.7	Sr $_{0.59}$ BePO $_{4.0}$ ·0.70 H $_2$ O
—CJ $_{10}$	5–6	158	6.1	Na $_{0.96}$ BePO $_{4.0}$ ·0.43 H $_2$ O
—CJ $_{11}$	8	150	6.0	Ca $_{0.48}$ BePO $_{4.0}$ ·0.62 H $_2$ O
—CJ $_{12}$	4–7	150	6.0	K $_{1.01}$ (NH $_4$) $_{0.35}$ BePO $_{4.0}$ ·0.15 H $_2$ O

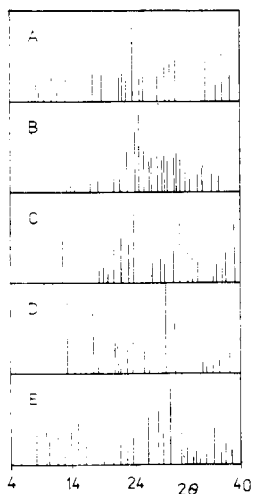


FIG. 1

X-Ray powder diffraction patterns of $\text{BePO}_4\text{—CJ}_{8-12}$; A, B, C, D and E for CJ_{8-12} , respectively

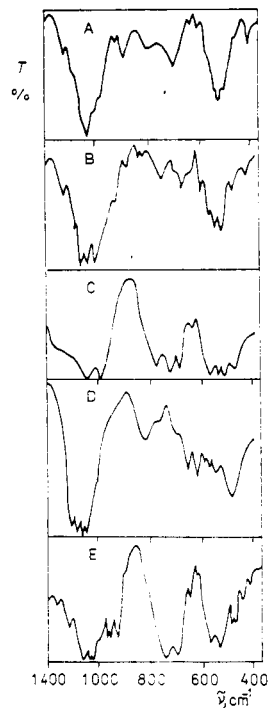


FIG. 2

IR spectra of $\text{BePO}_4\text{—CJ}_{8-12}$; A, B, C, D and E for CJ_{8-12} , respectively

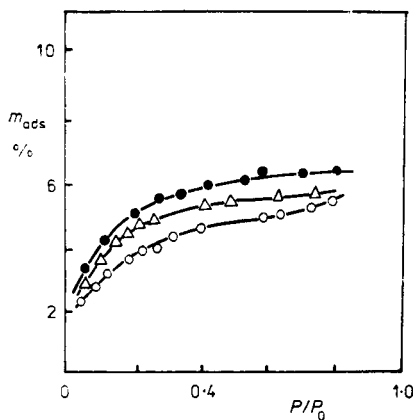


FIG. 3

H_2O adsorption isotherms at 20°C on $\text{BePO}_4\text{—CH}_n$; \bullet $n = 10$, \triangle $n = 11$, \circ $n = 12$

can be changed only slightly. The crystallization temperature, the type of organic amines and metal cations affect the product composition significantly, e.g. the formation of $\text{BePO}_4\text{—CJ}_8$ is favored in the system Ba^{2+} -cyclohexylamine, while in that of Sr^{2+} -cyclohexylamine, $\text{BePO}_4\text{—CJ}_9$ is preferentially formed. Similarly, Na^+ -pyrrolidine, Ca^{2+} -1-butylamine and K^+ -triethylamine give the samples —CJ_{10} , —CJ_{11} and —CJ_{12} , respectively. The optimum pH range is narrow (Table II).

The chemical composition of products obtained is given in Table II. The SEM shows that the crystals are homogeneous without any other phase than that of beryllophosphates. The X-ray powder diffraction patterns are depicted in Fig. 1. They show that the products are well crystallized and that they are of novel unique structure (when compared with the up-to-date known beryllophosphates). IR spectra of the samples obtained are shown in Fig. 2. The absorption peaks appear at the same wavenumbers as have been found for molecular sieves¹². For that reason we assume that the basic building units of $\text{BePO}_4\text{—CJ}_{8-12}$ are tetrahedral TO_4 , Be and P being the T elements.

DTA-TGA indicated that the structure collaps occurs at 376–476, 408–570, 324, 429 and 720°C for the beryllophosphates —CJ_8 , —CJ_9 , —CH_{10} , —CJ_{11} and —CJ_{12} , respectively. No organic species were found in the sample, in spite of the organic templates used for the synthesis. Effect of organic bases and/or amines should be studied in more detail.

The samples $\text{BePO}_4\text{—CJ}_{10-12}$ exhibit significant adsorption properties which are exemplified by water adsorption isotherms in Fig. 3. These samples exhibit the Langmuir-type reversible adsorption isotherms. We assume that they contain only micropores.

The charge-balancing cations can be completely or at least partially exchanged for smaller monovalent Na and Li cations. These ion-exchange properties resemble those of classical zeolites.

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