Synthesis and Characterization of a Novel Extra Large Ring of Aluminophosphate JDF-20

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A novel 20-membered ring channel aluminophosphate has been discovered; its synthesis and characterization are reported.

Since the first discovery of zeolite, numerous natural and synthetic zeolites,[1,2] silica polymorphs, aluminophosphate-based molecular sieves,[3,4] and microporous compounds built from MO_4 tetrahedra (where M is neither aluminium nor silicon, *e.g.* gallophosphate microporous crystal[5,6]) have been brought to light. These materials are prepared hydrothermally, and some of them possess new framework structures. VPI-5,[7] for example, is an extra-large ring aluminophosphate microporous material consisting of 18 tetrahedral (18 T) atoms. Recently, a synthetic gallophosphate molecular sieve with a 20T-atom pore opening, cloverite,[8] was reported. This is the largest ring among the natural and synthetic zeolite and zeolite-like materials. More recently, we have synthesized, for the first time, a microporous crystalline material possessing a 20 T-atom channel, designated as JDF-20.[9] This material has aluminophosphate composition whose channel is circumscribed with 20 T-atoms. We report here the synthetic procedures used to crystallize JDF-20, and some of the relevant characterization data on JDF-20.

JDF-20 was synthesized in the presence of template triethylamine from a predominantly non-aqueous system using a variety of glycols (*e.g.* triethylene glycol) as the solvent. Aluminium triisopropoxide and phosphoric acid (85 wt% H_3PO_4) were used exclusively as the aluminium and phosphorous starting materials, respectively. A typical synthesis procedure involves the following steps: (*i*) aluminium triisopropoxide is slurried in solvent, (*ii*) organic amine is added to the aluminous slurry, (*iii*) the phosphoric acid is added dropwise to the mixture, (*iv*) the whole mixture is stirred until it becomes homogeneous forming the final gel, which (*v*) is charged into the autoclave and heated in an oven, (*vi*) at specified times, the autoclave is removed from the oven and allowed to cool and products recovered by filtration with copious amounts of water or another solvent and dried in ambient air.

We have synthesized JDF-20 with a variety of organic solvents, such as di-, tri- and tetra-ethylene glycol and butane-1,4-diol. The synthesis recipes of JDF-20 are sum-

Table 1 Gel composition and crystallization conditions

	Gel composition (molar ratio)						
Entry	Al_2O_3	P_2O_5	Amine	Solvent[a]	*T*/°C	*t*/d	Product
1	1.0	1.8	4.7 Et_3N	18 TEG	180	5	JDF-20
2	1.0	3.0	7.1 Et_3N	18 TEG	180	30	Amorphous
3	1.0	1.8	4.7 Et_3N	26 DEG	180	10	JDF-20
4	1.0	1.8	5.9 Et_3N	14 tEG	180	10	JDF-20
5	1.0	1.2	5.9 Et_3N	14 tEG	180	50	JDF-20
6	1.0	1.8	4.7 Et_3N	28 BG	180	15	JDF-20
7	1.0	1.8	6.1 $(HOEt_3)N$	18 TEG	180	15	APO-5
8	1.0	1.8	4.8 Pr_2NH	18 TEG	180	3	APO-11
9	1.0	1.8	4.7 Et_3N	18 TEG	200	5	APO-5

[a] TEG = triethylene glycol; DEG = diethylene glycol; tEG = tetraethylene glycol; BG = butane-1,4-diol.

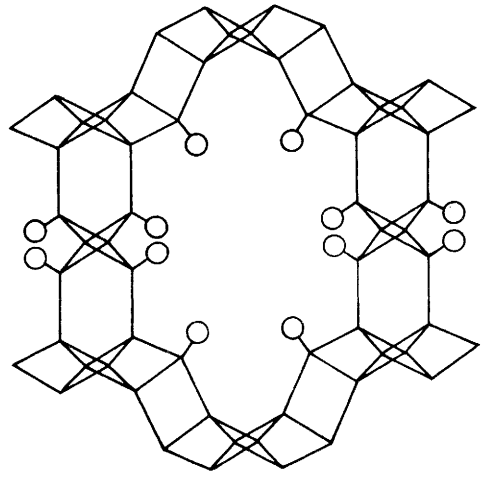

Fig. 1 View of the 20-ring channel showing the connectivity of the tetrahedral sites and location of the oxygen atoms (open circles) protruding into the channels

marized in Table 1. In the presence of other organic amines JDF-20 is not obtained but, instead, other aluminosphosphate molecular sieves are formed, *e.g.* 2,2′,2″-nitrilotriethanol and dipropylamine lead to the formation of APO-5 and APO-11, respectively. The crystallization of JDF-20 occurs over a wide range of temperature, 140–190 °C.

The formation of APO-5 is favoured over JDF-20 at high temperature from the same composition gel. This might be achieved by crystallization in autogeneous pressure at 200 °C or by direct high temperature crystallization—heating at above 300 °C in air.[10] Heteroatoms, such as Li, Mg, Mn, Ga, B, Si, Ti and Sn may be substituted into the JDF-20 lattice to form what are denoted M–JDF-20, *e.g.* Sn–JDF-20 for tin substitution.

The infrared spectrum of JDF-20 shows three bands at 1200–1000, 740–715 and 475–460 cm^{-1}, which are characteristic of aluminophosphate molecular sieves containing four- and six-membered rings.[11,12] The spectrum of JDF-20 is more complex than those of APO-5 and APO-11. The peaks around 1200–1000 cm^{-1} are similar with those of VPI-5.

The thermogravimetric analysis (TGA) for JDF-20 indicates that the weight loss (up to *ca.* 25 wt%) is caused by the removal of water and triethylamine (this result has been verified by elemental analysis and ^{13}C MAS NMR). The weight loss at relatively high temperature, *ca.* 200 °C (triethylamine boiling point 98 °C), implies interaction between triethylamine and the framework. This is in agreement with both the results of ^{13}C NMR spectroscopy and crystal structure analysis.

The ^{27}Al MAS NMR spectra of as-synthesized JDF-20 shows a resonance at δ 33, which is indicative of aluminium coordinated and linked to four oxygen atoms.[13] The ^{31}P spectrum of JDF-20 (a sharp resonance at δ −29 and a diffuse peak at −22) is rather similar to that of VPI-5 (δ −23.3, −33.1 and −27.2).[12]

The large ring structure of JDF-20 has been confirmed by[9] crystal structure analysis. A small single crystal with dimensions 25 × 100 × 175 μm was selected from the as-synthesized JDF-20 and used for data collection.† The crystal structure analysis shows that JDF-20 consists of an elliptically shaped main 20-membered ring channel. The entrance of the main channel has oxygen atoms projecting into it, see Fig. 1.

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† *Crystal data* for JDF-20: $Al_5HO_{24}P_6 \cdot 2Et_3NH \cdot 2H_2O$, space group *C2/c*, a = 32.035, b = 14.308, c = 8.852 Å, β = 104.65°, Z = 4.