Rapid Synthesis of Magnesium Aluminophosphate-5 by Microwave Dielectric Heating†

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A new microwave-hydrothermal technique has been used to synthesise magnesium aluminophosphate-5, which is formed in 20 min at pressures from 130 to 175 psi and has a significantly increased surface area compared to conventionally prepared samples; below 130 psi incomplete crystallisation occurred.

Aluminium phosphate molecular sieves were first synthesised by Wilson *et al.*[1] at the Union Carbide Corporation. Subsequently, the synthesis of silicon-substituted aluminophosphates and the incorporation of divalent metal cations into the aluminophosphate framework were reported by Lok *et al.*[2] and Flanigen *et al.*[3] respectively.

In this work the synthesis of magnesium aluminophosphate-5, MgAPO-5, outlined by Wilson and Flanigen[4] was followed with some modification. A series of identical reaction mixtures were prepared each having a composition of: 1.00 $C_6H_{15}N$:0.167 MgO:0.917 Al_2O_3:1.00 P_2O_5:39.8 H_2O:0.33 $MeCO_2H$:1.38 Pr^iOH. Aluminium isopropoxide (8.32 g) was mixed with 85% phosphoric acid (5.13 g) and water (11.01 g). A solution of magnesium acetate tetrahydrate (0.80 g) in water (3.51 g) was then added to the aluminium phosphate gel and stirred until a homogeneous mixture was obtained. Finally the templating agent, 2-(diethylamino)ethan-1-ol (2.60 g) was added. One of the prepared mixtures was placed in a stainless steel autoclave in a conventional oven and the remainder were thermally treated in CEM 120 ml TEFLON PFA® digestion vessels in a CEM model MDS-2100 microwave unit (1000 W); the temperature was measured by a fibre optic probe and a pressure feedback system was used. The reaction conditions are shown in Table 1. Once the vessels had cooled, the solids were recovered by vacuum filtration, washed with distilled water and dried in air at room temperature.

It was expected that as a result of the rapid heating capabilities of microwave ovens a reduction in the synthesis time would be observed. A considerable reduction has been demonstrated in the digestion times observed when heating mixtures of ore samples and acid in sealed vessels.[5]

The X-ray powder diffraction data confirmed that samples A and B were fully crystalline and comparison with the X-ray pattern obtained by Wilson and Flanigen[4] showed that they were consistent with the samples being MgAPO-5.

The structure of MgAPO-5 has been reported previously[6] and consists of the same framework structure as aluminium phosphate-5 ($AlPO_4$-5). The structure shows a strict rotation of aluminium and phosphorus and the unit cell comprises 24 tetrahedral oxide units, 12 Al and 12 P. The effect of pressure on the crystallinity of the samples was studied using microwave dielectric heating to determine the minimum pressure needed to synthesise MgAPO-5 under these conditions. The percentage crystallinity was calculated from the X-ray diffraction patterns. The results show that there is a limiting pressure of *ca.* 130 psi below which fully crystalline materials could not be formed. At pressures between 130 and 100 psi a mixture of crystalline MgAPO-5 (about 40%) and an amorphous material was obtained, while at less than 100 psi no evidence of crystalline material was found.

Table 1 Reaction conditions for the synthesis of MgAPO-5 and data from nitrogen adsorption and NMR studies

	Oven synthesis	Microwave synthesis			
Sample	A	B	C	D	E
Temperature/°C	200	174	165	150	142
Pressure/psi	*a*	175	130	100	75
Time of synthesis	24 h	20 min	20 min	20 min	20 min
Multi-point surface area/$m^2\ g^{-1}$	4.48	34.87	16.08	4.41	3.16
C	20.12	39.10	31.40	24.87	58.95
One-point surface area/$m^2\ g^{-1}$	4.00	32.75	14.92	4.02	3.02
^{27}Al NMR (δ)[c]	39.3(1)	37.3(1)	37.3(1)	42.1(1)	42.6(1)
^{31}P NMR (δ)[d]	−30.1, −24.4[e]	−29.3, −24.5[e]	−29.9, −25.0[e]	−29.2[f]	−18.6[f]

[a] Not determined. [b] *C* = Measure of interaction between nitrogen adsorbate and the surface of the sample. [c] Relative to $Al(H_2O)_6^{3+}$. Number of peaks in parentheses. [d] Relative to H_3PO_4. [e] Defined shoulder. [f] Broad shoulder also observed.

The nitrogen adsorption data in Table 1 show that both the value of *C* and the surface area has increased in the microwave-synthesised sample. The pore volumes of the solid when measured by nitrogen adsorption show the sample to be microporous and so the majority of the surface area measured is external surface. The increase in surface area in the microwave-synthesised sample, therefore, is a direct result of a decrease in particle size. When a lower pressure is used during the microwave synthesis (130 psi compared to 175 psi) the particle size is larger and therefore the surface area is lower.

When analysed by ^{27}Al solid-state NMR spectroscopy the samples of MgAPO-5 all show a single peak (δ_{Al} 37.3–42.6). The literature[6] value for the chemical shift relating to the Al(4P) environment is $\delta \approx 38$; those for the conventionally prepared sample and the two 100% crystalline microwave-prepared samples correspond to this value and hence this environment, and also show that this material obeys Lowenstein's rule,[7] which precludes Al–O–Al linkages.

† *Non-SI unit employed:* psi ≈ 6.895 × 10^3 Pa.

The shift in the peak in the ^{27}Al spectra observed for microwave-synthesised samples at 100 and 75 psi is probably due to the amorphous nature of the samples studied. When analysed by ^{31}P NMR spectroscopy the conventionally prepared materials and samples prepared at 175 and 130 psi by microwave heating show a major signal at $\delta_P \approx -30$ with a defined shoulder at $\delta_P \approx -25$. The major signal is indicative of the P(4Al) environment and the shoulder the P(3Al,1Mg) environment.

The less crystalline materials show a single resonance which corresponds to the P(4Al) environment and a much broader shoulder. The shoulder is indicative of a range of magnesium-containing environments, *i.e.* P(3Al,1Mg), P(2Al,2Mg) and P(1Al,3Mg). The major signal in the microwave sample prepared at 75 psi ($\delta_{Al} -18.6$) is consistent with a P(3Al,1Mg) environment. In this case it is expected that complete bonding has not occurred, hence the amorphous nature of the sample, the spectrum showing associations between the atoms rather than direct bonds.

From this work we have shown that there are two major advantages in using microwave-assisted synthesis of magnesium aluminophosphates. Firstly the reaction is much shorter, 20 min compared with 24 h under conventional hydrothermal conditions and secondly, the surface area of the material can be controlled by changing the pressure under which the sample is prepared. The increase in surface area will be advantageous in the catalytic applications of MgAPO-5,[8,9] for example in the conversion of methanol to light olefins. Work is continuing in order to investigate further the effects of pressure on the particle size and hence the surface area. Catalytic studies are also in progress.

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