Application of Microwave Dielectric Loss Heating Effects for the Rapid and Convenient Synthesis of Intercalation Compounds

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Intercalation compounds of α-$VO(PO_4)\cdot 2H_2O$ with pyridine, 4-methylpyridine, and 4-phenylpyridine have been synthesised two orders of magnitude more quickly using microwave dielectric loss heating effects than with conventional thermal methods; the samples retain a high degree of crystallinity and are therefore readily characterised by powder *X*-ray crystallographic techniques.

The intercalation of organic and organometallic compounds into layered oxide and sulphide structures has attracted considerable interest in recent years.[1] The kinetics of the intercalation processes are often slow and consequently even after refluxing at 150—200 °C for several days these reactions do not always proceed to completion. Ultrasound has been shown to enhance the rates of intercalation reactions, but, as with the thermal methods, can result in loss of crystallinity of the samples.[2,3] This makes structural characterisation of the intercalated compounds using *X*-ray powder techniques problematical. In this paper we demonstrate how microwave techniques can be used to accelerate greatly the rates of the intercalation processes and yet retain the crystallinity of the samples.

Examples of the application of microwave dielectric loss heating effects for accelerating organic reactions, organometallic reactions, the dissolution of geological samples by mineral acids, and solid state reactions have recently been reported.[4] Since some of the intercalation host lattices and guest molecules absorb microwaves strongly, *e.g.* WO_3 and MoO_3, and pyridine, we decided to investigate the effect of microwaves on these processes. For organic and organometallic solution reactions the most effective rate enhancements have been obtained using a Teflon container sealed in a commercially available autoclave made of polyethyrimide resin, which can sustain temperatures up to 250 °C and pressures of 80 atm.[5] Since these materials are transparent to microwaves at 2450 MHz a microwave oven operating at this frequency and a power level of 650 watts was used for these experiments.

Johnson *et al.*[6] have described co-ordination intercalation compounds in which pryridines are intercalated into the layered mixed oxide α-$VOPO_4$. Their experimental data provide a basis for comparison with our experiments. In a typical experiment 0.15 g of α-$VO(PO_4)\cdot 2H_2O$ and pyridine (py; 7 cm^3) or the same volume of a solution of pyridine in xylene were placed in the Teflon container of the autoclave and microwaves were applied for several minutes. The length of the microwave exposure was limited to *ca.* 5 min. by the pressure limitations of the autoclave. The maximum temperature achieved in the autoclave was 200 ± 5 °C. Table 1 summarises the results of the microwave experiments, together with the results of comparable control reactions which were carried out using conventional thermal tech-

Table 1. Comparison of syntheses of $VO(PO_4){\cdot}2H_2O$ intercalates using microwave and conventional thermal techniques.

	Microwave syntheses		Conventional syntheses		Lattice expansions of the *c* axis[c]	
Conditions:[a] Guest	*t*/min	Stoicheiometry	*t*/h	Stoicheiometry	*c*/Å	Δ*c*/Å
Pyridine (7 cm^3)	5	0.84	36 (120)[b]	0.35	9.55	5.44
4-Methylpyridine (2 cm^3 in 5 cm^3 xylene)	3	0.86	12 (140)	0.60	10.56	6.45
4-Phenylpyridine (1.5 g in 7 cm^3 xylene)	2 × 5	0.85	64 (140)	0.51	12.23	8.12[d]

[a] Host: $VOPO_4{\cdot}2H_2O$ (0.15 g). [b] We find that when more rigorously dried (CaH_2) pyridine is used, the thermal reaction is complete in 12 h, but results in a different product with a greater degree of reduction of the vanadium ions. Johnson *et al.*[6] also noted that the exact nature of the product depended on the water content of the pyridine. [c] Co-ordinated water is lost during the reaction of $VOPO_4{\cdot}2H_2O$ (c = 7.41 Å[1]). Δc represents the difference in the length of the c axis for the intercalation compound and that of anhydrous $VOPO_4$ (c = 4.11 Å[1]). [d] Another phase is also observed with a layer expansion of 9.89 Å (see Figure 2).

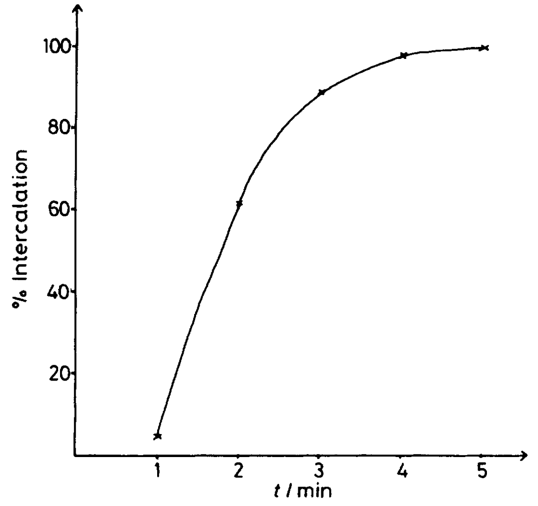

Figure 1. % Intercalation as a function of time for α-$VO(PO_4){\cdot}2H_2O$ with pyridine.

niques. The latter were done in sealed glass ampoules, where 100% intercalation corresponds to a stoicheiometry of $VO(PO_4){\cdot}py_{0.85}$. This was achieved after microwave irradiation for only five minutes (see Figure 1). Johnson *et al.*[6] have noted that the limiting stoicheiometry $VO(PO_4){\cdot}py$ is achieved only in an open system when the solid is refluxed with excess pyridine. The results summarised in Table 1 show that this acceleration rate is a general characteristic of these microwave syntheses and dramatic rate enhancements in the range 10^2 to 10^3 were generally observed. The powder *X*-ray diffraction patterns observed for the intercalated products were superior to those obtained by conventional thermal techniques, particularly for those samples which required many days of refluxing. This difference is illustrated in Figure 2, which compares the *X*-ray powder diffraction patterns for the 4-phenylpyridine intercalate. The *X*-ray diffraction pattern for the product resulting from the microwave experiments (Figure 2a) shows the presence of two tetragonal phases, which is not apparent from the lower quality data for the sample produced by conventional techniques (Figure 2b). The lattice expansions associated with the intercalation reactions are summarised in Table 1, and for pyridine are in close agreement with those reported previously by Johnson *et al.*[6] Similar rate enhancements were observed for reactions carried out under strictly anhydrous conditions.

Blank experiments established that $VOPO_4{\cdot}2H_2O$ does not absorb microwaves strongly, but the intercalated product and the pyridine and substituted pyridine solutions show rapid heating effects when exposed to microwaves. Therefore, in the initial stages of the reaction the high temperature rise associated with the solution is primarily responsible for the rate enhancement. These efficient heating effects very rapidly

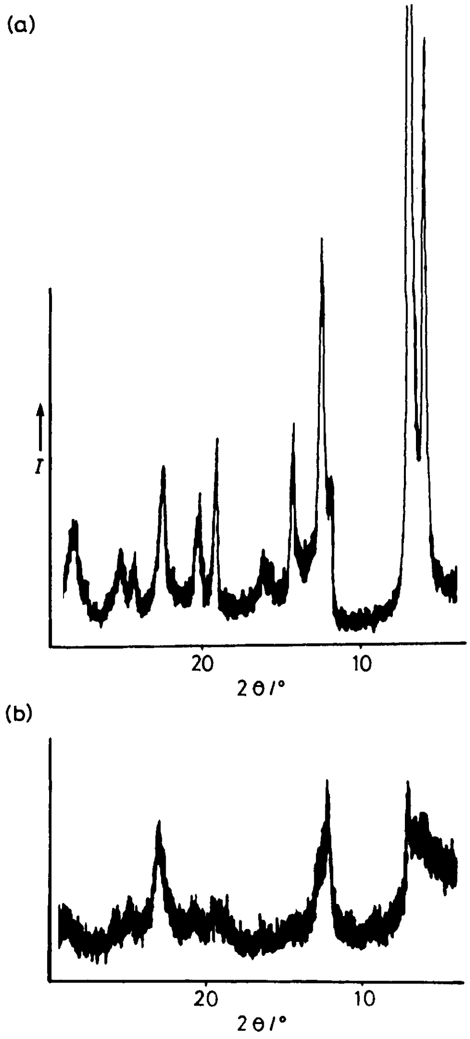

Figure 2. A comparison of the *X*-ray powder diffraction patterns for the intercalation compounds of α-$VO(PO_4)$ with 4-phenylpyridine: (a) microwave product and (b) conventional thermal product. The conditions used for the experiments are given in Table 1.

lead to the development of high pressures in the Teflon container due to the volatility of the solvents. Therefore, the reaction achieves average temperatures of 200 ± 5 °C and *ca.* 50 atm pressure within a minute. In the latter stages of the reactions autocatalytic effects associated with the strong absorption of microwaves by the intercalated product probably contribute to the completion of the intercalation reactions. These autocatalytic effects would have no analogues in conventional heating processes. The fact that the reactions are over within minutes and that no agitation of the samples is required means that the sample crystallinity is largely preserved.

The data we have presently are most complete for this system, although we have preliminary results for other host layered compounds which indicate the general applicability of this technique, *e.g.* with MoO_3.

Furthermore, preliminary *X*-ray data suggests that the technique can be used on single crystal samples of the host materials.

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