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LETTERS TO THE EDITOR

Preparation and Characterization of a New Layered Magnesium Phosphate: $MgHPO_4 \cdot 1.2H_2O$

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A new hydrated phosphate of magnesium with a layered structure was prepared hydrothermally under mild conditions. Provided it is not heated beyond 200°C, this solid undergoes reversible dehydration–rehydration with the layered structure remaining intact. The as-prepared precursor is orthorhombic (a = 9.274, b = 8.053, and c = 10.920 Å), the likely space group being $P2_12_12$. At ca. 500°C, the compound transforms to $Mg_2P_2O_7$.

Introduction

Layered clay-like materials have been extensively used as heterogeneous catalysts (*1–3*) because of their acidity and porosity. To meet the requirements of various reactions, new solid acid catalysts including layered ones (*4*) with different structures and acidities are of continuing academic and industrial interest. Condensed magnesium phosphates are components of, for example, cold-setting cements, refractory materials, and molding compositions (*5*). A variety of magnesium phosphates can be formed (*6*), the molar P/Mg ratios being 2, 1, $\frac{2}{3}$, and $\frac{1}{2}$. Whereas there are a large number of known species with P/Mg of 2, $\frac{2}{3}$, and $\frac{1}{2}$, magnesium phosphates with P/Mg = 1 are relatively rare. The best known is $MgHPO_4 \cdot 3H_2O$, the structure of which (*7*) consists of alternating P and Mg strata parallel to (1 0 0). Although the structure of $MgHPO_4 \cdot 3H_2O$ may be described in terms of hydrogen-bonded layers, the water molecules between the layers cannot be removed without the collapse of the whole structure. Quite a few uranyl phosphates (*8, 9*), as well as $Zr(HPO_4)_2 \cdot nH_2O$ type compounds (*10, 11*), possess a layered structure and some of them can undergo ion exchange and reversible hydration in the same way as zeolites. They are promising proton conductors and heterogeneous catalysts.

Here we report the preparation and the initial characterization of a new layered magnesium phosphate which undergoes reversible hydration up to 200°C.

Experimental

The title compound was prepared hydrothermally in the presence of diethylamine.

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Magnesium acetate tetrahydrate was mixed with phosphoric acid, water, and diethylamine in a composition of 2.0MgO : P_2O_5 : 4HAc : 1.07Et_2NH : 50H_2O. The reaction mixture was stirred until homogeneous, sealed in a PTFE-lined stainless steel autoclave, and heated at 180°C under autogeneous pressure for 3 days. The crystalline product was recovered by filtering and washing with water, and was dried at ambient temperature. Elemental analysis was carried out in the analytical center of Kingston University (England) by inductively coupled plasma (ICP)-atomic emission spectroscopy (AES) method. X-ray powder diffraction was carried out on a Siemens rotating-anode diffractometer using Cu*Kα* radiation. The 2*θ* stepsize was 0.02° and the count time was 4 sec. Quartz was used as an internal standard. To record the diffraction pattern *in situ* at elevated temperatures, an environmental cell was used. IR spectra were recorded on a Perkin–Elmer 1725X FTIR spectrometer and the differential thermal (DT)–thermal gravimetric (TG) analysis was performed on a Stranton–Redcroft STA 1500 thermal analyzer in flowing nitrogen at a heating rate of 5°C/min.

Results and Discussion

The X-ray powder diffraction (XRD) pattern (Fig. 1) and the corresponding data indicate that the as-prepared compound possesses a new structure. The XRD data are indexed on an orthorhombic cell with a = 9.274, b = 8.053, and c = 10.920 Å using an indexing program developed by Visser (*12*). The figure of merit is 22.7. Table I lists the XRD data for the as-prepared compound. The systematic absences (existence conditions: $h = 2n$ for h 0 0 and $k = 2n$ for 0 k 0) suggest that the probable space group is $P2_12_12$. From Fig. 1, we can also see that when the sample is heated at 100°C for 1 hr, it has an XRD pattern (we were not able to index the XRD data of this heated sample for yet unknown reasons) completely different from that of the as-prepared precursor. The first diffraction peak shifts toward high angle from 8.12° to 9.98° corresponding to a d-spacing decrease from 10.88 to 8.86 Å. Further heating to 200°C causes no significant change. However, when the temperature is increased to 300°C, the sample loses its crystallinity to a considerable degree, and some other phases start to form. After being heated at 500°C for 1 hr, the sample is transformed to the dense phase $Mg_2P_2O_7$ (*13*). Interestingly, when the sample is heated at 200°C and exposed to moist air for rehydration for 3–5 hr, it has an XRD pattern essentially identical to that of the as-prepared precursor. This phenomenon, in combination with the d-spacing decrease with increasing temperature, is characteristic of layered materials. Therefore, it is inferred that the as-prepared magnesium phosphate possesses a layered structure with water molecules between the layers.

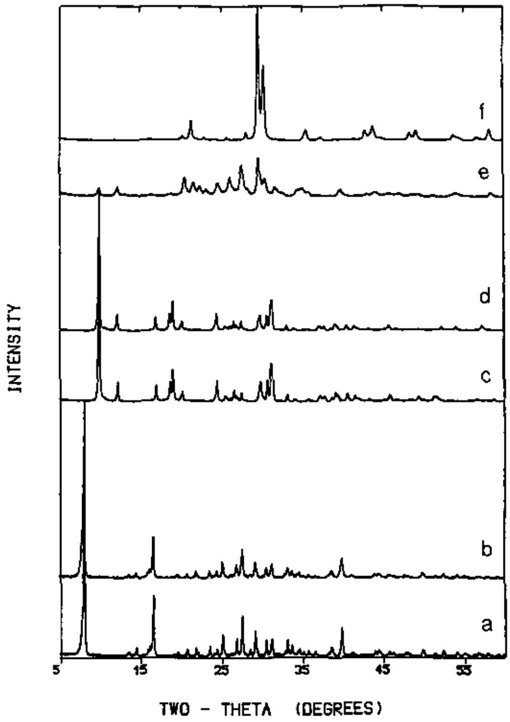

FIG. 1. X-ray powder diffraction patterns for $MgHPO_4 \cdot 1.2H_2O$ (a) at room temperature, (b) heated at 200°C followed by exposure to air, (c) at 100°C, (d) at 200°C, (e) at 300°C, (f) at 500°C.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $MgHPO_4 \cdot 1.2H_2O$

I_{obsvd}	d_{obsvd}(Å)	d_{calcd}(Å)	h	k	l
100	10.88	10.92	0	0	1
3	6.485	6.481	0	1	1
6	6.079	6.080	1	1	0
5	5.453	5.460	0	0	2
40	5.320	5.312	1	1	1
2	4.633	4.637	2	0	0
4	4.521	4.519	0	1	2
5	4.271	4.268	2	0	1
6	4.059	4.063	1	1	2
3	4.019	4.026	0	2	0
		4.018	2	1	0
7	3.773	3.778	0	2	1
		3.771	2	1	1
1	3.691	3.693	1	2	0
6	3.639	3.640	0	0	3
16	3.537	3.534	2	0	2
3	3.500	3.499	1	2	1
14	3.316	3.317	0	1	3
30	3.234	3.236	2	1	2
5	3.127	3.123	1	1	3
18	3.060	3.059	1	2	2
6	3.037	3.040	2	2	0
11	2.930	2.929	2	2	1
13	2.868	2.863	2	0	3
3	2.790	2.790	3	1	1
3	2.730	2.730	0	0	4
10	2.701	2.700	0	2	3
		2.698	2	1	3
8	2.657	2.656	2	2	2
3	2.606	2.607	0	3	1
5	2.586	2.586	0	1	4
3	2.554	2.551	3	1	2
4	2.509	2.509	1	3	1
2	2.491	2.491	1	1	4
4	2.452	2.452	3	2	0
1	2.391	2.392	3	2	1
2	2.352	2.353	2	0	4
6	2.331	2.333	2	2	3
		2.332	2	0	4
7	2.324	2.323	2	3	0
18	2.256	2.258	2	1	4
2	2.198	2.195	1	2	4
3	2.184	2.184	0	0	5
		2.183	4	1	1
3	2.055	2.055	1	1	5

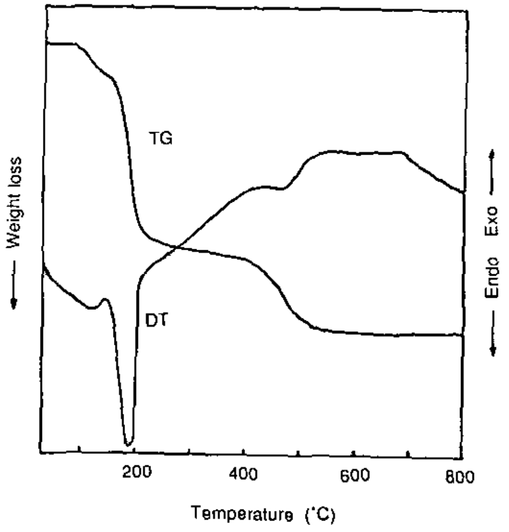

FIG. 2. DT–TG curves for $MgHPO_4 \cdot 1.2H_2O$.

Elemental analysis indicates that the sample contains 17.5% Mg and 21.4% P. Combined with the TG analysis, this result gives rise to an empirical formula of $MgHPO_4 \cdot 1.2H_2O$ for the as-prepared sample (the calculated contents of Mg and P on the basis of this formula are 17.1% and 21.8%, respectively).

The DT–TG curves (Fig. 2) exhibit three endothermic effects corresponding to three distinct weight losses. The first one occurs at around 100°C with a weight loss of 2.6% followed by the second one at ca. 180°C with a weight loss of 11.9%. The temperature for the third is ca. 470°C and the weight loss is 6.3%. The total weight loss is 22.3%, larger than the sum of the three individual effects due to the slow continuous weight losses between the three main effects. The first two effects can be attributed to the removal of the water molecules intercalated in the structure, and the third one to the removal of the hydroxyl groups associated with the protons. When the sample is heated up to 200°C and cooled down to room temperature, it can readsorb water from the air. Based on the DT–TG analysis, the dehydration–rehydration is completely reversible.

Figure 3 shows the IR spectra of the as-prepared sample and those treated at 200, 300, and 500°C for 1 hr, respectively. It can be seen that the IR absorption bands within 1400–700 cm^{-1}, which are believed to be

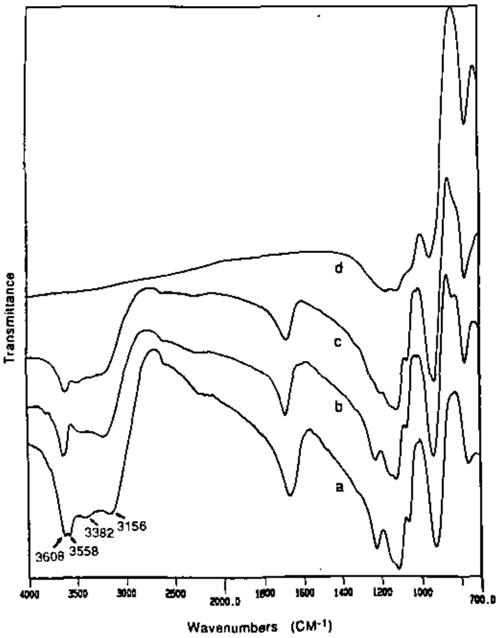

FIG. 3. IR spectra for $MgHPO_4 \cdot 1.2H_2O$.

associated with the $MgHPO_4$ layers, remain more or less unchanged as the sample is heated from room temperature to 200°C. Even at 300°C, the change for the adsorptions within this region is not marked. This suggests that below 300°C, the $MgHPO_4$ layers do not undergo dramatic network rearrangement with increasing temperature, although at 300°C the sample loses its crystallinity to a considerable degree. On the other hand, with increasing temperature, the absorptions within 4000–3000 cm^{-1}, which are related to hydroxyls and water molecules, undergo distinct changes. The as-prepared precursor exhibits twin absorptions at 3608 and 3558 cm^{-1} and two broad bands at 3382 and 3156 cm^{-1}, respectively. We assign the twin absorptions to the proton-related hydroxyls and the broad bands to the water molecules. When the sample is treated at 200°C, the twin merges into a single band and becomes more distinct, while the broad absorptions become much weaker. Obviously, most of, but not all, the intercalated water molecules are removed from the structure at this temperature. After the sample is treated at 300°C, the absorption at 3600 cm^{-1} becomes weaker as well, suggesting that part of the proton-related hydroxyls are removed. On the other hand, absorptions related to the water molecules are still observed. This indicates that even at 300°C, the intercalated water molecules cannot be removed completely. However, if the sample is treated at 500°C for 1 hr, all the absorptions within 4000–3000 cm^{-1} disappear completely, and the absorptions within 1400–700 cm^{-1} undergo distinct changes. This is in agreement with the XRD result that at 500°C, the sample is transformed to the $Mg_2P_2O_7$ phase, in which there are P–O–P as well as Mg–O–P linkages (*13*, *14*).

Acknowledgments

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