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Zirconium Phospho-sulfates with $NaZr_2(PO_4)_3$-type Structure

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Two new crystalline zirconium phospho-sulfates, α- and β-$Zr_2(PO_4)_2(SO_4)$ were prepared by the gel method followed by drying and calcining at controlled temperatures. Their X-ray patterns were indexed and their infrared spectra interpreted. They belong to the $NaZr_2P_3O_{12}$ or [NZP] structural family, and constitute the first example with S^{6+} in the tetrahedral site.

Introduction

There is an increasing interest in the properties of zirconium phosphate precipitates, in the form of gel as well as in the form of crystalline exchangers (*1–9*), mainly due to their power to adsorb radionuclide ions. In addition to the zirconium phosphate gel, others such as zirconium–titanium phosphate, titanium phosphate silicate, and zirconium silicate phosphate were prepared, (*6–8*) which shows that the substitution of zirconium and phosphorus by other elements with similar characteristics is possible.

Occasionally, sulfuric acid was used in the preparation of such gels (*5*, *6*), but no studies were conducted to determine the role of sulfates in the exchangers. The gels prepared in the presence of sulfuric acid were shown to have a greater effect in the adsorption of lanthanides and Sc than the gels prepared in the presence of other acids (*6*). Hence questions regarding the role of SO_4^{2-} can be raised: Are the sulfates adsorbed? Do they become a part of the structure of the exchanger? How do they affect the exchange capacity?

It is also known that the crystalline zirconium phosphates ZrP_2O_7 and $Zr_2P_2O_9$ react with sulfuric acid (*10*), but no characterization of the products was carried out.

The purpose of this paper is to show that depending on the concentration of the sulfates and the temperature used to dry the gel, the sulfate groups become a constitutional part of the structure, giving new crystalline zirconium phospho-sulfate compounds.

Experimental

Two kinds of experiments were carried out. First, samples of zirconium phosphates ZrP_2O_7 and $Zr_2P_2O_9$ were prepared by calcining the respective stoichiometric zirconium phosphate gels at 1200°C. Both these zirconium phosphates were refluxed in concentrated sulfuric acid for several days, taking small portions of the insoluble powder at several intervals for X-ray diffractometry. Second, zirconium phosphate

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gels with different stoichiometries were prepared in the presence of controlled amounts of sulfuric acid, starting from $NH_4H_2PO_4$ and zirconyl nitrate. Then, these amorphous gels were heated between 250 and 800°C in order to crystallize them. The starting gels were not washed before drying to avoid uncontrolled losses of the components by hydrolysis (*16, 17*).

Phase formation was followed by powder X-ray diffraction using a standard diffractometer. High precision X-ray diffraction of pure phases was carried out using an internal Si standard with a Philips APD 3600 X-ray diffractometer for indexing and refining the lattice parameters.

Infrared spectra of the new compounds and compositionally related materials were obtained to determine possible polymerization of the phosphate or sulfate groups.

Chemical analyses were performed on the phase-pure samples to determine the extent of sulfur incorporation.

Results

The zirconium pyrophosphate after refluxing in sulfuric acid did not transform into a gel as claimed by some (*10*). The powders were tested by X-ray diffraction every 24 hr for their crystallinity. The X-ray diffractograms showed that a new phase starts to appear during the refluxing process. This new phase was the same irrespective of the composition of the zirconium phosphate used. After a few days the reaction was complete yielding a new single phase. None of the XRD patterns described in the literature (*1–6*) match with this phase. Chemical composition of this phase revealed it to have $Zr_2(PO_4)_2(SO_4)$ stoichiometry. X-ray diffraction analysis of this new phase was carried out and the cell was indexed as monoclinic with $a = 15.263$, $b = 8.876$, $c = 8.963$, $\beta = 125.96$ (Table I). Thus a new zirconium phospho-sulfate, β-$Zr_2(PO_4)_2(SO_4)$ (Table I), was synthesized.

TABLE I

β-$Zr_2(PO_4)_2(SO_4)$: $a = 15.263$; $b = 8.876$; $c = 8.963$; $\beta = 125.96$

hkl	d_{hkl}	*I*
0 1 0	8.87	1
2 0 0	6.20	4
0 1 1	5.62	18
$\bar{2}$ 0 2	5.483	30
$\bar{3}$11, 111	4.416	100
$\bar{1}$ 0 2	4.217	2
$\bar{1}$ 2 1	3.976	18
$\bar{1}$12, 021	3.797	24
201, 310	3.737	36
0 0 2	3.621	2
2 1 1	3.448	14
0 1 2	3.358	22
$\bar{2}$ 2 2	3.152	45
4 0 0	3.090	22
$\bar{1}$ 2 2	3.055	9
130, 112	2.871	6
$\bar{1}$31, 022	2.809	4
$\bar{2}$ 1 3	2.759	17
$\bar{1}$ 1 3	2.574	16
1 3 1	2.558	35
202, 420	2.539	21
1 2 2	2.502	2
013, 231	2.327	1
$\bar{4}$ 0 4	2.241	1
222, $\bar{3}$04	2.206	7
023, 041	2.122	5
312, $\bar{3}$33, 421	2.099	1
$\bar{2}$ 3 3	2.070	2
$\bar{2}$ 1 4	2.047	1
$\bar{4}$ 2 4	2.001	7
$\bar{1}$33, $\bar{2}$42	1.989	19
$\bar{3}$ 2 4	1.974	9
5 1 1	1.957	21
3 2 2	1.945	7
5 3 0	1.898	3
033, 402	1.872	6
2 1 3	1.860	4

Another series of zirconium phosphate gels were prepared in the presence of sulfuric acid with a P/Zr ratio ranging from 1 to 2 and S/Zr from 0 to 2. A large excess of sulfuric acid was used in the preparation of some zirconium phosphate gels. The gels were dried at about 250°C, and then heated at higher temperatures to crystallize and check their stability. The calcined powders generally showed a mixture of several phases. Only the gels with starting composition ZrP_2O_7, $Zr_2P_2O_9$, $Zr_2(PO_4)_2(SO_4)$, and those with $P/Zr = 1$ and a large excess of sulfuric acid showed a single phase in their X-ray diffractograms. The first two of the above gel compositions produced crystalline phases of ZrP_2O_7 and the α-$Zr_2P_2O_9$ (low temperature form) (*11, 12*), respectively. The third composition resulted in a new crystalline phase which was identified as α-$Zr_2(PO_4)_2(SO_4)$ and is stable up to 750°C. Its stoichiometry was confirmed by chemical analysis which showed that the starting composition was maintained up to 750°C. Above 750°C, this phase started to decompose slowly by losing SO_3 and transformed to α-$Zr_2P_2O_9$. The structure of α-$Zr_2(PO_4)_2(SO_4)$ is nearly the same as the one that corresponds to sodium zirconium phosphate, $NaZr_2(PO_4)_3$ (*13*), and it can be indexed as hexagonal with a = 8.856 and c = 22.76 (Table II). The α phase has an X-ray diffractogram which is very similar to that of $NaZr_2(PO_4)_3$ and, therefore, these two compounds must have the same structure.

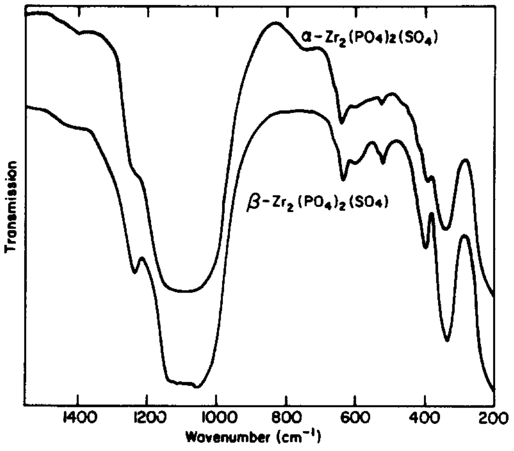

FIG. 1. ir spectra of zirconium phospho-sulfates.

TABLE II

α-$Zr_2(PO_4)_2(SO_4)$: a = 8.856; c = 22.76; Space Group $R\bar{3}c$

h	k	l	d_{hkl}	I
0	1	2	6.36	22
0	1	4	4.57	39
1	1	0	4.43	100
1	1	3	3.824	56
0	2	4	3.175	54
1	1	6	2.880	35
2	1	1		
2	1	4	2.583	30
3	0	0	2.556	30
2	2	0	2.214	6
3	0	6	2.120	4
1	2	8	2.030	10
1	3	4	1.992	22
0	1	10	1.959	11
2	2	6	1.910	13
2	1	10	1.791	11
3	2	4	1.679	18
4	1	0	1.675	15
2	2	9	1.668	26
0	4	8	1.589	3
1	3	10	1.554	4
3	2	7	1.547	4
4	1	6	1.531	4
3	0	12	1.523	4
3	1	11	1.483	5
3	3	0	1.476	5
1	0	16	1.410	3
5	1	4	1.338	10

The fourth phase found by using P/Zr = 1 and a large excess of sulfuric acid is the same as that obtained by refluxing zirconium phosphates with sulfuric acid, i.e., β-$Zr_2(PO_4)_2(SO_4)$. The β phase is more stable than the α phase as indicated by only partial decomposition even after calcining at 1200°C for 24 hr and yielding β-$Zr_2P_2O_9$ from the loss of SO_3 (*14*). Complete thermal decomposition of the phase takes place at 1200°C after 3 days of treatment. Both α- and β-$Zr_2(PO_4)_2(SO_4)$ have the same composition and the constitutional units in their ir spectra are identical (Fig. 1).

Since Hong's paper (*15*) a lot of work has been done showing how easy it is to substitute cations as well as anions in the $NaZr_2(PO_4)_3$-type structure. In this study we have shown the balanced substitution of $Na^{1+} \rightarrow \square^{0+}$ $PO_4^{3-} \rightarrow SO_4^{2-}$ in the $NaZr_2(PO_4)_3$-type structure. The $NaZr_2(PO_4)_3$ structure has been shown (*15*) to suffer a hexagonal to monoclinic distortion for some compositions. The lattice parameters of the distorted compounds are very similar to those of the β-$Zr_2(PO_4)_2(SO_4)$. Therefore, it seems reasonable to conclude that the β phase is the distorted version of the α phase. In the presence of high concentrations of sulfates, the β phase is apparently the most stable. The decomposition products, α- and β-$Zr_2P_2O_9$, have different X-ray diffractograms and very different infrared spectra, unlike the α- and β-$Zr_2(PO_4)_2(SO_4)$ compounds, which suggests that the $\alpha \rightarrow \beta$ transition in the former compounds is not due to simple hexagonal to monoclinic distortion as in the latter.

Conclusions

The formation of α- and β-$Zr_2(PO_4)_2(SO_4)$ from zirconium phosphate gels shows how strongly the sulfate ions are absorbed into these gels. When the gels were prepared in the presence of sulfuric acid, the absorption of sulfate ions was greater than when already formed $Zr-PO_4$ gels were treated with sulfuric acid.

The β phase is more stable than the α phase. Both the α and β phases have the structures of the hexagonal and monoclinic versions of $NaZr_2(PO_4)_3$ compound, respectively. However, neither of the two transforms into the other. Both these phases suffer thermal decomposition into the respective forms of $Zr_2P_2O_9$.

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