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New Preparative Methods and Characterization of Double Phosphates Containing Cerium(III) and Alkali Metals: $M_3Ce(PO_4)_2$*

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In our search for new reactions conducive to the development of thermochemical cycles for producing hydrogen from water [1, 2], we studied the reactions of CeO_2 with various alkali metal hydrogen *ortho*-phosphates, -*meta*phosphates, and -*pyro*phosphates at temperatures up to 1000 °C. It was found that CeO_2 was reduced to Ce(III), yielding nearly stoichiometric amounts of gaseous oxygen. Analysis of the solid products of these reactions by powder X-ray diffraction indicated the formation of $Na_3Ce(PO_4)_2$, which has just recently been identified elsewhere and prepared by alternate methods [3], and of $K_3Ce(PO_4)_2$, a new compound. Lithium phosphates also accomplished the reduction of Ce(IV), but yielded no corresponding lithium–cerium(III) double salt; instead, $CePO_4$ and Li_3PO_4 were identified as the reaction products.

In this communication, we describe a new method for the preparation of $Na_3Ce(PO_4)_2$ and $K_3Ce(PO_4)_2$ and their characterization, along with some of their physical and chemical properties.

Experimental

CeO_2 of 99.95% purity was purchased from Gallard-Schlesinger Chemical Company. Reagent grade sodium and potassium phosphates – $NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 7H_2O$, $Na_3PO_4 \cdot 10.5H_2O$, $Na_4P_2O_7 \cdot 10H_2O$, K_2HPO_4, and $K_3PO_4 \cdot 2.7H_2O$ – were analyzed by acidimetric titration and used without further purification. The lithium phosphates – LiH_2PO_4 and $Li_3PO_4 \cdot 0.8H_2O$ – were prepared from reagent-grade LiOH and H_3PO_4 and the solids were analyzed by acidimetric titration. Some condensed phosphates – $(NaPO_3)_3$, $(KPO_3)_3$, and $Li_4P_2O_7$ – were formed *in situ* from the acid *ortho*phosphates when the reaction mixtures were heated.

Cerium(III) phosphate was prepared in two ways: (a) Cerium(III) nitrate, $Ce(NO_3)_3 \cdot 6H_2O$, was dissolved in a minimum amount of water and treated with a concentrated, neutral solution of ammonium phosphate. $CePO_4$ precipitated as a fine white powder. This was washed with hot water, then acetone, and was fired in a platinum dish at 500 °C in air to remove any remaining ammonium nitrate, ammonium phosphate, or phosphoric acid. The absence of other phases was confirmed by X-ray powder diffraction and infrared (IR) spectroscopy. (b) Cerium(IV) oxide, CeO_2 was dissolved in concentrated aqueous HI. The resulting reddish solution was filtered to remove unreacted CeO_2, and treated with 50% H_3PO_4 to precipitate $CePO_4$. This solid was washed twice with boiling water to remove any soluble iodine-containing species, and then fired to 500 °C to remove traces of solid iodine. It was purified by retreatment with boiling water, followed by refiring in air. X-ray and IR analysis confirmed the formation of pure $CePO_4$.

Firing of reaction mixtures of cerium and alkali metal orthophosphates in air was performed in a platinum dish, while the reaction of acid or condensed phosphates with CeO_2 was carried out by firing under flowing argon or helium in a platinum boat located inside a quartz tube. Variation in heating rates had no significant effect on the formation of the double compounds. Measurements of $O_2(g)$ were made with a Backman Model 741 oxygen analyzer.

Hydrolysis of solid reaction products was performed either by treatment with excess boiling water, or by suspension of the solid in water at room temperature under a flow of $CO_2(g)$ at 1–2 atm. Weight losses due to hydrolysis were measured and the amounts of dissolved phosphate were confirmed by acid–base titrations. Sodium or potassium and cerium were determined by neutron activation; the results agreed well with the stoichiometry $M_3Ce(PO_4)_2$. Standard density measurements were made with a pycnometer. X-ray patterns were taken by means of a Debye-Scherrer camera and a General Electric diffractometer provided with a monochromator using copper Kα radiation.

Infrared spectra were recorded with KBr pellets on a Beckman IR 4240 instrument.

Results and Discussion

The solid products of the reaction of CeO_2 with excess NaH_2PO_4, Na_2HPO_4, $Na_4P_2O_7$, or $(NaPO_3)_3$ were extracted repeatedly with boiling water. In each case, the residue yielded the distinct X-ray powder pattern reported [3] for $Na_3Ce(PO_4)_2$. Similar experiments with potassium salts yielded the new double salt $K_3Ce(PO_4)_2$ which is more susceptible to hydrolysis than the sodium analog (see below). Thus,

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the preparations can be represented by the following equations:

$$2CeO_2 + 3M_4P_2O_7 \text{ (or } 6M_2HPO_4) \rightarrow$$
$$2M_3Ce(PO_4)_2 + 2M_3PO_4 + 1/2O_2 \ (+ 3H_2O) \quad (1)$$

$$2CeO_2 + (MPO_3)_3 \text{ (or } 3NaH_2PO_4) \rightarrow$$
$$M_3Ce(PO_4)_2 + CePO_4 + 1/2O_2 \ (+ 3H_2O) \quad (2)$$

The X-ray density of 3.60 g cm^{-3} based on 10 formulas per unit cell for the sodium salt agrees with the pycnometric density of 3.5 g cm^{-3}. The compound $K_3Ce(PO_4)_2$ does not appear to be tetragonal nor hexagonal and its X-ray powder pattern is described in Table I, its pycnometric density is 3.5 g cm^{-3}.

TABLE I. Powder X-ray Diffraction Pattern of $K_3Ce(PO_4)_2$.

d, Å	I	*d*, Å	I
9.604	5	2.305	16
9.205	3	2.282	5
8.750	2	2.252	9
7.929	2	2.225	14
7.481	89	2.188	12
6.804	2	2.149	2
5.941	4	2.125	17
5.712	5	2.109	14
4.857	32	2.045	26
4.287	2	2.032	31
4.066	74	2.004	4
3.922	2	1.977	4
3.751	2	1.953	7
3.652	5	1.913	6
3.469	9	1.889	9
3.258	24	1.867	17
3.200	3	1.847	17
3.113	11	1.831	6
3.071	5	1.791	6
2.960	100	1.773	2
2.880	10	1.748	12
2.820	56	1.735	7
2.781	68	1.705	2
2.699	4	1.698	4
2.620	9	1.663	7
2.597	7	1.653	21
2.546	5	1.641	2
2.489	2	1.622	9
2.447	7	1.604	5
2.412	21	1.586	5
2.348	2	1.558	10

Infrared spectra of $Na_3Ce(PO_4)_2$ show broad bands at 990–1300 cm^{-1} (P–O stretching) and at 530–660 cm^{-1} (Ce–O). Those for $K_3Ce(PO_4)_2$ have bands at 840–1300 cm^{-1} and 450–650 cm^{-1}. The P–O frequencies for these compounds are shifted from those for $CePO_4$ and Na_3PO_4 which appear at 1000–1150 cm^{-1} and 880–1050 cm^{-1}, respectively. The Ce–O band for $CePO_4$ lies at 550–625 cm^{-1}, and that for CeO_2 is at 310–600 cm^{-1}.

We also prepared $Na_3Ce(PO_4)_2$ and $K_3Ce(PO_4)_2$ by firing mixtures of M_3PO_4 (where M = Na or K) with $CePO_4$ to 500 °C in air, followed by further firing to 950 °C in flowing helium. This type of synthesis was used by Kizilyalli and Welch [3] to prepare $Na_3Ce(PO_4)_2$. The mixed phosphates are nearly white, but change (reversibly) to yellow-orange when heated.

No lithium–cerium(III) compound formed from Li_3PO_4 and $CePO_4$ nor, as indicated above, from other lithium phosphates and CeO_2. Similarly, no color change was observed when mixtures of Li_3PO_4 and $CePO_4$ were heated.

X-ray analysis showed no differences between compounds prepared from CeO_2 and those prepared from $CePO_4$. It was found, however, that oxygen evolution occurred when $M_3Ce(PO_4)_2$, prepared by firing the component phosphates in air, were fired in helium to about 950 °C. Since neither $CePO_4$ nor its mixtures with Li_3PO_4 show this behavior, it was concluded that some oxidation by air of Ce(III) to Ce(IV) took place during the formation of the double phosphates. This is indicated by the following reactions which occur simultaneously in air at about 500 °C:

$$CePO_4 + M_3PO_4 \rightarrow M_3Ce(PO_4)_2 \quad (3)$$

$$xM_3Ce(PO_4)_2 + xM_3PO_4 + \frac{x}{4}O_2 \rightarrow$$
$$xCeO_2 + \frac{3}{2}xM_4P_2O_7 \quad \text{(where } x \ll 1) \quad (4)$$

The release of oxygen at higher temperatures is represented by the reverse of equation (4).

Reaction (3), one of the preparative methods, has obviously been demonstrated. Reaction (4) was confirmed by IR with the detection of the sharp peak at 740 cm^{-1} which is characteristic of $M_4P_2O_7$; the presence of CeO_2 could not always be confirmed by X-ray diffraction since its concentration (calculated from the amounts of oxygen evolved) was usually below the limit of detection of the method. When the initial mixtures with $CePO_4/M_3PO_4 = 1$ were fired in air to 500 °C, the molar fraction of CeO_2 in the product $[X_{CeO_2}$ = mol CeO_2/mol CeO_2 + mol of $M_3Ce(PO_4)_2]$ varied from 0.05 for sodium compounds to 0.14 for potassium. Reaction (4) was further confirmed by two tests: (a) When pure $Na_3Ce(PO_4)_2$ which had been fired in helium to 950 °C was alternately fired in air to 500 °C and in helium, to 950 °C it evolved only a trace of oxygen. (b) When $Na_3Ce(PO_4)_2$ without excess alkali phosphate which had been fired in air to 500 °C in the presence of a large excess of Na_3PO_4 was then fired in helium at 950 °C, it evolved a significant amount of oxygen corresponding to X_{CeO_2} = 0.19; in this case the presence of CeO_2 was ascertained by X-ray diffraction.

The sodium double phosphate is extremely resistant to hydrolysis. Neither boiling it in excess water for 4 hr nor treatment overnight with H_2O and CO_2 (g) at room temperature yielded any significant dissolution of phosphate. Overnight treatment at room temperature with three equivalents of 1 *N* HCl dissolved 85% of the Na_3PO_4 in the compound. The potassium salt is less stable; 44% of the available K_3PO_4 is removed by overnight treatment with water at 25 °C. Acidimetric titration and qualitative tests show that some of the cerium in $K_3Ce(PO_4)_2$ dissolves, in contrast to the behavior of cerium in $Na_3Ce(PO_4)_2$ and $CePO_4$. This is analogous to a previously [3] reported situation where it was observed that the gadolinium in $Na_3Gd(PO_4)_2$ is more soluble in water than is the gadolinium in $GdPO_4$.

References

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