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THERMOCHEMICAL WATER-SPLITTING CYCLES BASED UPON REACTIONS OF CERIUM- AND ALKALINE EARTH PHOSPHATES*

MASTER

P. R. ROBINSON and C. E. BAMBERGER
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830 U.S.A.

ABSTRACT

Cerium(IV) oxide, CeO_2, reacts with derivatives of phosphoric acid, metaphosphate salts, and pyrophosphate salts at 600-1000°C to produce oxygen and cerium(III) phosphates. The cerium(III) phosphates are oxidized to CeO_2 by steam at 700-1200°C in the presence of alkaline earth oxides, carbonates, or halides. These two sets of reactions form the basis for a family of thermochemical cycles based upon the redox couple Ce(IV)/(III).

INTRODUCTION

We recently devised and experimentally confirmed two thermochemical cycles based upon the redox couple Ce(IV)/(III). The first of these [1] is outlined by Eqs 1-5, and is capable of splitting CO_2 into CO and oxygen as well as

$$2\mathrm{CeO_2} + 3\mathrm{Na_4P_2O_7} = 2\mathrm{Na_3Ce(PO_4)_2} + 2\mathrm{Na_3PO_4} + 1/2\ \mathrm{O_2} \qquad T_1 \simeq 800^\circ\mathrm{C} \qquad (1)$$

$$2\mathrm{Na_3Ce(PO_4)_2} + 3\mathrm{Na_2CO_3} = 2\mathrm{CeO_2} + 4\mathrm{Na_3PO_4} + 2\mathrm{CO_2} + \mathrm{CO} \qquad T_2 \simeq 800^\circ\mathrm{C} \qquad (2)$$

$$2\mathrm{Na_3Ce(PO_4)_2} + 3\mathrm{Na_2CO_3} + \mathrm{H_2O} = 2\mathrm{CeO_2} + 4\mathrm{Na_3PO_4} + 3\mathrm{CO_2} + \mathrm{H_2} \qquad T_2' \simeq 800^\circ\mathrm{C} \qquad (2')$$

$$6\mathrm{Na_3PO_4} + 6\mathrm{CO_2} + 6\mathrm{H_2O} = 6\mathrm{Na_2HPO_4} + 6\mathrm{NaHCO_3} \qquad T_3 \simeq 25^\circ\mathrm{C} \qquad (3)$$

$$6\mathrm{Na_2HPO_4} = 3\mathrm{Na_4P_2O_7} + 3\mathrm{H_2O} \qquad T_4 \simeq 270^\circ\mathrm{C} \qquad (4)$$

$$6\mathrm{NaHCO_3} = 3\mathrm{Na_2CO_3} + 3\mathrm{CO_2} + 3\mathrm{H_2O} \qquad T_5 \simeq 250^\circ\mathrm{C} \qquad (5)$$

splitting water into hydrogen and oxygen. The second of these cycles [1] is outlined by Eqs 6-9, where X = Cl, Br, or I.

$$2\mathrm{CeO_2} + \mathrm{H_4P_2O_7} = 2\mathrm{CePO_4} + 2\mathrm{H_2O} + 1/2\ \mathrm{O_2} \qquad T_6 \simeq 600^\circ\mathrm{C} \qquad (6)$$

$$2\mathrm{CePO_4} + 6\mathrm{LiX} + 4\mathrm{H_2O} = 2\mathrm{CeO_2} + 2\mathrm{Li_3PO_4} + 6\mathrm{HX} + \mathrm{H_2} \qquad T_7 \simeq 850^\circ\mathrm{C} \qquad (7)$$

$$2\mathrm{Li_3PO_4} + 6\mathrm{HX} = 2\mathrm{H_3PO_4} + 6\mathrm{LiX} \qquad T_8 \simeq 25^\circ\mathrm{C} \qquad (8)$$

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$$2H_3PO_4 = H_4P_2O_7 + H_2O \qquad T_9 \simeq 220°C \qquad (9)$$

Thermodynamic calculations predicted that alkaline earth oxides, carbonates, and halides would also drive the steam oxidation of $CePO_4$. This paper reports the results of experiments which confirm cycles based upon reactions similar to Eq 7, where LiX is replaced by alkaline earth halides.

EXPERIMENTAL

Unless otherwise indicated, all reagents were of analytical or reagent grade, and were used without further purification.

$CePO_4$ was prepared by reducing CeO_2 with 47% HI. The resulting solution was filtered, and then treated with excess H_3PO_4 (85%). Impure $CePO_4$ precipitated. This was collected by filtration and purified three times by boiling an aqueous suspension of the solid for an hour. The product was shown to be $CePO_4$ of greater than 98% purity by X-ray powder diffraction [2] and by neutron activation analysis.

In high temperature experiments, solid reactants were ground together and placed in a platinum boat which was covered with platinum foil; the boat was introduced into a fused quartz tube. A tube furnace was then used to heat the solids. A continuously flowing stream of argon at about one atm pressure was used to purge air from the tube, and to carry evolved gases away from the solids and into calibrated, continuously operating measurement devices — a Gow-Mac Model 20-150 thermal conductivity detector for H_2, and a Beckman Model 741 oxygen analyzer. Steam was pre-heated to 220°C and passed over the platinum boat at a rate equivalent to 3.2-4.8 ml of condensed $H_2O_{(\ell)}$ per minute. For reactions involving lithium halides, the resulting hydrogen halide was condensed from the 100 ml/min argon stream with the steam by a water-cooled condenser. The amounts of evolved hydrogen halides were determined by titration with standardized NaOH. For reactions involving MCO_3, the resulting $CO_{2(g)}$ was trapped in a solution of 2 N NaOH. In every case, a $CaSO_4$ column was used to remove any remaining water vapor from the Ar-H_2 or Ar-O_2 mixtures before they reached the gas-measuring devices.

A thermal controller was used to increase the reaction temperatures at a steady rate, usually about 5°C per min. Solid products were characterized by X-ray powder diffraction, and by acid-base titration.

RESULTS

Table 1 summarizes the results of experiments in which O_2 was evolved from reactions of CeO_2 with various acid phosphates. T-max is the temperature at which the pressure of evolved O_2 reaches a maximum. All reactions except those involving calcium and strontium pyrophosphates are at least 90% complete within 2.0-2.5 hrs at the indicated temperatures. The strontium and calcium reactions take up to 6 hrs to reach 90% completion. The question mark (?) indicates that we have not yet determined whether $CePO_4$ reacts with $Sr_3(PO_4)_2$ to form double phosphates.

Table 2 reports reactions in which $CePO_4$ is oxidized by steam in the presence of various bases. All of the reactions described in this table were conducted under a stream of argon (100 ml/min) and in the presence of a stream of steam corresponding to 3-5 ml condensed $H_2O_{(\ell)}$ per min.

Table 1. Thermal reduction of CeO_2 in the presence of acid phosphates.

Reaction	T-range (°C)	T-max (°C)
$2CeO_2 + H_4P_2O_7 = 2CePO_4 + 2H_2O + 1/2\ O_2$	580-800	600±50
$+ Na_3P_3O_9 = CePO_4 + Na_3Ce(PO_4)_2 + 1/2\ O_2$	550-800	670±10
$+ 3Na_4P_2O_7 = 2Na_3Ce(PO_4)_2 + 2Na_3PO_4 + 1/2\ O_2$	730-950	800±20
$+ 3Ca_2P_2O_7 = 2CePO_4 + Ca_3(PO_4)_2 + 1/2\ O_2$	930-1200	>1200
$+ 3Sr_2P_2O_7 =$ (?) $+ 1/2\ O_2$	900-1200	1100±80
$+ 3Ba_2P_2O_7 = 2Ba_3Ce(PO_4)_3 + 1/2\ O_2$	750-1200	1050±20

Table 2. Steam oxidation of $CePO_4$ in the presence of various bases.

Reaction	T-range (°C)	T-max (°C)
$2CePO_4 + 6NaOH = 2CeO_2 + 2Na_3PO_4 + 2H_2O + H_2$	350-600	380±10
$+ 3CaO + H_2O = 2CeO_2 + Ca_3(PO_4)_2 + H_2$	700-1150	750±80
$+ 3BaO + H_2O = 2CeO_2 + Ba_3(PO_4)_2 + H_2$	280-400	300±15
$+ 3Na_2CO_3 + H_2O = 2CeO_2 + 2Na_3PO_4 + 3CO_2 + H_2$	700-950	800±15
$+ 3CaCO_3 + H_2O = 2CeO_2 + Ca_3(PO_4)_2 + 3CO_2 + H_2$	700-1100	>1050
$+ 3BaCO_3 + H_2O = 2CeO_2 + Ba_3(PO_4)_2 + 3CO_2 + H_2$	700-1200	>1050
$+ 6LiCl + 4H_2O = 2CeO_2 + 2Li_3PO_4 + 6HCl + H_2$	680-960	860±15
$+ 3CaCl_2 + 4H_2O = 2CeO_2 + Ca_3(PO_4)_2 + 6HCl + H_2$	580-900	830±30
$+ 3SrCl_2 + 4H_2O = 2CeO_2 + Sr_3(PO_4)_2 + 6HCl + H_2$	580-920	760±30
$+ 3BaCl_2 + 4H_2O = 2CeO_2 + Ba_3(PO_4)_2 + 6HCl + H_2$	630-1050	>1050

The use of any pair of reactions from Tables 1 and 2 in thermochemical water-splitting cycles requires that orthophosphates be converted into acid phosphates. Eqs 10-13 represent possible ways of effecting this conversion (M = Ca, Sr, Ba):

$$M_3(PO_4)_{2(c)} + H_2O_{(\ell)} = MO_{(c)} + 2MHPO_{4(c)} \tag{10}$$

$$M_3(PO_4)_{2(c)} + CO_{2(g)} + H_2O_{(\ell)} + MCO_{3(c)} + 2MHPO_{4(c)} \tag{11}$$

$$M_3(PO_4)_{2(c)} + 2HCl_{(g)} = MCl_{2(c)} + 2MHPO_{4(c)} \tag{12}$$

$$M_3(PO_4)_{2(c)} + 6HCl_{(g)} = 3MCl_{2(c)} + 2H_3PO_{4(\ell)} \tag{13}$$

The designations (c), (ℓ), and (g) represent the crystalline, liquid, and gaseous states, respectively. Reactions 10 and 11 do not occur to any appreciable extent under standard conditions. However, in the presence of 5 atm $CO_{2(g)}$, partial conversion of an aqueous slurry of $Ba_3(PO_4)_2$ into $BaCO_3$ and $BaHPO_4$ occurs. A 22-34% conversion can be achieved under this condition. However, since both of these products are insoluble, their subsequent separation is extremely difficult.

Reactions 12 and 13 proceed readily at 25°C, with both $HCl_{(g)}$ and $HCl_{(aq)}$. Direct treatment of solid $M_3(PO_4)_2$ with excess aqueous HCl dissolves the alkaline earth orthophosphates quickly. However, the products — H_3PO_4 and MCl_2 — can be separated only with difficulty by fractional crystallization of the MCl_2, or by steam-distillation of the H_3PO_4.

We avoided these problems by treating aqueous suspensions of the orthophosphates with cation exchange resin (Dowex 50W) in the acid form. This effected a quantitative exchange of M^{2+} for H^+. The resulting H_3PO_4 was washed from the resin with distilled water. The adsorbed M^{2+} ions were eluted from the resin with excess aqueous HCl, which yielded $MCl_{2(aq)}$ and $HCl_{(aq)}$. Evaporation of these solutions to dryness at relatively slow rates yielded crystalline MCl_2 free of HCl and H_2O.

DISCUSSION

The first reaction in Table 1, the last three reactions in Table 2, and Eq 13 can be combined into feasible thermochemical cycles:

$$2CeO_2 + H_4P_2O_7 \xrightarrow{600°C} 2CePO_4 + 2H_2O + 1/2\ O_2$$

$$2CePO_4 + 3MCl_2 + 4H_2O \xrightarrow{750\text{-}1100°C} 2CeO_2 + M_3(PO_4)_2 + 6HCl + H_2$$

$$M_3(PO_4)_2 + [resin]\text{-}(6H^+) \xrightarrow{25°C} 2H_3PO_4 + [resin]\text{-}(3M^{2+})$$

$$[resin]\text{-}(3M^{2+}) + 6HCl \xrightarrow{25°C} 3MCl_2 + [resin]\text{-}(6H^+)$$

$$2H_3PO_4 \xrightarrow{220°C} H_4P_2O_7 + H_2O$$

In the last step of the cycle, $H_4P_2O_7$ may condense further to form other polyphosphoric acids such as HPO_3 or P_4O_{10}. For M = Ca or Sr, the temperatures for the cycle are well within the 950°C upper limit which is usually assumed for HTGRs (high-temperature gas-cooled reactors) [3]. For M = Ba, however, the 1050°C required for the oxidation of $CePO_4$ exceeds this limit.

The need to use ion exchange resins for the separation of H_3PO_4 from MCl_2 may make capital costs for cycles of this type prohibitively high.

REFERENCES

1. Bamberger, C. E., and Robinson, P. R., unpublished results.
2. X-ray powder patterns and neutron activation analyses were obtained by the Analytical Chemistry Division, Oak Ridge National Laboratory.
3. Quade, R. N., and Meyer, L., Int. J. Hydrogen Energy, 4, 101 (1979).