Cation effects in the conversion of methanol on calcium, strontium, barium and lead hydroxyapatites

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The effect of the nature of the cation on the surface and catalytic properties of calcium, strontium, barium and lead hydroxyapatites and dicationic analogs containing lead and strontium or barium has been studied with methanol and deuterated methanol. XRD, XPS and ^{31}P MAS NMR have been used to characterize the samples, and temperature programmed desorption of deuterated methanol has been employed to provide ancillary information. The dehydration/dehydrogenation of methanol is found to depend strongly on the nature of the divalent cation and is related to the binding strengths of methanol on the hydroxyapatites.

KEY WORDS: hydroxyapatite; cation effects.

1. Introduction

Calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is well-known as the mineral component of bones and teeth and as such is of considerable interest in dental and medical research [1,2]. Until recently relatively little work has been done on the surface and catalytic properties of this material [3–5]. Recently stoichiometric and nonstoichiometric calcium hydroxyapatites (CaHAp) have been examined as catalysts for the oxidation of methane [6,7], ethane [8] and propane [9,10]. Hydroxyapatites with other than calcium as cations, *e.g.*, barium and strontium, can be prepared through direct synthetic methods or through ion-exchange procedures [1,2]. While these hydroxyapatites are of lesser importance in biological terms, nevertheless their catalytic properties, particularly in oxidation processes, are of interest [11,12]. The present report compares the results from the conversion of methanol on several calcium, barium, strontium and lead hydroxyapatites, as well as on several dicationic analogs containing lead and either barium or strontium. Further information on the catalysts is obtained from X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), MAS nuclear magnetic resonance (NMR) spectroscopy and temperature programmed desorption (TPD) studies.

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2. Experimental

2.1. Materials

Stoichiometric and nonstoichiometric calcium hydroxyapatites were prepared from $Ca(NO_3)_2{\cdot}4H_2O$ (BDH AnalaR) and $(NH_4)_2HPO_4$ (BDH AnalaR) [13,14]. Strontium hydroxyapatites (SrHAp) were similarly prepared from the analogous strontium compound [15,16]. Barium hydroxyapatites (BaHAp) were synthesized from $Ba(OH)_2{\cdot}8H_2O$ and H_3PO_4 [17,18]. Lead hydroxyapatites (PbHAp) were prepared from the dehydration product of basic lead nitrate [19–21].

Dicationic hydroxyapatites PbSrHAp and PbBaHAp were prepared by ion exchange of the lead cation into SrHAp (Sr/P = 1.51) and BaHAp (Ba/P = 2.04) from aqueous solutions of lead nitrate. Methanol (CH_3OH, 99.9%) and deuterated methanol (CH_3OD, 99%) were purchased from Fisher Scientific and MSD isotopes, respectively.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT 2500X diffractometer using monochromatic Cu K_α radiation. Bulk concentrations of Ca, Sr, Ba, Pb and P were measured on the CaHAp samples dissolved in aqueous HNO_3 solutions by inductively coupled plasma (ICP) spectrometry (Shimadzu, ICPS-5000). Surface areas were calculated by application of the BET equation to N_2 adsorption isotherms (78 K) obtained with a conventional volumetric system. Surface compositions were measured with X-ray photoelectron spectroscopy

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(XPS; Shimadzu ESCA-1000AX) using Mg K_α radiation. The binding energies were corrected using 285 eV for C 1s as an internal standard. Argon-ion etching of the catalyst was carried out at 2 kV for 1 min with a sputtering rate estimated as 2 nm/min for SiO_2.

MAS NMR spectra were recorded on an AMX500 (Bruker) spectrometer operating at 500.14 MHz for ^1H and at 202.46 MHz for ^{31}P. Samples previously pretreated at 500 °C for 3 h were packed in 4 mm o.d. rotors and spun at ~5000 Hz.

2.3. Procedures

The conversion of methanol was investigated in a conventional fixed-bed continuous flow reactor operating under atmospheric pressure. The reactor consisted of a quartz tube of 7 mm i.d. and 35 mm in length, sealed at each end to 4 mm i.d. quartz tubes. The catalyst was sandwiched with quartz wool plugs, whose contribution to the reaction was found to be negligible. Methanol and water (when present) were supplied to the reactant stream from double (in series) and single saturators, respectively, with temperatures and flow rates separately controlled. The catalysts were pretreated, *in situ*, in a flow of helium (usually 15 ml/min) at 723 K. Reaction conditions were W (mass of catalyst) = 0.1, 0.2, 0.3 or 0.4 g, F (flow rate) = 20 ml/min, $P(CH_3OH)$ = 2.0, 4.0 or 7.3 kPa and $P(H_2O)$ = 0, 0.6 or 1.2 kPa, except as noted, with balance to atmospheric pressure provided by helium.

The reactants and products were analyzed with an on-stream gas chromatograph (HP 5880A) equipped with a thermal conductivity detector. A combination of three columns, Porapak T (2.7 m), Porapak Q (2.7 m) and molecular sieve 5 Å (0.09 m) was employed in the analyses. The conversion of CH_3OH was calculated from the quantities of CH_3OH introduced into the feed and the products formed. Carbon selectivities (mol%) were calculated on the basis of the carbon contents in the products as determined from the GC analyses. The carbon mass balances were $100 \pm 5\%$. The hydrogen selectivities (mol%) were calculated on an H1 basis.

For the temperature-programmed experiments the catalysts were first heated for 0.5 h at 450 °C in a flow (20 ml/min) of helium, followed by cooling to room temperature. After exposure to 4 kPa of CH_3OD diluted with helium for 0.5 h at room temperature, the flow of helium was maintained for 0.5 h. The sample was then held at 30 °C for 10 min under helium flow prior to heating at 10 °C/min. Desorbed products were analyzed by GC-MS (HP 5890-5970).

3. Results and discussion

The powder XRD patterns for the various samples, regardless of the cation, are typical of those expected for hydroxyapatites (not shown).

The surface areas of the hydroxyapatites each containing only the cations of one element are summarized in table 1. The calcium and strontium hydroxyapatites show little change in surface areas with bulk composition, except for that with Sr/P = 1.58 which has a markedly smaller area. The samples with either barium or lead as cation have surface areas markedly smaller than those containing calcium or strontium.

The XPS analyses of surface compositions of the monocationic materials show that the cation/phosphorus ratios are less than those found for the bulk values, although the former increase to values higher than the latter after etching (table 2). The O/P ratios are lower than those expected from the stoichiometry, with the exception of the calcium hydroxyapatite with a bulk Ca/P of 1.5. Etching effects on O/P are insignificant.

^{31}P MAS NMR spectra for all of the monocationic samples are essentially identical with a single ^{31}P resonance at approximately 3 ppm shift (relative to 85% H_3PO_4) (not shown) as reported previously [22]. Very weak sidebands in all samples can be interpreted as demonstrating the absence of chemical shift anisotropy and consequently little or no perturbation of the tetrahedral symmetry of the phosphate ions [1]. Since only one chemical shift was observed [22], all phosphate ions have similar environments. These observations are unexpected since it would be anticipated that non-stoichiometric hydroxyapatites would contain HPO_4^{2-} ions for which significantly different ^{31}P MAS NMR spectra have been reported.

^1H MAS NMR spectra of all monocationic samples displayed a sharp resonance with a chemical shift of approximately 0.1 ppm and a resonance at approximately 5 ppm, the former assigned to hydroxyl ions and the latter to adsorbed water [22–24].

The results obtained from the conversion of methanol on the catalysts of various compositions and at various reaction temperatures are shown in figure 1. The conversions of methanol are largely independent of the bulk compositions of CaHAp and SrHAp, although the results for CaHAp show an unexpected discontinuity.

Table 1
Surface areas [a] of the catalysts

Bulk composition [b] X/P	Cation			
	Ca	Sr	Ba	Pb
1.50	68.5	60.9	–	–
1.53	–	61.1	–	–
1.58	66.5	39.1	–	–
1.67	69.2	–	–	–
1.85	–	–	–	7.7
2.00	–	–	20.7	–

[a] m^2/g (BET).
[b] ICP (X = cation).

Table 2
Surface composition [a] of catalysts

Bulk composition [b] X/P	t [c]	Ca		Sr		Ba		Pb	
		Ca/P	O/P	Sr/P	O/P	Ba/P	O/P	Pb/P	O/P
1.50	0	1.4	4.3	1.5	2.3				
	1	1.7	4.3	1.6	2.2				
1.53	0			1.3	2.9				
	1			1.8	3.4				
1.58	0	1.4	3.4	1.6	2.2				
	1	1.6	3.5	1.7	2.0				
1.67	0	1.4	3.1						
	1	1.4	2.9						
1.85	0							1.6	3.7
	1							1.8	3.6
2.00	0					0.61	2.5		
	1					0.65	2.8		

[a] XPS.
[b] ICP (X = cation).
[c] Etching time (min).

The significantly higher conversion of methanol obtained with PbHAp (Pb/P = 2.00) at 723 K is noteworthy. The increase in conversion with temperature is as expected.

The selectivities to products from methanol display significant differences with changes in the cation of the catalyst (figure 2). Bimolecular dehydration to dimethyl ether appears to be the dominant process on the calcium and strontium hydroxyapatites, while with the barium analog the carbon oxides are the major product. At the lowest temperature studied (623 K) PbHAp produces only CO_x, but the selectivity to formaldehyde increases to 74% at 723 K. Similar results were found with the dicationic materials with selectivities of 73 and 80% to H_2CO obtained on PbSrHAp and PbBaHAp, respectively, at 723 K. Not surprisingly, hydrogen was also produced concomitantly with H_2CO.

Temperature-programmed experiments with deuterated methanol were performed to provide ancillary information on the catalysts and the conversion of methanol. The results are summarized in figure 3. A note of caution is appropriate here. The absolute values of data obtained from TPD experiments, particularly those involving water, should be discounted in favor of emphasis on the relative values of the results. In view of the small differences between and the absence of systematic changes of the quantities shown in figure 3, with Ca/P and Sr/P ratio only the averages of the aforementioned quantities are shown. The temperature at which the desorption of the alcohol reached a maximum was strongly dependent on the nature of the cation of the hydroxyapatite, increasing in the order Ca < Sr < Ba < Pb (figure 3(A)).

The peak maximum for the desorption of water was also dependent on the nature of the cation, with increases in the temperature at which the maximum appeared following the same order as seen with the desorption maxima for methanol (figure 3(B)). In contrast, the quantities of the various isotopic forms of water which were desorbed at the maximum decreased in the order Ca > Sr > Ba > Pb, the reverse of that seen with the maxima for methanol and water desorption, while the quantities of nondeuterated and singly deuterated water desorbed were substantially higher than that of D_2O (figure 3(C)).

Table 3
Surface areas and composition [a] of dicationic catalysts

Bulk composition [b] Pb/X		t [c]	PbXHAp			
			Pb/X	X/P	O/X	Surface area [d]
Pb/Sr	1.17	0	0.46	0.81	3.60	15.7
		1	0.14	0.98	2.83	
Pb/Ba	0.112	0	0.86	0.42	4.33	19.2
		1	0.33	0.80	3.41	

[a] XPS.
[b] ICP (X = cation).
[c] Etching time (min).
[d] m^2/g (BET).

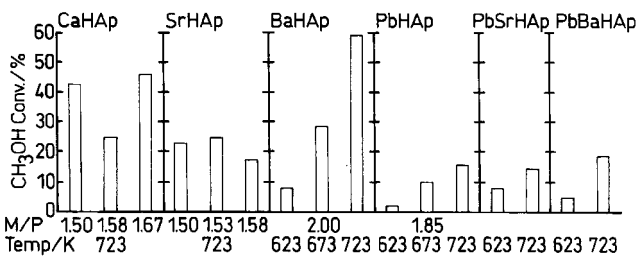

Figure 1. Conversion of methanol on the monocationic and dicationic hydroxyapatites at various temperatures. M/P: Cation/phosphorus ratio.

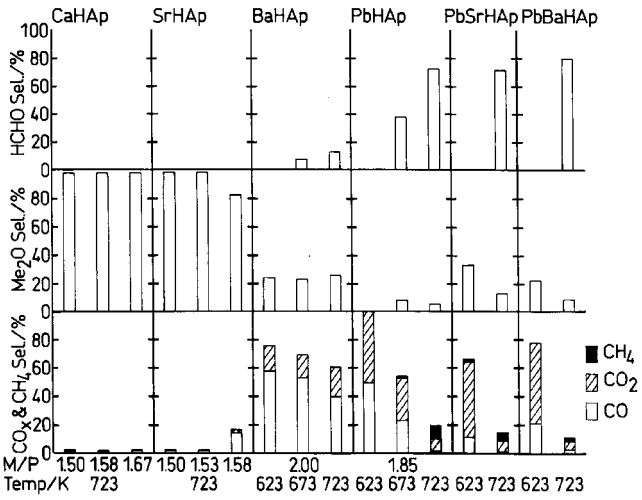

Figure 2. Selectivities to products on the monocationic and dicationic hydroxyapatites at various temperatures.

The variation with the nature of the cation in the quantities of the isotopes of water desorbed appears to be consistent with the changes in the selectivity to dimethyl ether (DME), the latter of which decreases in the order Ca > Sr > Ba > Pb. Although the formation of DME is suggestive of a bimolecular process, the significantly smaller quantities of D_2O desorbed, in comparison with those of HDO, from the TPD with CH_3OD demonstrate that the dehydration mechanism involves two steps, the interaction between the methanolic hydroxyl group and protium on the hydroxyapatite to form surface methoxy groups with release of HDO, followed by the interaction between CH_3OD and the surface methoxy groups to form DME with simultaneous deuteration of the site previously occupied by the methoxy group. It should be emphasized that although such a mechanism appears to be predominant, a gas-phase bimolecular process in which two molecules of methanol combine to form DME and water is undoubtedly also occurring. The formation of D_2O may result from the latter process as well as the associative desorption of surface deuteroxyl groups.

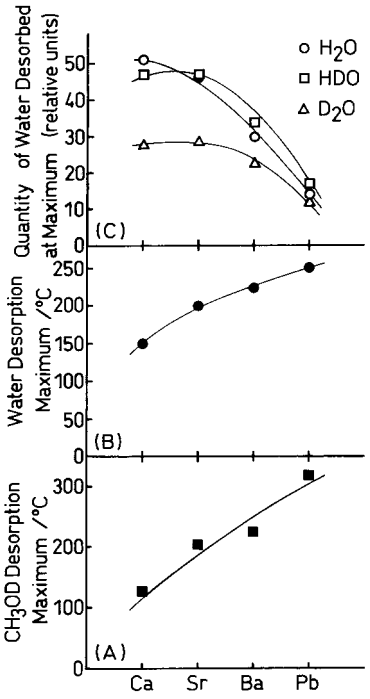

Figure 3. Temperature-programmed desorption pattern. (A) Temperature at which maximum of CH_3OD desorption occurs. (B) Temperature at which maximum of water desorption occurs. (C) Quantity of water desorbed at the maximum. (A, B, C for Ca and Sr are obtained from averages over the composition for a given cation.)

The strong dependence of the surface and catalytic properties of the hydroxyapatites on the nature of the cations is clearly evident. The data suggest that the dehydrogenation process to form formaldehyde is more prevalent on those catalysts where methanol is held more strongly, while the dehydration process to form DME occurs on the catalysts with weaker binding properties for methanol. The monoclinic structure of pure hydroxyapatite contains columns of calcium ions connected to their neighbors by three shared oxygen atoms. These columns are linked by phosphate tetrahedra to form a three-dimensional network of phosphate tetrahedra with enmeshed columnar Ca^{2+} ions [1]. Thus it is not unreasonable that the nature of the cation should have a strong influence on the properties of these solids. It is tempting to relate the observations in the present work to the charge densities of the cations, which increase as the atomic weight of the element increases, although the differences seen in the results for the hydroxyapatites of the various cations are undoubtedly dependent upon a number of factors.

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References

[1] J.C. Elliott, *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates* (Elsevier, Amsterdam, 1994).
[2] J.C. Elliott, in: *Calcium Phosphate Materials. Fundamentals*, eds. E. Brès and P. Hardouin (Sauramps Medical, Montpellier, 1998).
[3] C.L. Kibby, S.S. Lande and W.K. Hall, J. Am. Chem. Soc. 94 (1972) 314.
[4] C.L. Kibby and W.K. Hall, in: *Chemical Biosurfaces*, Vol. 2, ed. M.L. Hair (Marcel Dekker, New York, 1972), p. 663.
[5] J.A.S. Bett, L.G. Christner and W.K. Hall, J. Catal. 13 (1969) 332.
[6] S. Sugiyama, K. Abe, H. Hayashi, Y. Matsumura and J.B. Moffat, J. Mol. Catal. A, 144 (1999) 347, and references therein.

[7] S. Sugiyama, K. Abe, H. Hayashi and J.B. Moffat, Appl. Catal. A 183 (1999) 135.
[8] S. Sugiyama, T. Miyamoto, H. Hayashi and J.B. Moffat, J. Mol. Catal. A 135 (1998) 199.
[9] S. Sugiyama, E. Nitta, H. Hayashi and J.B. Moffat, Appl. Catal. A 198 (2000) 171.
[10] S. Sugiyama, T. Shono, E. Nitta and H. Hayashi, Appl. Catal. A 211 (2001) 123.
[11] H. Hayashi, H. Kanai, Y. Matsumura, S. Sugiyama and J.B. Moffat, Stud. Surf. Sci. Catal. 110 (1997) 673.
[12] H. Hayashi, S. Sugiyama and J.B. Moffat, Stud. Surf. Sci. Catal. 119 (1998) 325.
[13] E. Hayek and H. Newesely, Inorg. Synth. 7 (1963) 63.
[14] S. Sugiyama, T. Minami, H. Hayoshi, M. Tanaka, N. Shigemoto and J.B. Moffat, J. Chem. Soc., Faraday Trans. 92 (1996) 293.
[15] T. Ishikawa, H. Saito and K. Kandori, J. Chem. Soc., Faraday Trans. 88 (1992) 2937.
[16] Y. Matsumura, S. Sugiyama, H. Hayashi, N. Shigemoto, K. Saitoh and J.B. Moffat, J. Mol. Catal. 92 (1994) 81.
[17] A. Yasukawa, M. Kidokoso, K. Kandori and T. Ishikawa, J. Colloid Interface Sci. 191 (1997) 407.
[18] S. Sugiyama, T. Nakanishi, H. Hayashi and J.B. Moffat, Phosphorus Res. Bull. 8 (1998) 23.
[19] A. Bigi, M. Gandolfi, M. Gazzaro, A. Ripamonti, N. Roveri and S.A. Thomas, J. Chem. Soc., Dalton Trans. (1991) 2883.
[20] S. Sugiyama, K. Abe, H. Hayashi and J.B. Moffat, Catal. Lett. 37 (1999) 161.
[21] S. Sugiyama, T. Nakanishi, T. Ishimura, T. Moriga, H. Hayashi, N. Shigemoto and J.B. Moffat, J. Solid State Chem. 143 (1999) 296.
[22] S. Sugiyama, T. Moriga, H. Hayashi and J.B. Moffat, Bull. Chem. Soc. Jpn. 74 (2001) 18.
[23] W.P. Rothwell, J.S. Waugh and J.P. Yesinowski, J. Am. Chem. Soc. 102 (1980) 2637.
[24] J.P. Yesinowski and H. Eckert, J. Am. Chem. Soc. 109 (1987) 6374.