The conversion of methanol: a probe reaction for hydroxyapatite

S. Sugiyama* and J.B. Moffat

Department of Chemistry, University of Waterloo and Guelph-Waterloo Centre for Graduate Work in Chemistry and Biochemistry, Waterloo, ON N2L 3G1, Canada

Received 10 April 2001; accepted 2 July 2001

Stoichiometric and nonstoichiometric hydroxyapatites are characterized by surface area, ICP, XPS and NMR MAS. The dehydration of methanol is shown to be unimolecular but poisoned by both alcohol and water. Rate constants and the ratio of the adsorption equilibrium constants of alcohol and water are obtained with the former appearing to be related to the surface Ca/P values. Infrared spectroscopy and temperature-programmed desorption and reaction show that hydroxyapatite, after exposure to methanol, contains surface methoxy groups and related experiments with deuterated methanol show that the dehydration process involves the interaction of methanol with surface protium.

KEY WORDS: hydroxyapatite; methanol conversion

1. Introduction

Calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$; CaHAp] may well be one of the most studied phosphates, in large part as a result of its dominant role in the composition of bone and teeth [1,2]. The work to date has been largely concerned with various preparatory methods, structure and solid state properties of CaHAp. Until recently relatively few studies on the surface and catalytic properties of this material have been reported [3–5]. Recently stoichiometric and nonstoichiometric CaHAp have been examined as catalysts for the oxidation of methane [6,7], ethane [8] and propane [9].

The present work employs methanol as a probe molecule to investigate the surface properties of CaHAp of various compositions. XRD, XPS, MAS NMR and surface area measurements are employed to characterize the solid along with reactor studies, infrared spectroscopy, and temperature-programmed desorption of methanol and deuterated methanol to evaluate the interaction of the latter with the solid.

2. Experimental

2.1. Materials

Stoichiometric and nonstoichiometric calcium hydroxyapatites were prepared from $Ca(NO_3)_2 \cdot 4H_2O$ (WAKO) and $(NH_4)_2HPO_4$ (WAKO) [10–12]. A commercially prepared calcium hydroxyapatite was obtained from Anachemia and was used without further purification. 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 Kα radiation. Bulk concentrations of Ca 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 (XPS; Shimadzu ESCA–1000AX) using Mg Kα 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.

Infrared spectra were obtained with a Bomem MB-100 FTIR spectrometer. The sample was pressed into a self-supporting wafer and mounted in an IR cell fitted for heating under vacuum.

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 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 sin-

---

[*] Permanent address: Department of Chemical Science and Technology, The University of Tokushima, Minamijosanjima, Tokushima 770-8506, Japan.

1011-372X/01/0900-0075$19.50/0

gle 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 $W = 0.1$, 0.2, 0.3 or 0.4 g, $F = 20$ 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 5A (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 ± 5%. The selectivities to H_2 (mol%) were calculated on a hydrogen base.

Temperature-programmed experiments employed a gas chromatograph (HP 5890) equipped with a mass selective detector (HP 5970).

3. Results and discussion

3.1. Characterization

Powder X-ray diffraction patterns (not shown) are virtually identical for all samples and match those for calcium hydroxyapatite (JCPDS9-0432).

The bulk and surface compositions of the four samples of CaHAp are shown in table 1 together with the surface areas. The bulk compositions as determined from ICP range from calcium-deficient to stoichiometric (Ca/P equal to 1.67) while the surface areas are essentially identical. In contrast, the compositions of the surface layer for the three noncommercial samples show calcium deficiencies higher than those found for the bulk as reported earlier [6–9], while the values of O/P for the sample with a bulk Ca/P equal to 1.50 as well as the commercial sample are similar to that expected for a stoichiometric sample. With increasing values of the bulk Ca/P the surface O/P values decrease. Similar observations have recently been reported in studies of hydroxyapatite and other calcium phosphates [13]. Although some literature reports suggest that calcium hydroxyapatite is stable to temperatures in excess of 600 °C it is tempting to suggest that the orthophosphate may convert, at least partially, to the pyro-form (O/P equal to 3.5) and possibly to the metaphosphate (O/P equal to 3.0) or mixtures of these.

Table 1
Bulk and surface compositions and surface areas of CaHAp samples.

Bulk composition[a] Ca/P	t[b] (min)	Surface composition[c] Ca/P	O/P	Surface area[d] (m^2/g)
1.50	0	1.42	4.28	68.5
	1	1.65	4.28	
1.53[e]	0	1.68	4.32	65.0
	1	1.65	3.99	
1.58	0	1.37	3.40	66.5
	1	1.62	3.48	
1.67	0	1.40	3.08	69.2
	1	1.40	2.86	

[a] ICP.
[b] Etching time.
[c] XPS.
[d] BET.
[e] Anachemia.

The results of a number of studies on the effect of temperature on the properties of CaHAp have been reported [1,2,14–16] and most recently Tanaka *et al.* [17] have shown that, with a nonstoichiometric CaHAp (Ca/P equal to 1.62) the number of surface P–OH decreases by approximately 60% on heating to 500 °C, resulting in the formation of P–O–P groups as

$$2\text{P–OH} \rightarrow \text{P–O–P} + H_2O$$

the reverse of which can occur on addition of water. Such dehydroxylation/hydroxylation processes are, of course, reminiscent of those found with phosphates containing cations other than calcium, for example, boron [18]. Further, these authors noted that the thermal decomposition of nonstoichiometric CaHAp has been proposed to result in the conversion of a portion of the original orthophosphate groups to the pyrophosphate form as [3,17,19,20]

$$\begin{aligned} &Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x} \\ &\quad \rightarrow Ca_{10-x}(P_2O_7)_x(PO_4)_{6-2x}(OH)_2 \quad (0 < x < 1) \end{aligned}$$

with a further degradation, accompanied by the loss of water, to form the stoichiometric hydroxyapatite and calcium orthophosphate.

^{31}P MAS NMR spectra for all the samples pretreated at 500 °C for 3 h are virtually identical with a single ^{31}P resonance at approximately 3 ppm shift (relative to 85% H_3PO_4) (not shown). Very weak sidebands in all samples can be interpreted as indicative of the virtual absence of chemical shift anisotropy and hence little or no perturbation of the tetrahedral symmetry of the phosphate ions [1]. Since only one chemical shift was observed, all phosphate ions have similar environments. These observations are remarkable since it would be expected that nonstoichiometric CaHAp should contain HPO_4^{2-} ions for which significantly different ^{31}P NMR MAS spectra have been reported [21].

The 1.53 Ca/P sample, aliquots of which were heated to 700, 800 and 900 °C before the ^{31}P NMR MAS spectra were recorded at room temperature, showed no discernible differences from those found with the remaining compositions.

^{1}H NMR MAS spectra of all 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]. As expected the intensities of the latter resonances decreased with pretreatment temperature.

3.2. Methanol conversion

Preliminary experiments were performed to show that the homogeneous reaction contributed negligibly under the reaction conditions employed in the present work.

The effect of temperature on the nature of the products, the conversion of methanol and the coking of the catalyst was also examined in preliminary experiments to establish the appropriate range of reaction conditions. At a partial pressure of methanol of 4 kPa, a flow rate of 15 ml min^{-1} and reaction temperatures up to 723 K with all CaHAp compositions, the principal products from the conversion of methanol were dimethyl ether (DME), CO, CH_4 and CO_2, while under the same conditions but higher temperatures formaldehyde was also formed. At temperatures up to 773 K the selectivity to DME was greater than 90%. At temperatures greater than 773 K some evidence of coking was observed and at 873 K the catalyst was black after 30 min on-stream.

The effects of changes in the partial pressure of methanol, the residence time and the reaction temperature were examined in more detail. The conversions of methanol were found to be linear in W/F at 723 K as illustrated for the 1.53 Ca/P catalyst sample in figure 1. However, the conversion decreased with increase in the partial pressure of methanol (figure 2). The conversion was also found to be influenced negatively by the introduction of water vapour (figure 3). Finally, the reciprocal of the rate was shown to correlate linearly with $P(H_2O)/P(\mathrm{MeOH})$ (figure 4).

Evidently the reaction can be represented by a Langmuir–Hinshelwood expression of the form

$$r = \frac{kK_{\mathrm{MeOH}}P_{\mathrm{MeOH}}}{1 + K_{\mathrm{MeOH}}P_{\mathrm{MeOH}} + K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}}, \qquad (1)$$

$$\frac{1}{r} = \frac{1}{k} + \frac{K_{\mathrm{H_2O}}}{kK_{\mathrm{MeOH}}}\left(\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{MeOH}}}\right), \qquad (2)$$

when

$$(K_{\mathrm{MeOH}}P_{\mathrm{MeOH}} + K_{\mathrm{H_2O}}P_{\mathrm{H_2O}}) \gg 1,$$

from which the values of k (the rate constant) and $K_{\mathrm{H_2O}}/K_{\mathrm{MeOH}}$ (the ratio of the adsorption equilibrium constants) can be calculated.

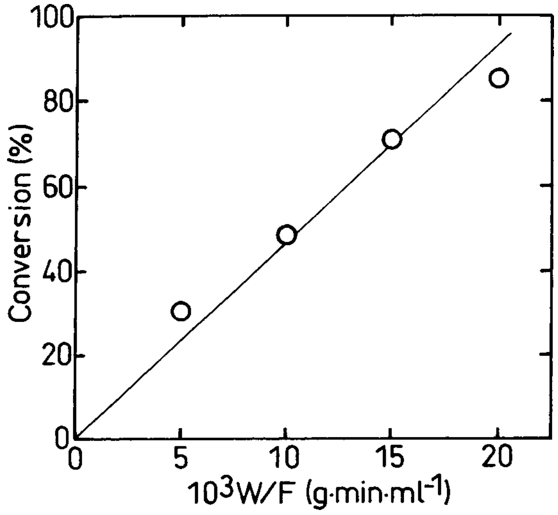

Figure 1. Conversion of methanol *versus* residence time on 1.53 CaHAp at 723 K, $P(CH_3OH) = 4$ kPa and 30 min on-stream.

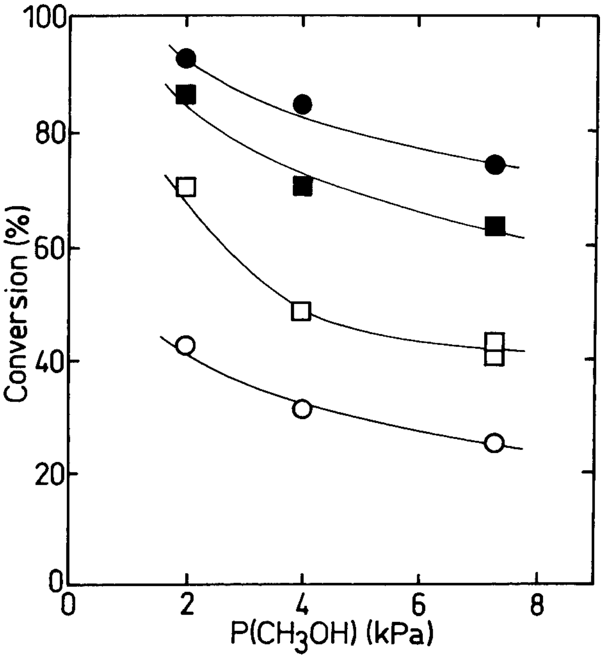

Figure 2. Conversion of methanol as a function of $P(CH_3OH)$ for various loadings of 1.53 CaHAp. Reaction temperature, 723 K. (○) $w = 0.1$ g; (□) $w = 0.2$ g; (■) $w = 0.3$ g; (●) $w = 0.4$ g.

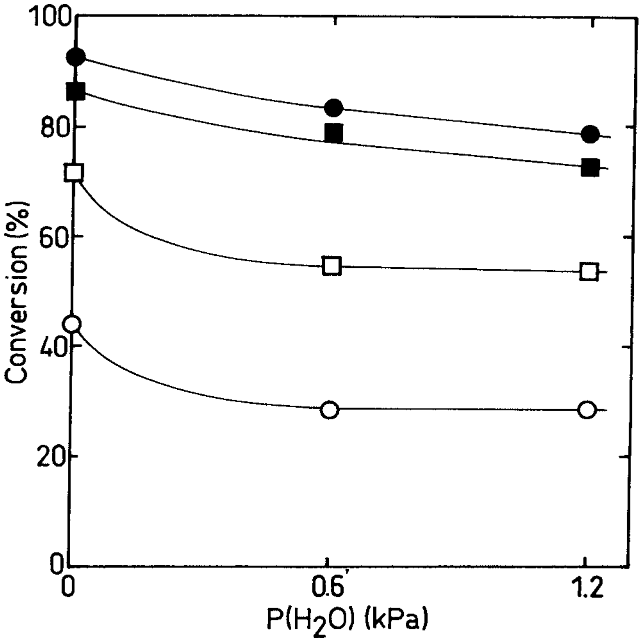

Figure 3. The effect of water on the conversion of methanol for various loadings of 1.53 CaHAp. Reaction temperature, 723 K. (○) $w = 0.1$ g; (□) $w = 0.2$ g; (■) $w = 0.3$ g; (●) $w = 0.4$ g.

Values of the conversion and the selectivities to products were obtained at 723 K and a methanol partial pressure of

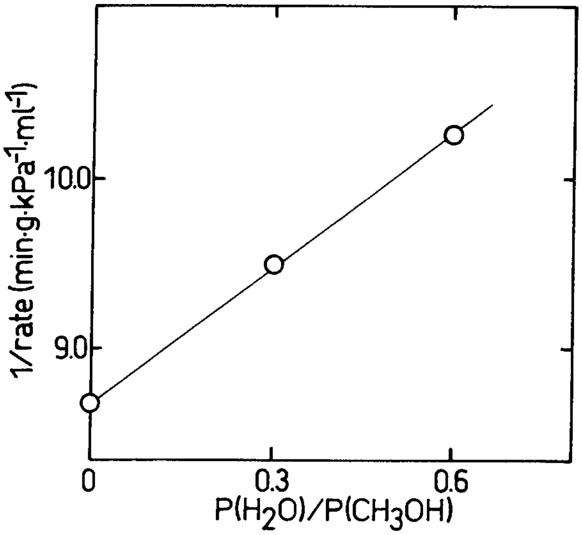

Figure 4. Correlation of 1/rate with $P(H_2O)/P(CH_3OH)$ on 1.53 CaHAp. Reaction temperature, 723 K.

Table 2
Kinetic data from application of LH equation.

Ca/P		k^c	$K(H_2O)/$
IC[a]	XPS[b]	((kPa ml)/(min g))	$K(CH_3OH)^d$
1.50	1.42	82	1.2
1.53	1.68	115	0.3
1.58	1.37	53	1.3
1.67	1.40	76	0.7

[a] From ion chromatography.
[b] From XPS.
[c] Rate constant.
[d] Ratio of adsorption equilibrium constants.

2.0 kPa by carrying out experiments at 0, 0.6 and 1.2 kPa of water and sample sizes of 0.1, 0.2 and 0.3 g for each of the four CaHAp compositions. The aforementioned conditions were selected to generate conversions which were in a range sufficiently low so as to justify application of equations (1) and (2) as well as minimizing catalyst deactivation. The results obtained are summarized in table 2.

Although values obtained from intercepts must be interpreted with caution, nevertheless it is of interest to compare the results reported in table 2. While no correlation is observed between any of the calculated values and the bulk composition of the catalysts, the rate constant for methanol conversion appears to increase with the surface Ca/P ratio. No such correlation exists for the ratio of adsorption equilibrium constants and it may be prudent to conclude that, within experimental error, the equilibrium constants for water and methanol are, at least approximately, equal for all four catalyst compositions. The nature of the surface sites and the effect of water and methanol as catalyst poisons will be discussed in more detail in the next section.

3.3. Infrared spectra

Infrared spectra of CaHAp provided further information on the conversion process (figure 5). After evacuation at 873 K for 2 h the catalyst was exposed to 4 kPa methanol at 298 K for 1/4 h followed by evacuation at the same temperature for 1/2 h. Bands at 2844, 2839 and 2943 cm^{-1} are attributed to the CH stretching vibration of methoxy groups while that at 2926 cm^{-1} may be related to a CH_3 bonding overtone [23–26]. The band at 2831 cm^{-1} is tentatively attributed to CH vibrations of $–O–CH_2–O$ or –O–CH–O species [26,27]. These bands decreased in intensity on evacuation at 473 K and vanished after evacuation at 723 K.

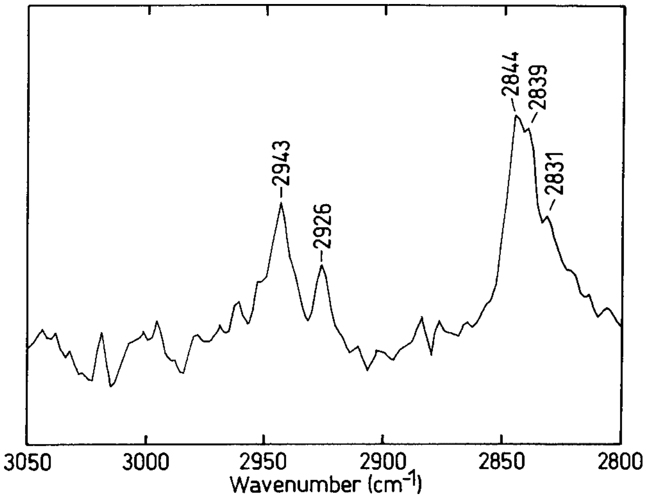

Figure 5. Infrared spectra of 1.53 CaHAp evacuated at 873 K for 2 h and exposed to 4 kPa methanol at 298 K for 1/4 h followed by evacuation at 298 K for 1/2 h.

After a similar treatment but exposure to 2 kPa of water IR bands (~3000 cm^{-1}) attributable to sorbed water appeared but vanished after evacuation at 473 K (not shown).

IR spectra obtained after adsorption of water (2 kPa) followed by methanol (4 kPa) displayed the bands found in the spectra of the individual species but the intensities of those due to methanol were considerably diminished showing that the adsorption of methanol is reduced by previously adsorbed water.

3.4. Temperature-programmed desorption

TPD of 1.53 CaHAp shows that both CO and CO_2 begin to desorb at approximately 120 °C (figure 6). Both of the carbon oxides show desorption maxima at 174 and 292 °C. The sorption properties of CaHAp for CO_2 are well known and measurements at 78 K have suggested that the oxide is both reversibly and irreversibly adsorbed [28–30]. It may be speculated that the aforementioned two peaks correspond to these forms. In contrast, water is steadily evolved in small quantities beginning at room temperature but increasing substantially at 350 °C.

For methanol TPD experiments, a sample of 1.53 CaHAp is at first heated for 1/2 h at 450 °C in a 20 ml/min flow of helium, held for 1/2 h at room temperature, exposed to 4 kPa methanol in the aforementioned helium flow at room temperature and finally retained in the flow of helium for 1/2 h. TPD experiments employed a heating rate of 10 °C/min.

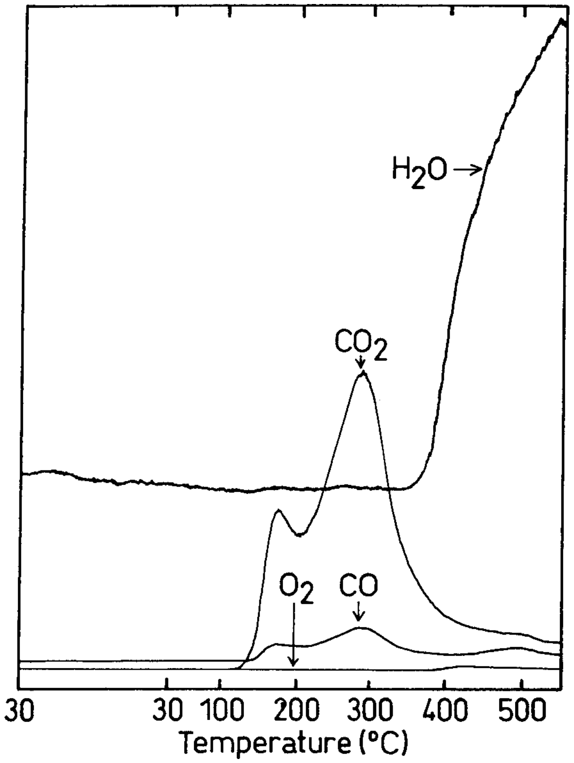

Figure 6. TPD of 1.53 CaHAp. Heated in a flow (20 ml/min) of helium at 303 K for 10 min followed by a temperature ramp of 10°/min.

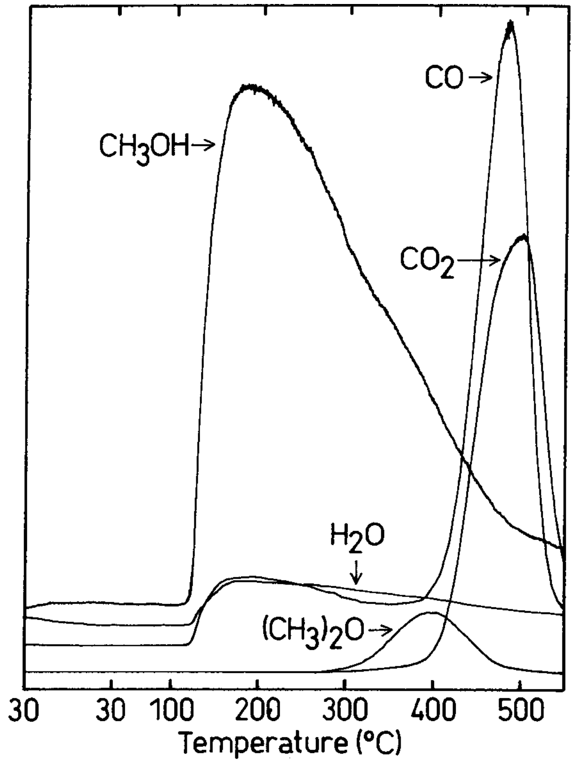

Figure 7. TPD of 1.53 CaHAp with preadsorbed methanol (conditions as in text).

At 120 °C methanol, water and CO begin to desorb (figure 7), the latter as observed with 1.53 CaHAp in the absence of methanol (*cf.* figure 6). The desorption of these species reached a maximum at 186 °C. It appears that these species are molecularly adsorbed. DME, evidently resulting from the combination of surface methoxy groups, and CO_2 began to desorb at 270 °C, the former showing a maximum at 398 °C, the latter at 500 °C. CO reached a secondary maximum at 483 °C. The latter corresponds, at least approximately, to the temperatures at which CO and H_2 were observed from methanol in the reactor experiments. It should be noted that water does not display a desorption maximum coincident with that of DME and is apparently produced in the course of the formation of surface methoxy groups which are the precursors to DME. Since, as observed in the reactor experiments no significant conversion of methanol occurs at temperatures below 350 °C the onset of the desorption of DME at 270 °C as observed in the TPD experiments implies that, as expected from the kinetic data, the rate of the reaction is controlled by the adsorption of methanol.

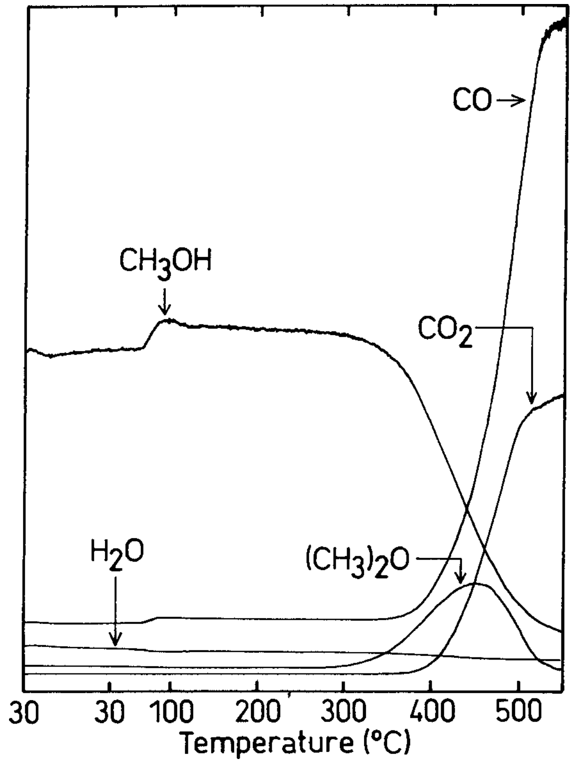

Figure 8. TP reaction of methanol on 1.53 CaHAp (conditions as in text).

Temperature-programmed reaction experiments in which 4 kPa of methanol diluted with helium were continuously passed over 1.53 CaHAp, previously heated for 1/2 h at 450 °C in a flow of helium, again displayed the desorption of DME beginning at 270 °C (figure 8), as found with the TPD experiments (*cf.* figure 7). Since little or no loss of methanol from the feed stream was observed at this temperature the DME is evidently being formed from methoxy groups already present on the surface. The gas phase concentration of methanol begins to decrease substantially at approximately 330 °C with CO_2 appearing at 370 °C and the maximum in the DME peak at 450 °C, somewhat higher than found in the TPD experiments.

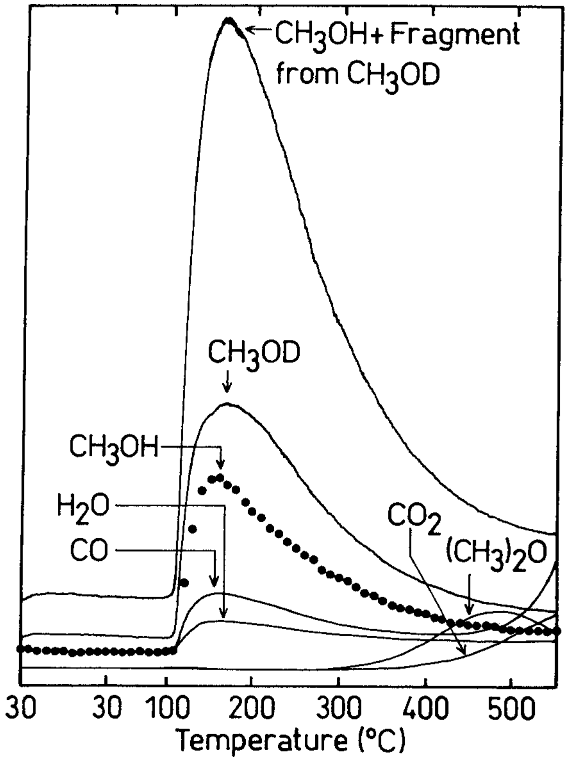

Figure 9. TPD of preadsorbed MeOD (conditions as in text).

TPD experiments with preadsorbed deuterated methanol (CH_3OD) produced patterns similar (figure 9), not surprisingly, to those observed with undeuterated methanol (*cf.* figure 7). Desorption of both CH_3OD and CH_3OH begins at approximately 105 °C, the presence of the latter being indicative of the deuterium/hydrogen exchange between the alcohols, either directly or indirectly.

Although care must be exercised in interpreting mass spectrometric data for the desorption of water, nevertheless some comments on these results may be of value. With all compositions of CaHAp the quantity of HDO exceeded that of the remaining isomers of water, at least initially (not shown). This suggests that the formation of the surface methoxy groups proceeds via the interaction between the protium contained on the surface and the oxygen of the deuterated methanol and not through a bimolecular pathway, a conclusion which is again consistent with the kinetics evidence.

Acknowledgement

The authors gratefully acknowledge funding from the Natural Sciences and Engineering Research Council of Canada to JBM and by the Japanese Ministry of Education to SS as an overseas researcher in the Department of Chemistry at the University of Waterloo.

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 (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] E. Hayek and H. Newesely, Inorg. Synth. 7 (1963) 63.

[11] S. Sugiyama, T. Minami, H. Hayoshi, M. Tanaka, N. Shigemoto and J.B. Moffat, J. Chem. Soc. Faraday Trans. 92 (1996) 293.

[12] S. Sugiyama, T. Yasutomi, T. Moriga, H. Hayashi and J.B. Moffat, J. Solid State Chem. 142 (1999) 319.

[13] H.B. Lu, C.T. Campbell, D.J. Graham and B.D. Ratner, Anal. Chem. 72 (2000) 2886.

[14] H.M. Rootare and R.G. Craig, Anal. Calorimetry 3 (1974) 381.

[15] S.S. Barton and B.H. Harrison, J. Colloid Interface Sci. 55 (1976) 409.

[16] H. Tanaka, T. Watanabe and M. Chikazawa, J. Chem. Soc. Faraday Trans. 93 (1997) 4377.

[17] H. Tanaka, M. Chikazawa, K. Kandori and T. Ishikawa, Phys. Chem. Chem. Phys. 2 (2000) 2647.

[18] J.B. Moffat and J.F. Neeleman, J. Catal. 34 (1974) 376;
J.B. Moffat, Catal. Rev. Sci. Eng. 18 (1978) 199.

[19] H. Monma, S. Veno and T. Kanazawa, J. Chem. Technol. Biotechnol. 31 (1981) 15.

[20] L. Winand, Ann. Chim. 6 (1961) 941.

[21] W.P. Rothwell, J.S. Waugh and J.P. Yesinowski, J. Am. Chem. Soc. 102 (1980) 2637.

[22] J.P. Yesinowski and H. Eckert, J. Am. Chem. Soc. 109 (1987) 6374.

[23] G.A.M. Hussein, N. Sheppard, M.I. Zaki and R.B. Fahim, J. Chem. Soc. Faraday Trans. 87 (1991) 2635.

[24] C. Chauvin, J. Saussey, J.C. Lavalley, H. Idriss, J.-P. Hindermann, A. Kiennemann, P. Chaumette and P. Courty, J. Catal. 121 (1990) 56.

[25] M.-Y. He and J.G. Ekerdt, J. Catal. 87 (1984) 381.

[26] Y. Matsumura and J.B. Moffat, J. Chem. Soc. Faraday Trans. 92 (1996) 1981.

[27] H. Idriss, J.P. Hindermann, R. Kieffer, A. Kiennemann, A. Vallet, C. Chauvin, J.C. Lavalley and P. Chaumette, J. Mol. Catal. 42 (1987) 205.

[28] T. Ishikawa, M. Wakamura and S. Kondo, Langmuir 5 (1989) 140.

[29] T. Ishikawa, Stud. Surf. Sci. Catal. 99 (1996) 301.

[30] Z.H. Cheng, A. Yasukawa, K. Kandori and T. Ishikawa, Langmuir 14 (1998) 6681.