ssue

Methanol adsorption and dehydrogenation over stoichiometric and non-stoichiometric hydroxyapatite catalysts

Yasuyuki Matsumura^a and John B. Moffat^{b,*}

^b Department of Chemistry and Guelph-Waterloo Centre for Graduate Work in Chemistry,

University of Waterloo, Waterloo, Ontario, N2L 3G1 Canada

On hydroxyapatite of stoichiometric composition (Ca/P = 1.65), methanol decomposes at 600 °C, in the absence of oxygen, to produce predominantly carbon monoxide. As the Ca/P ratio decreases, the selectivities to formaldehyde and dimethyl ether increase to *ca.* 80% at a value of Ca/P equal to 1.51. IR spectra show that methoxy groups are formed on the surface of both the stoichiometric and non-stoichiometric catalysts. Both IR and temperature-programmed desorption experiments suggest that for the decomposition of methanol, acidic sites are required for the dissociative adsorption whereas basic sites facilitate the C—H bond scission *via* carboxylate groups and the consequent formation of CO and H₂.

The conversion of methanol to formaldehyde is a process of both fundamental and practical interest.¹ Formaldehyde, which has become one of the world's most important industrial and research chemicals,¹ is commonly produced by two processes, one making use of a silver catalyst while the other is catalysed by a metal oxide. Two simultaneous reactions, one exothermic oxidation, the other endothermic, are believed to occur with the former catalyst:

CH₃OH +
$$\frac{1}{2}$$
O₂ → H₂CO + H₂O ($\Delta H = -156 \text{ kJ mol}^{-1}$)
CH₃OH → H₂CO + H₂ ($\Delta H = +85 \text{ kJ mol}^{-1}$)

but only the first reaction apparently occurs with the latter catalysts. While the mechanisms in either case are not completely understood, nevertheless, with the silver catalysts, the current consensus appears to favour the formation of formal-dehyde through the interaction of gas-phase methanol with dissociatively adsorbed oxygen.²

As a consequence of interest in both the methanol conversion process as well as the synthesis of methanol a number of publications concerned with the adsorption and decomposition of methanol have appeared in recent years. Studies of the adsorption and decomposition of methanol on solid surfaces have heretofore focused on single-crystal surfaces, for obvious reasons.³ However, reports of the results of work on a variety of oxides and related catalysts have also recently appeared.⁴⁻¹²

Hydroxyapatites $[Ca_{10-z} (HPO_4)_z (PO_4)_{6-z} (OH)_{2-z}, (0 \le z \le 1)]$ are known to catalyse acid-base reactions such as the dehydrogenation and dehydration of ethanol.¹³ The stoichiometric apatite (z = 0) has been shown to possess basic sites, while the non-stoichiometric forms function as acids.¹³⁻¹⁹

Recent work from this laboratory has shown that hydroxyapatites of various compositions display interesting properties in the catalysis of methane oxidation. Thus hydroxyapatite modified with lead catalyses the oxidative dehydrogenation of methane with high selectivity to C_2 compounds.^{20,21} In contrast, hydroxyapatite of approximately stoichiometric composition (Ca/P = 1.65) produces mainly carbon dioxide while the selectivity to formaldehyde increases with decrease in the Ca/P ratio, although carbon monoxide is the major product.²² Since hydrogen is also formed in the latter reaction, it appears that oxidation can proceed *via* intermediates resembling methanol.

In the present work, the results of studies of the adsorption

and decomposition of methanol on stoichiometric and nonstoichiometric hydroxyapatite are reported. It is shown that non-stoichiometric hydroxyapatite can catalyse the dehydrogenation of methanol to formaldehyde without further decomposition of the latter to carbon monoxide and hydrogen. To provide further information on the reaction intermediates and the mechanism by which methanol decomposes to carbon monoxide with concomitant reduction in the selectivity to formaldehyde, IR spectra of the surface species on both stoichiometric and non-stoichiometric apatites and profiles of the temperature-programmed desorption of these solids with previously adsorbed methanol have been obtained.

Experimental

Hydroxyapatites $(Ap_{1.65}, Ap_{1.61}, Ap_{1.55} \text{ and } Ap_{1.51};$ the numerical subscript indicates the Ca/P molar ratio of the apatites) were prepared from $Ca(NO_3)_2 \cdot H_2O(BDH AnalaR)$ and $(NH_4)_2HPO_4$ (BDH AnalaR) according to the method described in ref. 23. The resulting solid was heated in air at 500 °C for 3 h and crushed into 180-300 mesh. The Ca/P molar ratios of the hydroxyapatites were determined by analysing the concentrations of Ca^{2+} and PO_4^{3-} ions in the solution remaining from the synthesis by ion chromatography (Dionex 4500i). Formation of hydroxyapatite was confirmed by recording the X-ray diffraction (XRD) patterns for these samples.²⁴ The sample of β -calcium pyrophosphate $(Ca_2P_2O_7)$ was prepared by heating CaHPO₄ (BDH) in air at 860 °C for 3 h¹³ and β -tricalcium phosphate [Ca₃(PO₄)₂] was obtained by heating Ap_{1.51} at 1000 °C for 2 h.¹⁸ Calcium carbonate (CaCO₃, BDH AnalaR) and calcium oxide (CaO, Aldrich 99.995%) were heated in air at 500 °C for 2 h.

Methanol conversion was performed in a conventional fixed bed continuous flow reactor operated under atmospheric pressure. The reactor consisted of a quartz tube of 7 mm id and 35 mm in length, sealed at each end to 4 mm id quartz tubes. The catalyst was sandwiched with quartz wool plugs, the contribution of which to the reaction was negligible. Methanol was supplied from a saturator (CH₃OH, 2 kPa; total flow rate 0.9 dm³ h⁻¹). The catalysts (0.05–0.30 g) were preheated in a flow of helium (flow rate, 0.9 dm³ h⁻¹) at 600 °C for 1 h. The reactants and products were analysed with an on-stream gas chromatograph (HP 5880) equipped with a thermal conductivity detector (TCD). A combination of three columns, Porapak T (2.7 m), Porapak Q (2.7 m), and Molecular Sieve 5A (0.2 m) was employed in the analyses.

J. Chem. Soc., Faraday Trans., 1996, 92(11), 1981–1984 1981

^a Osaka National Research Institute, AIST, Midorigaoka, Ikeda, Osaka 563, Japan

Selectivities (in mol%) were calculated on the basis of the carbon contents in products determined by the GC analysis. Accuracies in the carbon balances were always better than 97%.

The surface areas of the catalysts were calculated by application of the BET theory to nitrogen adsorption isotherms obtained at 78 K.

Temperature programmed desorption of CD₃OD from hydroxyapatite was carried out in a vacuum system equipped with a ULVAC QMS-150A mass spectrometer. The sample was evacuated at 600 °C for 1 h before the adsorption. After exposure to *ca*. 5 kPa of CD₃OD (CEC, 99.8%) at 200 °C for 0.2 h, the sample was evacuated at 200 °C for 0.3 h. The sample was then heated at a rate of 10 °C min⁻¹ under evacuation (less than 0.03 kPa) and the desorbing gas was monitored with the mass spectrometer.

IR spectra of adsorption species were recorded with a Bomem MB-100 FTIR spectrometer at room temperature. The sample (0.03 g) was pressed into a self-supporting wafer and placed into an IR cell allowing heating under vacuum. The sample was evacuated at 600 °C for 1 h before adsorption of methanol (2 kPa) at 200 °C for 0.2 h followed by evacuation at the same temperature for 0.5 h.

Results

Decomposition of methanol

In the absence of oxygen, formaldehyde was produced from methanol with the hydroxyapatites at 600 °C and carbon monoxide, carbon dioxide, methane, hydrogen, dimethyl ether, water, methane, ethane and ethene were also detected (Table 1). The selectivities to formaldehyde and dimethyl ether decreased with increasing Ca/P ratio of the hydroxyapatite samples while those for the carbon oxides increased. Similar values of 40–50 m² g⁻¹ were found for the surface areas of the hydroxyapatite samples after use in the reaction. Since only 0.05 g of $Ap_{1.65}$ produced a methanol conversion of 94.9%, with carbon monoxide as the predominant product, it is evident that hydroxyapatite of this composition has significant activity in the decomposition process. Although catalytic activity was reasonably stable for a duration of 3 h, the colours of the catalysts, originally white, were found to be black after the reaction, indicating the formation of coke during the reaction.

Selectivities to formaldehyde as high as those observed with $Ap_{1.55}$ were also found with calcium phosphate and pyrophosphate while carbon monoxide was the predominant product with calcium carbonate and calcium oxide.

Temperature-programmed desorption (TPD) of CD₃OD from hydroxyapatite

To clarify the mechanism of the methanol decomposition, TPD measurements for CD_3OD adsorbed on $Ap_{1.65}$ and on

Ap_{1.51} at 200 °C were performed. With Ap_{1.51}, desorption of CD₃OD (m/e = 36) began at *ca*. 200 °C with the maximum appearing at *ca*. 250 °C (Fig. 1). Between 450 and 600 °C, both D₂CO (m/e = 32) and a species with m/e equal to 28 were desorbed. The latter species also exhibited a secondary maximum at *ca*. 680 °C. Although this species could be due to a fragment of D₂CO, no other fragment peak of D₂ (m/e = 4) or D (m/e = 2) was observed in this temperature range, suggesting that the desorbing species is primarily CO. Although the adsorbed methanol was fully deuteriated, no desorption of D₂ (m/e = 4) were desorbed with peak maxima at *ca*. 550 and 580 °C, respectively. Desorption of a small amount of CO₂ (m/e = 44) was observed above 600 °C.

With Ap_{1.65}, desorption of CD₃OD was also observed at 200-350 °C. Desorption of CO (m/e = 28), D₂ (m/e = 4), HD and H₂ was observed between 370 and 530 °C (Fig. 2). Small quantities of CO₂ (m/e = 44) and D₂CO (m/e = 32) were detected at and above 600 °C, respectively.

IR spectra of surface species

The adsorption and evacuation of methanol at 200 °C on $Ap_{1.51}$ produced IR bands at 2853, 2915, 2956 and 3005 cm⁻¹



Fig. 1 TPD profiles of CD₃OD adsorbed on $Ap_{1.51}$ at 200 °C. Rate of temperature increase, 10 °C min⁻¹.

Table 1 Methanol decomposition over hydroxyapatites and other calcium compounds^a

catalyst	amount /g	methanol conversion (%)	selectivity (%)						
			H ₂ CO	со	CO ₂	CH₄	(CH ₃) ₂ O	C ₂	SA ^b
Ap, .,	0.15	85.2	51.1	11.1	0.0	9.8	27.1	0.8	48.8
Ap. 55	0.15	96.6	36.8	46.1	0.6	4.9	11.0	0.7	43.1
Ap _{1.61}	0.15	95.0	9.3	60.7	3.8	19.7	6.2	0.8	46.0
Ap _{1.65}	0.15	100.0	0.2	79.1	10.4	8.3	1.9	0.0	38.1
Ap _{1.65}	0.05	94.9	2.7	68.9	12.7	11.0	3.9	0.8	
Ca,P,O,	0.30	14.7	43.0	8.9	0.0	12.3	35.8	0.0	<2
Ca (PO)	0.30	72.2	36.2	25.9	8.3	8.8	20.0	0.8	3.0
CaCO,	0.30	34.9	2.9	86.2	8.2	2.6	0.2	0.0	<2
CaO	0.15	100.0	0.0	96.3	2.5	1.2	0.0	0.0	<2

^{*a*} Reaction conditions unless otherwise noted: partial pressure of methanol, 2 kPa; total flow of reactant gas, 0.9 dm³ h⁻¹; reaction temperature, 600 °C; time-on-stream, 3 h. ^{*b*} BET surface area after reaction (m² g⁻¹).



Fig. 2 TPD profiles of CD₃OD adsorbed on Ap_{1.65} at 200 °C. Rate of temperature increase, 10 °C min⁻¹.

attributed to surface adsorption species [Fig. 3(a)]. Since the bands which appeared after the adsorption were weak and no significant changes in the original bands for hydroxyapatite were observed after the adsorption,²² the original bands were subtracted from the spectrum obtained after adsorption.

The bands at 2852 and 2956 cm⁻¹ can be assigned to the CH stretching vibration of methoxy groups,^{6.8,25} while that at 2915 cm⁻¹ is probably a CH₃ bending overtone.^{3a} Assignment of the band at 3005 cm⁻¹ is unclear but Hussein and Sheppard attributed the band to the CH stretching vibration of methane adsorbed on the surface.²⁶

The adsorption and evacuation of methanol on Ap_{1.65} at 200 °C also produced a spectrum similar to that obtained from Ap_{1.61} but with evident differences [Fig. 3(b)]. Peaks at 2845 and 2951 cm⁻¹ can, as before, be attributed to methoxy groups^{6,8,25} while those at 2788 and 2831 cm⁻¹ are tenta-



Fig. 3 IR spectra for the surface species on hydroxyapatites after methanol adsorption and evacuation at $200 \,^{\circ}\text{C}$

tively assigned to CH vibrations of $-O-CH_2-O-$ or -O-CH-O- species²⁷ with a small peak at 3008 cm⁻¹.

A new band at 1595 cm⁻¹ was also observed [Fig. 3(c)]. Although there were strong bands at 1300–1500 cm⁻¹ in the background spectra²² and subtraction of the background from the spectrum of the sample with methanol adsorbed at 200 °C was not perfect, a weak band at 1354 cm⁻¹ appeared in the background—corrected spectrum. Thus, the band at 1595 cm⁻¹ is assigned as an asymmetric stretching vibration of the carboxylate groups.^{25,28,29}

Discussion

The TPD profiles for $Ap_{1.51}$ and $Ap_{1.65}$ after adsorption of CD₃OD are strikingly dissimilar, not only in the desorption temperatures and the relative intensities of the desorption peaks, but also in the species which are desorbed. With Ap_{1,51}, diprotium was desorbed at temperatures rather higher than the desorption temperatures of formaldehyde and the quantity of HD desorbed is significantly smaller than that of H_2 (see Fig. 1), suggesting that the formation of a hydrogen molecule does not inevitably accompany the formation of a formaldehyde molecule. The production of formaldehyde requires the abstraction of a hydrogen atom from a surfacebound methoxy group. Since deuterium molecules are not concomitantly desorbed with formaldehyde molecules, it must be concluded that they remain on the surface. Two possibilities apparently exist. The deuterium atoms released from the surface-bound methoxy groups as evidenced in the IR spectra may deuteriate oxygen atoms attached to calcium or phosphorus atoms and/or exchange with protium atoms of previously existing hydroxy groups. In any event the emergence of HD and H₂ demonstrates the existence of protium atoms on the surface prior to and after the dissociative adsorption of methanol on Ap_{1.51}. Although it is conceivable that calcium hydride or deuteride existed on the surface before and after the decomposition, the IR spectrum provided no evidence for this.

With Ap_{1,65}, little or no formaldehyde is formed from the adsorption and decomposition of methanol (see Table 1). The TPD profiles are consistent with these results (see Fig. 2). Little or no formaldehyde is desorbed while CO, D₂, HD and H₂ are desorbed at approximately coincident temperatures. Furthermore, the temperature at which these species are desorbed on Ap_{1.65} is considerably lower than that at which formaldehyde emerges from Ap_{1.51}. A somewhat different sequence of events is required for the production of carbon monoxide and hydrogen on the stoichiometric hydroxyapatite, in contrast with those where formaldehyde is formed. Although the IR data provide evidence for the formation of methoxy groups on the surface of both the stoichiometric and non-stoichiometric catalyst and the peak intensities for the methoxy groups are comparable (see Fig. 3), the subsequent mechanistic steps with the former catalyst follow a different course. The remaining deuterium atoms in the surface methoxy group must be released, necessarily requiring the scission of the associated C-D bonds. A number of factors will be responsible for this process. The basic sites of the stoichiometric hydroxyapatite will exert an attractive interaction on the deuterium atoms of the surface methoxy group and will consequently weaken the C-D bonds. The deuterium atoms may become attached to the basic sites or combine with each other to form D_2 which is released to the gas phase. Alternatively, the deuterium atoms may extract protium atoms from the surface to emerge as HD. The presence of basic sites is thus essential for the dissociative process. Excess electrons resulting from the dissociation of the C-D bonds will be back-donated to the C-O bonds of the methoxy groups, increasing the electron density and hence the bond order in the internuclear region between the carbon and oxygen atoms.

A concomitant reduction in electron density between the oxygen atom and the surface will occur as that of the carbonoxygen bond approaches a value similar to that found in the free carbon monoxide molecule. The presence of a significant quantity of carboxylate groups on Ap_{1.65}, which correlates with the observation that the quantity of CO desorbed from Ap_{1.65} is greater than that of CO and D₂CO from Ap_{1.65}, provides additional evidence for the attractive interaction between hydrogen atoms (or protons) and the basic sites present on the surface of the stoichiometric hydroxyapatite. With other solids, such as calcium oxide, the carboxylate groups have been regarded as didentate structures.^{30,31} On vanadium-based catalysts it has been concluded that methoxy groups are converted to dioxymethylene species on heating, which are rapidly desorbed as formaldehyde.³²

Comments on the nature and source of the basic sites are relevant here. From a purely stoichiometric viewpoint, the existence of a Ca/P ratio of ca. 5/3 requires additional negative charges to provide charge balance. These are provided by basic hydroxy groups. Additionally, quantities of carbonate are present on the surface of the stoichiometric hydroxyapatite, in part at least resulting from the adsorption of CO₂, the amount decreasing with decrease in the Ca/P molar ratio of the apatite, as expected in view of the acidic properties of those catalysts with lower values of Ca/P.¹⁸ A portion of these carbonate groups may be decomposed to calcium oxide at 600 °C, thus producing CO₂ which is desorbed. Since it is known that carboxylate groups can exist on the surface of calcium oxide,²⁸ the formation of this oxide may contribute to the basic sites available on the stoichiometric hydroxyapatite. Since, on CaO and CaCO₃, carbon monoxide is the predominant product while formaldehyde is formed over $Ca_2P_2O_7$ and $Ca_3(PO_4)_2$, the surface oxide is apparently the active site for the decomposition of methanol to carbon monoxide (see Table 1).

Since the selectivity to carbon dioxide increases with increasing Ca/P ratio of hydroxyapatite (Table 1), formation of carbon dioxide may result, at least in part, from the decomposition of the surface carbonate species of hydroxyapatite. However, disproportionation of carbon monoxide to carbon dioxide and carbon and/or the water-gas shift reaction may also occur. The formation of methane may be partly due to hydrogenation of dimethyl ether formed by dehydration of methanol, probably on acid sites of hydroxyapatite, $^{13-15}$

$$(CH_3)_2O + 2H_2 \rightarrow 2CH_4 + H_2O^5$$

Finally it is of some interest compare the methanol adsorption and decomposition process with that of methane oxidation. As noted in the introduction, the selectivity to formaldehyde in methane oxidation increases with decrease in the Ca/P ratio of the calcium hydroxyapatite. In the present work with methanol, a similar observation has been made. Although basic sites have been suggested as necessary for the activation of methane,²¹ *i.e.* for C—H bond scission, the subsequent steps in the process apparently do not involve the adsorption of the methyl radical on the surface of the catalyst. Although highly speculative, it is tempting to argue that in the decomposition of methanol acidic sites are required for the dissociative adsorption whereas basic sites, as with the activa-

tion of methane, facilitate the C–H bond scission and in the case of methanol, the formation of CO and H_2 .

The authors sincerely thank Professor Seiichiro Imamura of Kyoto Institute of Technology for assistance in the TPD measurements. The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

References

- Kirk-Othmer Enyclopedia of Chemical Technology, Wiley-Interscience, New York, 4th edn., vol. 11, 1994, p. 929.
- 2 C. A. Bazilio, W. J. Thomas, U. Ullah and K. E. Hayes, Proc. R. Soc. London, A, 1985, 399, 181.
- 3 See, for example, (a) D. B. Clarke, D-K. Lee, M. J. Sandoval and A. T. Bell, J. Catal., 150, 81; (b) B-R. Sheu and D. R. Strongin, Langmuir, 1994, 10, 1801 and references cited therein.
- 4 N. Aas, T. J. Pringle and M. Bowker, J. Chem. Soc., Faraday Trans., 1994, 90, 1015.
- 5 S. G. Izmailov, I. V. Karetina, S. S. Khvoshchev and M. A. Shubaeva, J. Colloid Interface Sci., 1994, 165, 318.
- 6 G. A. M. Hussein, N. Sheppard, M. I. Zaki and R. B. Fahim, J. Chem. Soc., Faraday Trans., 1991, 87, 2655.
- 7 G. J. Millar, C. H. Rochester and K. C. Waugh, J. Chem. Soc., Faraday Trans., 1991, 87, 2795.
- 8 C. Chauvin, J. Saussey, J. C. Lavalley, H. Idriss, J-P. Hindermann, A. Kiennemann, P. Chaumette and P. Courty, J. Catal., 1990, 121, 56.
- 9 G. Busca, J. Mol. Catal., 1989, 50, 241.
- 10 G. Busca, P. F. Rossi, V. Lorenzelli, M. Benaissa, J. Travert and J-C. Lavalley, J. Phys. Chem., 1985, 89, 5433.
- 11 Y. Matsumura, K. Hashimoto and S. Yoshida, J. Catal., 1986, 100, 392.
- 12 K. W. Tawarah and R. S. Hansen, J. Catal., 1984, 87, 305.
- 13 C. L. Kibby and W. K. Hall, J. Catal., 1973, 31, 65.
- 14 C. L. Kibby and W. K. Hall, J. Catal., 1973, 29, 144.
- 15 C. L. Kibby, S. S. Lande and W. K. Hall, J. Am. Chem. Soc., 1972, 94, 214.
- 16 H. Monma, J. Catal., 1982, 75, 200.
- 17 Y. Izumi, S. Sato and K. Urabe, Chem. Lett., 1983, 1649.
- 18 J. A. S. Bett, L. G. Christner and W. K. Hall, J. Catal., 1969, 13, 33.
- 19 Y. Imizu, M. Kadoya and H. Abe, Chem. Lett., 1982, 415.
- 20 Y. Matsumura and J. B. Moffat, Catal. Lett., 1993, 17, 197.
- 21 Y. Matsumura, J. B. Moffat, S. Sugiyama, H. Hayashi, N. Shigemoto and K. Saitoh, J. Chem. Soc., Faraday Trans., 1994, 90, 2133.
- 22 Y. Matsumura and J. B. Moffat, J. Catal., 1994, 148, 323.
- 23 E. Hayek and H. Newesely, Inorg. Syn., 1963, 7, 63.
- 24 Index (Inorganic) to the Powder Diffraction File, ed. J. V. Smith, ASTM Publication No. PDIS-16i Philadelphia, 1966.
- 25 M-Y. He and J. G. Ekerdt, J. Catal., 1984, 87, 381.
- 26 G. A. M. Hussein and N. J. Sheppard, J. Chem. Soc., Faraday Trans., 1991, 87, 2655.
- 27 H. Idriss, J. P. Hindermann, R. Kieffer, A. Kiennemann, A. Vallet, C. Chauvin, J. C. Lavalley and P. Chaumette, J. Mol. Catal., 1987, 42, 205.
- 28 M. J. Holgado, C. Martin, I. Martin, V. Rives and S. S. Roman, React. Kinet. Catal. Lett., 1993, 49, 139.
- 29 C. Martin, I. Martin and V. Rives, J. Mol. Catal., 1992, 73, 51.
- 30 G. B. Deacon and R. J. Phillips, Coord. Chem. Rev., 1980, 33, 227.
- 31 J. A. Anderson and C. H. Rochester, J. Chem. Soc., Faraday Trans., 1986, 82, 1911.
- 32 G. Busca, J. Mol. Cat., 1989, 50, 241.

Paper 5/06925D; Received 19th October, 1995