

A high pressure, high temperature infrared study of CO hydrogenation over Rh/ZrO₂

James A. Anderson^{1,*}, Mahmoud M. Khader²

Department of Chemistry, The University, Dundee DD1 4HN, Scotland, UK

Received 5 May 1995; accepted 23 August 1995

Abstract

A Rh/ZrO₂ catalyst has been studied in the hydrogenation of CO in an in situ IR cell operating at high temperature and pressure, and using FTIR to follow the formation of surface and gas phase species as a function of reaction time. The reaction between CO and hydrogen was studied by varying the catalyst reduction temperature, reaction temperature, total pressure and hydrogen/CO ratio. Surface species identified were carbonyls on the rhodium surface, formates, carbonates and hydrocarbons. The relationship between adsorbed carbonate and formate is discussed in detail.

Keywords: Carbon monoxide; Hydrogenation; Infrared spectroscopy; Rhodium; Zirconia; Supported catalysts

1. Introduction

The conversion of synthesis gas to produce oxygenates has been shown to be highly selective only in the case of methanol formation. Many different catalysts have been tried, and many attempts have been made to determine operating conditions which would favour the selectivity to higher alcohol formation [1]. Among the various catalysts tested, rhodium has been shown to exhibit special behaviour in the CO/H₂ reaction, in that it appears very sensitive to many operative and preparative parameters [2]. Amongst the many variables which may cause changes in selectivity and activity of these catalysts, the role of the support appears to have a marked influence [2,3]. In the

case of a zirconia support, this has been shown to produce a product distribution with almost 60% selectivity to ethanol [4]. The role of zirconia in the hydrogenation of CO over rhodium has received attention [4–7], but little mechanistic detail is available [5,8]. For Rh/ZrO₂ catalysts it has been proposed that (CH_x)_n species, giving IR bands at 3000–2800 and 1450 cm⁻¹, react with CO to form the acyl precursor of ethanol [5], and that carbon monoxide bonded via both the C and O, giving an IR band at 1620 cm⁻¹ [8] may lead to enhanced CO dissociation probability and an increase in C₂ oxygenate formation [7]. It is apparent that IR spectroscopy is an ideal method to study these catalysts, and by operating under conditions of high temperature and high pressure, determine whether such species exist during reaction, and hence speculate as to whether they may play a part in the overall reaction mechanism.

* Corresponding author.

¹ Royal Society Research Fellow.

² Present address: Chemistry Department, U.A.E University, Al-Ain, United Arab Emirates.

2. Experimental

The catalyst was prepared by using a commercial zirconia supplied as the hydroxide by Magnesium Electron Ltd (XZO645/1). This material had a particle size of 1 μm and contained 3.5% SiO_2 as a stabilising agent. This material was converted to the oxide prior to impregnation with rhodium salt, by calcining in air at 773 K for 2 h. The resultant support had a BET surface area of $100 \text{ m}^2 \text{ g}^{-1}$, an average pore volume of $0.13 \text{ cm}^3 \text{ g}^{-1}$ and a mean pore radius of 20 \AA . An aqueous solution of rhodium nitrate was added to this zirconia, followed by heating to dryness while stirring. This was then dried overnight at 383 K in air followed by calcination for 3 h at 773 K. Catalyst samples after calcination at 773 K gave BET surface areas of $88.5 \text{ m}^2 \text{ g}^{-1}$.

For IR measurements, pressed powder discs of 25 mm were prepared. These were heated at 773 K for 30 min in a flow of dry nitrogen ($100 \text{ cm}^3 \text{ min}^{-1}$) before adjusting to reduction temperature (573 or 773 K). The nitrogen was then replaced by a flow of 3.5% H_2 in Ar before maintaining the temperature at 573 or 773 K for 2 h. The sample was then outgassed in dynamic vacuum while adjusting the reactor to reaction temperature followed by introduction of the CO/H_2 mixture at the desired ratio and total pressure.

3. Results

3.1. Catalyst characterisation

Catalysts which had been reduced in situ at 573 and 773 K were characterised by XPS and hydrogen chemisorption. Hydrogen adsorption isotherms measured at 298 K gave uptake values equivalent of 1.31 H:Rh and 1.22 H:Rh for catalysts reduced at 573 and 773 K, respectively. Assuming a stoichiometry of 2 hydrogen atoms to 1 rhodium atom, these would indicate dispersions of 65.3 and 60.9%, respectively. The Rh $3d_{5/2}$ peak position in X-ray photoelectron spectra indicate binding energies of 308.2 and 307.5 eV in

samples reduced at 573 and 773 K, respectively, compared with a value of 310.1 eV for a sample outgassed at 300 K. The value of 310.1 eV compares favourably with other values for calcined, supported rhodium catalysts [9] and indicative of Rh^{3+} , while the other values compare with reduced supported rhodium and rhodium foils [9]. The further lowering of binding energy by increasing the reduction temperature from 573 to 773 K has been observed for $\text{Rh}/\text{Al}_2\text{O}_3$ catalysts [10].

3.2. Reaction over ZrO_2

A pressed disc of the ZrO_2 support material was pretreated in the same manner as Rh/ZrO_2 and then exposed to a CO/H_2 (1:2) mixture at 20 bar and 513 K. Spectra obtained during the first 40 min of contact are shown in Fig. 1. Bands at 1620, 1580, 1440 (sh), 1417, 1386 (sh), 1365 (sh) and 1230 cm^{-1} are observed immediately on contact

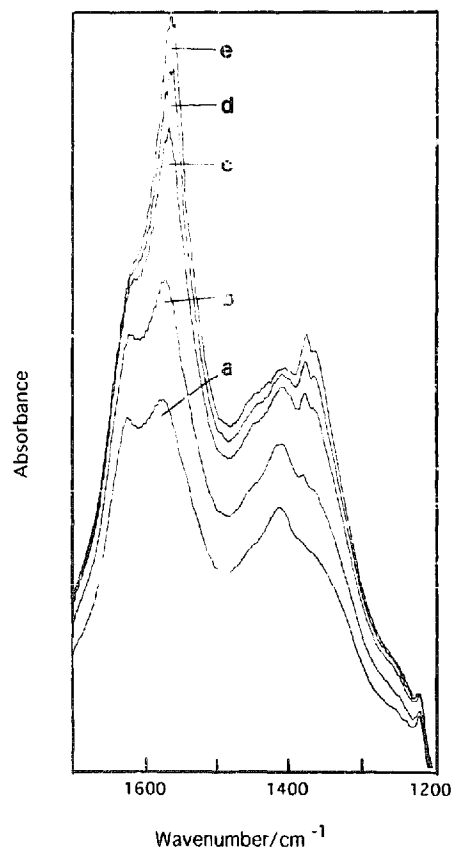


Fig. 1. FTIR spectra of reduced ZrO_2 in CO/H_2 (1:2) at 20 bar and 513 K at reaction times of (a) 1, (b) 4, (c) 20, (d) 30 and (e) 40 min.

between the reactant mixture and the ZrO_2 (Fig. 1a). All maxima grew up to a contact time of 20 min (Fig. 1c) whereafter only maxima at 1580, 1386 and 1365 cm^{-1} continued to grow. As a result of this, resolution between the various bands changed as a function of time with the 1620 cm^{-1} maximum, for example, present as a shoulder after extended contact times, but as a resolved feature at shorter times. The triplet at 1620, 1440, and 1230 cm^{-1} are assigned to the asymmetric ν_{CO} , the symmetric ν_{CO} and the COH bending mode, respectively, of the bicarbonate ion (HCO_3^-) by comparison with the frequencies of bands confirmed by isotopic substitution, to be due to bicarbonate ions on alumina [11]. Similar maxima are reported for adsorption of CO_2 , CO_2/H_2 and CO [12,13] on ZrO_2 at pressures of up to 1 atm. Maxima at 1580, 1386 and 1365 cm^{-1} are consistent with bands observed at 1580, 1390 and 1360 cm^{-1} following exposure of ZrO_2 to CO, CO/H_2 and CO_2/H_2 at pressure of 1 atm or less and assigned to bidentate formate species by comparing with bands observed for formic acid adsorption [13,14]. The band at 1417 cm^{-1} was not observed in previous low pressure studies [12,14]. In agreement with He and Ekerdt [13] but in contrast to Tre'yakov et al. [12] no maxima at ca. 1625 and 1300 cm^{-1} due to carbonate species (CO_3^{2-}) were detected.

3.3. Rh/ZrO₂ at 513 K in CO/H₂ (1:2) at 20 bar

Spectra of a rhodium zirconia catalyst which had been reduced at 573 K and exposed to CO/H₂ using the same conditions as for ZrO_2 are shown in Fig. 2. Bands at 1440, 1423, 1394 and 1376 cm^{-1} were observed (Fig. 2a) in addition to maxima at 1582 (sh), 1576 and 1561 cm^{-1} (not shown). Bands at ca. 1620 and 1230 cm^{-1} were not observed indicating that bicarbonate formation was not favoured in the presence of rhodium. During the initial period of contact, bands at 1440, 1423, 1394 and 1376 cm^{-1} all increased in intensity whereas at longer reaction times, maxima at 1440 and 1423 cm^{-1} decreased in intensity and were barely visible in spectra recorded after 150

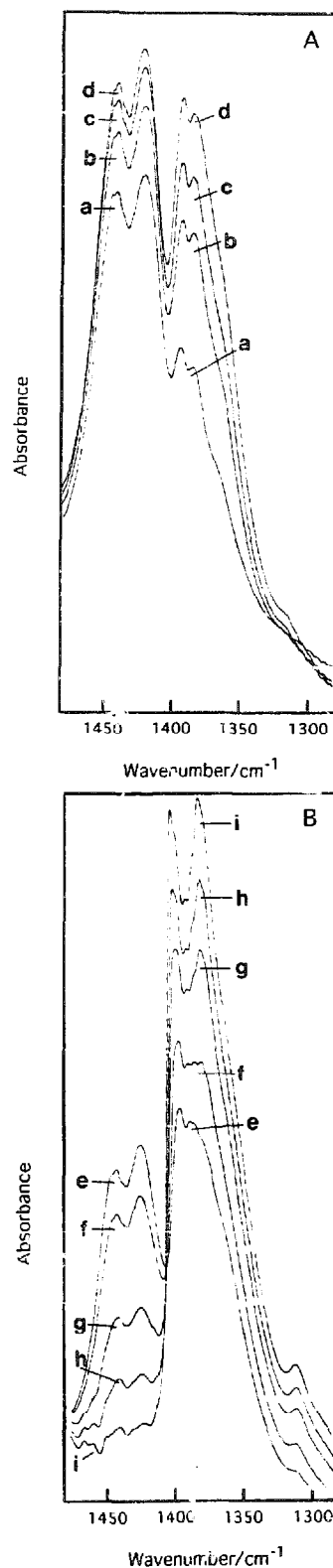


Fig. 2. FTIR spectra of Rh/ZrO₂ in CO/H₂ (1:2) at 20 bar and 513 K at reaction times of A (a) 0.5, (b) 2, (c) 4, (d) 8 mins and B (e) 16, (f) 30, (g) 60, (h) 90 and (i) 150 min.

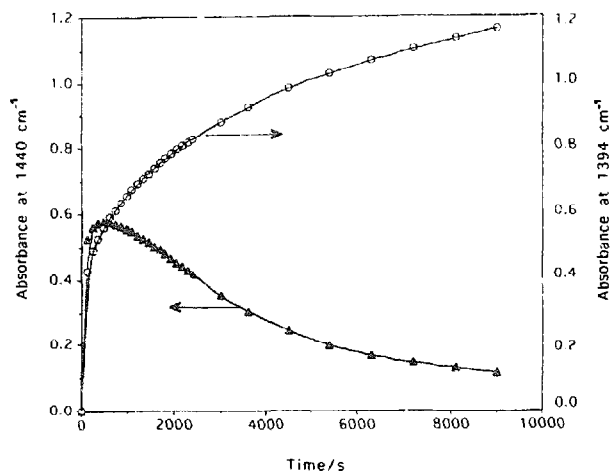


Fig. 3. Band intensities at 1440 and 1394 cm^{-1} as a function of reaction time in CO/H_2 (1:2) at 20 bar and at 513 K over Rh/ZrO_2 .

min (Fig. 2i). During this period, bands in the region, 1400–1350 cm^{-1} continued to grow, with 4 bands in this region at 1394, 1386, 1380 and 1376 cm^{-1} being detected (Fig. 2e–i). A weaker feature at 1310 cm^{-1} became apparent after extended reaction periods.

The relationship between band maxima at 1440 and 1394 cm^{-1} as a function of time is illustrated in Fig. 3. While the band intensity at 1440 cm^{-1} reaches a maximum after a period of reaction, the band at 1394 cm^{-1} continues to grow.

3.4. Rh/ZrO_2 in CO/H_2 (1:2) at 20 bar: influence of reaction temperature

The influence of reaction temperature on the formation and reactivity of the species giving the band maxima at 1440 and 1423 cm^{-1} was studied by monitoring the intensity of the former band during reaction at 513, 533 and 583 K. Absorbance values have been normalised at their maximum in intensity except in the case of the highest reaction temperature where the intensity had already passed through its maximum before the first scans were collected. Fig. 4 illustrates the time taken for the band intensity to drop to below 0.25 (i.e. concentration of the species is halved). A clear influence of temperature on the reactivity of the species is apparent indicating that the species is an intermediate in the reaction, although its role in formation of desired products is uncertain

at this stage. An approximate experimental activation energy for reaction of the species giving the band at 1440 cm^{-1} using rate constants calculated from the half-life of the species assuming first order, was 85 kJ mol^{-1} .

3.5. Adsorbed rhodium carbonyl species

The spectrum in the region 2300–1900 cm^{-1} where adsorbed rhodium carbonyls are expected is shown in Fig. 5a for a Rh/ZrO_2 catalyst reduced in H_2/Ar at 573 K and in a reaction mixture of 2:1 H_2/CO at 513 K at 20 bar pressure. After 2 h contact between catalyst and gas mixture, the region is dominated by the P (2115 cm^{-1}) and R (2175 cm^{-1}) branches of gas phase CO. Additionally, a lower frequency band at 2015 cm^{-1} is observed, which remains after reducing the pressure to 1 bar (Fig. 5b) and after brief evacuation at 513 K (Fig. 5c). The two latter treatments allowed a further component at 2089 cm^{-1} to be revealed. The presence of these two bands due to the two vibrational modes of the rhodium gem-dicarbonyl species [15,16] at 513 K and the detection of the lower frequency component in the presence of the reaction mixture at 20 bar (Fig. 5a) indicates that the species is present under reaction conditions. Similar maxima were detected for reaction temperatures of 533 and 583 K, when the total reaction pressure was 2 or 40

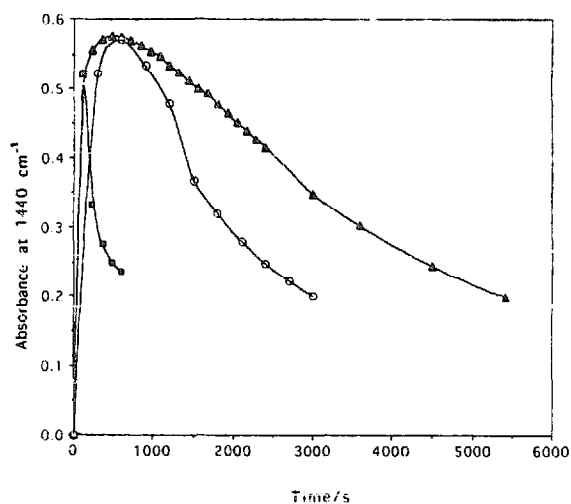


Fig. 4. Normalised band intensities at 1440 cm^{-1} as a function of reaction time for Rh/ZrO_2 in CO/H_2 (1:2) at 20 bar and reaction temperatures of 513 (\blacktriangle), 533 (\circ) and 583 K (\blacksquare).

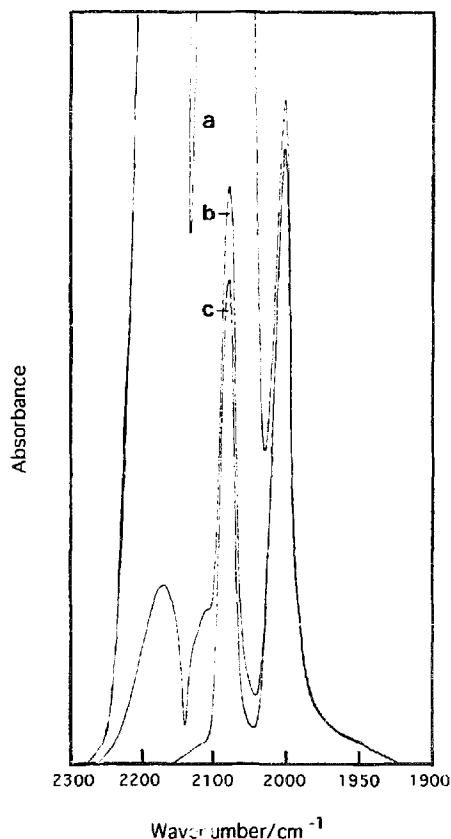


Fig. 5. Spectra of Rh/ZrO₂, reduced at 573 K then exposed to CO/H₂ (1:2) at 20 bar and 513 K. (a) After 2 h reaction time, (b) after 24 h reaction time and pressure lowered to 1 bar, and (c) evacuation at 513 K for 1 min.

bar instead of 20 bar, and when the reduction was performed in pure H₂ at 573 K instead of H₂/Ar mixture. The detection of this species for Rh/ZrO₂ reduced at 573 K is in agreement with one study [17] but in contrast to other results [8].

In the case of Rh/ZrO₂ catalyst reduced at 773 K, the feature resolved from the gas phase CO bands showed components at 2026 and 2015 cm⁻¹. On reducing the pressure to 1 bar, an additional maximum at 2100 cm⁻¹ was detected (Fig. 6a). Evacuation at 513 K to remove gaseous CO, left species that gave bands at 2100(sh), 2089, 2026(sh) and 2015 cm⁻¹ (Fig. 6b). The broad nature of the lower frequency component compared with its counterpart for the 573 K reduced sample (Fig. 5c), indicates that in addition to the rhodium gem-dicarbonyl species, favoured for the lower reduction temperature, linearly adsorbed carbonyl species on rhodium were also present under reaction conditions for the

higher temperature reduced samples. This is consistent with previous observations of CO adsorbed at room temperature on Rh/ZrO₂ samples reduced at 573 and 773 K [17] and with the lower dispersion measured for the 773 K reduced sample (see *catalyst characterisation*) since a decrease in dispersion favours the formation of linear bound carbonyls at the expense of gem-dicarbonyl species [3,18]. The detection of gem-dicarbonyl species at 513 to 583 K and in CO/H₂ mixtures at up to 40 bar pressure is significant given that above 473 K in CO at low pressures, rhodium sites for this species on an alumina support are lost by agglomeration with the formation of linear carbonyl bonding sites [19], and this process is enhanced by the presence of H₂ [20].

3.6. Rate of formation and reaction of species on 573 and 773 K reduced samples

As samples reduced at 573 and 773 K displayed differences in the nature of the dispersed metallic

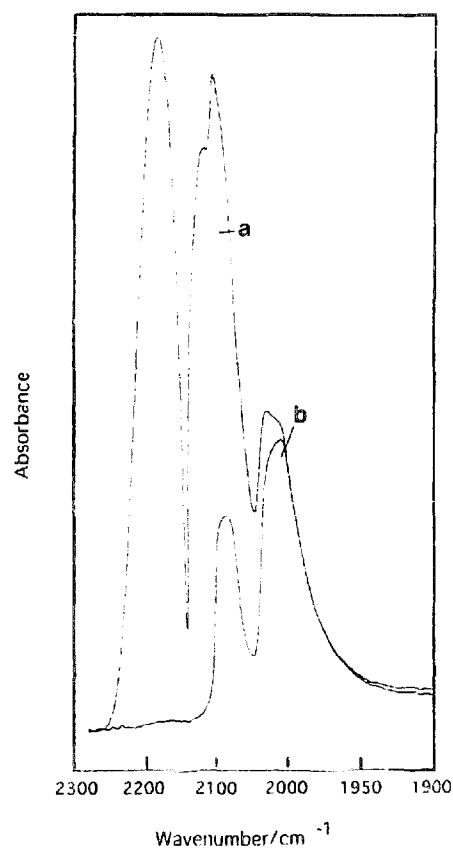


Fig. 6. Spectra of Rh/ZrO₂, reduced at 773 K then exposed to CO/H₂ (1:2) at 20 bar and 513 K. (a) After 24 h reaction time and pressure lowered to 1 bar, and (b) evacuation at 513 K for 1 min.

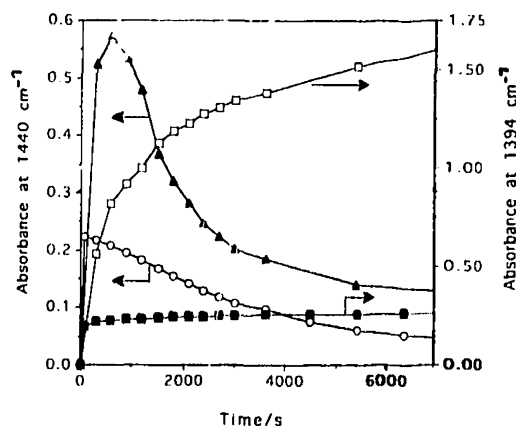


Fig. 7. Band intensities as a function of reaction time in reaction at 533 K in CO/H₂ (1:2) pressure 20 bar for Rh/ZrO₂ reduced at 573 K (□ 1394, ▲ 1440) and reduced at 773 K (■ 1394, ○ 1440).

function, it may be assumed that these samples should display differences in the rate at which bands grow or diminish, should the species responsible for these bands participate in the reaction. The intensities of bands at 1394 and 1440 cm⁻¹ as a function of time in reaction at 533 K, CO/H₂ = 2:1, total pressure 20 bar for Rh/ZrO₂ catalyst reduced at 573 and 773 K are shown in Fig. 7. The rate of formation of formate species (1394 cm⁻¹) on the 573 K reduced sample follows the trend shown for the sample in reaction at 513 K (Fig. 3) although the time taken to attain an equivalent absorbance value is clearly less for the higher reaction temperature. The general form of the plots produced for the 773 K reduced sample follow those of the 573 K reduced sample with an initial rapid growth in the band at 1394 cm⁻¹ and then a slow continual increase while for the 1440 cm⁻¹ band, a maximum is followed by a decrease in intensity. However, Fig. 7 clearly shows the amount of both species produced (i.e. maximum intensity) is considerably subdued for the higher temperature reduced sample.

4. Discussion

The absence of bicarbonate species on Rh/ZrO₂ in contrast to ZrO₂ and maxima due to formate species at 1394 in addition to those at 1386 and 1365 cm⁻¹ observed for ZrO₂ alone exposed to CO/H₂ mixtures at high temperature and pressure

indicates that the type of adsorbed species detected are influenced by the presence of the metal function. Of interest is the species giving the band pair at 1440 and 1423 cm⁻¹ whose formation and reaction are influenced by reaction temperature and reduction temperature, as these fulfil some of the criteria required for assignment of the species as a reaction intermediate. Bands within this range have been observed for CO₂ adsorption on Cu/SiO₂ [21] and assigned to carbonate species. Carbonate species give bands within the region 1630–1200 cm⁻¹ with the positions and separation of the vibrational modes depending on the mode of coordination. However as $\Delta\nu = \text{ca. } 160 \text{ cm}^{-1}$ between the asymmetric and symmetric stretching modes of a unidentate carbonate and ca. 320 cm⁻¹ between the C=O stretch and the asymmetric stretching mode of a bidentate carbonate [22,23] it is unlikely that the species is ligated in these modes. As a result of its D_{3h} symmetry, uncoordinated carbonate species shows only one IR band due to the asymmetric stretching mode at ca. 1470–1420 cm⁻¹ with the symmetric stretching mode at 1063 cm⁻¹ being infrared forbidden [22]. Unlike the case of Cu/SiO₂ [21], two maxima at 1440 and 1423 cm⁻¹ are detected here. One possibility is that two slightly different types of simple carbonate species exist, adsorbed on different types of site for example. These might then react further to form different types of formate species. Support for this would be the detection of 4 bands at 1394, 1386, 1380 and 1376 cm⁻¹ which grow as the 1440/1423 cm⁻¹ pair diminish (Fig. 2). However if this were the case, it is unlikely that their rates of formation and reaction would be identical (bands grow and decrease concomitantly) as seen here. The most likely explanation is that there is only one type of species that lays flat on the surface, but which involves a weak interaction between the surface and one of the oxygens resulting in a lowering of the symmetry from D_{3h}. The carbon–oxygen bonds involving the unperturbed oxygens would give rise to asymmetric and symmetric stretching modes (1440 and 1423 cm⁻¹, respectively) akin to a unidentate adsorbed carbonate,

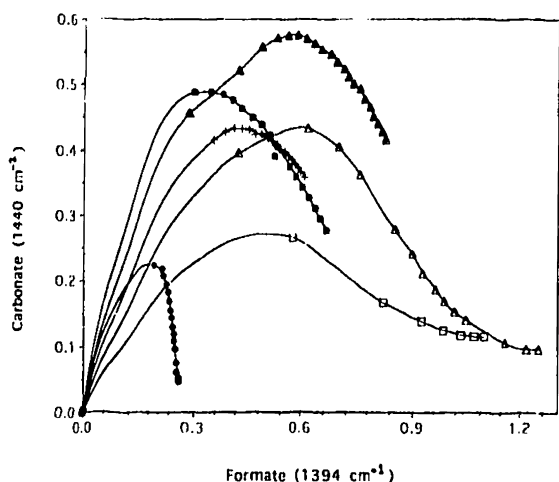


Fig. 8. Relationship between band intensities due to carbonate (1440 cm^{-1}) and formate (1394 cm^{-1}) species generated over a Rh/ZrO₂ catalysts reduced at 573 K and exposed to a 1:2 CO:H₂ mixture at 20 bar total pressure and at reaction temperatures of 513 K (\blacktriangle), 533 K (\triangle), and 583 K (\square), and at a reaction temperature of 513 K in a 1:10 (\blacksquare) and 2:1 ($+$) CO/H₂ mixture and a catalyst reduced at 773 K in a 1:2 CO/H₂ mixture at 20 bar and reaction temperature 513 K (\bullet).

but with a limited (17 cm^{-1}) value of $\Delta\nu$. The carbon oxygen bond (perturbed oxygen) would give a stretching mode at lower frequencies (unidentified).

If carbonate species are an intermediate in some process during CO hydrogenation, then the rate of its disappearance must be linked to the formation of some other species. Previous studies of zirconia in the absence of rhodium suggest that either a bicarbonate [13], a unidentate carbonate [24] or a bidentate carbonate [25] is converted into an adsorbed formate species. A linear relationship between bands ascribed to uncoordinated carbonate and bidentate formate species was established for Cu/SiO₂ [21], and between unidentate carbonate and formate species during CO₂ hydrogenation over ZrO₂ [24]. The relationship between formate and carbonate for a range of CO/H₂ ratios and temperatures and for two reduction temperatures is shown in Fig. 8. Results show that the general tendency is similar in all cases, although the position of the maximum varies according to conditions. This establishes that a relationship does exist between the two adsorbed species. The absence of a linear correlation between the two species [21,24] may be related to the fact that the

reaction here was studied under high pressure, high temperature conditions unlike those used in previous studies [21,24].

The form of the plots in Fig. 7 indicate that the relationship between the uncoordinated carbonate and the adsorbed formate species is of the consecutive reaction type where;



B and C are carbonate and formate species respectively, and the rate constant k_2 is less than k_1 . The attainment of maximum carbonate concentration at shorter reaction times (Fig. 7) indicates that an increase in reduction temperature leads to an increase in k_1 . Since all samples were heated at 773 K prior to reduction, and exhibited no difference in BET area whether reduction was performed at 573 or 773 K, it is possible that k_1 was altered due to a change in particle size that would inherently affect morphology and the number of interface sites. Certainly, a reduction in the number of interface sites for the 773 K reduced surface would be consistent with the diminished concentrations of formate and carbonate species, should these species be adsorbed at these sites. Studies by Baiker et al. [26] using Group IB metals and zirconia strongly suggest that ZrO₂ is involved in the reaction sequence and supports the proposal that the adsorbed species is located at the metal/support interface. The interrelationship between the two species as given in Eq. (1) relates to the two species adsorbed at the same type of site, hence the lesser quantities of both species on the high temperature reduced surface. High temperature reduction clearly modifies the surface in some manner as to restrict the number of adsorption sites available. Recent studies of Pt supported on an identical zirconia sample [27] indicate that at ca. 823 K, hydrogen is spilled over from the metal to the support. Some of this is adsorbed by the support while the rest results in a partial reduction of the zirconia. These processes may be those responsible for the modification of the surface indicated here leading to the depleted concentrations of adsorbed species.

A further possibility is that high temperature reduction resulted in a more fully dehydroxylated surface that would hinder the transfer of spillover hydrogen to hydrogenate the carbonate species, should this be located on the support surface. However such a scenario would lead to a build up in carbonate species for the 773 K reduced sample, which is not in keeping with the results presented in Fig. 7. Information regarding the formation of surface OH groups or Rh–H species was unobtainable due to the high scattering of the sample which resulted in low transmittance ($< 1\%$) in the range $4000\text{--}2900\text{ cm}^{-1}$. Reduction at 773 K resulted in improved transmittance in this region but the extreme broad nature of the band containing contributions from the OH vibration of surface hydroxyls meant that the subtle change in the concentration of OH species during reaction could not be determined.

The role of these species in the overall mechanism should be mentioned since, for Rh/SiO₂ at least, an equivalent change in dispersion to that observed here does not lead to significant changes in selectivity [2]. Although a link between carbonate and formate has been established here, the role of these species in the overall reaction process is less clear, i.e. the relationship and identity of A and D in Eq. (1). Millar et al. [21,28] in this laboratory, proposed that gaseous carbon dioxide and adsorbed oxygen generated the carbonate species that were subsequently hydrogenated to give adsorbed formate that was the pivotal intermediate in methanol synthesis over Cu/SiO₂ and Cu/ZnO₂/SiO₂ catalysts. The importance of carbonate species in the synthesis of methanol over Cu–Zn–Al catalysts has been identified [29], whereas, HCOO[−] was not considered to be an active intermediate for Group IB/ZrO₂ [26] or Re/ZrO₂ catalysts [30]. It is known that a relationship exists between surface carboxylate concentration and formation of the corresponding alcohol [2] although whether these carboxylates are reaction intermediates or merely an adsorbed form of the real reaction intermediate remains unclear. Should formate concentration be linked to methanol synthesis selectivity, results obtained

here would predict widely differing behaviour for Rh/ZrO₂ reduced at 573 and 773 K. Catalytic activity measurements are currently being carried out to determine whether this is in fact the case.

Acknowledgements

The authors thank Prof. C.H. Rochester for providing access to the high pressure IR facility, Prof. J.L.G. Fierro, C.S.I.C. Madrid, for carrying out the XPS analysis, Dr M. Lopez Granados, Madrid, for helpful discussions, P.J. Moles, Magnesium Electron Ltd for supplying the zirconia sample, Johnson Matthey for supplying the rhodium nitrate and the British Council, Abu Dhabi, U.A.E. for supporting a visit to Scotland (M.M.K.).

References

- [1] P. Forzatti, E. Tronconi and I. Pasquon, *Catal. Rev.-Sci. Eng.*, 33 (1991) 109.
- [2] J.P. Hindermann, J.G. Hutchings and A. Kiennemann, *Catal. Rev.-Sci. Eng.*, 35 (1993) 1.
- [3] J.R. Katzer, A.W. Sleight, P. Gajardo, J.B. Michel, E.F. Gleason and S. McMillan, *Faraday Discuss. Chem. Soc.*, 72 (1981) 121.
- [4] M. Ichikawa, *Bull. Chem. Soc. Jpn.*, 51 (1978) 2268, 2273.
- [5] M. Ichikawa and K. Shikakura, *Stud. Surf. Sci. Catal.*, 7 (1981) 925.
- [6] M. Ichikawa, K. Sekizawa and K. Shikakura, *J. Mol. Catal.*, 11 (1981) 167.
- [7] J.P. Hindermann, A. Kiennemann and S. Tazkritt, *Stud. Surf. Sci. Catal.*, 48 (1988) 481.
- [8] M.N. Bredikhin and Y.A. Lokhov, *Kinet. Catal.*, 28 (1987) 591.
- [9] S.E. Oh and J.E. Carpenter, *J. Catal.*, 80 (1983) 472.
- [10] J.A. Anderson, A. Guerrero Ruiz and J.L.G. Fierro, *Topics Catal.*, 1 (1994) 123.
- [11] Y. Amano, Y. Morikawa and G. Pleizier, *J. Catal.*, 46 (1977) 431.
- [12] N.E. Tret'yakov, D.V. Pozdnyakov, O.M. Oranskaya and V.N. Filimonov, *Russ. J. Phys. Chem.*, 44 (1970) 596.
- [13] M.-Y. He and J.G. Ekerdt, *J. Catal.*, 87 (1984) 381.
- [14] M.-Y. He and J.G. Ekerdt, *J. Catal.*, 90 (1984) 17.
- [15] A.C. Yang and C.W. Garland, *J. Phys. Chem.*, 61 (1957) 1504.
- [16] J.A. Anderson, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 3907.
- [17] Y. Tanaka, T. Iizuka and K. Tanabe, *J. Chem. Soc., Faraday Trans. 1*, 78 (1982) 2215.
- [18] R.R. Cavanagh and J.T. Yates Jr., *J. Chem. Phys.*, 74 (1981) 4150.
- [19] F. Selymosi and M. Pásztor, *J. Phys. Chem.*, 89 (1985) 4789.

- [20] F. Solymosi and M. Pásztor, *J. Phys. Chem.*, 90 (1986) 5312.
- [21] G.J. Millar, C.H. Rochester, C. Howe and K.C. Waugh, *Mol. Phys.*, 4 (1991) 833.
- [22] L.H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, London, 1966.
- [23] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Ed., J. Wiley and Sons, New York, 1986.
- [24] T. Chafik, D. Bianchi and S.J. Teichner, *Topics Catal.*, 2 (1995) 103.
- [25] T. Onishi, K. Maruya, K. Dornen, H. Abe and J. Kondo, in M.J. Phillips and M. Terman (Eds.), *Proc. 9th Int. Congr. Catal.*, Chemical Institute of Canada, Ontario, 1988, p. 507.
- [26] A. Baiker, M. Kilo, M. Maciejewski, S. Menzi and A. Wokaun, in L. Guzzi, F. Solymosi and P. Tetenyi (Eds.), *Proc. 10th Int. Congr. Catal.*, Elsevier, Amsterdam, 1993, p. 1257.
- [27] D.L. Hoang, H. Berndt and H. Lieske, *Catal. Lett.*, 31 (1995) 165.
- [28] G.J. Millar, C.H. Rochester and K.C. Waugh, *Catal. Lett.*, 14 (1992) 289.
- [29] P. Chaumette, P. Courty, J. Barbier, T. Fortin, J.C. Lavalley, C. Chauvin, A. Kiennemann, H. Idriss, R.P.A. Sneeden and B. Denise, in M.J. Phillips and M. Terman (Eds.), *Proc. 9th Int. Congr. Catal.*, Chemical Institute of Canada, Ontario, 1988, p. 585.
- [30] Z. Xu, Z. Qian, K. Tanabe and H. Hattori, *Bull. Chem. Soc. Jpn.*, 64 (1991) 1664.