

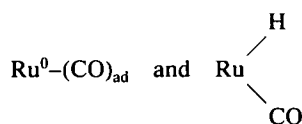
FTIR Spectroscopic Study of the Interaction of CO₂ and CO₂ + H₂ over Partially Oxidized Ru/TiO₂ Catalyst

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At least three distinct linearly bound carbonyl species are identified in the adsorption of CO₂ or CO₂ + H₂ over Ru–RuO_x/TiO₂ catalyst. The relative concentration and the growth of these species depend on metal oxidation state, presence of hydrogen, reaction temperature, and duration of exposure. The presence of preadsorbed or coadsorbed hydrogen promotes formation of



type species, the RuO_x–(CO)_{ad} species develop only on prolonged exposure to a dose of CO₂ or CO₂ + H₂. The oxygen or the hydrogen ligand bonded to ruthenium facilitates C–O bond scission. The widely reported lower temperature requirement for the CO₂ methanation reaction as compared to that of CO is attributed to the high reactivity of nascent carbonyl species which give methane directly via “active” carbon formation. As shown earlier (Gupta *et al.*, *J. Catal.* 137, 437 (1992)), the CO methanation requires multistep transformations, making the process energy intensive, particularly in the 300–450 K temperature range. The studies using ²H and ¹³C labeled adsorbates helped in the identification of oxygenated surface species having vibrational bands in the 1000–1800 cm⁻¹ region. These species are regarded as inactive side products formed on the support and/or at the Ru-support interfaces. © 1994 Academic Press, Inc.

INTRODUCTION

Some of the earlier studies have shown that CO₂ + H₂ interact with noble metals to form adsorbed CO in addition to formate or bicarbonate type oxygenated species (1–8). CO₂ is also reported to be dissociatively adsorbed over supported and single crystals of noble metals, such as Ru and Rh, even in the absence of hydrogen (1, 9–13). Some studies, on the other hand, have shown that the CO₂ adsorbs very weakly over clean Rh at room temperature

(14, 15) and its dissociation is assisted by the segregation of certain impurities at metal surface (15). Contradictory views have, similarly, been expressed regarding the role played by CO or by oxygenated species in the overall CO₂ methanation reaction. On the one hand, these species are considered as reaction intermediates (7), and on the other, they are regarded as catalyst poisons (8). Some other intriguing aspects include the lower temperature requirement for the methanation of CO₂ as compared to that of carbon monoxide (6, 16–22), even though the former reaction is believed to occur via CO as an intermediate.

In a recent publication (23) we reported on the surface species formed in the exposure of CO or CO + H₂ over titania supported partially oxidized ruthenium (Ru–RuO_x/TiO₂). The reduced and the oxidized metal sites, which were shown to coexist at a given temperature, act as independent CO chemisorption sites. It was also shown that the multicarbonyl species formed by interaction of CO or CO + H₂ undergo transformation to monocarbonyl form, which in turn acts as precursor for the methylene groups, which subsequently form hydrocarbons. The nature of the transient species was found to depend on the catalyst temperature and on the availability of hydrogen.

In the present paper we report on the surface species formed in the exposure of Ru–RuO_x/TiO₂ catalyst to CO₂ and CO₂ + H₂ at various temperatures. This catalyst is found to show high CO₂ methanation activity, particularly at low temperatures (7, 24, 25). For example, in a typical experiment employing a flow through microcatalytic reactor at 450 K, the methane yields from the CO₂ + H₂ and the CO + H₂ reactions were found to be 70% and 7%, respectively, under identical test conditions (25). The emphasis in the present study was to investigate the chemistry of reaction intermediates by evaluating the time and the temperature dependent modifications in the transient species using FTIR spectroscopy. Based on these data, some of the abovementioned fundamental aspects of CO₂ hydrogenation reaction are discussed.

EXPERIMENTAL

Catalyst

The partially oxidized ruthenium catalyst supported over TiO₂ (Degussa P25, ~80% anatase and 20% rutile, BET surface area 55 m² g⁻¹) was prepared using the method described earlier (7, 24). In this method, the metal is dispersed on the support in the form of 10–20 Å size RuO₂ particles using a deposition precipitation technique (24). The catalyst is then partially reduced at 495 K in a H₂/Ar (1 : 1) stream. The catalyst thus prepared contained about 3.8 wt% of Ru and the metal dispersion was estimated to be about 55%. About 25% of the metal was in zero valence state, the rest being in RuO_x form where $x \leq 2$ (8, 24).

IR Spectroscopy

The high pressure/high temperature stainless steel cell used in this study is described elsewhere (23). The cell is fitted with water-cooled CaF₂ windows fixed 6 cm apart. A self-supporting 2.5 cm diameter catalyst wafer weighing about 70 mg is fixed on a brass block located in between the CaF₂ windows. The sample could be heated at controlled temperatures up to 625 K either under vacuum or under a desired gas mixture.

A Mattson(USA) FTIR spectrophotometer (model Cygnus-100) equipped with a KBr beam splitter was employed to record IR spectra in transmission mode using either a DTGS or a MCT detector. For each spectrum 60 to 500 scans were coadded at a resolution of 4 cm⁻¹ or less as required.

The catalyst wafer was subjected to a 2–3 hr pretreatment in H₂ flow at 475 K and then evacuated at 575 K for 2–4 hr. A spectrum recorded with the wafer at the experimental temperature served as a background. The spectra were then recorded after introduction of an adsorbate either in the continuous flow (10 ml min⁻¹) or in the batch mode. The effect of exposure temperature and the effect of post-exposure thermal annealing on various IR bands were evaluated in detail. The effluents generated in the continuous flow experiments were analysed periodically by passing them through a gas cell placed in an external sample compartment of the spectrometer. The frequencies of various bands were reproducible within $\pm 1\text{--}4$ cm⁻¹ when different lots of the sample were used in repeated experiments.

High purity gases were used normally, and suitable purification treatments were carried out (23) when required.

RESULTS

Effect of hydrogen pretreatment. Without any pretreatment a Ru–RuO_x/TiO₂ wafer gave an IR spectrum

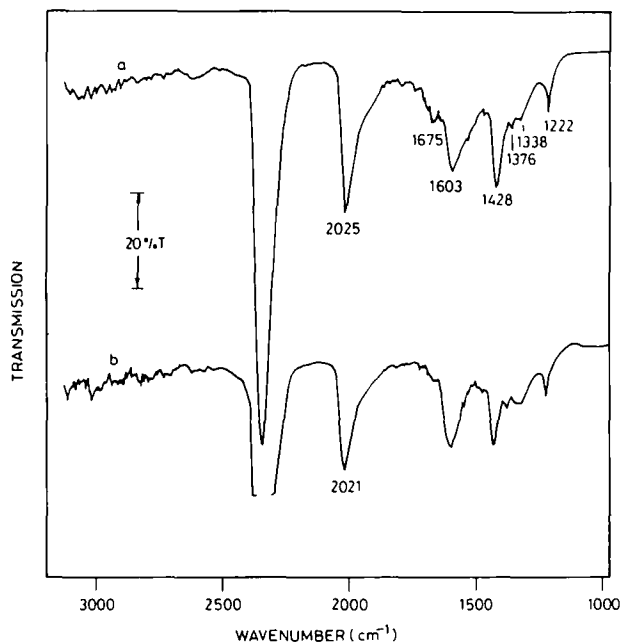


FIG. 1. (a) Infrared spectrum of partially oxidized Ru/TiO₂ catalyst recorded after 1 hr exposure at 300 K to 100 Torr CO₂. (b) IR Spectrum when the sample was exposed to a third successive 100 Torr CO₂ dose with 1 h evacuation at 575 K in between.

(air as reference) showing an intense band at 1630 cm⁻¹ as well as broad absorption in the 4000–3000 cm⁻¹ region due to adsorbed water and hydroxyl groups on the titania support. Hydrogen pretreatment at 475 K followed by evacuation led to removal of most of the adsorbed water as shown by the absence of H₂O bending mode vibration at 1630 cm⁻¹. The transmittance in the 4000–3000 cm⁻¹ region was about (1–2%) as compared to a transmittance of 6–8% in the 3000–1000 cm⁻¹ region.

CO₂ Exposure

Figure 1(a) shows the 1000–3000 cm⁻¹ region IR spectrum of a Ru/TiO₂ catalyst exposed to 100 Torr CO₂ at ambient temperature after hydrogen and vacuum treatments at 475 and 575 K respectively. Similar spectra, though with varying band intensities, were obtained for different gas pressures in the range of 50–300 Torr. Spectrum 1a shows the presence of adsorbed CO (1900–2100 cm⁻¹ region) in addition to the bands in 1000–1800 cm⁻¹ region. To assess the possible role of preadsorbed hydrogen in the generation of CO (Fig. 1a), a sample was exposed to successive doses of 100 Torr CO₂ without any hydrogen treatment in between two exposures. The sample was, however, heated each time under vacuum at 575 K to remove any surface adsorbed species before recording a background spectrum and dosing with 100 Torr CO₂. Figure 1b shows a typical spectrum obtained

after exposure to third such successive CO₂ dose. Similar spectra though with reduced intensity of C–O stretch bands were observed during further exposures to CO₂. This observation thus shows that the CO₂ reduction at catalyst surface may occur even in the absence of hydrogen.

A deconvolution of the C–O stretch region band (Fig. 1a) revealed the presence of at least three distinct bands appearing at around 2025, 1990, and 1952 cm⁻¹. A typical deconvolution of the C–O stretch region bands is shown in Fig. 2.

Most of the bands in Fig. 1a developed instantly after CO₂ exposure and except for the bands in the C–O stretch region, the intensity of all other bands remained unchanged when the catalyst was maintained under CO₂ for a prolonged period of approximately 2 hr. The C–O stretch bands, on the other hand, experienced significant changes in both intensity and frequency during this period, as shown by a typical set of spectra in Fig. 3. Thus, a spectrum recorded soon after CO₂ introduction consisted of a broad band with absorption maximum at 2000 cm⁻¹ and a shoulder band at around 1950 cm⁻¹ (Fig. 3a). The area under the C–O stretch band increased with time and reached a saturation level after about 1 hr exposure. Also, the main IR band shifted progressively to higher frequencies with time and attained a value of 2027 cm⁻¹ over 2 hr of exposure (Fig. 3b–f). The frequency of the 1950 cm⁻¹ band remained almost unchanged during this time. A weak band at 2075 cm⁻¹ is also noticeable in the spectra

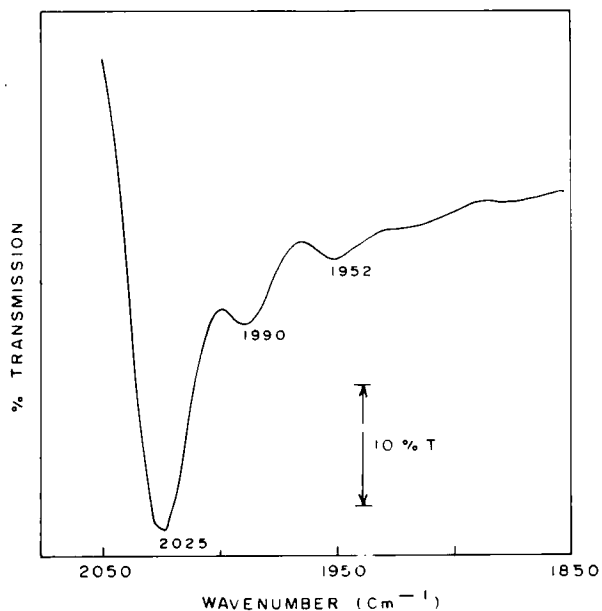


FIG. 2. Deconvolution and expansion of C–O stretch region bands formed on Ru/TiO₂ during 1 hr exposure to 100 Torr CO₂ at 300 K. Deconvolution parameters: $w = 40$ cm⁻¹, $k = 1.4$, $f = 0.4$, and Bessel function.

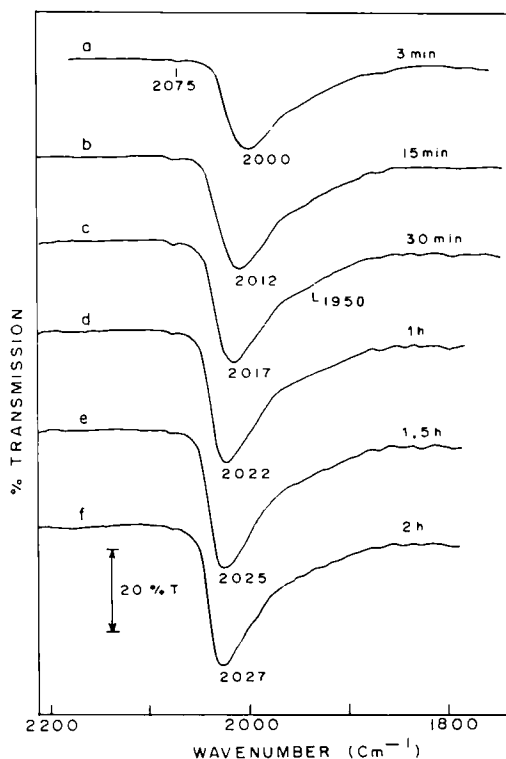


FIG. 3. The growth of C–O stretch region bands with time when a Ru/TiO₂ catalyst was exposed to 100 Torr CO₂ at 300 K.

of Fig. 3. The intensity and the frequency of this band remained unaltered during CO₂ exposure.

Effect of exposure temperature. Using the same sample employed for recording spectrum 1b, when the exposures to CO₂ were made at elevated temperatures (with in between heating under vacuum at 575 K but no hydrogen pretreatment), the intensity of various bands in 1000–1700 cm⁻¹ region reduced considerably and some of the bands in this region showed a frequency shift. Thus a band appearing at 1603 cm⁻¹ in Fig. 1a disappeared and a new band appeared at around 1618 cm⁻¹ when the sample was exposed to CO₂ at 370 and 470 K as shown in Fig. 4. The intensity of the 2025 cm⁻¹ band (Fig. 1a) was found to decrease with increasing exposure temperature, whereas its frequency showed a marginal shift to higher values (Fig. 4a,b). Figure 5 presents the time dependent development of C–O stretch bands during exposure to 100 Torr CO₂ at 370 K. Only a broad band centered at around 1957 cm⁻¹ was noted initially (spectrum a) and a new band at around 2005 cm⁻¹ developed over 15 min (Fig. 5b). The frequency of the 2005 cm⁻¹ band shifted progressively to 2026 cm⁻¹ during 1 hr of exposure (Fig. 5c–e). When the sample was subjected to a fresh pretreatment under hydrogen and then under vacuum before CO₂ exposure at 370 K, an intense CO stretch band as shown in Fig. 5f was observed.

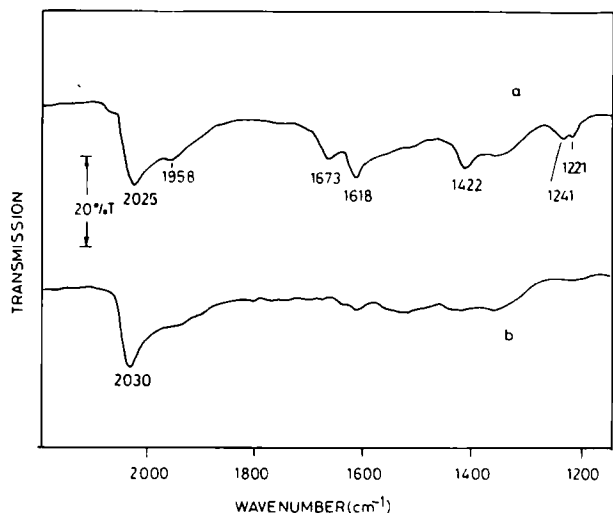


FIG. 4. Infrared spectra of Ru/TiO₂ catalyst on 1 hr exposure to 100 Torr CO₂ at (a) 370 and (b) 470 K.

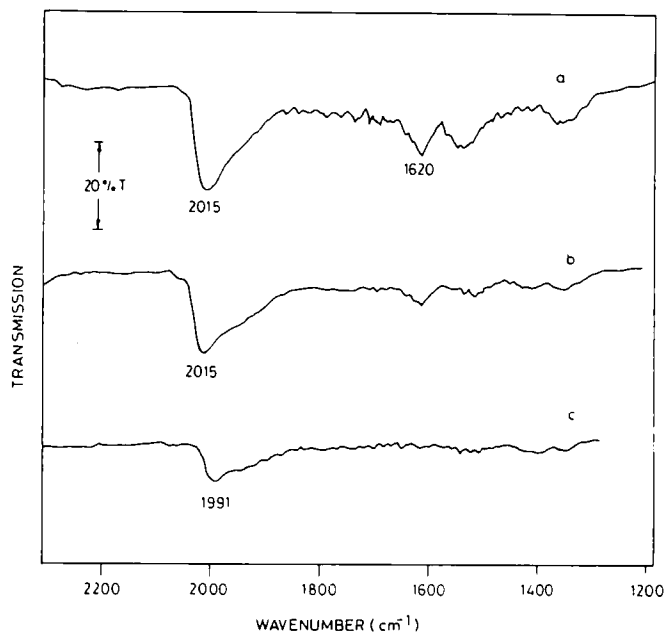


FIG. 6. Effect of 15–20 min evacuation on IR spectra formed on Ru/TiO₂ during exposure to 100 Torr CO₂ at (a) 300, (b) 370, and (c) 470 K.

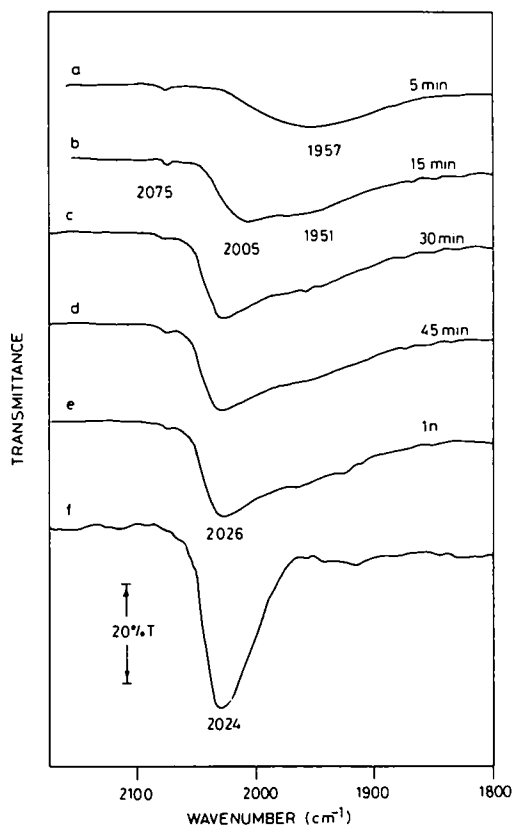


FIG. 5. Time dependent development of C–O stretch bands on Ru/TiO₂ during exposure to 100 Torr CO₂ at 370 K (a–e). Curve f shows the C–O stretch band when a sample freshly pretreated under hydrogen and then under vacuum was exposed to 100 Torr CO₂ at 370 K.

Effect of evacuation. When the sample was subjected to evacuation following CO₂ exposure, many of the bands in the 1000–1700 cm⁻¹ region and the IR bands due to gaseous CO₂ were removed immediately irrespective of the exposure temperature. Figures 6a–c show IR bands observed on Ru/TiO₂ after CO₂ adsorption at 300, 370, and 470 K respectively followed by 15–20 min evacuation at the sample temperature. The C–O stretch bands, on the other hand, were quite stable under evacuation even at elevated temperatures (Fig. 6b), though the frequency of the 2025 cm⁻¹ band shifted to lower values the extent of shift depending on exposure temperature. The C–O stretch bands were, however, removed easily when the surface of an evacuated sample was exposed to H₂ at all the sample temperatures in the range 300–470 K. Furthermore, the methane formation was also detected in the effluents during such hydrogen exposures at temperatures beyond 350 K.

Effect of surface oxidation. No CO was found to form in the CO₂ interaction over a catalyst surface which was pretreated under 5 Torr of oxygen at 475 K and then under vacuum at 575 K. Strong and overlapping bands due to oxygenated species with maxima at around 1667, 1617, 1424, 1241, and 1218 cm⁻¹ were, however, observed in the room temperature exposure to CO₂.

CO₂ + H₂ Exposure

Static mode. Figure 7a–d presents IR spectra of Ru/TiO₂ recorded after 1 hr exposure to 100 Torr of CO₂ +

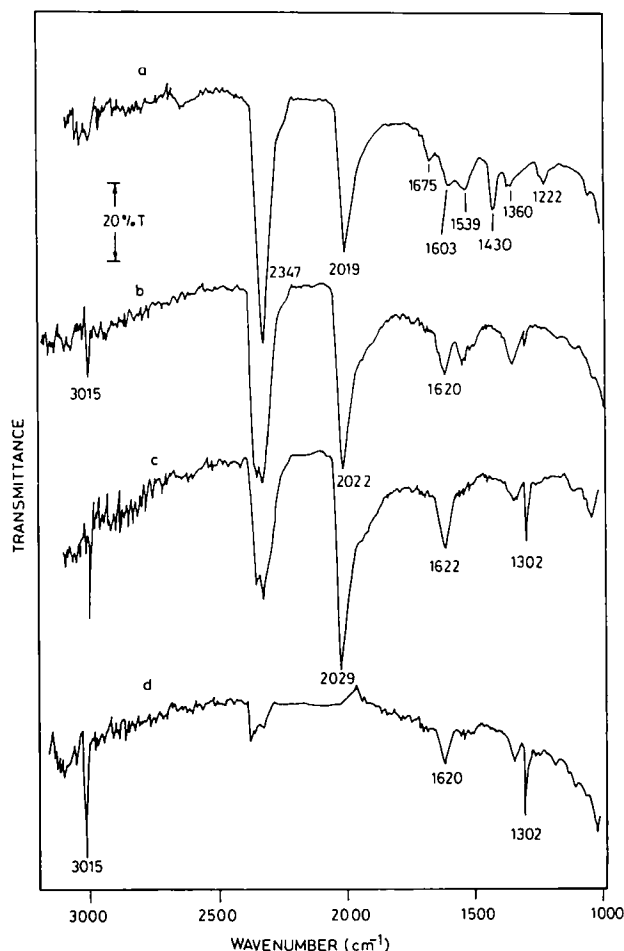


FIG. 7. IR spectra of Ru/TiO₂ after 1 hr exposure to 100 Torr CO₂ + H₂ (1 : 3) at different sample temperatures: (a) 300 K, (b) 370 K, (c) 420 K, and (d) 470 K.

H₂ (1 : 3) at different catalyst temperatures in the range 300–500 K. Spectra a–c in this figure reveal the formation of C–O stretch bands similar in nature and frequency to those in Figs. 1 and 4. The time dependent growth behaviour of C–O stretch bands was also similar to that observed for CO₂ exposure. Thus the CO₂ + H₂ exposure at room temperature gave rise initially to a main band at 2019 cm⁻¹ (Fig. 7a) along with a shoulder band to the lower frequency side which could be deconvoluted into two overlapping bands at around 1976 and 1937 cm⁻¹ (cf. Fig. 2). With time, the frequency of the 2019 cm⁻¹ band shifted progressively to higher values and reached a value of about 2021 cm⁻¹ after 1.5 hr of exposure. The deconvolution spectra of C–O stretch region bands indicated that all the three bands shifted to marginally higher frequency values with an increase in exposure temperature as is also reflected in the spectra of Fig. 7. The increase in exposure temperature also resulted in the initial enhancement of C–O stretch band intensity though with further increase

in temperature beyond 425 K their intensity reduced drastically (Fig. 7d).

Besides the C–O stretch region bands, various overlapping bands in the region 1000–1700 cm⁻¹ (Fig. 7) were detected. For exposure temperatures above 350 K, the presence of sharp methane bands (~3015 and 1302 cm⁻¹) was also observed (Fig. 7b–d) while the intensity of various 1000–1700 cm⁻¹ region bands (Fig. 7a) decreased progressively except for the 1620 cm⁻¹ band. The intensity of the methane bands was at a maximum at those temperatures when no C–O stretch bands were observed (Fig. 7d).

Evacuation effect. Evacuation of the sample resulted in the quick removal of many of the bands in the 1000–1700 cm⁻¹ region as was also observed in the case of CO₂ exposure. Effect of evacuation was, however, different in the case of C–O stretch region bands. In contrast to the experiments performed with CO₂ alone as adsorbate (Fig. 6a), the C–O stretch bands were less stable when formed during CO₂ + H₂ exposure and were removed on subsequent evacuation.

Pressure effect. Similar data were observed for other gas mixture pressures in the 100–760 Torr range. Though the intensity of C–O stretch region peak showed an increase with the pressure, the change in its frequency was only marginal. For example, the frequency of 2019 cm⁻¹ band observed during 100 Torr CO₂ + H₂ adsorption at room temperature (Fig. 7a) increased to 2025 ± 1 cm⁻¹ when the gas pressure was 760 Torr.

Effect of surface oxidation. Unlike in the case of results reported above for CO₂, the CO₂ + H₂ adsorption over oxidised catalyst surface gave rise to C–O stretch IR bands almost similar to those reported in Fig. 7 but with reduced intensity. The presence of intense bands due to adsorbed water was also observed in this case.

Continuous flow. Figure 8 gives IR spectra of Ru/TiO₂ when the CO₂ + H₂ mixture (1 : 3) was passed at a flow rate of 8–10 ml min⁻¹ at various catalyst temperatures. Though the nature of C–O stretch and 1000–1700 cm⁻¹ region bands in Fig. 8 is similar to that observed in batch mode experiments (Fig. 7), a few striking differences were observed. For instance, the main C–O stretch band appeared at 2042 cm⁻¹ when CO₂ + H₂ were passed over catalyst at 300 K, as compared to a frequency of 2019 cm⁻¹ observed in Fig. 7. Also, in contrast to the data in Fig. 7, the frequency of this band showed progressive decrease with increased exposure temperature and was observed at 2021 and 2011 cm⁻¹ for catalyst temperatures of 370 and 470 K respectively (Fig. 8b,c). Unlike the data of Fig. 7d showing no C–O stretch bands for the experiment at 470 K, the presence of these bands is noticeable in Fig. 8(c), indicating their continuing formation in

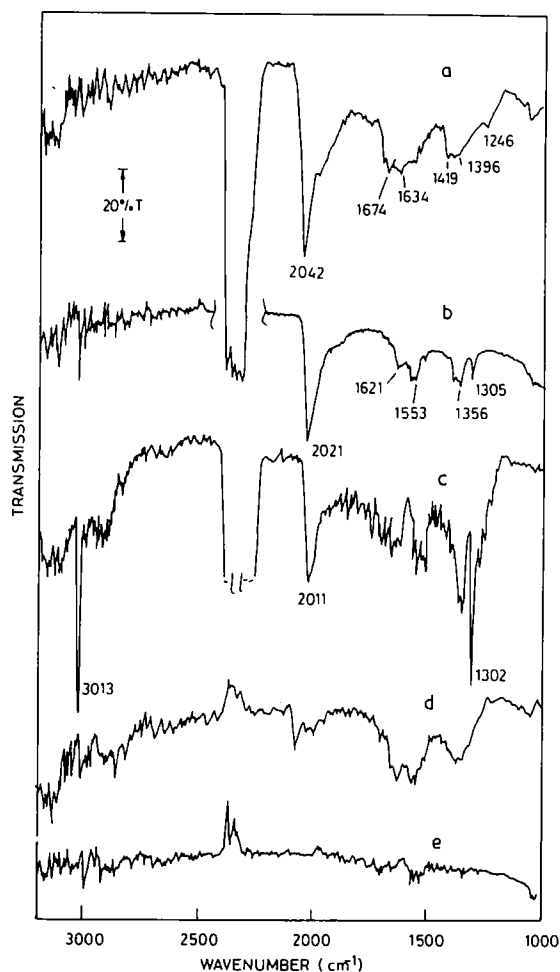


FIG. 8. IR spectra of Ru/TiO₂ when exposed for 30 min to flow (10 ml/min⁻¹) of CO₂ + H₂ gas mixture (1 : 3) at different sample temperatures: (a) 300, (b) 370, and (c) 470 K. (d) and (e) show IR spectra when the samples in (a) and (c) were subsequently evacuated at exposure temperature for 1 hr and 5 min respectively.

the CO₂ + H₂ reaction. Another important difference in the batch mode and the continuous flow experiments was reflected in the stability of C–O stretch bands. These bands were easily removed when a catalyst exposed to CO₂ + H₂ flow was subsequently evacuated and this removal was complete within a few minutes time for the higher exposure temperatures. Typical spectra obtained for the experiments performed at 300 and 470 K are shown in Fig. 8(d,e). These bands were removed only partially when the CO₂ alone was dosed (Fig. 6) and were removed at a slow rate in the static mode of exposure to CO₂ + H₂. Figure 8 also reveals that the appearance of IR bands due to methane is accompanied with reduced intensity of C–O stretch band.

Effluent analysis. The IR analysis of the effluents evolved on flowing CO₂ + H₂ over Ru/TiO₂ revealed

commencement of CH₄ formation at about 330 K. In addition to CH₄, the evolved gases also contained water vapour as reaction product. It is pertinent to mention here that the CH₄ formation in the parallel experiments performed with CO + H₂ flow was observable only at temperatures above 420 K (23).

CO₂ + D₂ reaction. Figure 9a shows the IR spectrum of a catalyst wafer exposed at ambient temperature to about 100 Torr of CO₂ + D₂ (1 : 4) mixture. A comparison with Figs. 7 and 8 reveals following salient features. The bands at around 1674 and 1246 cm⁻¹ observed in the CO₂ + H₂ reaction remained unchanged within ±2 cm⁻¹ for the CO₂ + D₂ reaction. Whereas no band at 1603 cm⁻¹ (Fig. 7) was formed, a new band is detected at around 1195 cm⁻¹ in Fig. 9. Also, a band at 1420–1430 cm⁻¹ is observed only as a weak band in Fig. 9a. Two prominent bands at around 1557 and 1360 cm⁻¹ in Fig. 7b are shifted to lower frequency values of 1542 and 1332 cm⁻¹, respectively, in the case of the CO₂ + D₂ reaction at 370 K (Fig. 9b). Two broad bands with maxima at 2667 and 2551 cm⁻¹ (Fig. 9a) represent two types of OD groups identifiable with the surface deuteroyl groups and molecular water formed during CO₂ deuteration. Subsequent heating of the samples led to CD₄ (2258 cm⁻¹ band) formation at temperatures above 350 K (Figs. 9b,c).

A comparative evaluation of various 1000–1700 cm⁻¹ region bands observed in this study is presented in Table 1.

Effect of ¹³C isotopic substitution. When the ¹³C labelled carbon dioxide was used as an adsorbate, IR band appearing at 2025 cm⁻¹ shifted to a lower value by about 53 cm⁻¹. Various bands in the 1000–1800 cm⁻¹ region (Fig. 1) also shifted to lower values and the extent of this shift is given in Table 1.

The shift in various IR bands was similarly observed on exposure of a catalyst wafer to 100 Torr of ¹³CO₂ + H₂ (1 : 4). Figure 10 gives 1000–2200 cm⁻¹ region IR bands obtained during ambient temperature exposure. Spectrum b in this figure presents comparative data for the exposure to 100 Torr ¹²CO₂ + H₂ (1 : 4) under identical conditions. The frequency shifts observed for various bands are reported in Table 1.

Exposure over titania. The room temperature exposure of metal free titania to both the CO₂ and CO₂ + H₂ resulted in the formation of several bands in the 1000–1700 cm⁻¹ region; the data are included in Table 1. The frequency of these bands matched with the corresponding IR bands formed over Ru/TiO₂ under similar test conditions (Fig. 8). The relative intensities, however, varied marginally. A few minutes evacuation led to removal of these bands as has been reported above in the case of Ru/TiO₂ samples.

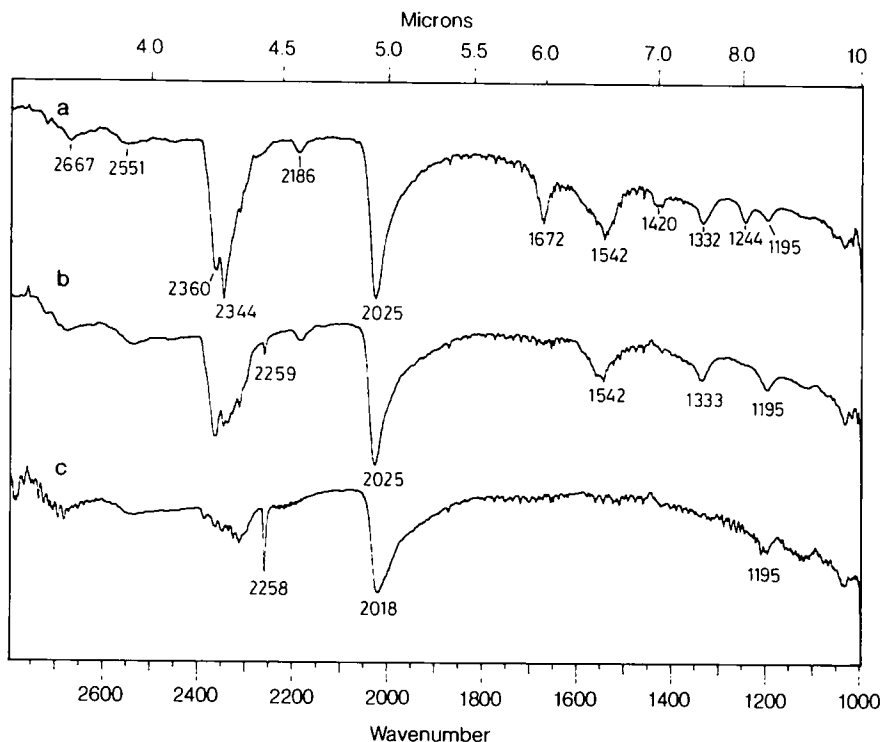
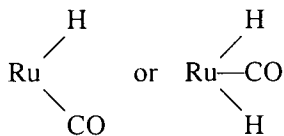


FIG. 9. IR spectra of Ru/TiO₂ when exposed for 30 min to CO₂ + D₂ (1 : 4) flow at different temperatures: (a) 300, (b) 370, and (c) 420 K.

DISCUSSION

1800–2200 cm⁻¹ Region Bands

There have been disagreements regarding the nature and the role of CO_{ad} species formed in the interaction of CO₂ + H₂ and CO₂ over supported noble metal catalysts including Ru (1–8, 10, 14, 26). Solymosi *et al.* (4, 5) reported formation of a weak IR band at around 1990 cm⁻¹ in the interaction of H₂ + CO₂ (1 : 1) on supported Ru. The frequency of CO formed in the H₂ + CO₂ surface reaction was found to be lower than that in the adsorption of CO alone (2030–2040 cm⁻¹) and has been attributed to the formation of



type surface species (4, 5). Solymosi and co-workers proposed a reaction mechanism where the importance of the above intermediates and also that of the formate type surface species was emphasized. Prairie *et al.* (7) and Highfield *et al.* (8) used diffuse reflectance infrared spectroscopy to investigate surface species formed in the CO₂ + H₂ reaction over a catalyst similar to that employed

in present study. The CO₂ + H₂ exposure at 323 K gave rise to C–O stretch bands at 2020 and 1995 cm⁻¹ along with the IR bands due to methane. The band at 1995 cm⁻¹ and another band appearing at 2015 cm⁻¹ on adsorption of hydrogen over CO_{ad} were identified with the hydrogen atoms associated with surface metal cations (8).

Various new features have now emerged in the present study of CO₂ or CO₂ + H₂ adsorption on Ru–RuO_x/TiO₂ catalyst using transmission FTIR spectroscopy. Findings of the present study are summarised below:

1. At least three C–O stretch bands, at around 2025, 1990, and 1950 cm⁻¹, are produced in the interaction of CO₂ over Ru/TiO₂ at ambient temperature (Fig. 2). Data in Figs. 1–5 show that these bands grow and disappear independently, thus indicating their distinct identity. Also, since all the three bands existed simultaneously during prolonged exposure to CO₂ or CO₂ + H₂ (Figs. 2, 5, 7, 8) and the cell pressure was kept constant during this period, the frequency shifts reported in our study (Figs. 3, 5, 7, 8) may therefore be attributed to the development of new transients at the catalyst surface and not to surface coverage effects. Further, as the bands reported above are formed during successive CO₂ exposures over the catalyst surface (Fig. 1b), it is implied that such species are formed in the interaction of CO₂ at metal sites even in the absence of hydrogen. The possible sites for CO₂

TABLE 1
Infrared Bands Observed on Adsorption of CO₂, ¹³CO₂, CO₂ + H₂, and CO₂ + D₂ over Ru/TiO₂ and TiO₂

No	Ru/TiO ₂ catalyst				TiO ₂ support		Assignment
	CO ₂	Isotopic shift ¹³ C/ ¹² C	CO ₂ + H ₂	Isotopic shift ¹³ C/ ¹² C	CO ₂ + D ₂	CO ₂ + H ₂	
1.	1679(w)	0.968	1672–1675 (s; sp)	0.976	1672 (s; sp)	1673 (m; sp)	complexed CO ₂ (see text)
2.	—		1620–1634 (s; sp)		1195 (m; sp)	1619 (w)	adsorbed H ₂ O/D ₂ O
3.	1602(s; b) (1560)	0.973	1600–1603 (m; b)		shifted	~1600(m)	bicarbonate
4.	—		1555 (s; b)	0.977	1542 (s; b)	—	formate
5.	1428 (s; sp)	0.973	1420–1430 (s; sp)	0.965	vw	1423(m)	bicarbonate
6.	Weak or absent		1360–1395 (s; b)	0.977	1332	w	formate
7.	sh; disappears on ¹³ C substitution		1243–1246 (s; sp)	0.977	1244 (m; sp)	1242 (s; sp)	complexed CO ₂ (see text)
8.	1222 (s; sp)	0.995	sh	no shift	—	sh	bicarbonate

Note. All bands except (4) and (6) disappeared on evacuation, and also failed to form above around 335 K. VW—very weak, w—weak, m—medium, s—strong, b—broad, sh—shoulder, sp—sharp.

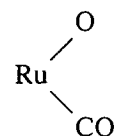
reduction could include both the Ru⁰ and the Ti₂₋₈ moieties at Ru/TiO₂ interfaces (27, 28).

2. The surface species formed during CO₂ or CO₂ + H₂ adsorption are different in many ways from those formed during CO or CO + H₂ adsorption under identical conditions (23). For example, no methylene group containing surface species were detected at any stage of the CO₂ + H₂ reaction (Fig. 8), whereas such species were predominant in the initial stages of the CO + H₂ reaction (23). A comparison of the C–O stretch region bands clearly shows that no IR bands at frequencies higher than 2040 cm⁻¹, identified widely with multicarbonyl species (29, 30), were formed during CO₂ or CO₂ + H₂ interaction, in contrast to the experiments performed with CO as adsorbant (23). Also, an intense band appearing at ~2020 cm⁻¹ in Fig. 7a was observed at around 2050 cm⁻¹ for the corresponding experiment performed using CO + H₂. The recent studies carried out in our laboratories on coadsorption of CO, CO₂, and H₂ over title catalyst have unequivocally shown that the distinct surface species were formed during the hydrogenation of CO and CO₂ (31). The stability and the reactivity of these species were also different in the two cases.

3. As the 1950 and 1990 cm⁻¹ bands are formed on freshly reduced surface (Figs. 3, 5), they may be assigned mainly to Ru⁰(CO) type linear species. The confirmation about the assignment of these bands to linear form rather than to bridge bonded species comes from our data obtained with the S-poisoned catalysts (32). These bands

were found to develop, though with reduced intensity, when a catalyst wafer dosed with CS₂ vapour was evacuated and then exposed to CO₂ + H₂ at 300 K.

The time dependent growth of the 2026 cm⁻¹ band as seen in Figs. 3 and 5 suggests the weakening of Ru–CO bonding and it can therefore be ascribed to the progressive formation of oxygen perturbed



type species, where the oxygen is generated during CO₂–Ru⁰ interaction. A band in the 2038–2020 cm⁻¹ region has been reported on CO adsorption over incompletely reduced or on oxygen dosed Ru/TiO₂ by Guglielminotti *et al.* (30) and is attributed to the carbonyls associated with Ru²⁺. The parallel experiments carried out recently in our laboratory have supported this assignment. Figure 11a shows a typical IR spectrum obtained on exposure of a catalyst wafer to 100 Torr of CO after pretreatments under H₂ (475 K, 2 hr) and then under vacuum (575 K, 2 hr). In the experiment, when a sample pretreated as above was dosed with 20 Torr of O₂ at 300 K followed by repeated pumping and exposure to 100 Torr of CO, a spectrum shown in Fig. 11b was obtained. Figure 11c shows the IR spectrum of the residual surface

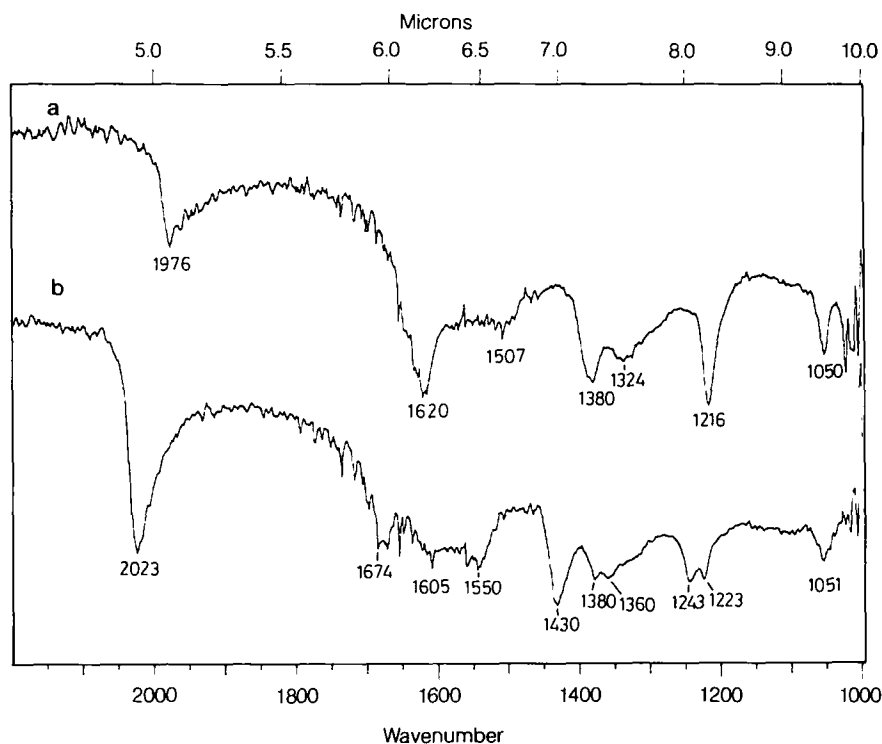


FIG. 10. Infrared spectra of Ru/TiO₂ developed on 1 hr exposure at 300 K to 100 Torr of (a) ¹³CO₂ + H₂ (1 : 4) and (b) ¹²CO₂ + H₂ (1 : 4).

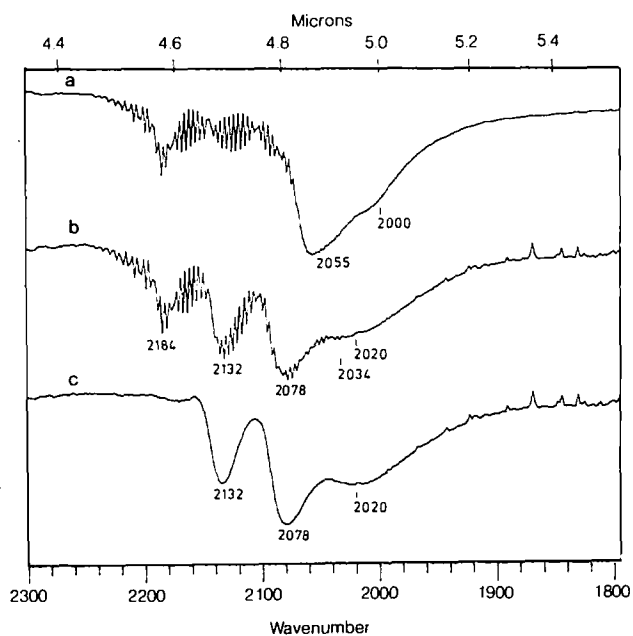


FIG. 11. Adsorption of 100 Torr CO over Ru/TiO₂ after different pretreatments (a) H₂ (475 K, 2 hr) and then vacuum (575 K, 2 hr); (b) as in (a) dosed with 20 Torr O₂ at 300 K and then evacuated; (c) shows residual surface species on CO adsorption over samples followed by 5 min evacuation.

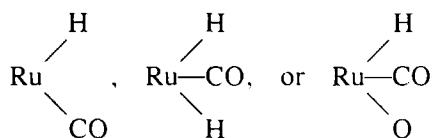
species when the cell was subsequently evacuated at room temperature. The appearance of a band at ~ 2032 cm⁻¹ and a similar increase in the intensity of high frequency bands at 2136 and 2080 cm⁻¹ as shown in Fig. 11b have been reported by other workers also during CO adsorption over oxidized Ru (29). The 2020–2025 cm⁻¹ IR band appearing in Figs. 1–5 compares well with the data in Fig. 11c and therefore its assignment to CO held at O-perturbed ruthenium sites is in order.

A deconvolution of the spectrum in Fig. 11c clearly showed that the bands appearing in Fig. 11a at 2001 cm⁻¹ and at lower frequencies are diminished after oxygen pretreatment and must therefore be assigned to CO bonded at Ru⁰ sites and not to the oxidized ruthenium as suggested earlier (23).

4. Since the CH₄ formation is accompanied by the simultaneous decrease of C–O stretch bands (Figs. 7, 8) and methane formation is observed when the surface covered with these bands is exposed to hydrogen, it is suggested that the adsorbed CO is precursor to methane.

5. A comparison of the data in Figs. 1–3 with those in Fig. 8 reveals that the C–O stretch band at a higher frequency of 2042 cm⁻¹ was formed during continuous flow of CO₂ + H₂ at 300 K. This band appeared at around 2020–2025 cm⁻¹ when the sample was exposed to CO₂ (Fig. 1) or to a dose of CO₂ + H₂ in batch mode (Fig. 7). This shift cannot be ascribed to pressure effects as a

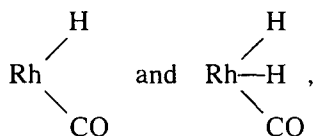
change of cell pressure from 100 to 760 Torr in our experiments resulted in a shift of only 5–6 cm^{-1} . The higher frequency of this band is indicative of a stronger C–O bonding and therefore a weakening of the Ru–CO bond. This may therefore be attributed to the surface structures such as



as proposed by Solymosi *et al.* (4, 5). Such species would form only in the presence of excess H_2 . Also the comparison of Figs. 1 and 7 shows that even though the frequency of this band was similar, its intensity was greater in the presence of hydrogen, suggesting that the coadsorption of H_2 and CO_2 promoted the formation of carbonyl species, which is in agreement with the data in Fig. 5f. Similarly, the stability of CO_{ad} species is affected considerably by the coadsorbed or gaseous H_2 , as becomes evident by the comparison of spectra in Figs. 6a and 8d. Thus, the CO formed in the exposure to CO_2 is bonded strongly and is not removed easily even on evacuation at elevated temperatures. On the other hand, the C–O stretch bands formed during $\text{CO}_2 + \text{H}_2$ flow are easily removed even at room temperature (Fig. 8d). It may therefore be concluded that the adsorbed CO is very reactive to preadsorbed or gaseous hydrogen. This is further confirmed by the observation that the adsorbed CO formed during CO_2 adsorption, though stable under vacuum at elevated temperatures, is very reactive to subsequently dosed H_2 .

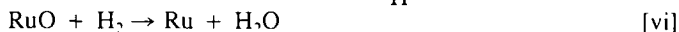
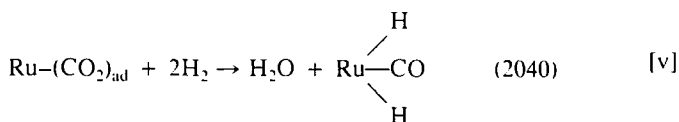
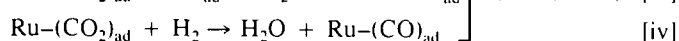
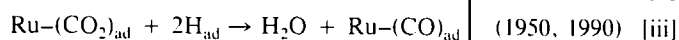
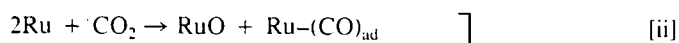
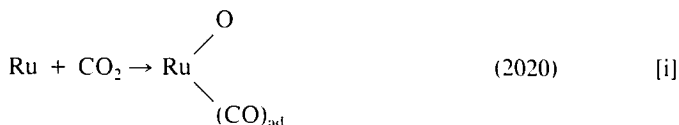
The referee has pointed out that the greater reactivity of $(\text{CO})_{\text{ad}}$ in the $\text{CO}_2 + \text{H}_2$ experiments could arise due to its reaction with adsorbed moisture, i.e., the water-gas shift reaction, as has also been suggested in an earlier study (7). If the water-gas shift reaction is to proceed under the reported conditions, then the $(\text{CO})_{\text{ad}}$ species would be unstable because of reaction with adsorbed moisture which was not found to happen in our study. To further check on this point, when a $(\text{CO})_{\text{ad}}$ covered catalyst surface was exposed to water vapour at room temperature, the carbonyl IR bands were found to be unaffected and a measurable amount of CO_2 was formed only on raising the sample temperature above 375 K.

In support of our model, the *ab initio* calculations of McKee *et al.* (33) have indeed shown that the bent rhodium carbonyl hydride species, such as



are long lived and the presence of a hydride ligand facilitated C–O bond dissociation.

6. The surface reactions occurring at catalyst surface during CO_2 or $\text{CO}_2 + \text{H}_2$ interactions leading to adsorbed CO species may thus be visualized to be the following:



The figures included in parentheses indicate the likely C–O stretch frequencies of surface species formed. The observation that the $\text{CO}_2 + \text{H}_2$ adsorption over both the oxidised and the reduced catalyst surface gave rise to similar bands, whereas CO_2 alone was not adsorbed/reduced over oxidised surface, suggests the occurrence of step vi. A temperature dependent red shift in the C–O stretch frequency as seen in Fig. 8, also, show that the coadsorbed hydrogen helps in reduction of both the metal sites and the $(\text{CO})_{\text{ad}}$ species (steps V and VI).

7. The following picture thus emerges from the observations summed up above. Initial adsorption of CO_2 or of $\text{CO}_2 + \text{H}_2$ gives rise to formation of linear $\text{Ru}-(\text{CO})_{\text{ad}}$ species with subsequent development and growth of $\text{RuO}_x(\text{CO})_{\text{ad}}$ or metal–carbonyl–hydride type surface species. The nascent carbonyl species are very reactive to coadsorbed or gaseous hydrogen and are viewed as precursors to methane. In the case of CO hydrogenation, adsorbed carbonyl species are known to first form a methylene group chain, which in turn yields to methane at an appropriate temperature (23). This explains the observed lower energy requirement for the $\text{CO}_2 + \text{H}_2$ reaction (16–22) as compared to that for CO methanation. The higher reactivity of nascent species towards hydrogen may also account for the selective CH_4 formation from CO_2 via active carbon formation rather than the formation of long chain hydrocarbons as observed during $\text{CO} + \text{H}_2$ reaction (23).

1000–1700 cm^{-1} Region Bands

Bands in this spectral region have been reported widely in the adsorption of CO_2 or $\text{CO}_2 + \text{H}_2$ over various supported noble metals. For example, Solymosi *et al.* observed IR bands at 1230, 1450, and 1620–1640 cm^{-1} in

the interaction of CO₂ over Ru/Al₂O₃ and attributed them to carbonate type species (4). On the other hand, CO₂ + H₂ (1 : 1 mole ratio) interaction resulted in the appearance of new bands at 1377, 1396, 1596, and 1640 cm⁻¹, the relative intensity of which depended on catalyst temperature. These bands were found to be stable under evacuation and were assigned to formate ions. The formate ions were considered to be inactive species in the methanation of CO₂ (4).

Prairie and co-workers (7) saw no bands in this region on the exposure of Ru/TiO₂ catalyst to CO₂ at 383 K. The CO₂ + H₂ (1:4) exposure, however, resulted in the two prominent bands at 1553 and 1359 cm⁻¹. As similar bands developed in the exposure of Ru/TiO₂ to formic acid under identical conditions, these were assigned to formate ions (HCOO⁻), which in turn were considered as reservoirs giving rise to CO_{ad} species and then to CH₄ formation. No such bands were observed by these authors in the exposure of metal free titania to CO₂ or CO₂ + H₂.

The data presented in Table 1 prompt us to highlight the following important features.

The two bands at around 1357 and 1555 cm⁻¹ seen clearly at 370 K (Figs. 7b and 8b) are not observed with CO₂ alone or on TiO₂ and were assigned to formate ions by earlier workers (7). This is confirmed in the present experiments also, since they show a small expected shift with D₂ substitution (Fig. 9b, Table 1). The observed isotope shifts of ¹³C/¹²C, ~0.969 for the 1555 cm⁻¹ band assigned to asymmetric COO stretch and a value of ¹³C/¹²C = 0.977 for the 1355 cm⁻¹ band due to symmetric stretch (Table 1) are in agreement with this assignment.

Two bands at around 1675 cm⁻¹ and 1245 cm⁻¹ are observed only weakly with CO₂ alone, but are strong for adsorption of CO₂ + H₂, or that of CO₂ + D₂. These bands can not be attributed to bicarbonate or any hydrogenous systems since they do not show any isotope shift on deuteration (Table 1). We assign these bands to complexed CO₂ species (or bridged carbonate) as suggested by Solymosi *et al.* (2). This is confirmed from the observed ¹³C isotope shifts of ~0.976 and 0.977 which is similar to that observed for formate bands.

Three bands at around 1603, 1428, and 1225 cm⁻¹ appear strongly with CO₂ alone, and with moderate strength with CO₂ + H₂, and were also observed on TiO₂. The first two bands seem to have shifted on deuteration but are masked by the formate bands, while the 1225 cm⁻¹ band seems to have disappeared (i.e., shifted below 1000 cm⁻¹). Both the 1603 cm⁻¹ and 1428 cm⁻¹ bands show ¹³C isotope shift (Table 1). These results strongly suggest that these bands may originate from bicarbonate species (34), with the 1225 cm⁻¹ band being assigned to the C–OH in plane bend.

A band at 1620 cm⁻¹ develops progressively during evacuation and shows considerable stability at higher temperatures (Figs. 4, 7, 8). A corresponding band is seen at 1195 cm⁻¹ in CO₂ + D₂ experiments (Fig. 9) and may therefore be assigned to adsorbed H₂O/D₂O.

A study of Table 1 shows that whereas bands ascribed to bicarbonate or adsorbed CO₂ species were formed during adsorption of CO₂ + H₂ or CO₂ + D₂ over metal free titania, no detectable formate type species were formed under identical conditions. Spectra in Fig. 8 show that the formate type species were unstable even at ambient temperature and were not detected during continuous exposure to CO₂ + H₂ at temperatures above 370 K when the simultaneous formation of both the (CO)_{ad} and the methane was observed. Though the contribution of formate intermediates as a source of CO_{ad} species may not be completely ruled out at present, the above arguments prompt us to conclude that the oxygenated species are formed as side products at the titania or Ru/titania interfaces and by and large play no significant contribution to the catalytic methanation process.

CONCLUSION

In conclusion, we may state that the mode in which transient carbonyl species are bonded with ruthenium is a deciding factor in their reactivity towards adsorbed or the gaseous hydrogen. The nature of the transient species in turn depends on the metal oxidation state at the time of interaction, the catalyst temperature, and the composition of the reacting stream. The linearly held monocarbonyls formed during CO₂ + H₂ interaction are envisaged to be very reactive in nascent form and are regarded as direct precursors to methane via "active" carbon formation. The thermal behaviour of the carbonyl stretch bands suggests that a hydrogen or an oxygen ligand cobonded to ruthenium facilitated the C–O bond scission. The CO methanation, on the other hand, is governed by a multicarbonyl → methylene group route, particularly in the 300–450 K range (23). This multistep reaction route requires additional energy thus making the process energy intensive in this temperature range (24, 25). At the higher reaction temperatures the direct disproportionation of (CO)_{ad} species may govern the methanation of both the CO and CO₂. As far as oxygenated surface species are concerned, most of them are formed identically on Ru/TiO₂ and metal free titania. These species were very unstable and were not observed under actual reaction conditions i.e., at exposure temperatures above 370 K when a catalyst was active for methanation reaction (Figs. 7, 8). We therefore regard these species as side products which play no significant role towards methane formation from CO₂ + H₂.

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