Catalysis Letters 21 (1993) 245–255

FTIR studies on the CO, CO_2 and H_2 co-adsorption over $Ru–RuO_x/TiO_2$ catalyst

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Received 20 March 1993; accepted 24 May 1993

FTIR spectra of a $Ru–RuO_x/TiO_2$ catalyst obtained on co-adsorption of CO, CO_2 and H_2 in the temperature range of 300–500 K were found to be the sum total of corresponding spectra observed during methanation of individual oxides. The two oxides compete for metal sites and at each temperature they reacted simultaneously to form distinct transient $Ru(CO)_n$ type species even though the nature, the stability and the reactivity of these species were different in the two cases. The monocarbonyl species formed during adsorption/reaction of CO alone or of CO + H_2 were bonded more strongly than those formed during $CO_2 + H_2$ reaction.

Keywords: Infrared spectroscopy; ruthenium/TiO_2 catalyst; IR spectra of adsorbed CO and CO_2

1. Introduction

In recent communications [1,2] we reported that even though carbon dioxide methanation occurred via CO as an intermediate, the nature of transition species was different in the hydrogenation of CO and CO_2. Thus, whereas adsorption/hydrogenation of CO gave rise to multiple CO binding states corresponding to $RuO_x(CO)_n$, where $x = 0–2$ and n varies from 1 to 3, only monocarbonyl species were formed during CO_2 hydrogenation. The frequency and the reactivity of monocarbonyl species (identified as direct precursors of methane) were also found to be different in the two cases. Another distinct feature was observed in the formation of a long methylene group chain over catalyst surface during CO + H_2 reaction which served as a building block to higher hydrocarbon products. No such species were formed in the $CO_2 + H_2$ reaction under similar conditions.

We have now performed in situ FTIR spectroscopic studies on CO, CO_2 and H_2 co-adsorption over a partially oxidised ruthenium on titiana catalyst (represented as Ru–RuO$_x$/TiO$_2$ and referred to as Ru/TiO$_2$ in the text for brevity) to understand how surface species formed during simultaneous adsorption and hydrogenation of CO and CO$_2$ would differ from those formed during the hydrogenation of individual oxides. The adsorption properties of catalyst surface covered a priori with one of the carbon oxides were investigated in detail. Experiments were also performed using ^{13}C labelled carbon oxides and the results are included in this paper. Salient features of IR spectra obtained using $CO + H_2$ and $CO_2 + H_2$ adsorbates are also included for a comparative evaluation.

2. Experimental

The transmission IR spectra were recorded using a 25 mm diameter self-supporting catalyst wafer weighing $\sim$ 70 mg. The time dependent transformations in IR spectra were followed in the sample temperature range of 300–500 K during exposure to $CO + CO_2 + H_2$ (1 : 1 : 6) under both the continuous flow ($\sim$ 8–10 ml min^{-1}) and the batch modes. The samples were pretreated under vacuum (575 K, 2 h) and then under H$_2$ (475 K, 2 h) before exposure to adsorbate gases. The spectrum of such a pellet recorded after cooling to exposure temperature served as a background.

A Mattson-Cygnus 100 FTIR spectrophotometer equipped with a DTGS or a MCT detector was employed and 100–500 scans were co-added at 4 cm^{-1} resolution as required. The frequency values were reproducible within $\pm$1–2 cm^{-1} for the experiments repeated with different lots of a sample. More details about the methods are given in ref. [1].

Titania supported Ru catalyst was prepared using a previously described method [3]. It contained $\sim$ 3.8 wt% of ruthenium and showed a metal dispersion of about 55% [3,4]. About 25% of ruthenium existed in an oxide form and the metal particle size ranged between 10 and 30 Å [3–5]. High purity gases were used after proper purification [1,2].

3. Results and discussion

3.1. CO+CO$_2$+H$_2$ ADSORPTION

Fig. 1 (a) shows the IR spectrum of Ru/TiO$_2$ observed under $CO + CO_2 + H_2$ (1 : 1 : 6) gas mixture flow (10 ml min^{-1}) at ambient temperature. In addition to IR signals due to gaseous CO or CO$_2$, various overlapping signals in the 2200–1900 cm^{-1} region due to chemisorbed CO and in the 1700–1000 cm^{-1} region due to oxygenate species are observed in fig. 1 (a). When the exposures were made at elevated catalyst temperatures, IR bands typical of a methylene group chain (2927 and 2850 cm^{-1}) and also due to methane (3014 and 1302 cm^{-1}) were observed. The rela-

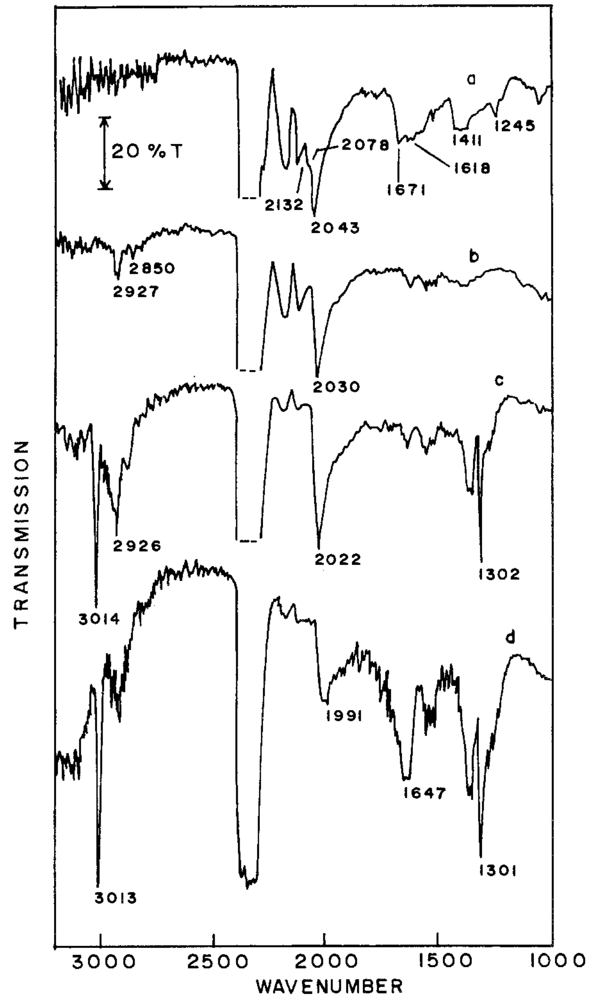

Fig. 1. Infrared spectra of partially oxidised Ru/TiO$_2$ catalyst on 15 min exposure to CO + CO$_2$ + H$_2$ (1 : 1 : 6) flow at the following temperatures: (a) 300 K, (b) 400 K, (c) 420 K and (d) 470 K.

tive intensity of these bands depended on sample temperature. Thus, whereas at the sample temperatures in the 375–410 K range only methylene bands and no methane was observed at temperatures between 410 and 450 K both the methylene group and the methane IR bands were detected. With the further increase in exposure temperature, the intensity of methylene bands decreased and at the temperatures above 460 K only methane bands were predominant. Curves b–d of fig. 1 show typical IR spectra obtained for exposure temperatures of 400, 420 and 470 K respectively. The experiments at progressively increasing temperatures were performed using the same catalyst wafer which was each time given a regeneration pretreatment as described in the experimental. It may also be mentioned that the spectra in fig. 1 were recorded after equilibration of a sample for 10–15 min under adsorbate flow.

As is seen in fig. 1, the rise in exposure temperature resulted in the initial increase of the C–O stretch band intensity until temperatures of about 420 K (fig. 1 (c)) followed by a decrease on further rise in the temperature (fig. 1 (d)). Also, the frequency of this band acquired a progressively decreasing value with the rise in sample temperature as shown in the spectra b–d.

On comparing the data in fig. 1 with those obtained on exposing Ru/TiO_2 to CO + H_2 and CO_2 + H_2 mixtures [1,2], it becomes apparent that the spectra b–d in fig. 1 carry features which are a combination of results obtained during individual hydrogenation of CO and CO_2. This is substantiated by the presence of IR bands due both to methylene bands and methane in fig. 1 (c). As stated in section 1, the methylene group formation is found to occur on this catalyst only from CO + H_2 reaction and not from CO_2 + H_2 [1,2]. A comparative catalyst behaviour is shown in fig. 2 (a)–(c) which gives IR spectra of Ru/TiO_2 at 420 K obtained after 10 min exposure to CO + CO_2 + H_2, CO + H_2 and CO_2 + H_2 streams respectively. The data in fig. 2 (b), (c) show that whereas no substantial amount of methane formed from CO + H_2 at 420 K, significant amount of methane from CO_2 was detected under identical conditions. Similar results were obtained at other reaction tempera-

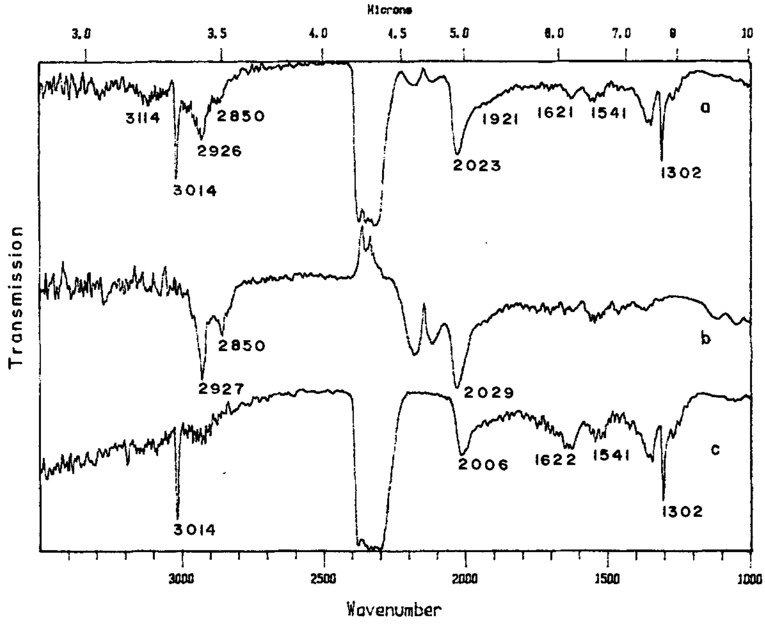

Fig. 2. Comparison of infrared spectra of Ru/TiO_2 recorded after 15 min exposure to the flow of various gas mixtures at 420 K: (a) CO + CO_2 + H_2 (1 : 1 : 6); (b) CO + H_2 (1 : 3); (c) CO_2 + H_2 (1 : 3).

tures. The presence of intense 3014, 2926 and 2850 cm^{-1} bands in fig. 2 (a) thus confirms that both the CO and CO_2 are amenable to simultaneous hydrogenation over Ru/TiO_2 catalyst.

3.2. C–O STRETCH REGION BANDS

Interesting features were noticed on comparison of C–O stretch region bands recorded on exposing a catalyst to different gas mixtures. Spectrum (a) in fig. 3 shows vibrational bands developed on Ru/TiO_2 soon after exposure to $CO + CO_2 + H_2$ stream at ambient temperature. Fig. 3 (b) shows a subtraction spectrum: spectrum a minus IR spectrum of metal free TiO_2 exposed to gas stream under identical condition. Spectrum b thus represents C–O stretch vibrational bands due to species formed at metal sites during initial stages of adsorption. Spectra c–e of fig. 3 are similar subtraction spectra developed with time during prolonged catalyst exposure to gas mixture. These data show that whereas the frequency of 2144 and 2132 cm^{-1} bands remained unaltered, the low region bands showed remarkable variation. Thus, the two overlapping bands at 2062 and 2038 cm^{-1} were formed in the initial stages (fig. 3 (b), (c)) and the prolonged exposure resulted in the appearance of strong bands at around 2082 and 2044 cm^{-1} as shown in spectra d and e recorded after 20 and 30 min of exposure respectively. The spectrum as shown in fig. 3 (e) remained unchanged on continued exposure.

The parallel data obtained on exposure of Ru/TiO_2 to $CO + H_2$ and $CO_2 + H_2$ gas mixtures are reported by us earlier [1,2] and a brief description is given here for comparative evaluation. Thus, the $CO + H_2$ exposures resulted initially in the formation of strong bands at 2144, 2132, 2085 and 2050 cm^{-1} in addition to low frequency bands at around 2000 and 1950 cm^{-1} [1]. Prolonged exposure led to the formation of a weak band at around 2175 cm^{-1} and in the further growth of 2050/2051 cm^{-1} band. Curve f in fig. 3 gives a typical vibrational spectrum of Ru/TiO_2 recorded after continuous 30 min exposure to $CO + H_2$ flow at ambient temperature. In the case of $CO_2 + H_2$ exposures, no bands at frequencies higher than 2100 cm^{-1} were observed even after several hours of exposure [2]. Two bands, a weak band at around 2070 cm^{-1} and an intense band at around 2015 cm^{-1} were observed in the initial stages of $CO_2 + H_2$ exposure. In addition, an asymmetric broadening below 2000 cm^{-1} in the C–O stretch band was also noticeable. The intensity of all these bands increased during further $CO_2 + H_2$ exposure and reached a saturation level in about 30 min time. At the same time the 2015 cm^{-1} band acquired a higher value of about 2041 cm^{-1}. Fig. 3 (g) presents typical data obtained on 30 min exposure of a Ru/TiO_2 wafer to $CO_2 + H_2$ flow at room temperature.

A comparison of the spectra e, f and g in fig. 3 again confirms that the C–O stretch region vibrational bands formed on Ru/TiO_2 during $CO + CO_2 + H_2$ interaction at beam temperature may be considered as the sum total of IR bands obtained during adsorption of $CO + H_2$ and $CO_2 + H_2$. For instance, the high fre-

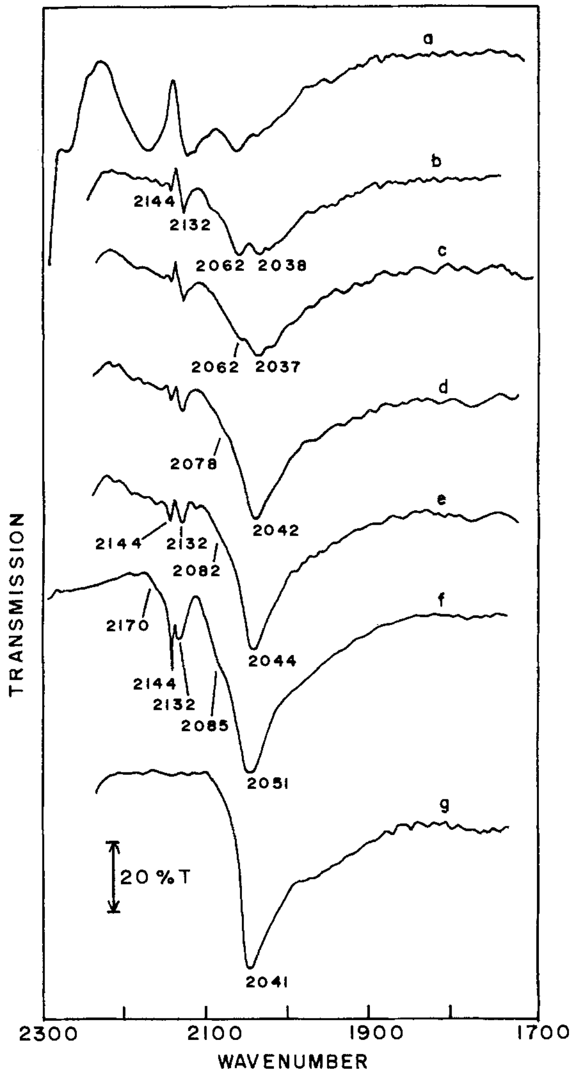

Fig. 3. Growth of C–O stretch region bands when Ru/TiO_2 catalyst was under CO + CO_2 + H_2 (1 : 1 : 6) flow at 300 K for varying periods of time: (a) within 0.5 min of switching gas flow, (b) difference spectrum: spectrum (a) minus spectrum of TiO_2 under identical flow conditions, (c)–(e) difference spectra recorded after 5, 20 and 30 min of exposure respectively. Curves (f) and (g) show comparative difference spectra recorded after 30 min exposure at 300 K to the flow of CO + H_2 (1 : 3) and CO_2 + H_2 (1 : 3) respectively.

quency (HF) bands at around 2144 and 2132 cm^{-1} (fig. 3 (e)) are characteristic of CO + H_2 adsorption (fig. 3 (f)). As has been discussed in ref. [1] in detail, these bands in conjunction with a strong band at 2087 cm^{-1} are attributed to multicarbonyl $[M(CO)_n]$ type species held at ruthenium sites of different oxidation states. No such species are formed during $CO_2 + H_2$ adsorption [2]. On the other hand, the low frequency (LF) bands in the 1900–2045 cm^{-1} region (fig. 3 (e)) identified with the linear monocarbonyl species [1,2], bear resemblance in frequency and shape with the bands observed during $CO_2 + H_2$ adsorption under identical conditions (fig. 3 (g)).

As has been brought out in our earlier publications [1,2], the vibrational bands due to monocarbonyl species appeared at different frequencies in the adsorption of $CO + H_2$ and $CO_2 + H_2$ suggesting a difference in their bonding characteristics. The thermal stability and the reactivity of these bands formed in the two cases and identified as methane precursors were also found to be different. These species were easily removed and were more reactive towards hydrogenation in the case of $CO_2 + H_2$ adsorption/reaction [1,2]. The effect of evacuation on the species left behind on the catalyst surface following exposure to different gas streams is shown in fig. 4. Spectra a–c in fig. 4 exhibit C–O stretch vibrational bands from species remaining on Ru/TiO$_2$ after 1 h of evacuation of IR cell following 30 min exposure to $CO + CO_2 + H_2$, $CO + H_2$ and $CO_2 + H_2$ respectively. As mentioned above, $CO + H_2$ interaction led to more strongly bonded species giving rise to 2132, 2070

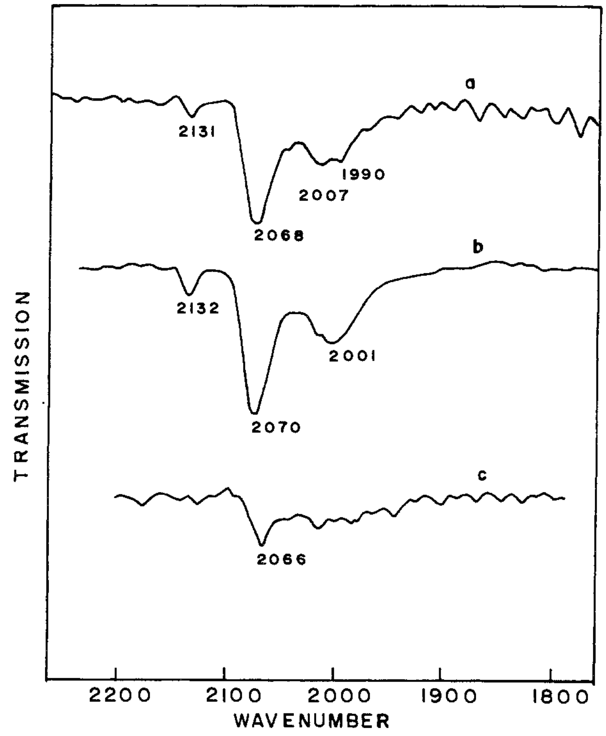

Fig. 4. Effect of 1 h evacuation on the C–O stretch bands formed on Ru/TiO$_2$ in 30 min exposure at 300 K to a flow of (a) $CO + CO_2 + H_2$ (1 : 1 : 6), (b) $CO + H_2$ (1 : 3) and (c) $CO_2 + H_2$ (1 : 3).

and 2001 cm^{-1} bands (fig. 4 (b)) as compared to those species formed during CO_2 + H_2 exposure and responsible to weak IR bands at 2066 cm^{-1} in fig. 4 (c). The 2068 cm^{-1} band in fig. 4 (a) may thus be considered as overlap of similar bands seen in figs. 4 (b) and (c). Similarly, whereas the IR bands at 2131, 2007 and 1990 cm^{-1} in fig. 4 (a) are typical of surface species formed on CO + H_2 interaction (fig. 4 (b)) a number of weak vibrational bands in the 1750–2000 cm^{-1} region due to adsorbed moisture are observed at room temperature in the CO_2 + H_2 reaction only (fig. 4 (c)). These observations thus confirm again that both the adsorbates react simultaneously and leave behind distinct species on the catalyst surface.

Similar conclusions could be drawn in the studies performed at elevated temperatures in the range of 300–500 K. Fig. 5, for example, presents a comparative evaluation of IR bands observed during exposure to three gas mixtures at 420 K. The intense band at 2022 cm^{-1} observed during CO + CO_2 + H_2 adsorption (fig. 5 (a)) may be regarded as overlap of bands at 2027 and 2006 cm^{-1} observed during adsorption of CO + H_2 (fig. 5 (b)) and that of CO_2 + H_2 (fig. 5 (c)). Also, the strong absorbance in the 2000–1900 cm^{-1} region (fig. 5 (a)) is characteristic of IR bands observed during CO_2 + H_2 exposures [2] again confirming that both the CO and CO_2 interact simultaneously and independently over Ru/TiO$_2$ at different temperatures.

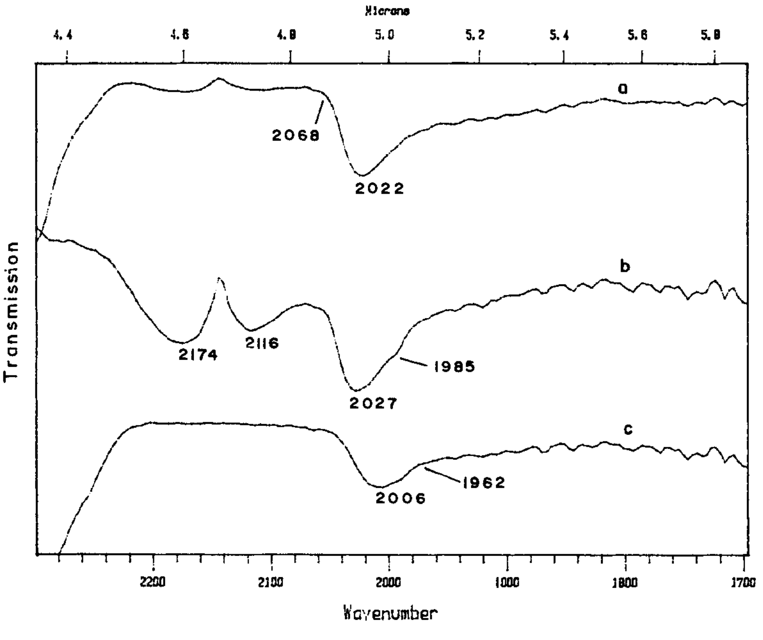

Fig. 5. C–O stretch region bands from Ru/TiO$_2$ catalyst on 30 min exposure to different gas mixtures at 420 K: (a) CO + CO_2 + H_2, (b) CO + H_2, (c) CO_2 + H_2.

3.3. CO-ADSORPTION OF $^{12}CO + ^{13}CO_2 + H_2$

IR spectra of Ru/TiO$_2$ obtained on exposure to 20 Torr of CO + CO$_2$ (60% ^{13}C) + H$_2$ (1 : 1 : 6) in batch mode at different sample temperatures carried all the features similar to those shown in fig. 1 except the presence of two distinct methane peaks at 3015 and 3008 cm^{-1} corresponding to $^{12}CH_4$ and $^{13}CH_4$ respectively. The relative intensity of these two peaks again demonstrated simultaneous interaction and hydrogenation of CO and CO$_2$.

3.4. REACTION OF $^{12}CO_2 + H_2$ ON A CATALYST SURFACE PRECOVERED WITH $^{13}CO + H_2$

To evaluate if a catalyst surface covered already with CO would be accessible to CO$_2$ adsorption and hydrogenation, a Ru/TiO$_2$ wafer was exposed to 100 Torr of ^{13}CO (60% ^{13}C) + H$_2$ (1 : 3) gas mixture at a sample temperature of 420 K. Most of the gas mixture reacted in about 1.5 h and gave rise to strong methylene bands of 2925 and 2853 cm^{-1} in addition to a broad band in the C–O stretch region with maximum at around 2017 cm^{-1} and weak bands in the 2200–2400 cm^{-1} range due to $^{12}CO_2 + ^{13}CO_2$ (fig. 6 (a)). No measurable isotopic shift is observed in CH$_2$

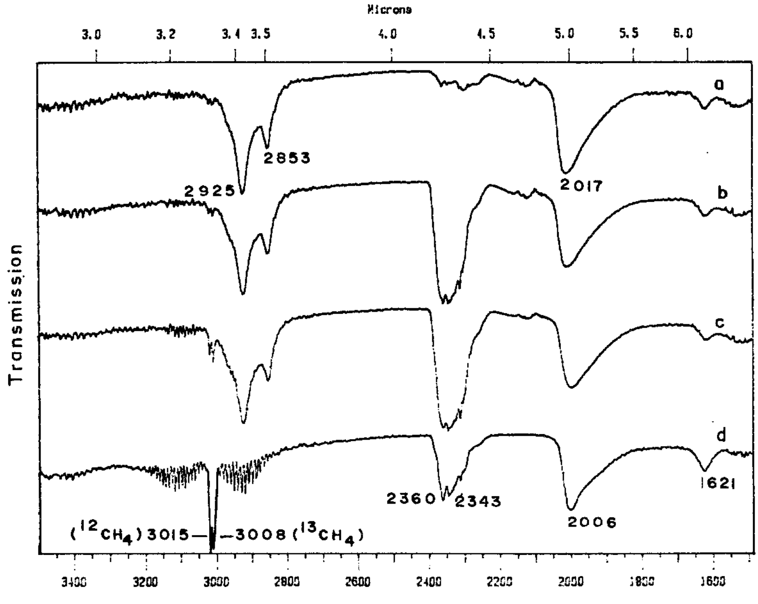

Fig. 6. Effect of preadsorbed CO on the adsorption/hydrogenation of CO$_2$: IR spectra of Ru/TiO$_2$ following (a) 1.5 h exposure at 420 K to 100 Torr of ^{13}CO (60% enriched) + H$_2$, (b) further addition of 100 Torr $^{12}CO_2 + H_2$, (c) and (d) on subsequent rise in sample temperature to 450 and 470 K respectively.

group frequencies possibly because of overlap of shifts due to ^{12}C–^{12}C, ^{12}C–^{13}C and ^{13}C–^{13}C type various combinations each giving rise to different isotopic shift. Subsequent to exposure of the catalyst to $CO + H_2$ for 1.5 h at 420 K, when 100 Torr of $CO_2 + H_2$ (1 : 3) were introduced into the IR cell, a spectrum as shown in fig. 6 (b), recorded 15 min after $CO_2 + H_2$ addition, was observed. It may be noticed that as compared to copious CH_4 formation from $CO_2 + H_2$ reaction at 420 K over clean catalyst surface (fig. 2 (c)), no detectable methane from CO_2 was formed over CO covered surface (fig. 6 (b)). Methane formation commenced on raising catalyst temperature to 450 K. The relative intensity of 3015 and 3008 cm^{-1} bands due respectively to $^{12}CH_4$ and $^{13}CH_4$, however, suggests that even at a catalyst temperature of 450 K, methane formed predominantly from CO (fig. 6 (c)). Further rise in sample temperature to 470 K led to a significant increase in the intensity of the $^{12}CH_4$ IR band (fig. 6 (d)) suggesting complete methanation of CO_2 along with that of CO.

The methane formation from CO_2 could, however, be observed at a lower temperature when the catalyst surface was pre-exposed to lower $CO + H_2$ pressures. For instance, in a typical experiment when a catalyst wafer was exposed to 50 Torr of $^{13}CO + H_2$ at 420 K, measurable methane formation was detected during subsequent 50 Torr $CO_2 + H_2$ introduction (cf. fig. 6 (b)).

3.5. REACTION OF $^{13}CO + H_2$ ON A CATALYST SURFACE COVERED WITH $^{12}CO_2 + H_2$

Contrary to the behaviour reported above, the presence of carbon dioxide in the reaction cell appeared to have little effect on the subsequent adsorption/hydrogenation of $CO + H_2$. Thus, in a typical experiment when a catalyst wafer was equilibrated with 100 Torr of $CO_2 + H_2$ at 420 K followed by inclusion of 100 Torr of $CO + H_2$, strong bands at 2925 and 2853 cm^{-1} characteristic of methylene groups were detected. Since such species are formed during $CO + H_2$ reaction only and not during $CO_2 + H_2$ reaction, it is evident that the presence of CO_2 or that of surface species formed in the $CO_2 + H_2$ reaction causes no hinderance to CO hydrogenation.

The above results thus reveal that the monocarbonyl species formed during $CO + H_2$ adsorption are bonded more strongly than the similar species developed during $CO_2 + H_2$ adsorption under identical conditions. This view is substantiated if we compare the evacuation effect on C–O stretch bands formed in different experiments (fig. 4). As mentioned above the C–O stretch region bands formed during $CO_2 + H_2$ adsorption are removed easily on pumping while these bands showed fairly high stability when formed during $CO + H_2$ exposure. These conclusions are in agreement with our contention that even though $CO_2 + H_2$ reaction proceeds via adsorbed monocarbonyls as intermediate, the bonding and the reactivity of these transient species are different than those formed during $CO + H_2$ reaction.

4. Concluding remarks

Based on the data presented above, we may conclude that the CO and CO_2 compete for adsorption and hydrogenation at a particular metal site. At each temperature, the two oxides may simultaneously give rise to distinct transient CO_{ad} species during hydrogenation at metal sites even though the nature, the stability and the reactivity of these species may vary in the two cases. The monocarbonyl species formed during $CO + H_2$ adsorption are bound strongly and inhibit the $CO_2 + H_2$ reaction at temperatures lower than 450 K (fig. 6 (b)). At higher catalyst temperatures both the oxides appear to react unhindered.

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