Methanation and adsorption of CO, CO + H₂, CO₂ and CO₂ + H₂ over Ru-RuOₓ/TiO₂ catalyst: TDS and FTIR studies

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The adsorption of CO and CO + H₂ over Ru-RuOₓ/TiO₂ catalyst gives rise to at least three binding states identifiable with Ru(CO)ₙ and the linearly bonded monocarbonyl species. The fraction of monocarbonyl species increases considerably in the presence of co-adsorbed hydrogen and also at higher exposure temperatures. Whereas CO₂ is weakly adsorbed over catalyst surface, the exposure of catalyst to CO₂ + H₂ results in abundant formation of linearly-bound monocarbonyl species and adsorbed water. The CO molecules adsorbed as monocarbonyl are envisaged to be direct precursor of ‘active’ carbon and, hence, of methane. The lower temperature needed for CO₂ + H₂ reaction as compared to that for CO + H₂ reaction, particularly for catalyst temperatures in the range 300-450K, is attributed to the higher reactivity of nascent Ru{(CO)}ₙ ad species generated directly during CO₂ + H₂ interaction. In the case of CO methanation under similar conditions, these species are produced during thermal transformation of multicarbonyls thus making the process energy intensive. The promotional effect of hydrogen is due to its role in the extraction of oxygen from Ru{(CO)}ₙ or Ru{(CO)ₙ}_ad species thus facilitating the formation of active ‘CO’ or ‘C’ reaction intermediates.

The yields of hydrocarbons in the hydrogenation of CO and CO₂ have been found to be higher when titania supported noble metals, such as Ru, are used as compared to the yields obtained using corresponding metals supported on zirconia, silica or alumina. The influence of titania on the adsorption and catalytic properties of a dispersed metal has been attributed to the occurrence of strong metal support interaction, though the precise nature of this interaction has been a matter of controversy. For example, whereas some authors believe that titania based catalysts owe their peculiar behaviour to electronic charge transfer between the metal and the support, others propose that geometric factors play a crucial role. Some other explanations are based on changes in metal crystallite morphology, encapsulation of the metal crystallites by support and the hydrogen spillover, etc.

Even though a large number of investigations have been devoted to the study and review of CO hydrogenation reaction over supported noble metals, much less attention has been paid to the corresponding reaction of CO₂ (ref. 18-21). Some other issues pertaining to these reactions remain unresolved. For example, it is reported that carbon dioxide methanation over supported rhodium catalyst proceeds via formation of carbon monoxide and its subsequent dissociation. A question then arises as to why CO₂ methanation requires a lower temperature as compared to that for CO under identical test conditions, as has been widely reported. Another intriguing aspect concerns observed enhancement in catalytic activity when a part of noble metal is present in the oxide form.

It has been shown in earlier studies that the activity of a titania-based catalyst may be improved by adopting suitable preparative procedures which modify support characteristics and also the oxidation state and dispersion of active metal. Thus, following a procedure called deposition/precipitation, a partially reduced ruthenium oxide on titania represented as Ru-RuOₓ/TiO₂ has been developed which shows considerable low temperature (<375K) activity, particularly for CO₂ hydrogenation. A part of ruthenium in the oxide form was found to be essential for the low temperature catalytic activity.

In the present study we aimed at investigating the surface processes occurring in the interaction of CO or CO₂ over supported ruthenium. The thermal desorption and the infrared spectroscopy studies were, therefore, undertaken to investigate
the binding states and the nature of species formed in the interaction/adsorption of CO and CO₂ over Ru-RuOₓ/TiO₂ catalyst at different temperatures in the absence and in the presence of hydrogen. The catalyst activity for the CO and CO₂ hydrogenation reactions was also evaluated using a flow through microcatalytic reactor.

Materials and Methods

The preparation and characterization of the catalyst used in this study have been described in detail elsewhere. In brief, TiO₂ powder (Degussa p 25, 55 m² g⁻1 BET area) was suspended in an aqueous solution of ruthenium trichloride and the mixture was hydrolysed at 345K by adjusting the pH to 4-4.5 with KOH under constant stirring. After evaporation at 365K, the residue was calcined in air at 445K for 18h and then at 650K for 18h. Residual KCl was then removed by dialysis and the sample was dried at 385K. The catalyst was reduced in hydrogen at an optimized temperature in the range 475-525K and consisted of about 3.8 wt % of ruthenium. The catalyst having surface area of ~55 m² g⁻¹ consisted of about 3.8 wt % ruthenium. The XPS analysis showed that about 70% of the metal existed in oxide form. Electron microscopy revealed that the ruthenium particle size ranged between 10 and 30Å.

Though the proper representation of the used catalyst is Ru-RuOₓ/TiO₂, it is referred to as Ru/TiO₂ catalyst in the text for brevity.

Catalytic activity

The catalytic activity was evaluated in the range 300-600K using a flow-through tubular quartz reactor operating at atmospheric pressure. A fixed bed of 500 mg of the catalyst (particle size 0.1-0.15mm) was pretreated at 575K for 1-2h under hydrogen flow (~30 ml min⁻¹) and was then exposed at required temperature to CO+H₂ (1:4) or CO₂+H₂ (1:4) stream at a flow rate of about 15 ml min⁻¹. The reaction products sampled at regular intervals were analysed with a gas chromatograph employing a thermal conductivity detector and a Porapak-Q column maintained at 300K. The experiments were also performed in pulse mode where 100 µl pulses of CO or CO₂ were introduced at regular intervals while the catalyst bed was maintained under hydrogen flow (~15 ml min⁻¹) at a particular temperature.

Thermal desorption spectroscopy (TDS)

For TDS measurements, about 200 mg of a sample was packed in a stainless steel tube reactor (i.d. 5 mm) connected at one end to a gas manifold. The catalyst could be heated in this set up under H₂, He or vacuum in a desired sequence without exposure, in between, to air. The desorbed effluents were fed simultaneously to a mass spectrometer (Micromass-2 from Micromass Ltd, U.K., scanning range 1-60 amu) and a Perkin-Elmer gas chromatograph. The gases were directly introduced to the detector by eliminating the GC column. As far as possible, stainless steel tubings of 1.58 mm diameter were employed for connections to avoid the dead volume effect on the two analyses by GC and MS. Whereas GC signal was recorded continuously during a particular desorption cycle, the mass spectra were recorded in 1-60 mass batches after every 15K. The mass signals were calibrated using standard mixtures and the CO and H₂O signals were multiplied by a factor of 0.9 and 0.73 respectively to compensate for sensitivity factors. Even though the mass spectra thus reconstituted were not well resolved and one to one correspondence with GC response profiles was not seen in some cases, they nevertheless gave important information about the composition of gases evolved during different stages of thermal desorption.

The following procedure was adopted to record each thermal desorption profile. The sample was first heated under hydrogen flow (40 ml min⁻¹) at about 525K for 1h and then under helium for about 1.5h. These pretreatment conditions were chosen to maintain conditions similar to those employed for the catalyst activity measurements. No moisture was found to be released after above pretreatments as was ascertained by mass spectral analysis. The sample, cooled to ambient temperature, was then exposed to CO or CO₂ flow (10 ml min⁻¹) for about 10-15 min. For the exposure of CO+H₂ or CO₂+H₂, the sample was cooled under hydrogen and CO or CO₂ was introduced along with H₂ flow. No CH₄ was formed during gas mixture flow. In both the cases, the sample was then maintained under helium flow (40 ml min⁻¹, 1-1.5h) to remove loosely held adsorbates, the removal of which was confirmed again by mass spectrometry. Profiles were obtained from detector response on heating the sample at a linear rate of about 6K min⁻¹ under helium flow and the effluent composition was analysed using mass spectrometer. The mass signal at 28 amu was compensated for the small contribution of carbon dioxide to this signal.

Fourier-transform infrared spectroscopy

A high temperature-high pressure stainless steel
IR cell (path length 6 cm) described elsewhere in detail was used in these studies. The cell had calcium fluoride windows and permitted in situ treatment of a sample at temperatures up to 625 K under a flowing inert or reactive gas stream or alternatively under vacuum of up to $10^{-5}$ Torr.

About 80 mg of finely powdered catalyst sample was pressed into a self-supporting wafer of 25 mm diameter. The catalyst wafer was subjected to a pretreatment in H$_2$ at 500 K and then under vacuum at 575 K. A spectrum recorded after cooling the sample to ambient temperature served as a background. The spectra were then recorded after introduction of an adsorbate. The effects of exposure temperature and post-exposure thermal annealing on the appearance of different IR bands were also evaluated.

A Mattson (USA) model Cygnus 100 FTIR using DTGS detector was employed to record infrared transmission spectra. About 100-200 scans at 4 cm$^{-1}$ resolution were collected for each spectrum as per requirement.

High purity He and H$_2$ gases were used after suitable purification treatments. The gases were found to be free of H$_2$O and CO$_2$ impurities within the detection limits of mass spectrometer. Carbon monoxide and carbon dioxide gases of 99.99% purity were used without further purification.

**Results**

**Catalytic activity**

Curves a and b in Fig. 1 show methane yields during reaction of CO$+H_2$ and CO$_2$+$H_2$ gas streams at different temperatures. Whereas detectable amounts of methane formed from CO$_2$ at catalyst temperatures as low as 340 K, CO methanation commenced only at temperatures above 450 K (Fig. 1a). Complete conversion of both CO and CO$_2$ to methane was observed at reaction temperatures above 500 K. Small yields of C$_2$H$_6$ (~1%) and CO$_2$ were also observed some times during CO hydrogenation in the temperature range 400-475 K. The C$_2$H$_6$ yield, however, increased when CO and H$_2$ were reacted in 1:3 stoichiometry. On the other hand, no ethane formed in the CO$_2$+$H_2$ reaction at all the temperatures under study. A similar behaviour was observed when the experiments were performed in pulse mode. For instance, on employing a similar catalyst in a pulse mode reactor, only 5% of a CO pulse was methanated at 375 K, the methane yield from CO$_2$ being about 25% under identical conditions.

**Thermal desorption spectroscopy**

**CO exposure:** Figs 2(a) and 3(a) give thermal desorption profiles for Ru/TiO$_2$ catalyst exposed to CO at 305 and 355 K respectively. The constituents of the eluted gas as revealed by mass spectral data are also shown in these figures. The profiles 2(a) and 3(a) could be roughly resolved into at least 4 individual bands as shown by the broken curves in these figures. Thus, for the CO exposure at 305 K, the profile consisted of overlapping bands with the maxima at around (±5 K) 375, 425, 495 and 560 K appearing mainly due to evolution of CO$_2$, though a small amount of CO was also evolved. A small amount of water was...
released at the sample temperatures greater than 550K (Fig. 2). The water release as shown in Fig. 2 remained unaffected even when a prolonged pretreatment was given to a sample at 575K. Also, similar profiles, though with reduced intensities, were observed when the same sample was reused for successive adsorption/desorption cycles.

With the increase in CO exposure temperature, the lower temperature desorption peaks progressively disappeared and relatively more intense peaks, mainly due to CO₂, appeared at 500 and 560K (Fig. 3). Thus, the ratio of desorption bands 495/375 and 495/425 was found to be 0.4 and 0.3 in the CO exposure at 305K, the corresponding values in the case of 355K exposure being about 4.5 and 0.9 respectively.

The desorption profiles were more intense when the catalyst was exposed to CO+H₂ (1:2) gas mixture. Fig. 4 shows the desorption profile and the mass signals after a Ru/TiO₂ sample was exposed to CO+H₂ at 300K for 10 min. The profile could be seen as consisting of at least 4 distinct overlapping bands centered at around 375, 430, 495 and 550K. An interesting feature of these data is the evolution of a large amount of carbon monoxide in contrast to the results obtained for CO exposure under helium (Fig. 2). Mass analysis also indicated the existence of multiple CO binding states responsible for desorption peaks in the range 350-550K (Fig. 4). The CO₂ in this case was released only in the 450-650K temperature range. Another noticeable feature of Fig. 4 is the release of at least two times more water than that shown in the Figs 2 and 3. It may be mentioned here that no hydrogen or methane release was observed at any stage of the desorption process.

When the CO+H₂ exposure was made at higher sample temperatures, the lower temperature peaks at 375 and 430K due to release of CO disappeared progressively. Typical data obtained for CO+H₂ exposure at a sample temperature of 400K are given in Fig. 5. The areas under different peaks reveal that the 495/375 and 495/425
band ratio increases by about three times when the exposure temperature is raised from 300 to 400K.

CO\textsubscript{2} exposure: Only a small amount of carbon dioxide was adsorbed when exposed over Ru/TiO\textsubscript{2} under flowing helium carrier gas (Fig. 6). The detector response curve in Fig. 6 reveals the existence of three weak desorption bands at around 350, 440 and 510K. The increase in the sample temperature led to further reduction in the CO\textsubscript{2} adsorption and to the near absence of 350K peak in the desorption profile.

When Ru/TiO\textsubscript{2} was exposed to CO\textsubscript{2} in the presence of hydrogen, large amounts of CO\textsubscript{2} and water desorbed during subsequent thermal treatment. A very small amount of CO was also released. Fig. 7 shows a desorption profile and the mass signals of constituent gases when a Ru/TiO\textsubscript{2} sample was exposed to CO\textsubscript{2} + H\textsubscript{2} at 300K and then equilibrated under He. Bands with maxima at 350 and 425K arising due mainly to CO\textsubscript{2} and bands with the maxima at around 485 and 530K due both to H\textsubscript{2}O and CO\textsubscript{2} may clearly be discerned in these data. The water release profile appeared to comprise two overlapping bands at around 520 and 570K.

The amount of desorbed H\textsubscript{2}O and CO increased further when the CO\textsubscript{2} + H\textsubscript{2} mixture was passed over Ru/TiO\textsubscript{2} at higher temperatures whereas desorption peaks below 450K became less intense as was the case in CO + H\textsubscript{2} experiments.

**FTIR spectroscopy**

Figure 8a shows infrared spectrum of Ru/TiO\textsubscript{2} recorded at ambient temperature with the sample under CO + H\textsubscript{2} (1:3) flow. In addition to the overlapping bands in C–O stretch region, IR bands at 2358 and 2340 cm\textsuperscript{-1} due to CO\textsubscript{2}, and at around 1620 and 1378 cm\textsuperscript{-1} due to oxygenate species were observed. CO\textsubscript{2} + H\textsubscript{2} exposure under similar conditions resulted in the formation of adsorbed CO giving rise to a prominent CO stretch at 2041 cm\textsuperscript{-1} and overlapping shoulder bands in the 1850-2000 cm\textsuperscript{-1} region (Fig. 8b). In addition, various overlapping bands were observed in the region 1000-1700 cm\textsuperscript{-1} due to oxygenated surface species and also in the hydroxyl group region (not shown in the figure) indicating the formation of large amounts of free and adsorbed water.
A new pair of bands at 2928 and 2853 cm⁻¹ assignable to a long chain of methylene groups was also detected in CO + H₂ interaction at the exposure temperatures in the range 370-420K. At higher sample temperatures, these bands were replaced by IR bands due to CH₄. The 2928 and 2853 cm⁻¹ bands were, however, not observed in the CO₂ + H₂ adsorption at all the sample temperatures, as has been described elsewhere in detail.

Figure 9 presents the C - O stretch region spectra obtained after compensating for the presence of gaseous adsorbates in the cell. For this purpose, spectra were recorded under identical conditions using metal free titania and these were then subtracted from the respective spectra in Fig. 8. Thus, spectrum a in Fig. 9 shows C - O stretch vibrational bands generated over Ru/TiO₂ in room temperature exposure to CO + H₂. At least six bands around 2144, 2133, 2085, 2052, 1995 and 1940 cm⁻¹ can be located, the presence of which was further confirmed by spectrum deconvolution and also by parallel investigations using ¹³C labelled carbon monoxide. These bands have been discussed in detail in our earlier communication and they have been attributed to Ru(CO)ₙ and RuOₙ(CO)ₙ type species (where n = 1-3 and x ≤ 2). Whereas the IR bands appearing at frequencies greater than 2080 are identified with multicarbonyl form, the lower frequency bands are known to arise due to monocarbonyl species. Almost similar bands were observed when CO alone was adsorbed over Ru/TiO₂, as is reported earlier. The C - O stretch bands due to adsorbed CO over Ru have been reported by various other research groups also and have been reviewed in reference 34.

The C - O stretch bands appearing as a result of CO₂ + H₂ interaction were, however, quite different in frequency from those reported above. In this case a prominent band was observed at 2041 cm⁻¹ with weaker and overlapping bands at both the higher and lower frequency sides (Fig. 9b). Deconvolution of spectrum 9b, as shown in Fig. 9c, clearly revealed presence of distinct bands at 2082, 2041, 2009 and 1975 cm⁻¹. These bands have been attributed to monocarbonyl species bonded linearly at different metal sites. Infrared studies by other research groups have also reported CO formation in the CO₂ + H₂ adsorption over ruthenium and other noble metals.

**Thermal stability**

Effects of exposure temperature and post-annealing on different IR bands are reported elsewhere by us in detail and only salient features are mentioned below to help in understanding our TDS data.

**Effect of exposure temperature:** The increase in the exposure temperature above 370K resulted in almost complete disappearance of IR bands in the region 1000-1700 cm⁻¹ in the case of both the CO + H₂ and CO₂ + H₂ experiments. In the C - O stretch region, the higher frequency (2000-2145 cm⁻¹) bands observed from CO or CO₂ + H₂ adsorption were removed progressively on raising the sample temperature, while the intensity of low frequency bands attributable to monocarbonyls showed a considerable increase. For instance, at an CO + H₂ exposure temperature of 420K, no C - O stretch bands were observable in the region 2145-2050 cm⁻¹. Instead, a prominent peak was observed at 2029 cm⁻¹ in addition to the shoulder bands at lower frequency. With the further increase in sample temperature to 470K,
only a weak band at about 1980 cm\(^{-1}\) was observed. Similar progressive removal of higher frequency C–O stretch band was observed in the CO\(_2\) + H\(_2\) exposure at elevated temperatures\(^{35}\).

**Effect of post-exposure annealing:** The IR bands due to oxygenate species, formed during both the CO + H\(_2\) and CO\(_2\) + H\(_2\) exposures, disappeared in post-exposure annealing at 370K. In the C–O stretch region, the stability of various bands depended on the composition of adsorbate. The higher frequency bands formed in the CO or CO + H\(_2\) adsorption were removed progressively with the increasing temperature, the process being promoted by the presence of coadsorbed hydrogen\(^{34}\). Thus, when CO alone was adsorbed the C–O stretch bands due to adsorbed CO were very stable even at a temperature of 470K and were removed only after prolonged pumping of the cell. On the other hand, these bands formed during CO + H\(_2\) exposure were removed after evacuation for 15-20 min at 470K. The CO stretch bands formed in the CO\(_2\) + H\(_2\) interaction were also easily removed on evacuation of the sample at the exposure temperature\(^{35}\).

**Discussion**

The desorption profile shown in curve “a” of Fig. 2 and the progressive removal of lower temperature bands at higher exposure temperatures (Fig. 3a) reveal the existence of at least three distinct binding states for adsorption of CO over Ru/TiO\(_2\) under an inert medium of helium. The mass spectral data in these figures show that the CO is held irreversibly and converts to CO\(_2\) on thermal treatment. The source oxygen responsible for CO oxidation may be identified with the titania support, hydroxyl groups and the suboxides of ruthenium. The conversion of Ru to a lower oxidation state and that of titania support to TiO\(_2\)-5 species as a result of CO interaction is well documented\(^{1,12,17,39,43}\). Some of the desorbed gases, particularly those evolved at temperatures higher than 450K, may have their origin in the carbonate or bicarbonate type species which are known to form over reducible oxide based catalysts during CO/CO\(_2\) interaction\(^{3,8,19,34}\). Though the studies using CO\(^{18}\) are now planned to unequivocally establish lattice oxygen participation, recent microcalorimetric investigations\(^{36}\) support our point of view. The Boudouard disproportionation reaction may, however, contribute to CO\(_2\) formation at elevated temperatures\(^{1}\).

The decreasing intensity of low temperature bands in TDS profile recorded for higher exposure temperatures (Fig. 3a) has striking similarity with the disappearance of higher frequency C–O stretch bands (2085-2144 cm\(^{-1}\) region) as a result of thermal activation. The temperature required for the removal of lower frequency bands, which are attributed to monocarbonyl species, corresponds with 495K desorption band (Fig. 2a). We may thus attribute the 375 and 425K desorption bands to multicarbonyl (Ru(CO)\(_n\)) species and the 495/500K band to the CO bonded in monocarbonyl form. The relative areas under various desorption bands show that the disappearance of 375 and 425K peaks on thermal activation is accompanied by the growth of 495K band (Fig. 3a). These results thus show that the multicarbonyl species transform to monocarbonyl form at metal sites on thermal activation, as was also concluded in our previous IR study\(^{34}\).

A comparison of TDS profiles in Figs 2(a) and 3(a) with those in Figs 4(a) and 5(a) shows that the CO binding states are similar in the absence and in the presence of hydrogen which again is in agreement with our IR results\(^{34}\). The distinct features in Figs 4 and 5 are, however, the large intensities of desorption bands at temperatures above 500K and the release of large amounts of CO and H\(_2\)O. These observations suggest that the basic role of hydrogen lies in the abstraction of oxygen from adsorbed carbonyl species thus promoting their transformation from one form to the other. The hydrogen may also reduce a part of CO\(_2\) formed during CO-RuO\(_x\) or CO-TiO\(_2\) interactions as is evident from the large CO mass spectral bands in Figs 4 and 5. The surface processes occurring in the CO + H\(_2\) adsorption may thus be represented as follows:

\[
\begin{align*}
\text{Ru}(\text{CO})_n + \text{H}_2 & \rightarrow \text{Ru}(\text{CO})_{n-1} + \text{Ru} + \text{C} + \text{H}_2\text{O} \quad \text{... (i)} \\
\text{Ru}(\text{CO})_n + \text{H}_2 & \rightarrow \text{Ru} - \text{C} + \text{H}_2\text{O} \quad \text{... (ii)} \\
\text{RuO}_x + \text{H}_2 & \rightarrow \text{RuO}_{x-1} + \text{H}_2\text{O} \quad \text{... (iii)} \\
\text{Ru} - (\text{CO}_2)_{\text{ads}} + \text{H}_2 & \rightarrow \text{Ru} + \text{CO} + \text{H}_2\text{O} \quad \text{... (iv)}
\end{align*}
\]

These conclusions find support from recent studies of Hoffman and Robbins\(^{44}\) based on the use of ruthenium single crystals.

Desorption profiles in Figs 6 and 7 show that whereas a very small amount of CO\(_2\) adsors under inert atmosphere, an intense desorption profile is observed after CO\(_2\) + H\(_2\) exposure due to the release of CO, H\(_2\)O and CO\(_2\) (Fig. 7a). This is in agreement with an earlier study which showed that H\(_2\) and CO\(_2\) chemisorption exhibit strong co-adsorption synergy\(^{30}\). The data in Fig. 7 reveal CO formation during CO\(_2\) + H\(_2\) reaction on catalyst surface. IR spectroscopy studies have similar
ly shown that a large amount of CO is generated in the exposure of Ru/TiO\textsubscript{2} to CO\textsubscript{2} + H\textsubscript{2} (Figs. 8, 9).

The following picture thus emerges from the observations made above. The CO and the CO + H\textsubscript{2} interactions lead to formation of both the multicarbonyl and the monocarbonyl species whereas the CO\textsubscript{2} + H\textsubscript{2} interaction results primarily in the formation of linearly held Ru-CO type species (Figs 8, 9). These species are stabilized in the presence of oxygen in RuO\textsubscript{x} moieties as has also been suggested by Lane and Wólf\textsuperscript{45} and by Yokomizo and coworkers\textsuperscript{37}. It has been suggested that the linearly held carbon monoxide is more reactive than the bridge-bonded CO, and is a direct precursor of methane either via formation of methylene groups or via active carbon formation\textsuperscript{14,36}. This concept helps in explaining the catalytic behaviour of supported Ru as shown in Fig. 1. We may thus argue that in the case of CO + H\textsubscript{2} reaction, a large portion of CO is held as multicarbonyls which may not participate in the hydrogenation reaction until converted to methylene groups or to monocarbonyl form. Such transformation is complete only at temperatures around 450K (for IR evidence, see ref. 34). On the other hand, in the case of CO\textsubscript{2} + H\textsubscript{2} reaction, linearly bonded monocarbonyls are formed even at room temperature and this explains why CO\textsubscript{2} + H\textsubscript{2} methanation proceeds at a significant rate at temperatures lower than 450K (Fig. 1). CO methanation may, therefore, be considered to follow the multistep processes, i.e., Ru(CO)\textsubscript{4} \rightarrow Ru(CO) \rightarrow Ru - C \rightarrow CH\textsubscript{x}, or Ru(CO)\textsubscript{3} \rightarrow Ru(CH\textsubscript{3}) \rightarrow C\textsubscript{n}H\textsubscript{2n+2} thus requiring higher energy than that for the CO methanation where the monocarbonyls are formed directly. It is also of interest to note that the prominent band due to CO stretch appears at frequencies 2052 and 2041 cm\textsuperscript{-1} in Figs 9a and 9b respectively indicating that the CO formed during CO\textsubscript{2} + H\textsubscript{2} reaction is bonded differently than the CO adsorbed directly from CO + H\textsubscript{2}. Therefore, the higher catalytic activity for CO\textsubscript{2} + H\textsubscript{2} reaction may also be attributed to higher reactivity of nascent ‘CO’ molecules generated from CO\textsubscript{2}.

It may be argued that the higher methane yields from CO\textsubscript{2} + H\textsubscript{2} reaction could arise because of lower ambient CO pressures. The CO methanation reaction over Ru has a strong positive dependence on H\textsubscript{2} (1 to 2 order) and is strongly inhibited by CO (-1/2 to -1 order) (see ref. 9, for example); consequently, operating with CO\textsubscript{2} + H\textsubscript{2} may produce a low CO pressure as compared to that in the reaction with CO + H\textsubscript{2}, and may thus facilitate competitive H\textsubscript{2} adsorption thus increasing the reaction rate. However, since the higher methane yields from CO\textsubscript{2} were observed in our pulse mode experiments also when the amounts of reacting CO or CO\textsubscript{2} were negligibly small as compared to that of H\textsubscript{2}, it is implied that the nature and the reactivity of transient species rather than the concentration effect play an important role, particularly in the temperature range 320-420K.

At the higher reaction temperatures (> 450K), no multicarbonyls are formed in the CO or CO + H\textsubscript{2} interaction\textsuperscript{14} thus accounting for almost similar catalyst activity for the CO and CO\textsubscript{2} methanation reactions (Fig. 1).

Conclusions

Following conclusions may be reached on the basis of the present studies.

(i) CO molecules are irreversibly bound in at least three distinct states corresponding to multicarbonyl and monocarbonyl species when Ru-RuO\textsubscript{x}/TiO\textsubscript{2} is exposed to CO or CO + H\textsubscript{2}. Subsequent thermal treatment in the absence of hydrogen leads to multicarbonyl - monocarbonyl transformation and the carbon monoxide is eventually converted to CO\textsubscript{2} by abstracting oxygen from the support or from the ruthenium suboxides.

(ii) Adsorbed hydrogen facilitates transformation of multicarbonyl species to methylene groups or to monocarbonyls which in turn are identified as precursors to methane via active carbon formation.

(iii) CO\textsubscript{2} is weakly adsorbed over Ru-RuO\textsubscript{x}/TiO\textsubscript{2} whereas CO + H\textsubscript{2} leads to large amounts of adsorbed monocarbonyl species and water.

(iv) It is suggested that the CO methanation occurs via multistep process at lower temperatures via multicarbonyl - monocarbonyl - Ru - C, or multicarbonyl - methylene groups - hydrocarbon route whereas CO\textsubscript{2} hydrogenation proceeds via direct monocarbonyl formation thus requiring lesser energy. At higher reaction temperature (>450K) disproportionation of adsorbed CO (Boudouard reaction) may contribute to methanation of both the CO and CO\textsubscript{2}.

(v) It is also suggested that the nascent (CO)\textsubscript{ad} species formed \textit{in situ} during CO\textsubscript{2} + H\textsubscript{2} reaction may have higher reactivity than the similar species formed during CO or CO + H\textsubscript{2} interaction.

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References

31 King D L, J Catal, 51 (1978) 386.
32 Brown M F & Gonzalez R D, J phys Chem, 80 (1976) 1731.