Elementary steps involved in the hydrogenation of the linear CO species adsorbed on a Ru/Al$_2$O$_3$ catalyst

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Abstract

The adsorption of CO on a reduced 3.5% Ru/Al$_2$O$_3$ catalyst in the temperature range (300–478 K) leads mainly to the formation of a linear CO species (denoted by L) adsorbed on Ru sites characterized by an IR band at 2047 cm^{-1} at 300 K. The linear CO species is hydrogenated to CH$_4$ in the temperature range 443–478 K in a flow of pure hydrogen. The rate of appearance of CH$_4$ as a function of the time in hydrogen follows a decreasing exponential profile which indicates that a limiting elementary step at the surface controls the overall process. It is shown that this step is the hydrogen-assisted dissociation of CO, while the other elementary steps leading to CH$_4$ are fast. In the course of the hydrogenation reaction, the hydrogen surface concentration does not change significantly with the removal of the L species (no competition between the L species and hydrogen). This is due to the fact that in the presence of adsorbed CO on the surface, hydrogen is adsorbed in an amount similar to that determined on a surface without any adsorbed CO but the sites involved are different. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; CO species; Ru/Al$_2$O$_3$ catalyst

1. Introduction

This research paper is dedicated to Professor H. Knözinger, for both his 65th birthday and retirement after a long and fruitful career in the science of heterogeneous catalysis. He made an outstanding work in the field of vibrational spectroscopy applied to solid catalysts and elementary steps. In particular, he developed the infra-red analytical tools and methods to the study of the surface of catalytic materials (chiefly acid–base surface properties). He wrote several reviews which are considered as seminal contributions to our science [1–4]. The present paper has the objective to show that combining FTIR spectroscopy studies of the catalyst surface in the course of a catalytic reaction (the hydrogenation of linearly adsorbed CO species) and experiments in the transient regime constitute a powerful tool to characterize the elementary steps controlling the reaction.

In the past two decades, the adsorbed carbonaceous species formed in the course of the CO/H$_2$ reaction on supported metal catalysts were widely studied by experiments in the transient regime [5]. The isothermal [6,7] and temperature programmed hydrogenations [8] into CH$_4$ are of particular interest because these adsorbed species can be characterized according to their reactivities with hydrogen. In previous works [6–8], it has been shown that the profiles of the curves giving the production of CH$_4$

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either after a switch $x\%$ $CO/H_2 \rightarrow H_2$ at a given temperature [6,7] or during the increase in the reaction temperature in pure hydrogen [8], can be used for the determination of various parameters linked to the hydrogenation process such as: (a) the number of adsorbed CO species hydrogenated; (b) the number of elementary steps with similar rate constants involved in the reaction; and (c) the activation energies of hydrogenation of the adsorbed species. The above studies [6–8] were performed with a reduced Fe/Al_2O_3 catalyst and it has been shown [9] that the coverage of the surface by undissociated adsorbed CO species was very small during the 10% CO/H_2 reaction (at 1 atm total pressure and with $T > 478$ K) and mainly surface carbon and adsorbed C_xH_y species were present at the surface of the iron particles. On Ru-containing catalysts (Refs. [10–14] and references therein), it is known that in the course of the CO/H_2 reaction: (a) various undissociated adsorbed CO species (Linear, Bridged, geminal dicarbonyl) can be present on the surface associated to adsorbed C_xH_y species; and (b) that some of these species can be hydrogenated to CH_4 at the reaction temperature. In the present study, combining experiments in the transient regime (using both FTIR and mass spectroscopy) and kinetic models we show that the elementary steps controlling the hydrogenation of the linear CO species adsorbed on a Ru/Al_2O_3 catalyst can be revealed. Moreover, this procedure is a source of information on the composition of the surface during the hydrogenation (i.e. the evolution of the hydrogen surface concentration during the hydrogenation of CO). It is known that adsorbed C_xH_y species [10–14] accumulates on the Ru particles in the course of the CO/H_2 reaction on Ru-containing catalysts. To prevent the difficulties in the kinetic model linked to the simultaneous presence of these species with the undissociated CO species, we study the hydrogenation of the linear CO species formed in absence of hydrogen (CO/He mixture).

2. Experimental

A 3.5% Ru/Al_2O_3 (in wt.%) catalyst was prepared using the incipient wetness method. Alumina (Degussa C γ-Al_2O_3) was impregnated with an ap-

propriate amount of an aqueous solution of $RuNO(NO_3)_3$, 2 H_2O (Johnson Matthey). After drying for 24 h at room temperature and then for 12 h at 383 K, the solid was treated in air for 12 h at 623 K leading to a BET surface area of 90 m^2/g. The metal content was obtained using the Inductively Coupled Plasma technique after dissolution of the catalyst with an acid solution. For the FTIR study, the catalyst was compressed to form a disk ($\Phi = 1.8$ cm, $m = 40–90$ mg) which was placed in the sample holder of a small internal volume stainless steel IR cell described elsewhere [15], allowing in-situ treatments (293–900 K) of the solid, at atmospheric pressure, with a gas flow rate in the range of 150–2000 cm^3/min. The rate of the CH_4 production in the course of the hydrogenation or the amount of adsorbed CO were obtained with another parallel analytical system by the determination of the composition of the gas mixture (1 atm total pressure) at the outlet of a quartz microreactor using a quadrupole mass spectrometer [6–8].

Before the adsorption of CO, the solid was treated in situ in the two analytical systems according to the same following procedure: He, 298 K $\rightarrow$ He, 383 K $\rightarrow$ H_2, 383 K (1 h) $\rightarrow$ H_2, 523 K, (1 h) $\rightarrow$ H_2, 713 K (2 h) $\rightarrow$ He, 713 K (5 min) $\rightarrow$ He, 298 K. After this treatment, the metallic dispersion determined by the irreversible hydrogen chemisorption at 383 K [16] using a volumetric method (ASAP 2000 Micromeritic) and assuming a ratio $H/Ru(s) = 1$ was 43%, in agreement with the data found in the literature on supported Ru catalysts prepared with a free chlorine precursor [17,18]. The same sample of catalyst was used for several experiments, and before each experiment, it was treated according to the following procedure: He, 713 K $\rightarrow$ O_2, 713 K (10 min) $\rightarrow$ He, 713 K (10 min) $\rightarrow$ H_2, 713 K (1 h) $\rightarrow$ He, 713 K (10 min) $\rightarrow$ He; T_a and T_r are the adsorption and reaction temperature, respectively. For instance, an experiment of hydrogenation was performed as follows: after cooling in He at $T_a = 478$ K, CO was adsorbed using a switch He $\rightarrow$ $x\%$ CO/He for a time t_a, then after a short He purge, a switch is performed between helium and pure hydrogen. During those various switches, either the composition of the gas at the outlet of the quartz reactor was determined or the FTIR spectra of the adsorbed species were recorded.

3. Results

3.1. Adsorption of CO in the temperature range 300–480 K

The identification of the adsorbed CO species has been obtained by FTIR spectroscopy. Fig. 1 shows the FTIR spectra recorded on the reduced 3.5% Ru/Al_2O_3 catalyst in the course of the adsorption (1% CO/He) in the range 300–480 K. Spectrum (a) recorded at 300 K shows a strong IR band at 2047 cm^{-1} which is ascribed to a linear CO species (denoted by L) (Refs. [19–21] and references therein) and a weak IR band at 2135 cm^{-1} which must be ascribed to one of the two IR bands of the geminal dicarbonyl or multicarbonyl species (denoted by G/M) probably on $Ru^{+\delta}$ (Ref. [22] and references therein). The strong IR band of the L species overlaps with the second IR band of the G/M species at ≈ 2080 cm^{-1} [22]. The G/M species are probably formed by the CO induced oxidation of some Ru^0 sites [20,22]. The very weak IR band at 1750 cm^{-1} in Fig. 1 has already been observed by Kellner and Bell [23] on a Ru/Al_2O_3 catalyst and has been assigned to μ-bonded carbonyls in which coordina-

tion occurs through both the carbon and oxygen atoms of CO. The increase in T_a (Fig. 1b) leads to the increase in the intensity of the IR band of the L species for temperatures lower than 450 K alongside with a shift to 2039 cm^{-1} at 445 K and 2032 cm^{-1} at 538 K, while a shoulder is detected at 1960 cm^{-1}. The IR bands of the G/M species decrease but without any significant shift. The results in Fig. 1 show that the ruthenium surface is modified by the CO adsorption (increase in the intensity of the IR band of the L species, detection of the shoulder at 1960 cm^{-1} and disappearance of the G/M species). The origin of this modification is not within the scope of the present study but it can be due, for instance, to a reconstruction of the surface of the ruthenium particles or to the dissociation/disproportionation of CO leading to adsorbed carbon and maybe adsorbed oxygen. If after heating from 300 to 538 K, the catalyst is cooled in the presence of 1% CO/He, the IR band area of the L species remains constant, indicating that the modifications of the surface are irreversible. Moreover, the intensities of the G/M IR bands remain low after cooling indicating that the $Ru^{+\delta}$ sites are involved in the reconstruction of the CO/Ru system.

The amount of CO adsorbed at 300 K during a switch He → 10% CO/5% Ar/He according to Fig. 2 is 68 μmol/g. The same experiment (not shown) performed at 478 K indicated an amount of CO adsorbed of 69 μmol/g. There is no significant formation of CO_2 at 478 K indicating that the dissociation/disproportionation reaction of CO must be very slow at this temperature. The absence of differences between the amounts of CO adsorbed at 298 and 478 K, while the IR band of the L species increases with the adsorption temperature, is due to the fact that the reconstruction is a slow process and cannot be revealed within the short time of the experiment of Fig. 2. However, it is shown below by isothermal hydrogenation that the amount of CO adsorbed on the Ru/Al_2O_3 surface increases with the duration of the adsorption at 478 K in agreement with the FTIR observations.
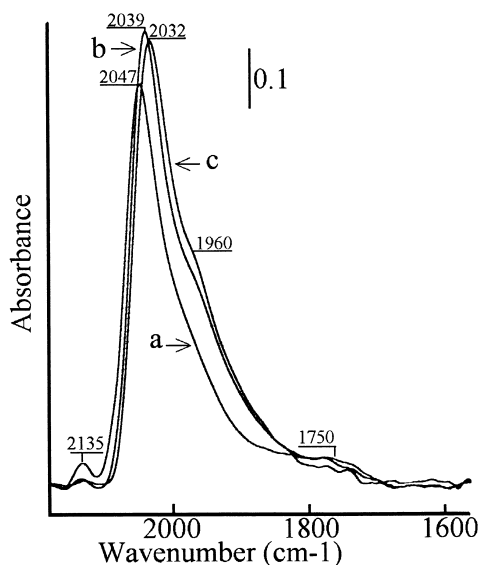
3.2. Hydrogenation of the linear CO species

Fig. 3 shows the CH_4 production at 478 K according to the following experiment. CO is adsorbed

Fig. 1. FTIR spectra recorded on 3.5% Ru/Al_2O_3 in the course of the CO adsorption at various temperatures with a 1% CO/He mixture: (a) 300 K; (b) 450 K; (c) 480 K.
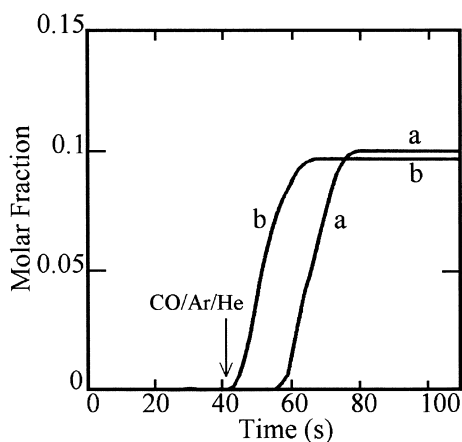
Fig. 2. Composition of the gas mixture at the outlet of the microreactor during the adsorption of CO on Ru/Al_2O_3 at 300 K using a CO/Ar/He mixture: (a) CO, (b) Ar (with a factor of 2).

at 478 K during a time t_a, here 80 s, 5 and 15 min in Fig. 3a–c, respectively, and then after a purge in He during 60 s, pure hydrogen is introduced and the production of CH_4 is recorded with a mass spectrometer. We have detected neither CO nor CO_2 during the CH_4 production, while water was not
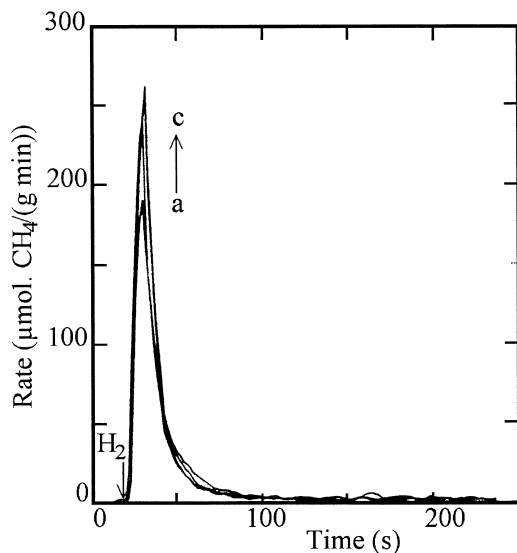
studied due to the difficulties for its quantitative analysis with a mass spectrometer. Fig. 3 shows that whatever t_a, the profile of the rate of CH_4 production follows a similar decreasing exponential profile. However, an increase in the initial rate of CH_4 production with the increase in t_a can be observed. This is also associated to an increase in the total amount of CH_4 produced from 56 $\mu mol/g$ for $t_a = 80$ s to 62 $\mu mol/g$ for $t_a = 15$ min. This increase can be linked to the reconstruction of the CO/Ru system or/and to a slight carbon deposition due to the CO dissociation/disproportionation reaction. For a given duration of the adsorption at 478 K ($t_a = 15$ min), if the hydrogenation is performed at lower temperatures, the evolution of the rate of the CH_4 production with the time of hydrogenation also follows a decreasing exponential profile. However, the initial rate decreases with the decrease in reaction temperature (478, 453 and 443 K in Fig. 4a–c, respectively) as observed in Fig. 4. It can be observed that the amount of CH_4 produced (56 to 62 $\mu mol/g$) during the hydrogenation is lower than the amount of CO adsorbed (68 $\mu mol/g$). This is due to the fact that: (a) a small fraction of the linear CO species desorbs during the short purge in He at 478 K; and (b) some adsorbed CO species are not hydrogenated at 478 K (see below).
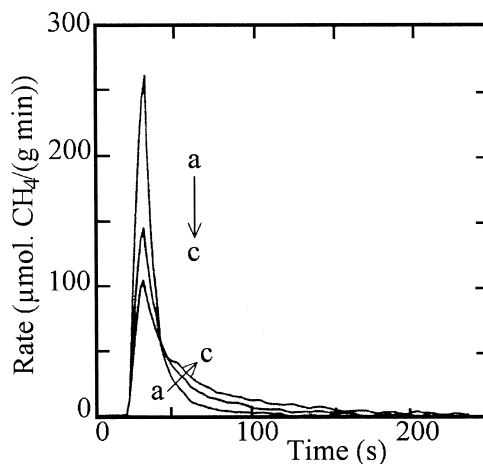

Fig. 3. Evolution of the rate of the CH_4 production at 478 K in the course of the hydrogenation of the Linear CO species as a function of the time of adsorption t_a: (a) 80 s; (b) 5 min; (c) 15 min.

Fig. 4. Evolution of the rate of the CH_4 production in the course of the hydrogenation of the Linear CO species as a function of the reaction temperature for $t_a = 15$ min: (a) 478 K; (b) 453 K; (c) 443 K.

The FTIR spectra recorded during the hydrogenation at 478 K are shown in Fig. 5. After adsorption of CO at 478 K, a purge is performed with He during 3 min and then pure hydrogen is introduced. Spectra a–g in Fig. 5 show that the IR band intensity of the L species rapidly decreases with time on stream alongside a shift to lower wave numbers, while two IR bands at 2047 and 1966 cm^{-1} remain after 10 min in H$_2$. Similar IR bands ($\approx$ 2040 and $\approx$ 1960 cm^{-1}) have been observed after the decomposition in vacuum of several Ru carbonyl complexes adsorbed on Al$_2$O$_3$ [24] and also after the hydrogenation of adsorbed CO species on a Ru/Al$_2$O$_3$ catalyst [23]. Therefore, these two IR bands have been ascribed to a complex structure (diadsorbed CO structure) involving Ru (individual atom or small Ru clusters) and the alumina support [23,24]. These adsorbed species are not hydrogenated in pure hydrogen at $T < 487$ K as observed by Kellner and Bell [23]. In the course of the hydrogenation, we did not detect any IR bands in the 3100–2800 cm^{-1} range which is characteristic of C$_x$H$_y$ adsorbed species. The FTIR spectra in Fig. 5 indicate that it is mainly the L species which leads to the CH$_4$ production.
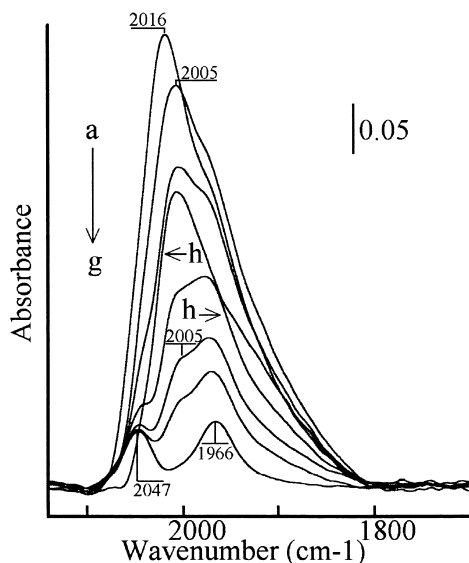

Fig. 5. FTIR spectra recorded during the hydrogenation of the linear CO species at 478 K: (a) in He; (b–g) in H$_2$, (a) 20 s, (b) 30 s, (c) 60 s, (d) 85 s, (e) 110 s, (g) 10 min; (h) spectrum obtained after subtraction (c)−(g).

4. Discussion

The above results are now analyzed to obtain more insight on the elementary steps involved in the hydrogenation of the L species. It is also shown that this offers a way to characterize the surface state of the catalyst during the hydrogenation process.

4.1. Elementary steps in the hydrogenation of the linear CO species

The decrease in the intensity of the IR band of the L species (Fig. 5) after the introduction of hydrogen clearly indicates that it is this species which is hydrogenated to CH$_4$. Moreover, the decreasing exponential profile of the rate of CH$_4$ production observed in Fig. 3 shows that a limiting step controls the overall process [6,7]. The various elementary steps that can be considered for the hydrogenation of this species are:

(a) Desorption of CO: $CO_{(ads)} \rightarrow CO_{(gas)}$, rate constant k_0'
(b) Dissociation of CO: $CO_{(ads)} \rightarrow C_{(ads)} + O_{ads}$, rate constant k_0
(c) Hydrogen chemisorption: $H_{2(g)} \rightarrow 2\ H_{(ads)}$
(d) Hydrogenation of $C_{(ads)}$: $C_{(ads)} + H_{(ads)} \rightarrow CH_{(ads)}$
(e)–(g) Successive hydrogenation of the CH$_x$ intermediates: $CH_{(ads)} + H_{(ads)} \rightarrow CH_{2(ads)} \cdots \rightarrow CH_{4(ads)}$
(h) Desorption of CH$_4$: $CH_{4(ads)} \rightarrow CH_{4(g)}$.

Steps (a) and (b) can be studied separately using the change in the intensity of the IR band according to an experiment similar to Fig. 5 (not shown) but performed with a helium flow. The rate of disappearance of the L species is then given by:

$$\frac{-d\left[CO_{(ads)}\right]}{dt} = (k_0' + k_0)\left[CO_{(ads)}\right] \quad (1)$$

where [CO$_{(ads)}$] is the superficial concentration of the L species and t the time of desorption. Expression (1) leads to:

$$\ln\left(\frac{\left[CO_{(ads)}\right]}{\left[CO_{(ads)}\right]_0}\right) = -(k_0' + k_0)t \quad (2)$$

where [CO$_{(ads)}$]$_0$ is the superficial concentration of the L species at time 0. Assuming that the IR band

areas (denoted by A) are proportional to the amount of L species on the surface, expression (2) indicates that $\ln(A(t)/A(0))$ must be a straight line. This is well observed in Fig. 6a. There is a controversy on the above assumption, in particular, on single crystals the linear relationship between the area of the IR band and the coverage is mainly observed for $\theta < (\approx 0.8/0.5)$. However, in a previous study [25], we have discussed this point for supported metal catalysts taking into account various data in the literature. It must be noted that in Fig. 6a we present the experimental data for a short duration of the experiment ($t < 160$ s) because the straight line is no more observed for a longer period. This is due to the fact that the heat of adsorption of the L species (equal to the activation energy of desorption E_d) increases linearly with the decrease in coverage from 175 kJ/mol at $\theta = 0$ to 115 kJ/mol at $\theta = 1$ as previously studied [25]. This means that a large decrease in the coverage decreases the rate constant of desorption at a given desorption temperature. During the experiment leading to Fig. 6a, the coverage of the L species varies from $\theta \approx 0.8$ to $\theta \approx 0.4$ and the average of the heat of adsorption in this range of coverage is ≈ 140 kJ/mol [25]. The slope of curve a in Fig. 6 leads to $k_0' + k_0 = 2.1 \times 10^{-3}$ s^{-1}, in good agreement with the result found by Cant and Bell [26] on a 4.3% Ru/SiO$_2$ catalyst (0.7×10^{-3} s^{-1} at 473 K) and by Winslow and Bell [11] on a Ru powder (1×10^{-3} s^{-1} at 443 K). Note that assuming a pre-exponential factor of 10^{13} s^{-1} for the rate constant of desorption of the L species, and consider-
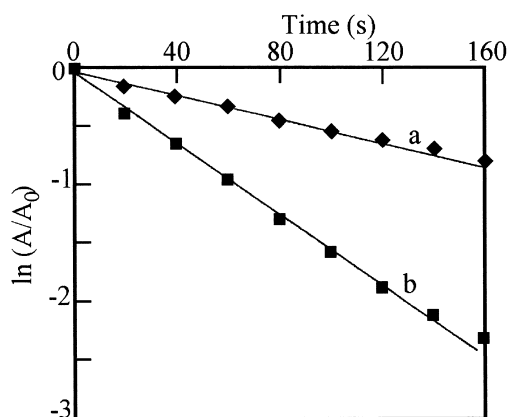
ing that the activation energy of desorption is ≈ 140 kJ/mol, it is then found that the rate constant of desorption is $\approx 5 \times 10^{-3}$ s^{-1} at 478 K and is in very good agreement with the above experimental values. This also leads to the conclusion that the rate constant of dissociation/disproportionation of CO at 478 K is probably significantly lower than the rate constant of desorption. This is in agreement with the study of Winslow and Bell [11] who indicated a factor of 10 in favour of the rate of desorption on a Ru powder.

Curve b in Fig. 6 gives the plot of $\ln(A(t)/A(0))$ in the course of the hydrogenation using the results in Fig. 5. The $A(t)$ values are determined after subtraction of the contribution of the two IR bands observed after 10 min of hydrogenation. For instance, spectrum h in Fig. 5 is obtained after subtraction of spectrum g to spectrum c. The slope of the straight line observed in Fig. 6b leads to a rate constant of disappearance of the L species of 1.6×10^{-2} s^{-1}, a value greater than the one determined for the desorption (Fig. 6a). This cannot be attributed to a higher rate of desorption of the L species due for instance to a competition with the hydrogen chemisorption because we did not detect CO$_{(g)}$ during the hydrogenation process (Fig. 3). The increase in the rate constant of disappearance of the L species in the presence of hydrogen indicates that a new elementary step must be involved. We consider that this new step is the hydrogen-assisted dissociation of CO [27]:

(i) $CO_{(ads)} + H_{(ads)} \rightarrow C_{(ads)} + OH_{(ads)}$ rate constant k_0''.
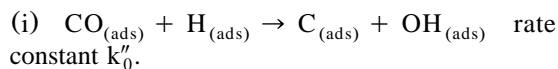
The rate of disappearance of CO in the presence of hydrogen is now linked to steps (a), (b) and (i):

$$\frac{-d[CO_{(ads)}]}{dt} = \left(k_0' + k_0 + k_0''[H_{(ads)}] \right)[CO_{(ads)}]$$

where $[H_{(ads)}]$ is the superficial concentration of adsorbed hydrogen. Assuming that $[H_{(ads)}]$ is constant during the hydrogenation, the slope of curve b in Fig. 6 leads to $(k_0' + k_0 + k_0''[H_{(ads)}]) = 1.6 \times 10^{-2}$ s^{-1} and then to $K_0'' = k_0''[H_{(ads)}] = 1.4 \times 10^{-2}$ s^{-1}. This last value is also in good agreement with that of 0.72×10^{-2} s^{-1} determined in similar experimental conditions by Cant and Bell [26] on a 4.3% Ru/SiO$_2$ catalyst at 473 K.

Fig. 6. Determination of the rate constant of disappearance of the L species at 478 K: (a) in helium, (b) in hydrogen.

The fact that IR bands corresponding to adsorbed C_xH_y species are not detected during the hydrogenation of the L species indicates that the elementary steps (d) to (h) are fast compared to the hydrogen-assisted dissociation of CO. This is in agreement with the exponential decreasing profile of the CH_4 production during the isothermal hydrogenation (Fig. 3) which clearly indicates that a limiting step controls the process. Note that considering that the H_2 assisted dissociation of CO is this limiting steps as in the case of Pd catalysts [27], the evolution of the rate of the CH_4 production with time on stream of the hydrogenation reaction is given by $v(CH_4) = K_0''$ $[CO_{(ads)}]_0 \exp(-K_0''t)$ leading to an initial rate equal to $K_0''[CO_{(ads)}]_0$. Fig. 3 shows that the maximum of the rate of production is 190 μmol/(g min) for $t_a = 80$ s at 478 K, while the amount of L species (amount of CH_4 production) is ≈ 57 μmol/g. This leads to $K_0'' \approx 5 \times 10^{-2}$ s^{-1} in reasonable agreement with the value obtained from Fig. 6b and it confirms that the L species is hydrogenated via the hydrogen-assisted dissociation step which is the rate determining step in the CH_4 production.

4.2. On the hydrogen surface concentration during the hydrogenation of the L species

In the above section, we have assumed that the hydrogen surface concentration is constant during the hydrogenation of the L species. This assumption is obviously in contrast to the idea that there is a competition between L species and hydrogen. For instance, it can be considered as in Ref. [11], that the coverage of the L species during the hydrogenation is initially high while the number of sites for the hydrogen chemisorption is very small and that the number of these sites increases with the removal of the L species by hydrogenation. This interpretation of the mechanism of hydrogenation of the L species leads to the conclusion that the rate of the CH_4 production is initially small and increases with time on stream, until a maximum appears at a time t_m and finally decreases. We have shown in a previous study [7] that the value of t_m is a function of several kinetic parameters such as the rate of increase in the number of sites for the hydrogen chemisorption or the reaction temperature (the lower the reaction tem-

perature, the higher the value of t_m). The decreasing exponential profile of the CH_4 production observed in Fig. 3, which is also observed at lower reaction temperatures in Fig. 4, is incompatible with this kinetic model. In contrast, the results lead to the conclusion that the hydrogen surface concentration $[H_{(ads)}]$ must be high even in the presence of a large amount of L species on the surface and that $[H_{(ads)}]$ is roughly constant during the hydrogenation of the L species. Some complementary experiments have been performed to confirm this point. In particular, we have studied the CO adsorption on a surface saturated by hydrogen, and then the hydrogen chemisorption on a surface saturated by CO.

Hydrogen chemisorption on the present catalyst is a slightly activated process and the saturation is rapidly obtained for a chemisorption at 383 K followed by cooling to 300 K [28]. A TPD experiment in a helium flow from 300 to 800 K indicates that the total amount of hydrogen desorbed from the ruthenium surface during the TPD is 76 μmol H_2/g of catalyst [28]. Assuming the following ratio H/Ru(s) = 1 and CO/Ru(s) = 1, it appears that the adsorption of CO at 300 K (68 μmol/g) only involves 45% of the sites adsorbing hydrogen. This value is in the range of those reported by other studies: 63% on a Ru powder and 52% on a 5% Ru/Al_2O_3 solid [29], 25% on 6.2% Ru/Al_2O_3 catalyst [30] and 67% on a Ru powder [31]. Fig. 7 gives the TPD spectra in a helium flow (5 K/s)
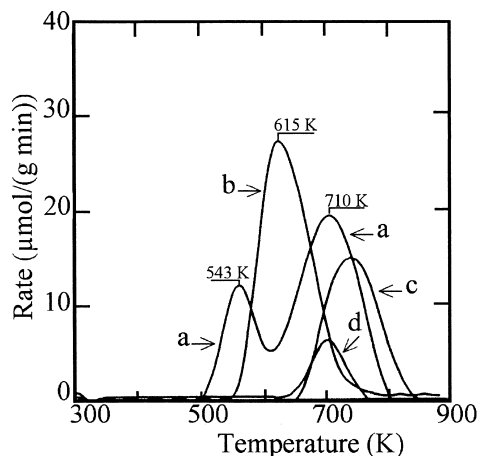
Fig. 7. DTP spectra after adsorption of CO at 300 K on the Ru/Al_2O_3 solid: (a) CO; (b) CO_2; (c) H_2; (d) CH_4.

recorded after adsorption of CO at 300 K on a reduced catalyst. The peaks of hydrogen and CH_4 (3 μmol CH_4/g) detected at high temperatures are due to the decomposition of H_2O coming from Al_2O_3 support on the Ru particles when the temperature of the TPD experiment is higher than that used for the pretreatment of the catalyst [28]. The two CO peaks (4 + 30 μmol/g) and the CO_2 peak (24 μmol/g) indicate that there are probably several processes involved in the TPD experiment (i.e. desorption and dissociation/disproportionation of adsorbed CO species). The adsorption of CO on a surface saturated by hydrogen is shown in Fig. 8 according to the following procedure. After adsorption of hydrogen at 383 K, the solid is cooled down to 300 K in hydrogen and then, after a helium purge, a CO/Ar/He mixture is introduced. It can be observed (in Fig. 8) that CO displaces a fraction of the chemisorbed hydrogen (42 μmol/g), while the amount of CO adsorbed is not affected (68 μmol/g). Fig. 9 gives the TPD results after the adsorption of CO on a surface saturated by hydrogen (TPD done after the experiment in Fig. 8). The two CO peaks (4 + 25 μmol/g) and the CO_2 peak (24 μmol/g) appear at higher temperatures than in Fig. 7, while the peak of CH_4 is detected at lower temperature and in larger amount (10 μmol CH_4/g). This CH_4 production is due to the hydrogen that remained adsorbed on the surface after CO chemisorption. Note that the hydrogen mass balance between hydrogen desorbed at 300 K and that involved in the CH_4 production is 60 μmol/g, which is in reasonable

Fig. 9. DTP spectra after the experiment in Fig. 8: (a) CO; (b) CO_2; (c) H_2; (d) CH_4.

agreement with the amount of hydrogen adsorbed on a clean surface (76 μmol/g). The above results show that there is a competition between hydrogen and CO on certain sites of the surface, and this seems, at first sight, in contradiction with the assumptions involved in the kinetic model. However, the following experiments show that the situation is more complex.

After the reduction, the solid is cooled down in helium to 383 K and CO is adsorbed. After a short purge in helium, hydrogen is chemisorbed during 15 min. Fig. 10 shows the changes in the FTIR spectra
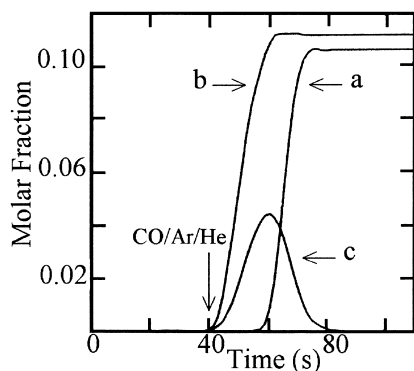

Fig. 8. Composition of the gas mixture at the outlet of the microreactor during the adsorption of CO at 300 K on Ru/Al_2O_3 saturated by hydrogen: (a) CO; (b) Ar (with a factor of 2); (c) H_2.
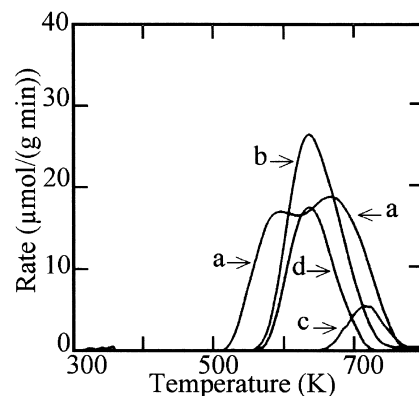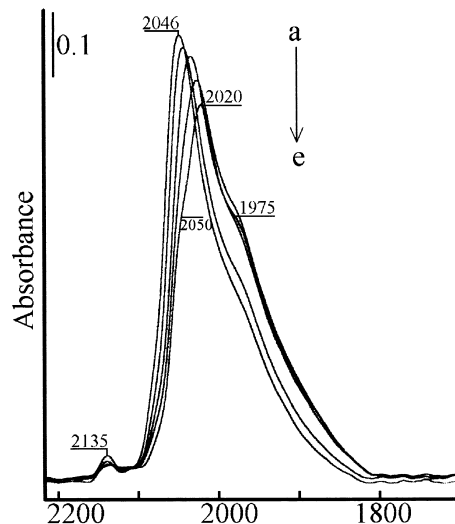

Fig. 10. FTIR spectra recorded during the adsorption of hydrogen at 383 K on the Ru particles saturate in CO: (a) in 1% CO/He; (b–e) in H_2, (b) 30 s, (c) 50 s, (d) 4 min, (e) 10 min.

during this experiment. It can be observed that the presence of hydrogen leads to a modification in the profile of the IR band of the L species which shifts to lower wave numbers (from 2046 to 2020 cm^{-1} after 10 min) while two shoulders are well detected at ≈ 2050 and ≈ 1975 cm^{-1}. The total IR band area in the range 2100–1800 cm^{-1} is unchanged during the hydrogen chemisorption indicating that: (a) the L species is not significantly hydrogenated at 383 K; and (b) the chemisorbed hydrogen interacts with the L species (shift in the IR band) but without any significant desorption of this species. Fig. 11 shows the TPD spectra after adsorption of hydrogen on a surface saturated by CO. After adsorption of CO at 383 K, hydrogen is chemisorbed for 10 min and then the solid is cooled down to 300 K in hydrogen. After a short purge in helium, the temperature is increased to perform a TPD experiment. A large hydrogen peak is observed at 473 K (43 μmol/g) in Fig. 11, which is not observed in Fig. 9 and a CH$_4$ peak (13 μmol/g) similar to that already observed in Fig. 9. The hydrogen mass balance for the TPD experiment is 70 μmol H$_2$/g, a value close to that observed in the absence of CO on the surface. The C mass balance is 60 μmol/g (CO peak 16 μmol/g, CO$_2$ peak 25 μmol/g and CH$_4$ peaks (13 + 6) μmol/g), it confirms that CO was not displaced during the hydrogen chemisorption.

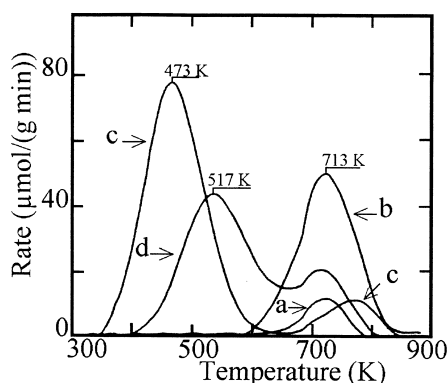The above results show that the adsorption of CO on a surface saturated by hydrogen leads to the desorption of 45% of the adsorbed hydrogen. However, hydrogen can be adsorbed on a surface saturated by CO without any significant desorption of the linear CO species and with an amount similar to that determined on a surface without any CO. Using another experimental procedure, Winslow and Bell [11] also have observed on a Ru powder that nearly a monolayer of CO may coexist with a 0.8–0.9 monolayer of hydrogen at 443 K and similar observations were made in early works (Ref. [11] and references therein). The present results lead to the following conclusions: (a) the Ru sites adsorbing hydrogen are probably different in the presence and in the absence of linear CO species on the surface; and (b) in the course of the hydrogenation of the linear CO species, the hydrogen surface concentration can be considered as constant because there is no competition with the L species. This explains that we observe a decreasing exponential profile for the CH$_4$ production as a function of time on stream irrespective of the reaction temperature (range 453–478 K) and not a CH$_4$ peak with a maximum appearing at a time t_m as expected for a kinetic model assuming a competitive adsorption. Note that the simultaneous presence of high concentrations of linear CO species and hydrogen on the Ru surface constitutes another argument to validate the hydrogen-assisted dissociation of CO.

5. Conclusions

The present study has shown that combining transient regime experiments (using both FTIR and mass spectroscopy as detectors) in the course of the hydrogenation of the adsorbed CO species on a Ru/Al$_2$O$_3$ catalyst with a kinetic model constitutes a well adapted tool to characterize the catalytic process.

The following conclusions can be derived from the present study:

- CO adsorbs mainly as linear CO species at 478 K on the reduced Ru/Al$_2$O$_3$ catalyst,
- this species is hydrogenated to CH$_4$ via a complex process with a limiting step,
- this step is the hydrogen-assisted dissociation of CO,

Fig. 11. DTP spectra after the adsorption of hydrogen at 383 K on the Ru particles saturated by CO: (a) CO; (b) CO$_2$; (c) H$_2$; (d) CH$_4$.

- there is no competitive adsorption between CO and hydrogen,
- the surface concentration of hydrogen during the hydrogenation of the linear CO species can be considered as constant,
- in the presence of adsorbed CO on the surface, hydrogen is adsorbed on other sites aside from those involved in the absence of CO.

Acknowledgements

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