

## TRANSIENT DRIFT SPECTROSCOPY FOR THE DETERMINATION OF THE SURFACE REACTION KINETICS OF CO<sub>2</sub> METHANATION

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**Abstract**—Transient experiments were applied to the study of the adsorbed CO intermediate, (CO)<sub>a</sub>, formed during the CO<sub>2</sub> methanation reaction on a 2% Ru/TiO<sub>2</sub> catalyst at 383 K. Step-up experiments showed that the (CO)<sub>a</sub> formation steps are inhibited by H<sub>2</sub>O and enhanced by H<sub>2</sub>. Step-down experiments showed that the (CO)<sub>a</sub> hydrogenation is not influenced by the partial pressure of water. Based on the fact that water inhibits the overall CO<sub>2</sub> methanation, it is deduced that the rate limiting process in the overall reaction is (CO)<sub>a</sub> formation.

### INTRODUCTION

Heterogeneous catalytic reactions studied under steady-state conditions lead to overall lumped kinetic models that do not reflect a unique mechanistic physicochemical reality (Carberry, 1976; Baerns *et al.*, 1992). The transient behavior of the reaction is more sensitive to the elementary step rate constants (Renken, 1990). Therefore, dynamic experiments are used in order to distinguish between different models describing steady-state behavior.

The simultaneous measurement of the surface-adsorbed species and the gas phase reactant-products considerably increases the amount of information available for the establishment of a kinetic model. Yet it is important to distinguish reactive-adsorbed species from spectator-surface species that do not participate in the reaction (Tamaru, 1991). Dynamic experiments can be used as a tool to understand the role of these observed species.

In this work, the kinetics of a surface reaction intermediate was studied by transient infrared experiments and compared to the steady-state kinetics obtained for the overall reaction. The aim was to gain more insight on the mechanism of formation and reaction of the observed reaction intermediate, as well as to determine which process is rate limiting in the overall reaction.

The reaction studied was the CO<sub>2</sub> methanation reaction at 383 K on a 2% Ru/TiO<sub>2</sub> catalyst. It is established in the literature that (CO)<sub>a</sub> is an important reaction intermediate in the CO<sub>2</sub> methanation reaction (Henderson and Worley, 1985; Erdöhelyi *et al.*, 1986). In this paper the kinetics of the (CO)<sub>a</sub> surface intermediates formed during the CO<sub>2</sub> methanation

reaction on a 2% Ru/TiO<sub>2</sub> catalyst are determined by diffuse reflectance infrared spectroscopy (DRIFTS) and are compared with the steady-state kinetics for the overall CO<sub>2</sub> methanation reaction.

### MATERIALS

Transient experiments were performed in a single pass setup (Fig. 1) composed of a water evaporator and a controlled-environment DRIFTS cell. Feed was supplied through one of two banks of mass flow controllers that could be selected using a low-volume, four-way switching valve across which pressure and flow rate were equilibrated to avoid surges during switching. Reactor effluent composition was determined with a Balzers QMG 420 quadrupole mass spectrometer coupled with a two-stage continuous atmospheric sampling system. The DRIFTS cell (Harrick HVC-DR2 vacuum chamber with DRA-1200 diffuse reflectance accessory) was located in a Nicolet 710 FTIR spectrometer equipped with a mid-range MCT detector and a KBr beamsplitter. The instrument was operated at a scan speed of 1 scan s<sup>-1</sup>, a resolution of 4 cm<sup>-1</sup>, and a number (10–40) of interferograms were co-added depending on the time interval between each spectrum collection.

The water evaporator was made of a stainless steel U-tube filled with 1 mm glass beads and a small quantity of water. It was maintained at a temperature between 245 K and 283 K in order to vary the feed water pressure from a P<sub>H<sub>2</sub>O</sub> value of 0.8 to 12.3 mbar.

The apparatus for the steady-state experiments consisted of a recycle reactor linked to the DRIFTS cell and is described elsewhere (Marwood *et al.*, 1994). CO<sub>2</sub> (99.995%), H<sub>2</sub> (99.9999%) and He (99.9999%) gases were used after passing through Oxisorb traps that reduce oxygen impurity levels to less than 0.1 ppm.

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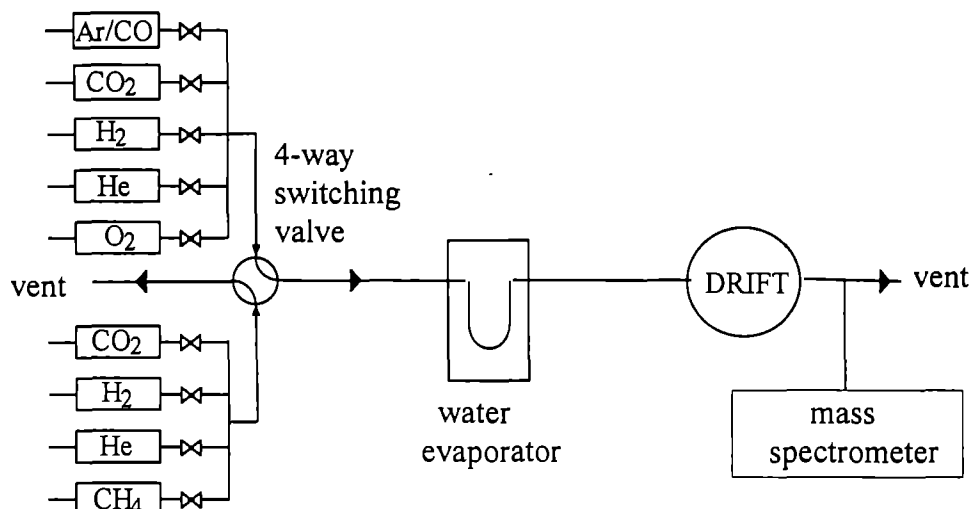


Fig. 1. Schematic layout of experimental apparatus.

## METHODS

### Catalyst preparation

The catalyst was ruthenium (2.13 wt%) dispersed on TiO<sub>2</sub> (Degussa P25) as described by Thampi *et al.* (1987). Standard pretreatment consisted of heating the catalyst to 498 K in flowing 40% O<sub>2</sub> for 1 h followed by a brief purge in He and a reduction in 20% H<sub>2</sub> at 498 K. The catalyst was then cooled to 383 K in 20% H<sub>2</sub> and left to stabilize for 20 min before exposure to the reaction mixture. A 30 min exposure to 20% H<sub>2</sub> at 498 K, as well as 20 min stabilization at 383 K, was performed to clean the catalyst surface in between each transient experiment.

### IR data

Infrared (IR) spectra were baseline corrected and represented in Kubelka–Munk (K–M) form, with a reference spectrum consisting of the clean catalyst in flowing 20% H<sub>2</sub> as described by Prairie *et al.* (1991b). The (CO)<sub>a</sub> data is represented by the integral of the IR band in the range 2070–1750 cm<sup>-1</sup>. The validity of such a representation was verified. Gaseous CO was adsorbed and the catalyst exposed to small pulses of H<sub>2</sub>. Consequently (CO)<sub>a</sub> reacted to form CH<sub>4</sub> and the (CO)<sub>a</sub> IR band decreased. A linear relationship was observed between the 2070–1750 cm<sup>-1</sup> band area and the CH<sub>4</sub> formed for θ<sub>CO</sub> between 0.1 and 1.

### Transient experiments

Step-up and step-down transient experiments were performed where the feed composition was changed from an initial to a final feed composition. The effects of the H<sub>2</sub> and H<sub>2</sub>O partial pressures as well as the reaction temperature on the transient response were studied for a total flow rate of 50 Nml/min. The experiments are summarized in Table 1.

Surface IR spectra were acquired at 20 s intervals during the first 5 min of the experiments and at 3 min intervals for the rest of the 40 min duration of the step-up experiments.

The step-down experiments were performed starting from the steady state with surface IR spectra acquired at 1 min intervals during the first 5 min period and at 3 min intervals for the rest of the experiment.

## RESULTS

### Identification of adsorbed intermediates

Figure 2e shows the spectrum obtained on the surface of 2% Ru/TiO<sub>2</sub> under steady-state CO<sub>2</sub> methanation conditions. The interpretation of this IR spectrum is proposed by comparing it with the spectra of each of its individual components.

Figure 2d shows the spectrum of 2% Ru/TiO<sub>2</sub> exposed at 383 K to flowing 40% CO for 10 min followed by a 10 min He purge to eliminate the gas phase CO absorbance bands, and H<sub>2</sub> pulses in the He

Table 1. Feed mixtures for transient experiments

No.	Feed initially	Switched to	mol% H <sub>2</sub>	P <sub>H<sub>2</sub>O</sub> (mbar)	T(K)
1†	H <sub>2</sub>	H <sub>2</sub> , 10% CO <sub>2</sub>	5 < x < 50	2.4	383
2	H <sub>2</sub>	H <sub>2</sub> , 10% CO <sub>2</sub>	20	0.8–12.3	383
3	20% H <sub>2</sub> , 10% CO <sub>2</sub>	H <sub>2</sub>	2 < x < 50	1.6	383
4	20% H <sub>2</sub> , 10% CO <sub>2</sub>	H <sub>2</sub>	20	0.8–12.3	383
5	20% H <sub>2</sub> , 10% CO <sub>2</sub>	H <sub>2</sub>	20	6.1	363–413

† Total flow rate of 100 Nml/min instead of 50 Nml/min.

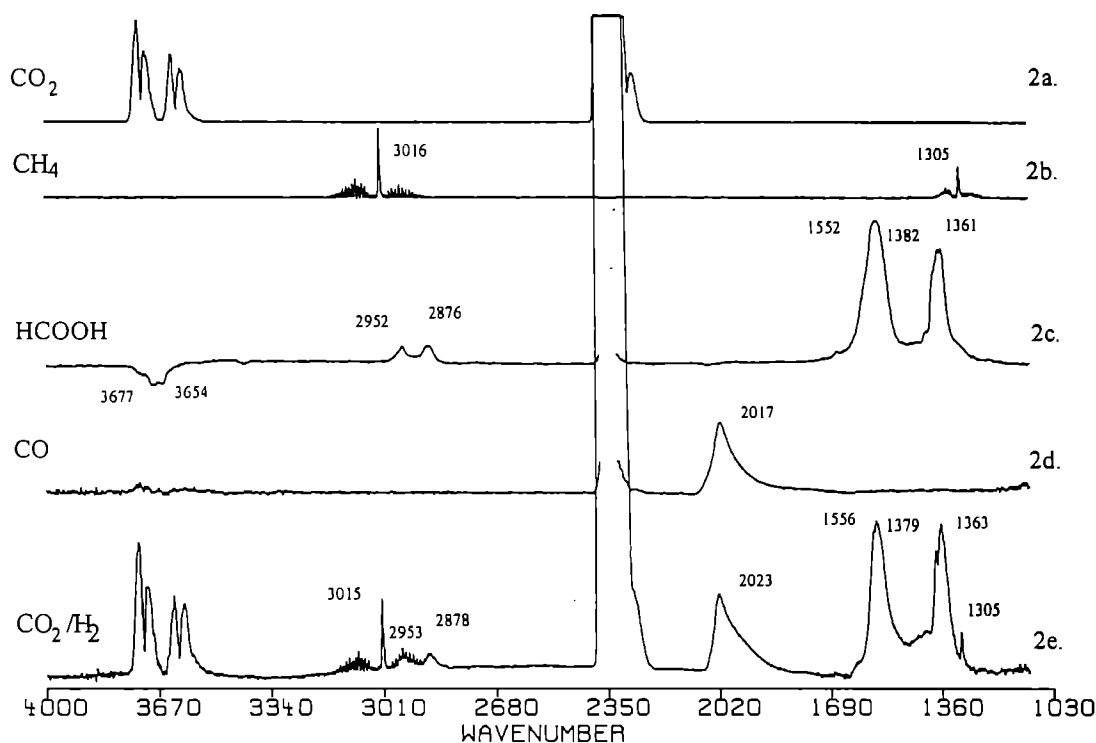


Fig. 2. DRIFTS spectra: a, gas phase  $\text{CO}_2$ ; b, gas phase  $\text{CH}_4$ ; c,  $\text{HCOOH}$  adsorption on 2%  $\text{Ru/TiO}_2$ ; d,  $\text{CO}$  adsorption on 2%  $\text{Ru/TiO}_2$ ; e,  $\text{CO}_2$  methanation on 2%  $\text{Ru/TiO}_2$ ; spectra recorded at 383 K.

carrier in order to diminish the  $(\text{CO})_a$  surface coverage. A large band was observed at  $2045\text{ cm}^{-1}$  for total  $\text{CO}$ -coverage ( $\theta_{\text{CO}} = 1$ ) (Cant and Bell, 1982; Gupta *et al.*, 1992). This coverage effect is well documented for  $(\text{CO})_a$  adsorbed on a metal surface (Sheppard and Nguyen, 1978). The  $(\text{CO})_a$  peak presented in Fig. 2e, with a maximum at  $2017\text{ cm}^{-1}$ , corresponds to  $\theta_{\text{CO}} = 0.6$ .

Figure 2c shows the spectrum of  $\text{TiO}_2$  at 383 K where  $2\text{ }\mu\text{l}$  of  $\text{HCOOH}$  were injected into the flowing He carrier. Two large bands at  $1552\text{ cm}^{-1}$  and  $1361\text{ cm}^{-1}$  arise from asymmetric and symmetric O–C–O stretching vibrations of adsorbed  $(\text{HCOO}^-)_a$  species (Busca *et al.*, 1987). The  $1382\text{ cm}^{-1}$  and  $2876\text{ cm}^{-1}$  bands are attributed to the CH bending and stretching vibrations. The band at  $2952\text{ cm}^{-1}$  results from a combination or overtones of  $\nu_{(a)\text{CO}_2} + \delta_{\text{CH}}$ . The two negative bands at  $3677\text{ cm}^{-1}$  and  $3654\text{ cm}^{-1}$  correspond to a decrease of free hydroxyls on the  $\text{TiO}_2$  surface. This decrease is due to  $(\text{HCOO}^-)_a$  formation by a condensation mechanism between  $\text{HCOOH}$  and these hydroxyl groups.

Figure 2b shows the spectrum of gaseous  $\text{CH}_4$  characterized by two bands at  $3016$  and  $1305\text{ cm}^{-1}$  associated with their rotational structure, and Fig. 2a shows the spectrum of gaseous  $\text{CO}_2$ . The spectrum in Fig. 2e, obtained on 2%  $\text{Ru/TiO}_2$  under steady-state  $\text{CO}_2$  methanation conditions, can therefore be decomposed into two adsorbed species:  $(\text{CO})_a$  ( $2023\text{ cm}^{-1}$ ) and  $(\text{HCOO}^-)_a$  ( $1360$ ,  $1379$ ,  $1555$ ,  $2870$ ,  $2948\text{ cm}^{-1}$ ) as well as gaseous  $\text{CO}_2$  (reactant) and  $\text{CH}_4$  (reaction product).

#### Steady-state kinetics

At 383 K, the  $\text{CO}_2$  steady-state methanation rate can be described by:

$$R_{\text{CH}_4} = 0.0167 (P_{\text{CO}_2})^{0.22} (P_{\text{H}_2})^{0.57} (P_{\text{H}_2\text{O}})^{-0.28} \quad (\mu\text{mol g}_{\text{Ru}}^{-1}\text{s}) \quad (1)$$

where the reaction rate is almost of order  $\frac{1}{2}$  in hydrogen concentration and is inhibited by water—water being a reaction product. A good correlation is obtained between measured and calculated data [eq. (1)]. The calculated values were found within a 10% interval relative to the measured data. An activation energy  $E_a = 80 \pm 4\text{ kJ mol}^{-1}$  was measured for the overall methanation reaction. This value is in good agreement with the value of  $79\text{ kJ mol}^{-1}$  found by Prairie *et al.* (1991a) for this reaction on a 3.8%  $\text{Ru/TiO}_2$  catalyst.

#### Step-up experiments

In Fig. 3, gaseous  $\text{CO}_2$ ,  $\text{CH}_4$  and surface  $(\text{CO})_a$  are plotted together for a step-up experiment. A  $\text{CO}_2 \Rightarrow (\text{CO})_a \Rightarrow \text{CH}_4$  sequence can be established. In additional experiments (Marwood, 1994) it was verified that  $\text{CH}_4$  is not adsorbed on the catalyst and  $\text{CO}$  adsorption from the gas phase is fast compared to  $(\text{CO})_a$  formation from  $\text{CO}_2$ . ( $\text{CO}$  coverage was found to follow the gas phase concentration in transient experiments without any time delay.) Besides  $\text{CH}_4$ , water is formed and detected in the gas phase qualitatively following the methane curve. Due to the

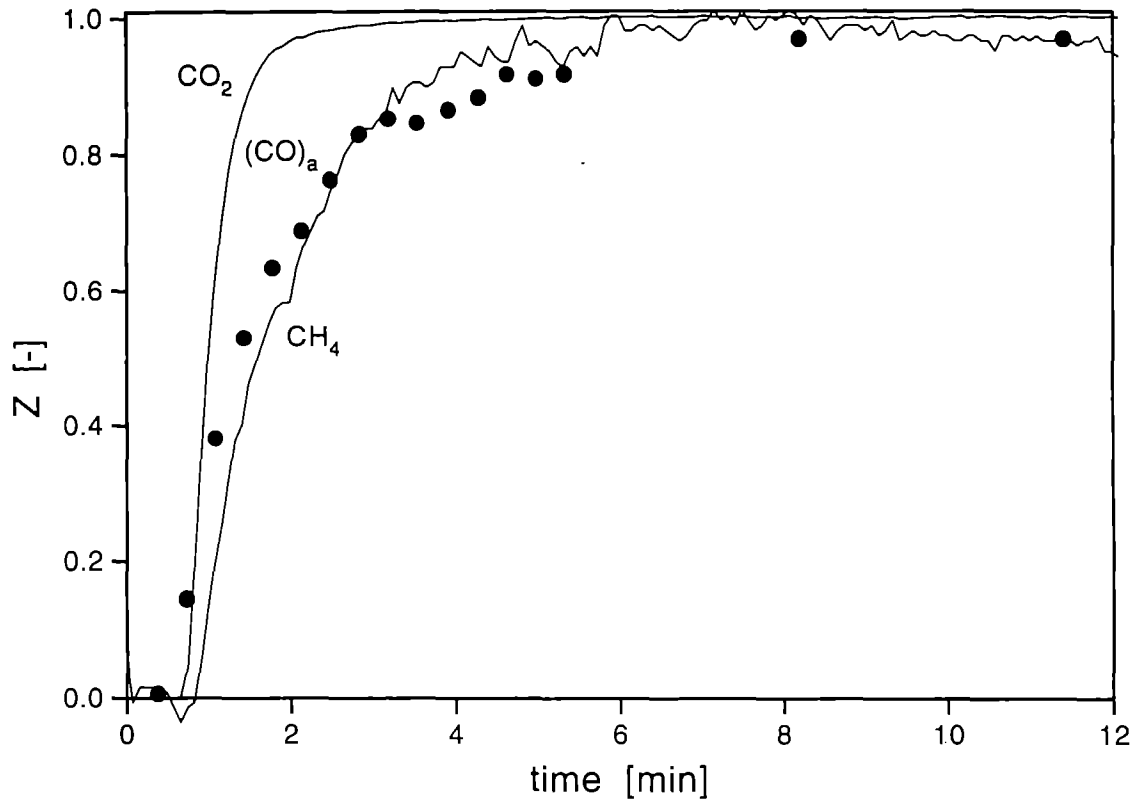


Fig. 3. Transient step-up experiment; feed switched from an initial composition of 20% H<sub>2</sub> in He to 10% CO<sub>2</sub> and 20% H<sub>2</sub> in He at 383 K and  $P_{\text{H}_2\text{O}} = 0.8$  mbar.

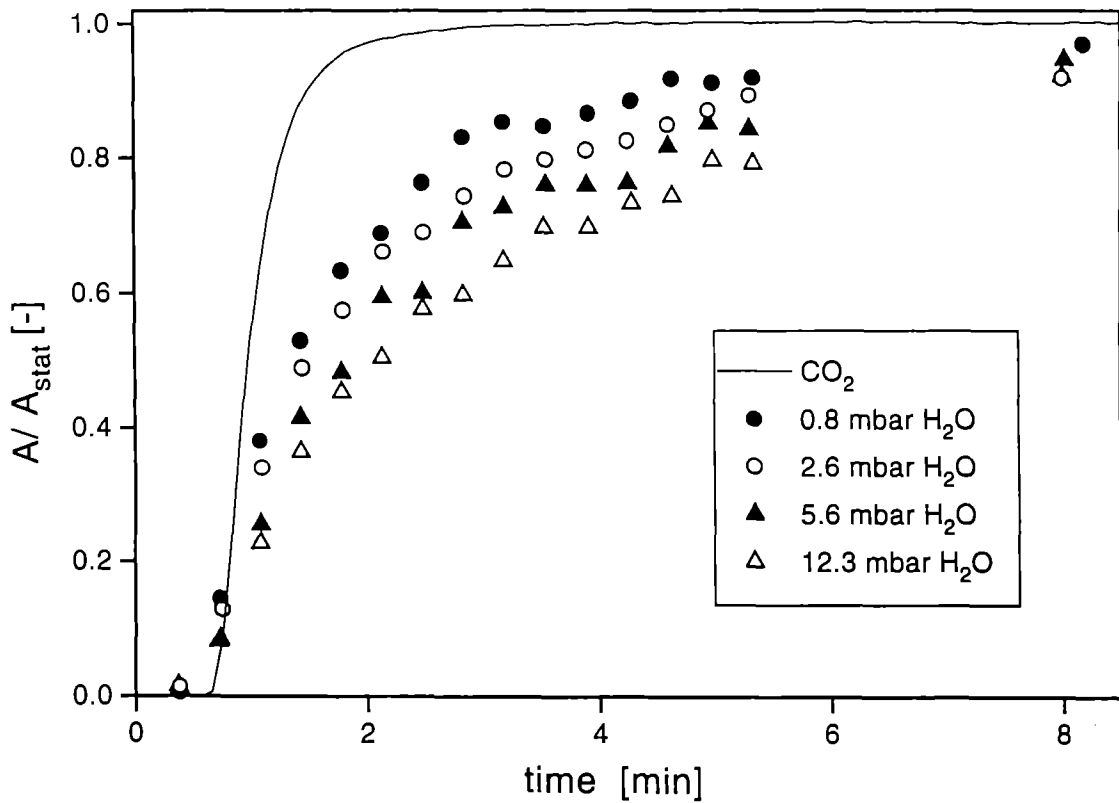


Fig. 4. Effect of  $P_{\text{H}_2\text{O}}$  on the transient step-up experiment; normalized (CO)<sub>a</sub> band integrals for a feed switched from an initial composition of 20% H<sub>2</sub> in He to 10% CO<sub>2</sub> and 20% H<sub>2</sub> in He at 383 K;  $P_{\text{H}_2\text{O}}$  varying between 0.8 and 12.3 mbar.

very low  $\text{CO}_2$  conversion in the DRIFTS cell, a quantitative determination of  $\text{H}_2\text{O}$  by mass spectrometry is difficult. The transient response for water was therefore omitted in Fig. 3.

An inhibiting effect of  $P_{\text{H}_2\text{O}}$  on the  $(\text{CO})_a$  formation is shown in Fig. 4. The  $(\text{CO})_a$  data presented were normalized by the steady-state value obtained after 40 min of reaction. A definite effect of  $\text{H}_2\text{O}$  on the  $(\text{CO})_a$  formation rate is observed. A decrease of this rate is observed with an increasing value of  $P_{\text{H}_2\text{O}}$ .

The  $(\text{CO})_a$  formation is also influenced by the  $\text{H}_2$  concentration. An increasing value of  $P_{\text{H}_2}$  results in an increase of the  $(\text{CO})_a$  formation rate. The step-up experiments show that  $\text{H}_2$ , as well as  $\text{H}_2\text{O}$ , plays an important role in the  $\text{CO}_2$  dissociation mechanism to form  $(\text{CO})_a$ .

#### Step-down experiments

Typical IR data are presented in Fig. 5 for  $(\text{CO})_a$  hydrogenation at 383 K in 20 mol%  $\text{H}_2$ . These spectra were acquired at 3 min intervals. The uppermost spectrum was recorded during steady-state operation just before the switch.  $(\text{CO})_a$  band integrals were normalized against the spectrum recorded 2 min after the switch to account for the gas phase  $\text{CO}_2$  residence time in the system.

Figure 6 shows a semi-log plot of a normalized band area against time for varying  $\text{H}_2$  molar fractions. Good linearity is obtained up to 20%  $\text{H}_2$ . For 50%  $\text{H}_2$  an order of 1.5 more adequately describes the data. The linearity of these data in a certain  $\text{H}_2$  concentration range suggests that  $(\text{CO})_a$  hydrogenation depends to first order on  $\theta_{\text{CO}}$  within this range. Such a first-order dependence is in good agreement with

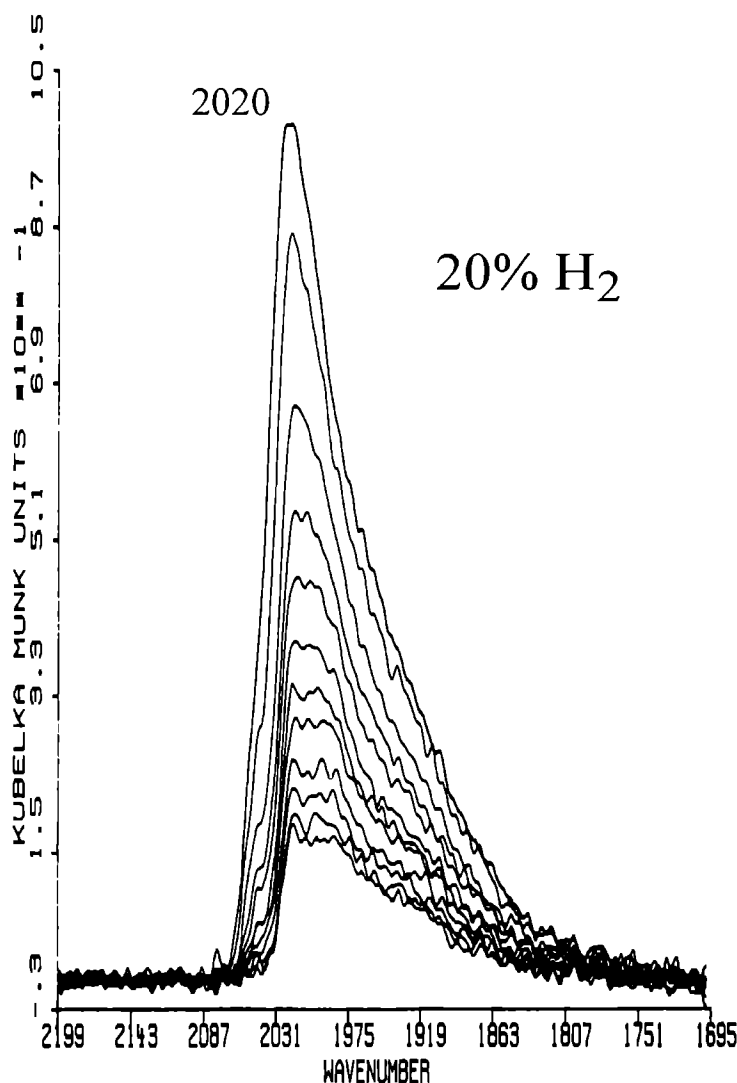


Fig. 5. DRIFTS spectra of  $(\text{CO})_a$  on 2%  $\text{Ru}/\text{TiO}_2$  during a transient step-down experiment. The spectra are recorded at 3 min intervals after a switch from an initial composition of 10%  $\text{CO}_2$  and 20%  $\text{H}_2$  in He to 20%  $\text{H}_2$  in He at 383 K;  $P_{\text{H}_2\text{O}} = 2.4$  mbar. The uppermost spectrum was recorded at steady state in the  $\text{CO}_2/\text{H}_2$  mixture immediately prior to the switch.

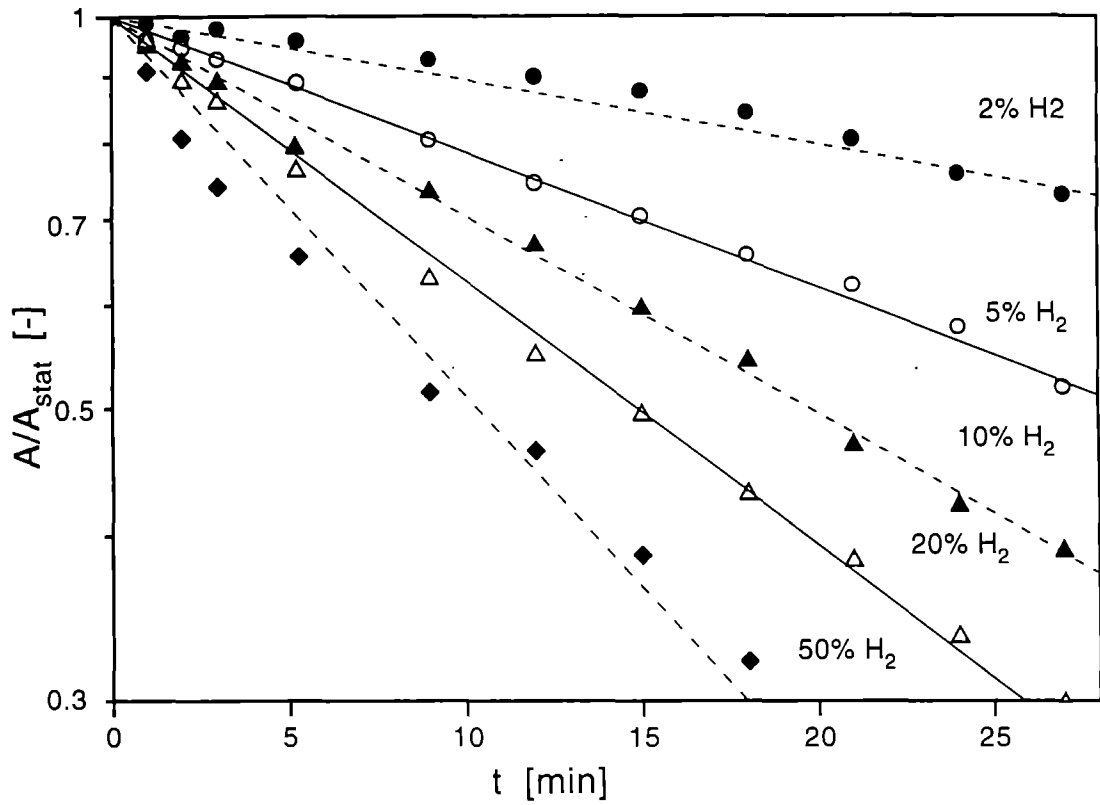


Fig. 6. Effect of  $P_{H_2}$  on the transient step-down experiment. Normalized  $(CO)_u$  band integrals for a feed switched from an initial composition of  $x\%$   $H_2$  and  $10\%$   $CO_2$  in He to  $x\%$   $H_2$  in He ( $2 < x < 50$ ) at  $383\text{ K}$ ;  $P_{H_2O} = 1.6\text{ mbar}$ .

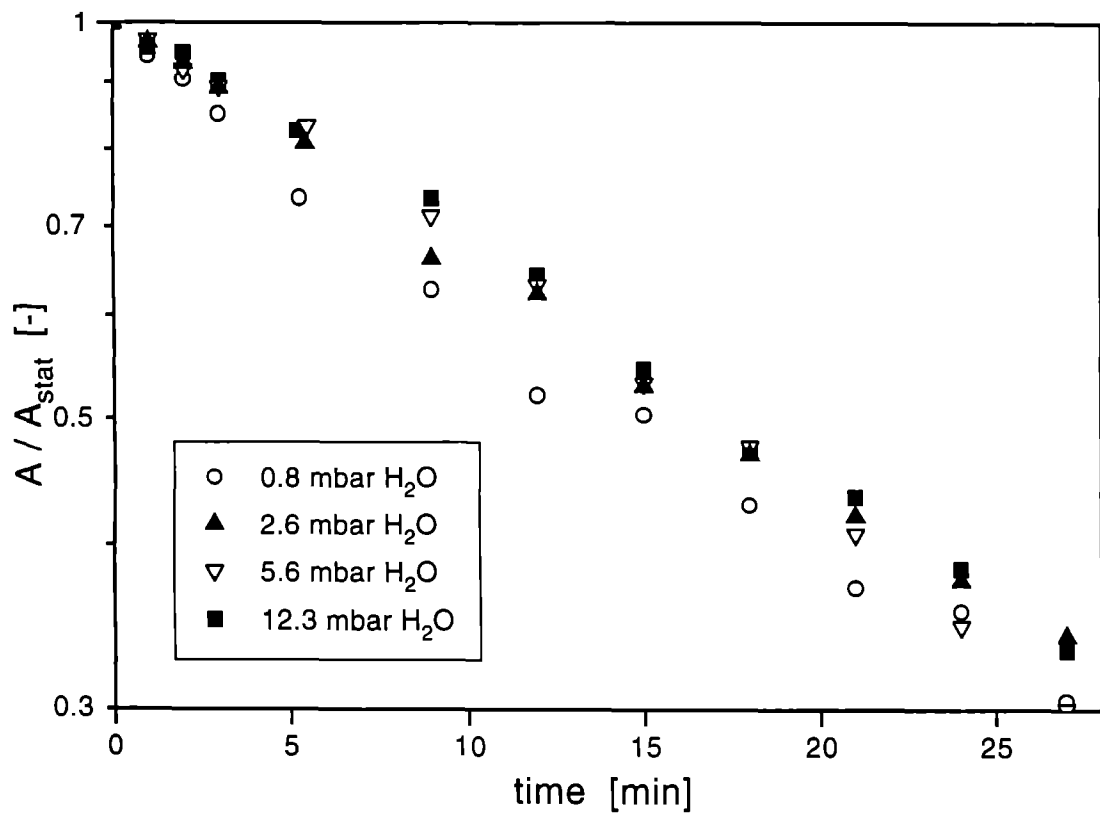


Fig. 7. Effect of  $P_{H_2O}$  on the transient step-down experiment. Normalized  $(CO)_u$  band integrals for a feed switched from an initial composition of  $20\%$   $H_2$  and  $10\%$   $CO_2$  in He to  $20\%$   $H_2$  in He at  $383\text{ K}$ ;  $P_{H_2O}$  varying between  $0.8$  and  $12.3\text{ mbar}$ .

results presented by Cant and Bell (1982) on a Ru/SiO<sub>2</sub> catalyst, or by Mori *et al.* (1982) and Tahri *et al.* (1993) on a Ni/SiO<sub>2</sub> catalyst:

$$\frac{d\theta}{dt} = k\theta_{\text{CO}} P_{\text{H}_2}^n = k'\theta_{\text{CO}} \quad (2)$$

$$k' = kP_{\text{H}_2}^n$$

Slopes  $k'$  in a log-log plot vs hydrogen concentration show that the hydrogenation of (CO)<sub>a</sub> has a half order dependence on hydrogen concentration.

The hydrogenation of (CO)<sub>a</sub> is independent of the H<sub>2</sub>O partial pressure as is shown in Fig. 7. This observation is important if it is combined with the fact that water inhibition was measured under steady-state conditions for the overall CO<sub>2</sub> methanation reaction.

Figure 8 shows a semi-log plot of the normalized band area against time for six temperatures. The slopes in this figure represent the reaction rate constant  $k'$  which is an intrinsic function of temperature. Plotting  $k'$  vs temperature in the Arrhenius form yields an apparent activation energy of  $62 \pm 3 \text{ kJ mol}^{-1}$ .

In summary, the hydrogenation of metal-adsorbed CO on the 2% Ru/TiO<sub>2</sub> catalyst obeys the following kinetic expression at atmospheric pressure and temperatures up to 413 K.

$$r = cst \exp(-62,000/RT) \theta_{\text{CO}} P_{\text{H}_2}^{0.5} \quad (3)$$

## DISCUSSION

The CH<sub>4</sub> production in the step-up experiment shown in Fig. 3 is delayed, indicative of CH<sub>4</sub> production through a series of consecutive reaction steps. The comparatively faster initial rate of formation of (CO)<sub>a</sub> makes this surface species a very plausible surface intermediate. The observation that H<sub>2</sub> catalyses while H<sub>2</sub>O inhibits (Fig. 4) the (CO)<sub>a</sub> formation rate has to be taken into account in the establishment of a mechanism leading to (CO)<sub>a</sub>. Clearly these observations show that (CO)<sub>a</sub> is not formed by simple CO<sub>2</sub> dissociation. The reverse water-gas shift reaction (RWGS) proposed by Prairie *et al.* (1991a) on the basis that the steady-state (CO)<sub>a</sub> concentration is negatively influenced by H<sub>2</sub>O is consistent with the observed H<sub>2</sub> and H<sub>2</sub>O effect in the transient step-up experiments. The mechanism of the RWGS is thought to either go through a formate intermediate (Schild *et al.*, 1991; Shido and Iwasawa, 1993) or through a "surface redox" process (Ernst *et al.*, 1992; Fujita *et al.*, 1992). Spectroscopic surface experiments performed in this system where (HCOO<sup>-</sup>)<sub>a</sub> surface adsorbates are measured tend to favor the formate mechanism in the following form:

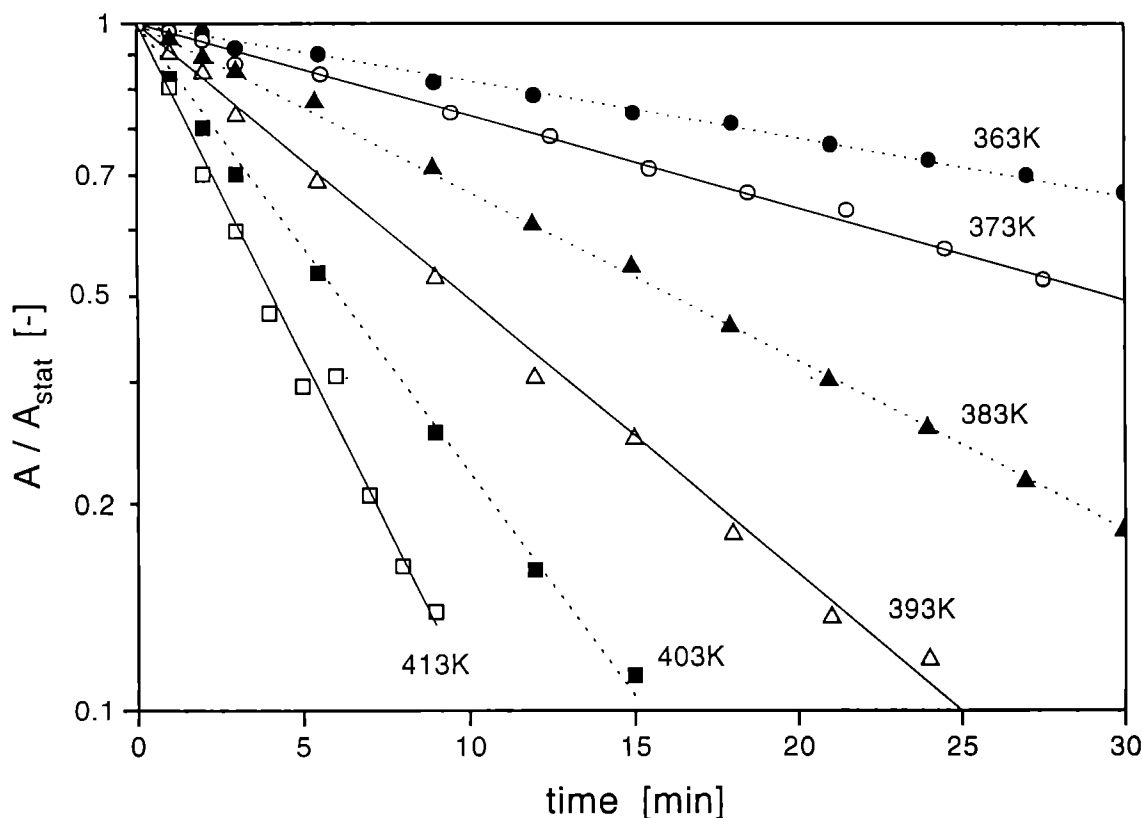
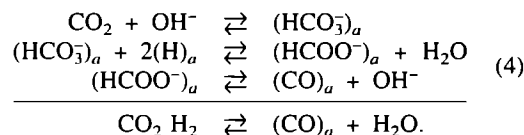


Fig. 8. Effect of the reaction temperature on the transient step-down experiment. Normalized (CO)<sub>a</sub> band integrals for a feed switched from an initial composition of 20% H<sub>2</sub> and 10% CO<sub>2</sub> in He to 20% H<sub>2</sub> in He;  $P_{\text{H}_2\text{O}} = 6.1 \text{ mbar}$  with reaction temperature varying between 363 and 413 K.

This mechanism is based on the observations that:

- (1)  $(\text{HCOO}^-)_a$  is not formed in the absence of  $\text{H}_2$  or Ru to dissociate the  $\text{H}_2$ .
- (2)  $(\text{HCO}_3^-)_a$  is observed on the catalyst surface or on a blank composed of the  $\text{TiO}_2$  support upon exposure to  $\text{CO}_2$ . A  $\text{CO}_2 \Rightarrow \text{CO}_2/\text{H}_2$  switch results in the decrease of the  $(\text{HCO}_3^-)_a$  while  $(\text{HCOO}^-)_a$  appears on the catalyst surface. No modification of  $(\text{HCO}_3^-)_a$  is observed on the blank  $\text{TiO}_2$  surface.
- (3) Negative hydroxyl bands are measured on the IR spectrum of the catalyst surface after steady-state reaction.
- (4) The positive effect of  $\text{H}_2$  concentration on the  $(\text{CO})_a$  formation as well as the inhibiting effect of  $\text{H}_2\text{O}$  are compatible with this mechanism.

A similar mechanism was proposed by Fu *et al.* (1989) for the water-gas shift reaction on a K-Os/ $\text{Al}_2\text{O}_3$  catalyst.

The observation of a one-half order dependence on  $\text{H}_2$  concentration for the  $(\text{CO})_a$  hydrogenation process indicates that  $(\text{CO})_a$  methanation has a first-order relationship with adsorbed  $(\text{H})_a$  concentration which is in equilibrium with gas phase  $\text{H}_2$  via a dissociative adsorption process. Neither  $(\text{CO})_a$  coverage nor methanation seem to perturb this equilibrium. Similar results for  $(\text{CO})_a$  methanation on Ru/ $\text{SiO}_2$  were also reported by Cant and Bell (1982). Water concentration has no effect on the hydrogenation of  $(\text{CO})_a$ . Water inhibition was measured under steady-state conditions for the overall  $\text{CO}_2$  methanation reaction. Inhibition by water must act on the  $(\text{CO})_a$  formation steps if  $(\text{CO})_a$  is to be a reaction intermediate in the  $\text{CO}_2$  methanation reaction. Such an inhibiting effect of water on the  $(\text{CO})_a$  formation was indeed observed during the step-up experiment. This indicates that the rate limiting process of the overall methanation reaction is the  $(\text{CO})_a$  formation.

The overall  $\text{CO}_2$  methanation reaction exhibits an activation energy of  $80 \text{ kJ mol}^{-1}$  for 2% Ru/ $\text{TiO}_2$ . This value is in good agreement with the literature where values ranging between  $67$  and  $88 \text{ kJ mol}^{-1}$  are reported. For the process of  $(\text{CO})_a$  methanation, an activation energy of  $62 \text{ kJ mol}^{-1}$  is measured. Thus, no elementary step in the pathway between  $(\text{CO})_a$  and  $\text{CH}_4$  can be the limiting step in the overall  $\text{CO}_2$  methanation reaction. However,  $(\text{CO})_a$  accumulation is observed on the catalyst surface under steady state. The accumulation of a reaction intermediate placed after the rate limiting step in a consecutive reaction scheme is controlled by the ratio of the rate limiting step reaction constant by the reaction intermediate consumption rate. The observed  $(\text{CO})_a$  accumulation thus indicates that the  $(\text{CO})_a$  hydrogenation process is of the same order of magnitude as the  $(\text{CO})_a$  formation process. A similar conclusion was reached with periodic variations of  $\text{CO}_2$  in the  $\text{H}_2$  feed (Marwood *et al.*, 1994).

## CONCLUSIONS

The transient kinetic study of the  $(\text{CO})_a$  surface intermediate shows that the  $(\text{CO})_a$  formation steps are inhibited by  $\text{H}_2\text{O}$  and enhanced by  $\text{H}_2$ . A RWGS mechanism, based on spectroscopic observations, is postulated and can explain the observed  $\text{H}_2\text{O}$  and  $\text{H}_2$  trends. Although the transient behavior of catalysts differs from steady state (Renken, 1993), the following conclusion can be drawn.

The fact that  $(\text{CO})_a$  hydrogenation in the transients is independent of  $\text{H}_2\text{O}$  concentration, as opposed to the observation of  $\text{H}_2\text{O}$  inhibition under steady-state conditions, may indicate that the rate limiting process in the overall  $\text{CO}_2$  methanation reaction is the formation of  $(\text{CO})_a$ . A similar conclusion is reached by comparing the apparent activation energies for  $(\text{CO})_a$  hydrogenation and the overall steady-state reaction.  $(\text{CO})_a$  accumulation on the catalyst surface reflects a  $(\text{CO})_a$  hydrogenation rate constant of a similar order of magnitude to the rate limiting process.

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## NOTATION

$A$	integrated $(\text{CO})_a$ infrared band between $2070$ and $1750 \text{ cm}^{-1}$
$A_{\text{stat}}$	steady-state value of the integrated $(\text{CO})_a$ infrared band under $\text{CO}_2$ methanation
$E_a$	apparent activation energy
$k'$	rate coefficient for the $(\text{CO})_a$ hydrogenation step
$P_{\text{H}_2}$	hydrogen partial pressure
$P_{\text{H}_2\text{O}}$	$\text{H}_2\text{O}$ partial pressure
$r$	$(\text{CO})_a$ hydrogenation rate
$R_{\text{CH}_4}$	methane formation rate
$Z$	dimensionless variable, normalized by the steady-state value of the variable

## Greek letter

$\theta_{\text{CO}}$	fractional surface coverage by CO
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