

## C<sub>1</sub>-oxygenated molecules adsorbed on rhodium containing catalysts. Identification of a formyl species

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### Abstract

The adsorption of methanol, (D<sub>4</sub>) methanol and formaldehyde on rhodium containing catalysts is studied by FTIR. Besides the well characterized methoxy and formate species, new bands could be observed on the CeO<sub>2</sub> and Pr<sub>6</sub>O<sub>11</sub> supported catalysts. Comparison with results obtained by chemical trapping enables us to identify the new species as a stabilized formyl. The mechanism of methanol dissociation is discussed.

**Keywords:** Carbon monoxide; Hydrogen; Methanol; Formaldehyde; FTIR; Formyl; Adsorption; Rhodium

### 1. Introduction

Many studies have been undertaken to study the influence of the supports and promoters on the reactivity and selectivity of rhodium catalysts in CO–H<sub>2</sub> reactions. Many models have been proposed to explain the drastic changes with the support for Rh catalysts which were first reported by Ichikawa [1,2]. Among them electronic and/or electrostatic interaction, built up of new catalytic sites, maintaining the metal in a higher oxidation state, stabilization of reaction intermediates have been invoked. These aspects have been discussed in details in Ref. [3]. In a recent work it has been shown by TPD and TPSR that two reaction mechanisms may be involved in methane formation on Rh/SiO<sub>2</sub> [4]. Borer and Prins [5] have recently proposed that, on Rh/La<sub>2</sub>O<sub>3</sub>, formates

located on the support could be the reaction intermediate in CH<sub>3</sub>OH formation. Chinchén et al., [6] concluded also that formates might be involved in methanol synthesis on rhodium containing catalysts. However, on Rh/TiO<sub>2</sub>, Takeuchi and Katzer [7] did not observe isotopic mixing on the oxygen when starting from C<sup>18</sup>O to produce methanol thus excluding formates as intermediates in methanol formation on their catalyst.

In presence of some promoters the adsorption of carbon monoxide is also affected. The adsorption mode of carbon monoxide can have an effect on the formation of some adsorbed species. Sachler and Ichikawa [8] reported that bridge bonded CO is preferentially suppressed in presence of the promoter. Further, several authors have also observed that a new absorption band appears in the IR spectra of adsorbed carbon monoxide [8–15]. The band is situated at a lower frequency

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than usually observed for CO adsorption on pure metals. This new adsorption mode of CO is related to an increased dissociation probability of the C–O bond and has been ascribed to the coordination of CO through both ends of the CO molecules. A C and O coordinated species has been proposed to be a key intermediate in the CO hydrogenation reactions [16,17]. This is evident for the CO dissociation, since for dissociation carbon monoxide must at one moment tilt towards the surface as suggested by de Koster and van Santen [18] by theoretical calculations. Further, Anderson and Dowd [19] have shown that the tilting with respect to the surface normal enhances the electron back-donation into the  $2\pi^*$  orbital of CO and decreases the C–O bond strength. The C and O coordination can also favour the CO migratory insertion into a metal–alkyl or a metal–hydrogen bond [8,20–22]. This has been confirmed by theoretical calculations for iron complexes [23]. Recently, the stabilization of a surface acetyl species has been observed during the adsorption of acetaldehyde on promoted rhodium catalysts which are effective in ethanol synthesis from CO + H<sub>2</sub> [24]. Schild et al., [25] have shown that an  $\eta^2(\text{C},\text{O})$  CH<sub>2</sub>O species is formed during the adsorption of methanol or formaldehyde or by CO + H<sub>2</sub> reaction on Pd/ZrO<sub>2</sub>. On Pd/CeO<sub>2</sub>, Diagne et al., [26] proposed from chemical trapping and TPD experiments that formyl species are involved in methanol formation from CO–H<sub>2</sub>. Despite careful research, no formyl species were observed by IR in CO + H<sub>2</sub> reaction on catalytic surfaces until Saussey et al., [27] reported their formation on ZnO and on ZnO supported copper catalysts.

The adsorption of formaldehyde on oxides is well documented in the literature. Formates are the predominant adsorbed form on oxides such as Fe<sub>2</sub>O<sub>3</sub> [28], Al<sub>2</sub>O<sub>3</sub> [29], MgO [30], TiO<sub>2</sub> [30–32], SiO<sub>2</sub> [33], ZrO<sub>2</sub> [33,34], ThO<sub>2</sub> [32,33]. Additionally methoxy and dioxymethylene entities have been observed at higher coverages [32,33]. Dioxymethylene together with formate were produced from adsorption of HCHO on CeO<sub>2</sub> at 300 K. Band intensities of dioxymethy-

lene and methoxy species increased markedly when cerium oxide was partially reduced prior to the adsorption [35]. The adsorption of formaldehyde has also been studied by EELS on metals. On Ni(110), the primary surface intermediate has been shown to be a methoxy species [36]. At higher coverages solid formaldehyde and polymeric paraformaldehyde are detected. Anton et al., [37] have adsorbed formaldehyde on clean and oxygen precovered Ru(001) single crystals.  $\eta^2$  formaldehyde was observed on clean Ru(001) and the  $\eta^1(\text{O})$  configuration is favoured in presence of oxygen. Upon decomposition on these surfaces,  $\eta^2(\text{C},\text{O})$  formyl species are formed. On a Pt(110)–(1 $\times$ 2) surface molecularly adsorbed formaldehyde,  $\eta^2(\text{C},\text{O})$  formyl species, hydrogen adatoms and chemisorbed carbon monoxide are surface intermediates in the decomposition reaction of formaldehyde [38]. Davis and Barteau [39] propose the intermediacy of a formyl species in the decomposition of H<sub>2</sub>CO on Pd(111). Houtman and Barteau [40] observed that CH<sub>2</sub>O is decomposed to CO and H<sub>2</sub> at  $T < 130$  K on clean Rh(111) and paraformaldehyde appears at high coverage. On an O-predosed surface paraformaldehyde, CO, formate and  $\eta^1(\text{O})$  formaldehyde are detected.

Adsorption of methanol on oxides has also been widely studied. Two kinds of methoxy species were detected by Li et al., [35] when CeO<sub>2</sub> was exposed to CH<sub>3</sub>OH at 300 K. Binet et al., [41] have observed that three kinds of methoxy species are formed on CeO<sub>2</sub> after CH<sub>3</sub>OH adsorption.

Solymosi et al., [42] have investigated the adsorption of CH<sub>3</sub>OH on a clean Rh(111) surface. They evidenced the formation of CH<sub>3</sub>O species which can be hydrogenated to CH<sub>3</sub>OH or decomposed to adsorbed CO and H<sub>2</sub> at 200–220 K. In presence of oxygen, Solymosi et al., [43] observed an increase of the surface concentration of irreversibly bound methoxy species and a slight stabilization effect of this methoxy moieties. Parmer et al., [44] studied the adsorption of methanol on Rh(100) by EELS. At 200–220 K they observed an OH bond cleavage to form an O-bonded methoxy species. Between 250 and 320 K

a fraction of the methoxy species decomposed to form CO and H adatoms. Pre-adsorbed Cu on Rh(100) stabilizes the methoxy species and shifts the methoxy decomposition product from adsorbed CO to HCHO(g) [45].

The present study has been done to show that indeed formyl species can exist on oxide supported and promoted rhodium catalysts and thus that the mechanism through CO insertion into a metal–hydrogen bond is possible on promoted catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

The rare earth oxides were prepared from their nitrate ( $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ) ( $\text{Ln}$  = rare earth). 10 g  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 400 ml distilled water, heated under stirring at 80°C. The pH was adjusted to 7 by ammonia. The precipitate was filtered, dried at 120°C and calcined in air at 400°C for 10 h. The BET specific surface area of the oxides were about 35 m<sup>2</sup>/g. The silica was obtained from Roth (0201, 100 mesh) and contains less than 100 ppm of Na, K and Fe.

The catalysts were prepared by a conventional impregnation of the support ( $\text{SiO}_2$ ,  $\text{CeO}_2$ ,  $\text{Pr}_6\text{O}_{11}$ ) by the suitable amount of an aqueous solution of  $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$  from Johnson Matthey to obtained 3 wt% Rh/support. The catalysts were dried at 120°C, and calcined in air at 450°C for 10 h.

### 2.2. Catalyst reduction

In the infrared experiments the catalysts were reduced in situ at 400°C by hydrogen which was admitted into the cell. The hydrogen atmosphere was then pumped off and the procedure was repeated 5 times.

Metal particle size and dispersion (in brackets) as measured by carbon monoxide adsorption by pulse techniques were Rh/ $\text{SiO}_2$ :3.1 nm (35%); Rh/ $\text{CeO}_2$ :2.5 nm (43%); Rh/ $\text{Pr}_6\text{O}_{11}$ :1.9 nm (60%).

These results are in good agreement with TEM measurements.

### 2.3. FTIR spectroscopy

10 to 20 mg of catalyst were pelleted in form of a disk of 12 mm in diameter. The spectra were taken in a vacuum device similar to that used by Lamotte [46]. The spectra were recorded on a Nicolet MX1 FTIR spectrometer after 100 scans with a 4 cm<sup>-1</sup> resolution. 3 to 5 kPa of methanol, formaldehyde or formic acid were introduced into the vacuum device and a first spectrum was taken after 5 min at room temperature. The pellet was then lifted into the heating part for 10 min. The pellet was reintroduced into the beam in the part at room temperature. The pressure was maintained constant during the measurement (3 to 5 kPa). The reported values are therefore for an important coverage. Experiments were made after pumping the gas atmosphere, but the band at 1665 cm<sup>-1</sup> disappears rapidly with time. The reported spectra are obtained after subtraction of the catalytic pellet and the gas phase spectra.

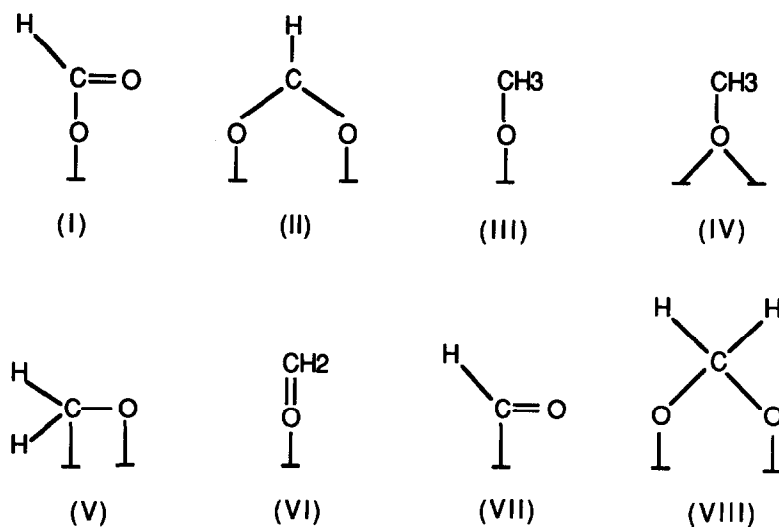
Introduction of formaldehyde: trioxymethylene was introduced into a vacuum vessel, dried under vacuum and depolymerized by heating. The formaldehyde vapors were introduced into the IR cell.

### 2.4. Chemical trapping experiments

The device used for the chemical trapping has been reported elsewhere [47]. Methanol or formaldehyde was adsorbed on the catalyst and then heated to 120°C, temperature at which appears the band at 1665 cm<sup>-1</sup> in the infra red spectra on the promoted samples.  $\text{ICH}_3$  or  $\text{ICD}_3$  is added in large excess. The formed products are analyzed by GC with a FID detector [47].

## 3. Results and discussion

In order to make easier the reading of this part, the various proposed surface species are depicted in Scheme 1.



Scheme 1. Proposed surface structures. I: monodentate formate, II: bidentate formate, III: monodentate methoxy, IV: bidentate methoxy, V:  $\eta^2(\text{C},\text{O})$  formaldehyde, VI:  $\eta^1(\text{O})$  formaldehyde, VII: formyl, VIII dioxymethylene.

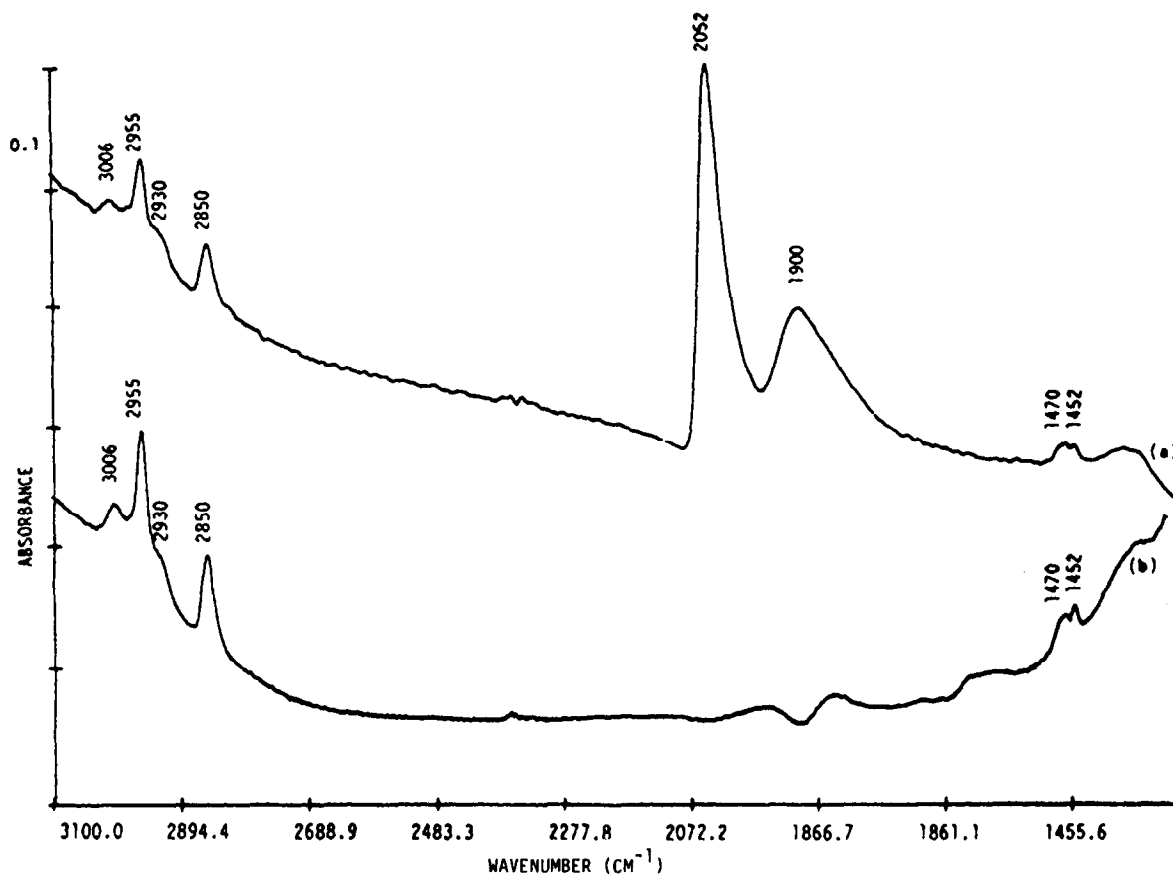


Fig. 1. FTIR spectra of  $\text{CH}_3\text{OH}$  adsorption and heating to  $120^\circ\text{C}$  (a) on  $\text{Rh}/\text{SiO}_2$  (b) on  $\text{SiO}_2$ .

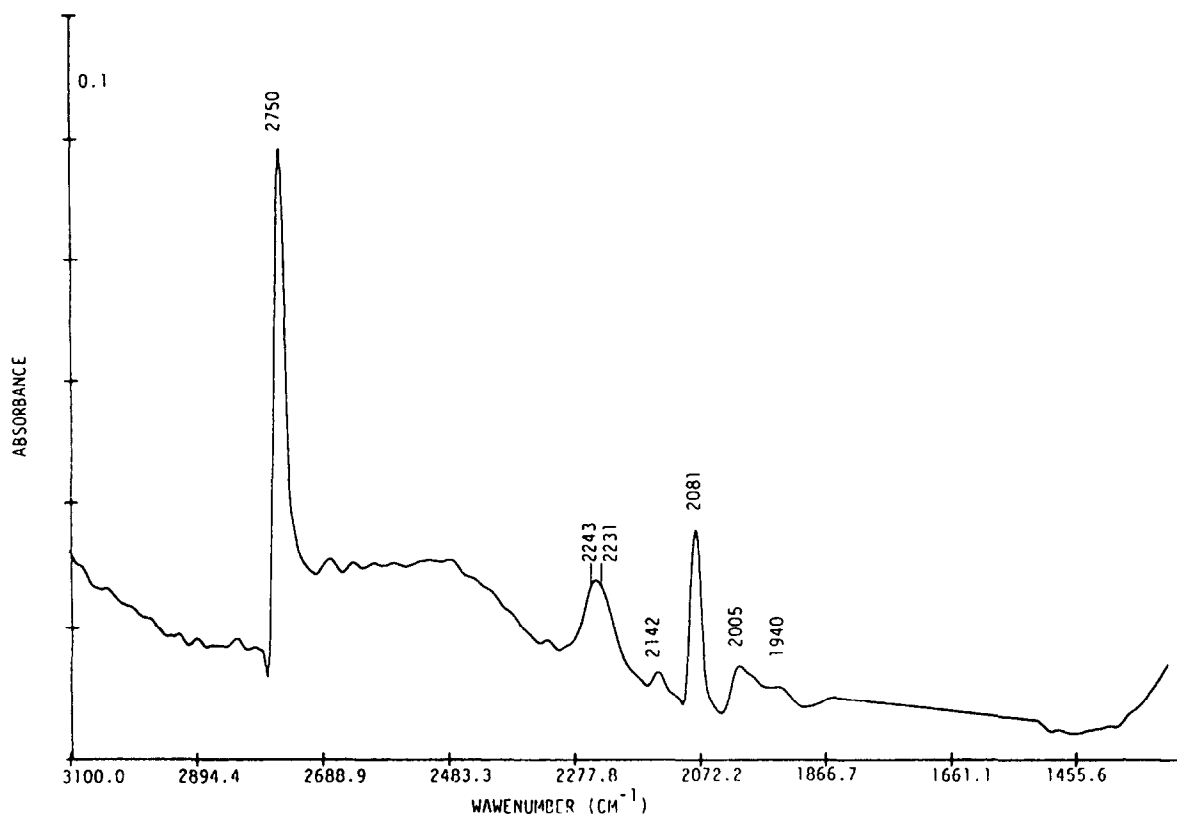


Fig. 2. FTIR spectra of CD<sub>3</sub>OD adsorption and heating to 120°C on Rh/SiO<sub>2</sub>.

### 3.1. Adsorption of methanol on the reduced Rh/SiO<sub>2</sub>

Bands appear at 3006, 2955 (with a shoulder at 2930), 2850, 1470 and 1452 cm<sup>-1</sup> (Fig. 1a). These bands resist evacuation at room temperature. According to the literature they can be attributed to the formation of methoxy species (III) ( $\nu_a\text{CH}_3$  3015 and 2955,  $\nu_s\text{CH}_3$  2857,  $\delta_a\text{CH}_3$  1470 cm<sup>-1</sup> and  $\delta_s\text{CH}_3$  1457 cm<sup>-1</sup>) (Refs. [48,49]). No other bands are observed except two bands at 2052 cm<sup>-1</sup> and 1900 cm<sup>-1</sup>, which can be ascribed to CO formed by decomposition of methanol. The spectrum taken after adsorption of methanol on silica in the same conditions gives rise to the same peaks except for that corresponding to adsorbed carbon monoxide (Fig. 1b). It can therefore be concluded, that the methoxy species (III) observed on Rh/SiO<sub>2</sub> are located on the silica support. Adsorption of deuterated methanol

(Fig. 2) on the Rh/SiO<sub>2</sub> catalyst in the same conditions gives bands at 2243, 2142 cm<sup>-1</sup> which can respectively be ascribed to  $\nu_a\text{CD}_3$  and  $\nu_s\text{CD}_3$  vibrations of a deuterated methoxy species. This confirms the results for non-deuterated methanol. Further CD<sub>3</sub>OD adsorption gives rise to bands at bands at 2750 ( $\nu\text{OD}$ ), 2231 ( $\nu_a\text{CD}_3$ ) and 2081 ( $\nu_s\text{CD}_3$ ) cm<sup>-1</sup>. These bands correspond fairly well to that reported in the literature for gas phase CD<sub>3</sub>OD: 2724 ( $\nu\text{OD}$ ), 2228 ( $\nu_a\text{CD}_3$ ), and 2080 ( $\nu_s\text{CD}_3$ ) cm<sup>-1</sup> [48,49]. The band at 2750 cm<sup>-1</sup> is at a higher position than the band  $\nu\text{OD}$  of gas phase (D<sub>4</sub>) methanol. It may correspond to the  $\nu\text{OD}$  of silica hydroxyl which would cover the band at 2724 cm<sup>-1</sup> of the gas phase methanol. No other species appear by heating the sample except bands at 2005 and 1940 cm<sup>-1</sup> which can be ascribed to adsorbed carbon monoxide in linear and bridged modes respectively.

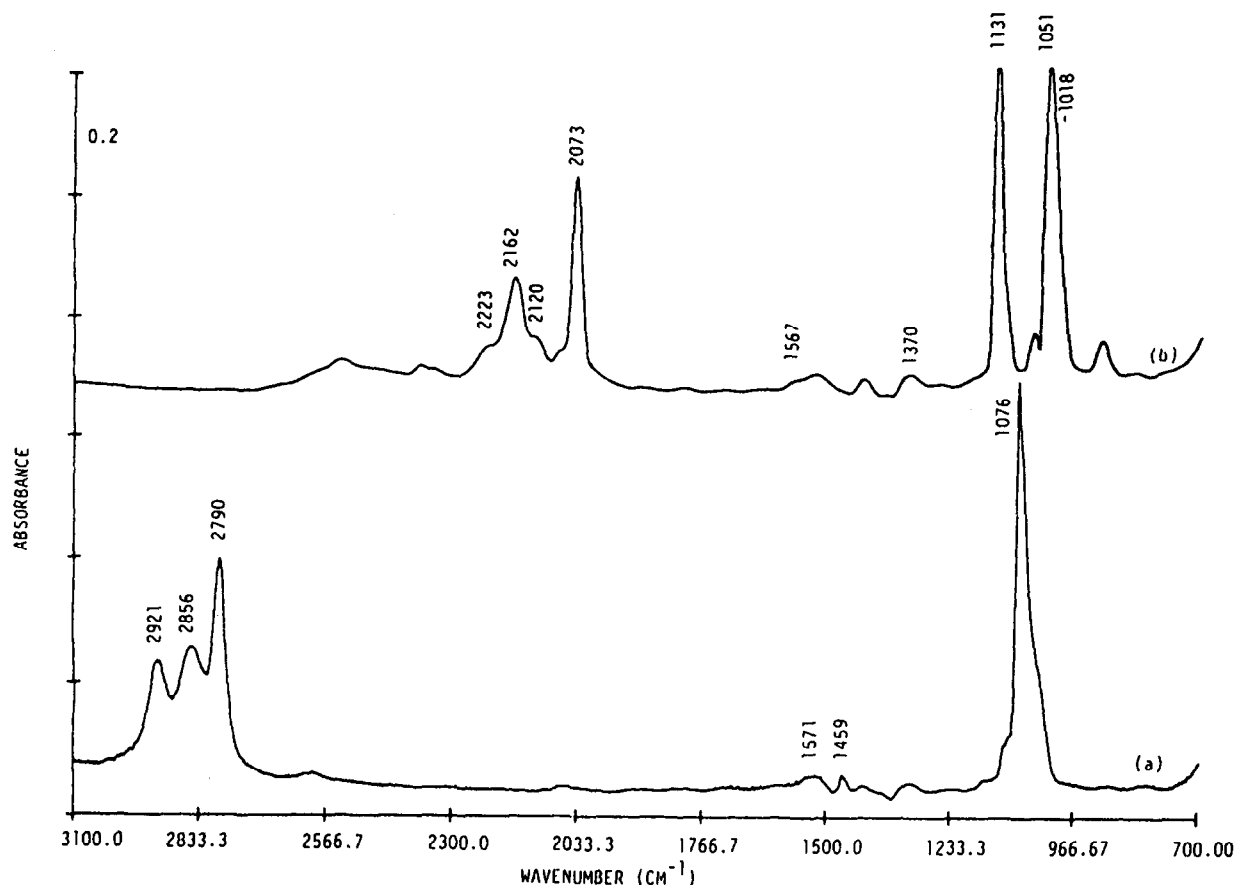


Fig. 3. FTIR spectra: (a) after  $\text{CH}_3\text{OH}$  adsorption and heating to  $120^\circ\text{C}$  on  $\text{CeO}_2$ , (b) after  $\text{CD}_3\text{OD}$  adsorption and heating to  $120^\circ\text{C}$  on  $\text{CeO}_2$ .

### 3.2. Adsorption of methanol on $\text{CeO}_2$ and $\text{Pr}_6\text{O}_{11}$

In order to make the difference between the species formed on the support and that obtained on the supported rhodium, methanol was also adsorbed on the pure supports (i.e.,  $\text{CeO}_2$  and  $\text{Pr}_6\text{O}_{11}$ ). Adsorption of methanol on  $\text{CeO}_2$  results in the appearance of medium bands at 2921, 2856, 2790  $\text{cm}^{-1}$  and weak bands at 1571, 1459 and a strong band at 1076  $\text{cm}^{-1}$  (Fig. 3a). These bands resist evacuation at room temperature. After evacuation, no band is observed in the area of the OH bending ( $1194 \text{ cm}^{-1}$ ) of methanol in gas phase. Therefore, most of the bands can be attributed by comparison with the results of Binet et al., [41] to bidentate methoxy species (IV) adsorbed on  $\text{CeO}_2$  ( $\nu_a\text{CH}_3$  2921  $\text{cm}^{-1}$ ,  $\nu_s\text{CH}_3$  2790  $\text{cm}^{-1}$ ,  $\nu\text{C-O}$  1076  $\text{cm}^{-1}$  and  $\delta\text{CH}_3$  1459  $\text{cm}^{-1}$ ). The

band at 2856  $\text{cm}^{-1}$  arises according to Binet et al., [41] from the Fermi resonance between  $2\delta\text{CH}_3$  and  $\nu_s\text{CH}_3$ . The slight band at 1571  $\text{cm}^{-1}$  appears by heating from room temperature to  $120^\circ\text{C}$  and could correspond to the formation of a surface formate species. Deuterated ( $\text{D}_4$ ) methanol was also admitted on the surface of cerium oxide (Fig. 3b). Bands at 2223  $\text{cm}^{-1}$  and 2073  $\text{cm}^{-1}$  correspond to  $\nu_a\text{CD}_3$  and  $\nu_s\text{CD}_3$  of gas phase methanol in the literature [49] and indeed they disappear by evacuation. Bands at 2162, 1131, 1051 and 1018  $\text{cm}^{-1}$  are more resistant to evacuation and according to the literature could be ascribed to  $\nu_s\text{CD}_3$  (2162  $\text{cm}^{-1}$ ),  $\delta_a\text{CD}_3$  (1131  $\text{cm}^{-1}$ ),  $\delta_s\text{CD}_3$  (1051  $\text{cm}^{-1}$ ) and  $\nu\text{C-O}$  (1018  $\text{cm}^{-1}$ ) of a bidentate surface methoxy species (IV) [41]. According to Binet et al., [41], the position of the bands attributed to methoxy species can change with the reduction of  $\text{CeO}_2$  and the

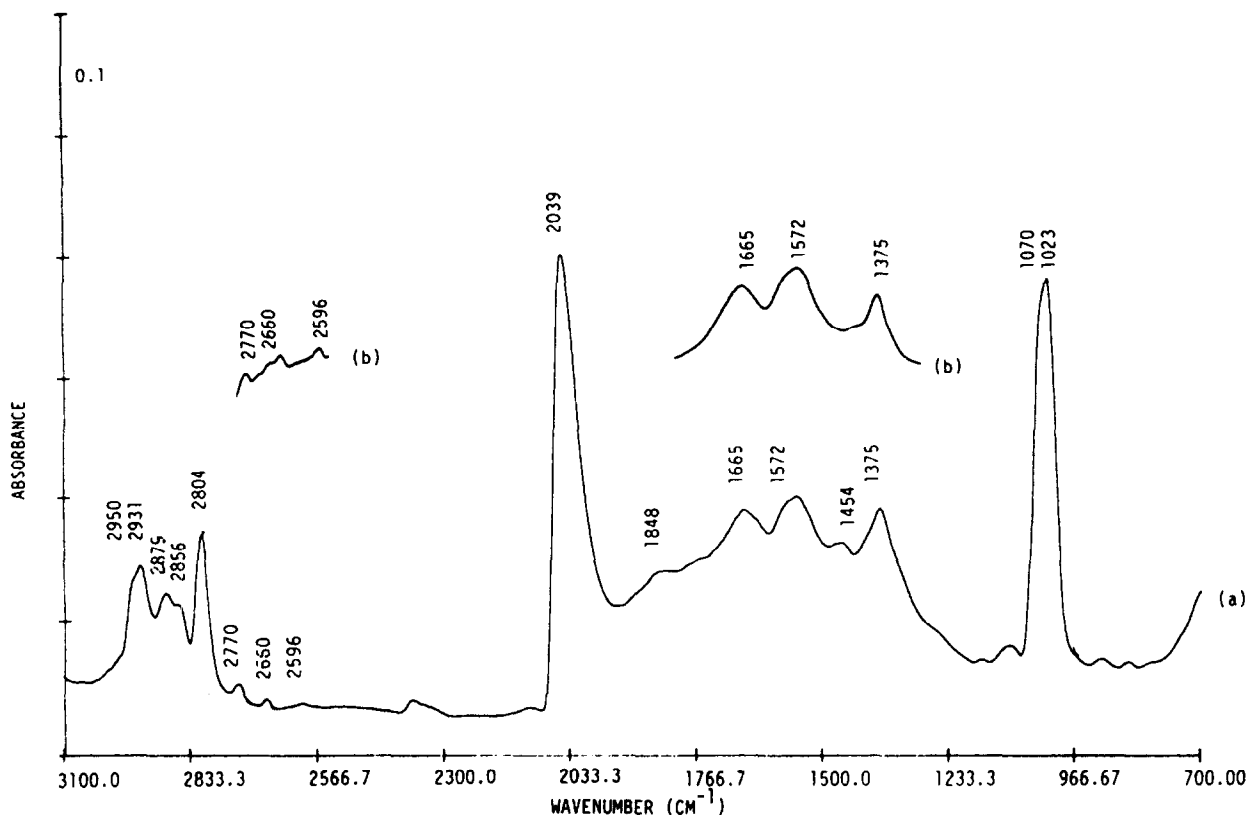


Fig. 4. FTIR spectra: (a) after  $\text{CH}_3\text{OH}$  adsorption and heating to  $120^\circ\text{C}$  on  $\text{Rh}/\text{CeO}_2$ . (b) difference spectra between  $120^\circ\text{C}$  and room temperature after  $\text{CH}_3\text{OH}$  adsorption on  $\text{Rh}/\text{CeO}_2$ .

$\text{Ce}^{4+}/\text{Ce}^{3+}$  surface ratio. The bands in the present work are in accordance with a bidentate methoxy (IV) on reduced ceria. Three bands are increased upon heating and could correspond to the formation of formates by oxidation of the methoxy species ( $\nu_a\text{OCO}$   $1567\text{ cm}^{-1}$ ,  $\nu_s\text{OCO}$   $1370\text{ cm}^{-1}$ ,  $\nu\text{CD}$   $2120\text{ cm}^{-1}$ ) [27,50]. The results obtained during adsorption of  $\text{CH}_3\text{OH}$  and  $\text{CD}_3\text{OD}$  thus confirm that methoxy and formate species are formed on  $\text{CeO}_2$ .

The same type of spectra (not reported here) is observed during methanol adsorption on  $\text{Pr}_6\text{O}_{11}$ . Bands at  $2926\text{ cm}^{-1}$ ,  $2846\text{ cm}^{-1}$ ,  $2790\text{ cm}^{-1}$ ,  $1431$  and  $1065\text{ cm}^{-1}$  can be attributed to a monodentate surface methoxy (III) ( $\nu_a\text{CH}_3$ , Fermi resonance  $2\delta\text{CH}_3$  and  $\nu_s\text{CH}_3$ ,  $\delta\text{CH}_3$  and  $\nu\text{C-O}$ ). Upon heating, bands appear at  $1595$  and  $1351\text{ cm}^{-1}$  and correspond to the formation of a bidentate formate (II).

### 3.3. Adsorption of methanol on $\text{Rh}/\text{CeO}_2$ and $\text{Rh}/\text{Pr}_6\text{O}_{11}$

The spectra of adsorbed methanol on  $\text{CeO}_2$  and  $\text{Pr}_6\text{O}_{11}$  supported rhodium catalysts are more complicated. The bands in the  $\nu\text{CH}_3$  area can be attributed by comparing the spectra obtained on the pure support and on silica supported rhodium catalysts. On  $\text{Rh}/\text{CeO}_2$  (Fig. 4a) a band at  $2950\text{ cm}^{-1}$  could correspond to the  $\nu_a\text{CH}_3$  vibration of a methoxy species located on rhodium, this attribution is in agreement with the existence of two bands in the C–O area of methoxy species. The feature at  $1023\text{ cm}^{-1}$  could be ascribed to a methoxy located on Rh, together with that at  $2950$ . By comparing with the result on pure  $\text{CeO}_2$ , the bands at  $2931$  ( $\nu_a\text{CH}_3$ ),  $2856$  (Fermi resonance between  $2\delta\text{CH}_3$  and  $\nu_s\text{CH}_3$ ),  $2804$  ( $\nu_s\text{CH}_3$ ),  $1454$  ( $\delta_s\text{CH}_3$ ) and  $1070\text{ cm}^{-1}$  ( $\nu\text{C-O}$ ) are probably that of a bidentate methoxy species (IV) on the

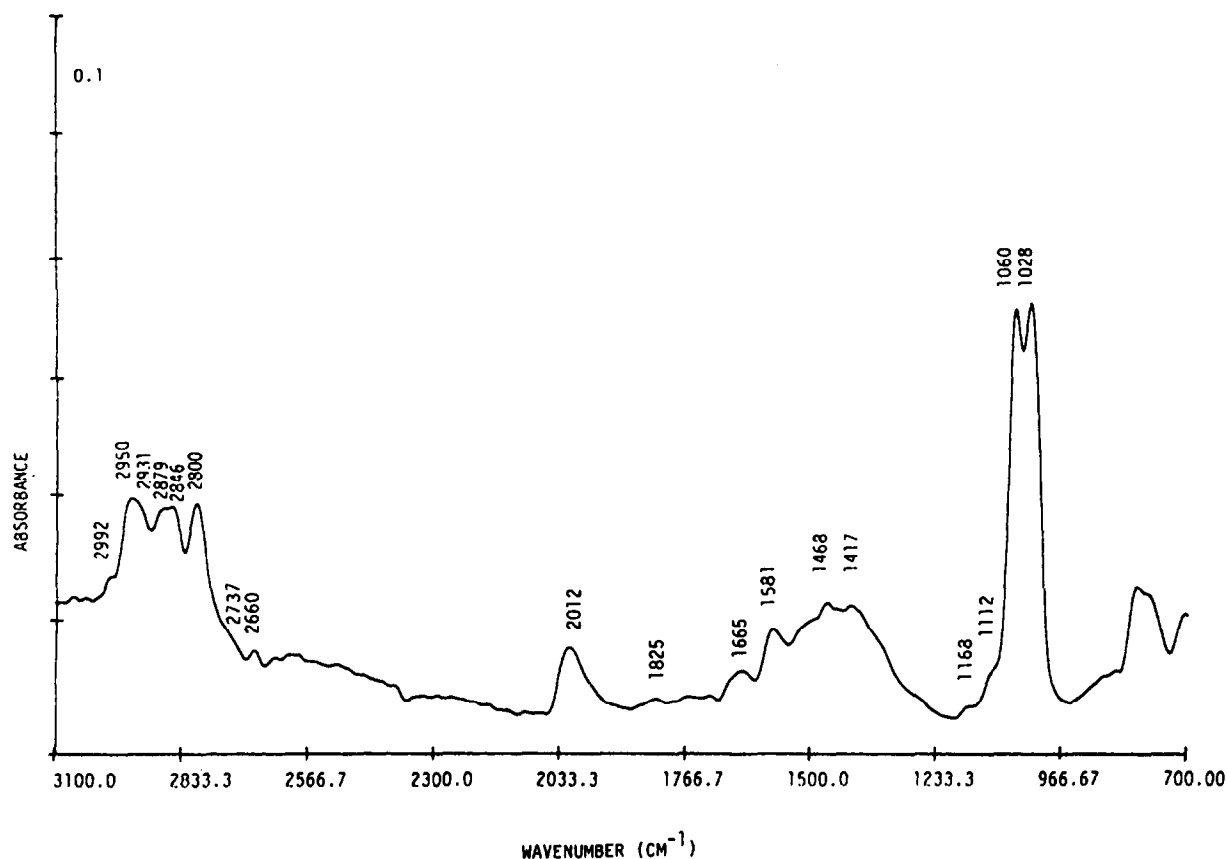


Fig. 5. FTIR spectra after  $\text{CH}_3\text{OH}$  adsorption and heating to  $120^\circ\text{C}$  on  $\text{Rh}/\text{Pr}_6\text{O}_{11}$ .

$\text{CeO}_2$  support. Bands at  $1572$  ( $\nu_a\text{O}-\text{C}-\text{O}$ ),  $1375$  ( $\nu_s\text{O}-\text{C}-\text{O}$ ) and  $2879$  ( $\nu_s\text{CH}$ ) can be compared to that of bidentate formate (II) species in the literature. By heating the sample to  $60$ – $120^\circ\text{C}$  new bands appear simultaneously at  $1665$  and  $2770$ ,  $2660$  and  $2596$   $\text{cm}^{-1}$ . The appearance of these bands are clearly shown on the difference spectra between  $120^\circ\text{C}$  and room temperature as given in Fig. 4b. The features corresponding to formates ( $1572$  and  $1375$   $\text{cm}^{-1}$ ) increase too. These bands will be discussed in detail in connection with the results of chemical trapping. Bands at  $2039$  and  $1848$   $\text{cm}^{-1}$  can be attributed to carbon monoxide adsorbed linearly and in a bridging configuration respectively. Very similar results are obtained on  $\text{Rh}/\text{Pr}_6\text{O}_{11}$  as can be seen in Fig. 5. The attribution of the bands was strengthened by the study of the adsorption of  $\text{CD}_3\text{OD}$ . Bands at  $2176$  ( $\nu_a\text{CD}_3$ ),  $2078$  ( $\nu_s\text{CD}_3$ ),  $1121$  ( $\delta_s\text{CD}_3$ ) and  $1070$   $\text{cm}^{-1}$  ( $\nu\text{C}-\text{O}$ ) can be attributed to a monodentate meth-

oxy species (III) (Fig. 6a). The formates are located at  $2134$   $\text{cm}^{-1}$  ( $\nu\text{CD}$ ),  $1557$  ( $\nu_a\text{O}-\text{C}-\text{O}$ )  $1378$  ( $\nu_s\text{O}-\text{C}-\text{O}$ )  $\text{cm}^{-1}$ . Upon heating to  $60$ – $120^\circ\text{C}$  new bands appear at  $1960$   $\text{cm}^{-1}$ , corresponding to the bands obtained at  $2770$  or  $2660$ , and  $1656$   $\text{cm}^{-1}$  corresponding to that at  $1665$   $\text{cm}^{-1}$  for  $\text{CH}_3\text{OH}$ . They will be attributed hereafter. The increase of the features at  $1960$  and  $1656$   $\text{cm}^{-1}$  is confirmed by the difference spectra between  $120^\circ\text{C}$  and  $60^\circ\text{C}$  (Fig. 6b) which shows a shoulder at  $1960$   $\text{cm}^{-1}$  and a band at  $1656$   $\text{cm}^{-1}$ . Similar spectra are obtained on  $\text{Rh}/\text{CeO}_2$  but the band at about  $1960$   $\text{cm}^{-1}$  is only observed as a shoulder of the band at  $2050$   $\text{cm}^{-1}$  corresponding to adsorbed carbon monoxide on Rh.

### 3.4. Adsorption of formaldehyde

Formaldehyde was also adsorbed on the surface of the supports and on the supported rhodium cat-



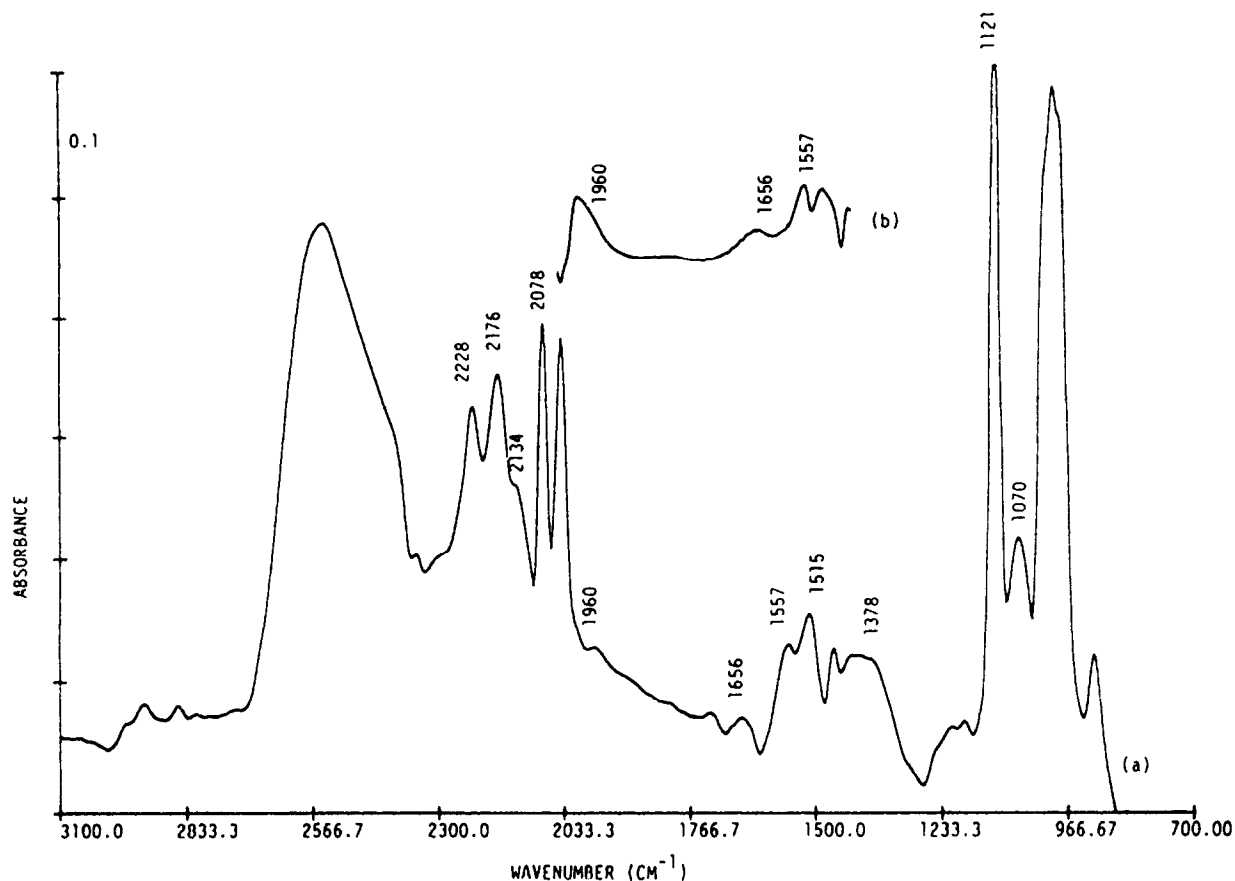


Fig. 6. FTIR spectra: (a) after  $\text{CD}_3\text{OD}$  adsorption and heating to  $120^\circ\text{C}$  on  $\text{Rh}/\text{Pr}_6\text{O}_{11}$ , (b) difference spectra between  $120^\circ\text{C}$  and  $60^\circ\text{C}$  after  $\text{CD}_3\text{OD}$  adsorption on  $\text{Rh}/\text{Pr}_6\text{O}_{11}$ .

alysts. On  $\text{SiO}_2$  (spectra non reported here) only bands corresponding to methoxy bands appears like in Fig. 1b; on  $\text{Rh}/\text{SiO}_2$  feature corresponding to adsorbed carbon monoxide can be observed. In Fig. 7, the spectrum for formaldehyde adsorbed on  $\text{Pr}_6\text{O}_{11}$  after heating to  $120^\circ\text{C}$  is reported. The adsorption at room temperature and  $120^\circ\text{C}$  give rise to bands at  $2921\text{ cm}^{-1}$ ,  $2850\text{ cm}^{-1}$ ,  $2800\text{ cm}^{-1}$ ,  $1430\text{ cm}^{-1}$  and  $1065\text{ cm}^{-1}$ . These bands correspond well to those observed in the present work for methanol adsorption on  $\text{Pr}_6\text{O}_{11}$  and have been attributed to methoxy species (III) ( $2926\text{ cm}^{-1}$   $\nu_a\text{CH}_3$ ,  $2846\text{ cm}^{-1}$  (Fermi resonance between  $2\delta\text{CH}_3$  and  $\nu_s\text{CH}_3$ ),  $2790\text{ cm}^{-1}$   $\nu_s\text{CH}_3$ ,  $1431\text{ cm}^{-1}$   $\delta\text{CH}_3$  and  $1065\text{ cm}^{-1}$   $\nu\text{C-O}$ ). Bands at  $2865\text{ cm}^{-1}$ ,  $1605$ ,  $1567$ ,  $1375\text{ cm}^{-1}$  and  $740\text{ cm}^{-1}$  can be observed and increase upon heating to  $120^\circ\text{C}$ . For methanol adsorption only traces of these bands are

observed. Comparing these bands to those observed by Li et al., [35] during adsorption of formic acid on  $\text{CeO}_2$  these bands can be ascribed to monodentate and bidentate formate species. Further, features are obtained at  $2940$ ,  $1430$ ,  $1159$ ,  $967$  and  $864\text{ cm}^{-1}$  and decrease upon heating at  $120^\circ\text{C}$ . These bands are in good agreement with bands observed during adsorption of formaldehyde on  $\text{Ru}(001)$  by Anton et al., [37]. These authors assigned these frequencies to  $\nu_a\text{CH}_2$ ,  $\delta\text{CH}_2$ ,  $\omega\text{CH}_2$ ,  $\nu\text{C-O}$  and  $\rho\text{CH}_2$  of an adsorbed  $\text{CH}_2\text{O}$  in the  $\eta^2(\text{C,O})\text{CH}_2\text{O}$  (V) configuration. As can be seen in Fig. 8a, the same bands can be formed for formaldehyde adsorbed on  $\text{Rh}/\text{Pr}_6\text{O}_{11}$ . Additional bands at  $1492$ ,  $1407$ ,  $1112$  and  $925\text{ cm}^{-1}$  are very similar to that reported by Busca et al., [33] for the adsorption of formaldehyde on  $\text{ThO}_2$ . These authors attributed these features to a

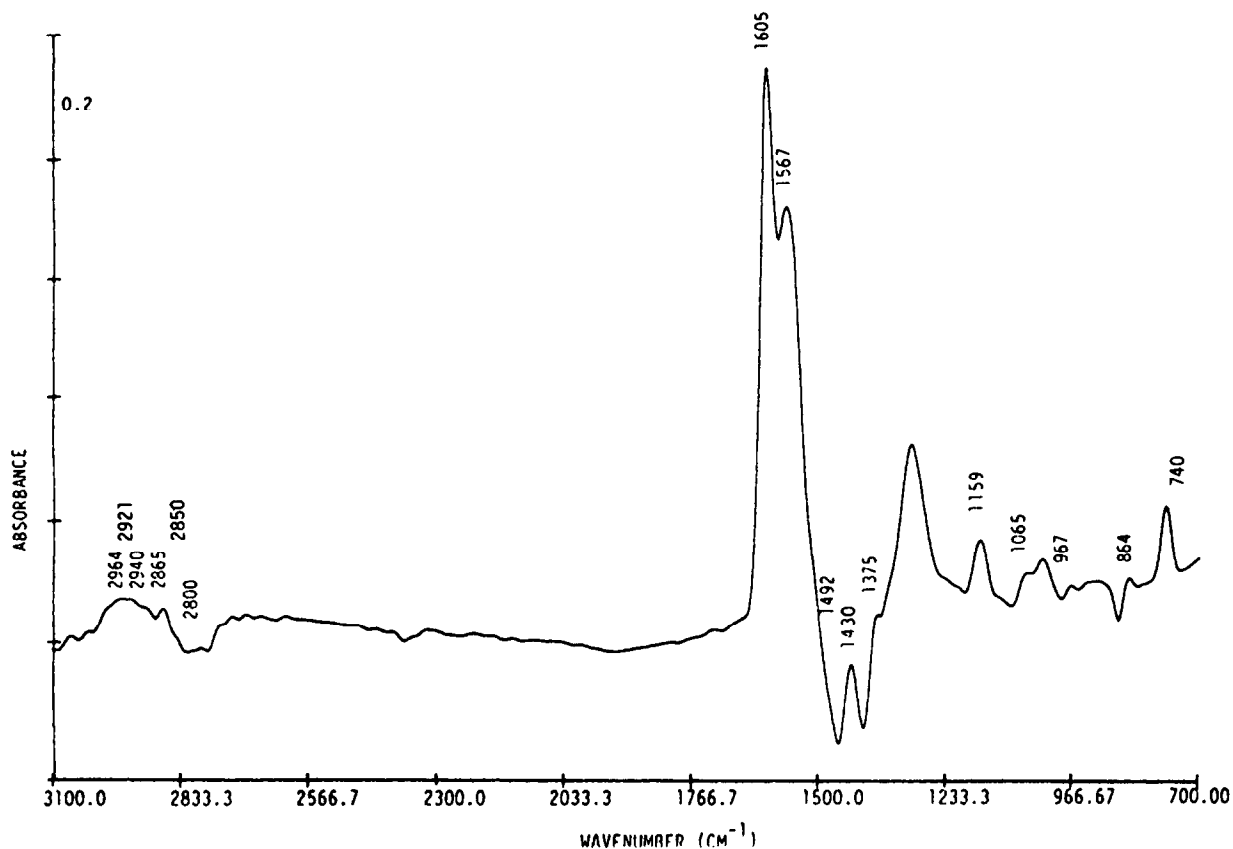


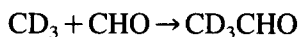
Fig. 7. FTIR spectra after  $\text{CH}_2\text{O}$  adsorption and heating to  $120^\circ\text{C}$  on  $\text{Pr}_6\text{O}_{11}$ .

surface dioxymethylene species (VIII). However upon heating to  $60$ – $120^\circ\text{C}$  new bands develop simultaneously at  $2762$ ,  $2645$ ,  $2556$  and  $1665\text{ cm}^{-1}$  as can be seen clearly from the difference spectra between  $120^\circ\text{C}$  and  $60^\circ\text{C}$  (Fig. 8b).

### 3.5. Discussion of the bands at $1665\text{ cm}^{-1}$

According to the literature bands at  $1665\text{ cm}^{-1}$  could be attributed to an  $\eta^1(\text{O})\text{CH}_2\text{O}$  species (VI) [37]. However these species are only present at very low temperatures about  $80\text{ K}$ .  $\eta^2(\text{C},\text{O})\text{CH}_2\text{O}$  (V) is present on the catalysts as shown in the part on formaldehyde adsorption. Further, monodentate formates (I) have also been observed in that area on  $\text{Cu}/\text{SiO}_2$  [51] and  $\text{Cu}(100)$  [50]. However, as indicated before, the bands at  $2770$  ( $2762$ ),  $2660$  ( $2645$ ),  $2596$  ( $2556$ )  $\text{cm}^{-1}$  are developed simultaneously to the band at  $1665\text{ cm}^{-1}$  upon heating and obviously all these

features correspond to the same species. Further, monodentate formate give rise to a  $\nu\text{O}-\text{C}-\text{O}$  band at around  $1600\text{ cm}^{-1}$  as shown in Ref. [35]. Chemical trapping experiments by  $\text{CD}_3\text{I}$  have shown that  $\text{CD}_3\text{CHO}$  is formed in the conditions where these bands appear [14,47] ( $400\text{ K}$ ). The formation of  $\text{CD}_3\text{CHO}$  would be in accordance with the reaction of a formyl species (VII) with a  $\text{CD}_3$  species formed during the decomposition of  $\text{CD}_3\text{I}$ , in agreement with the following scheme:



In acetaldehyde adsorption on the same catalyst, in the same conditions, an acetyl species has been evidenced [24].

As compared to the band at  $\sim 1600\text{ cm}^{-1}$  found by Saussey et al., [27] on  $\text{ZnO}$  and  $\text{Cu}/\text{ZnO}$ , the band at  $1665\text{ cm}^{-1}$  seems at a high frequency. However, most of the formyl species found in the literature are stabilized by the interaction of the

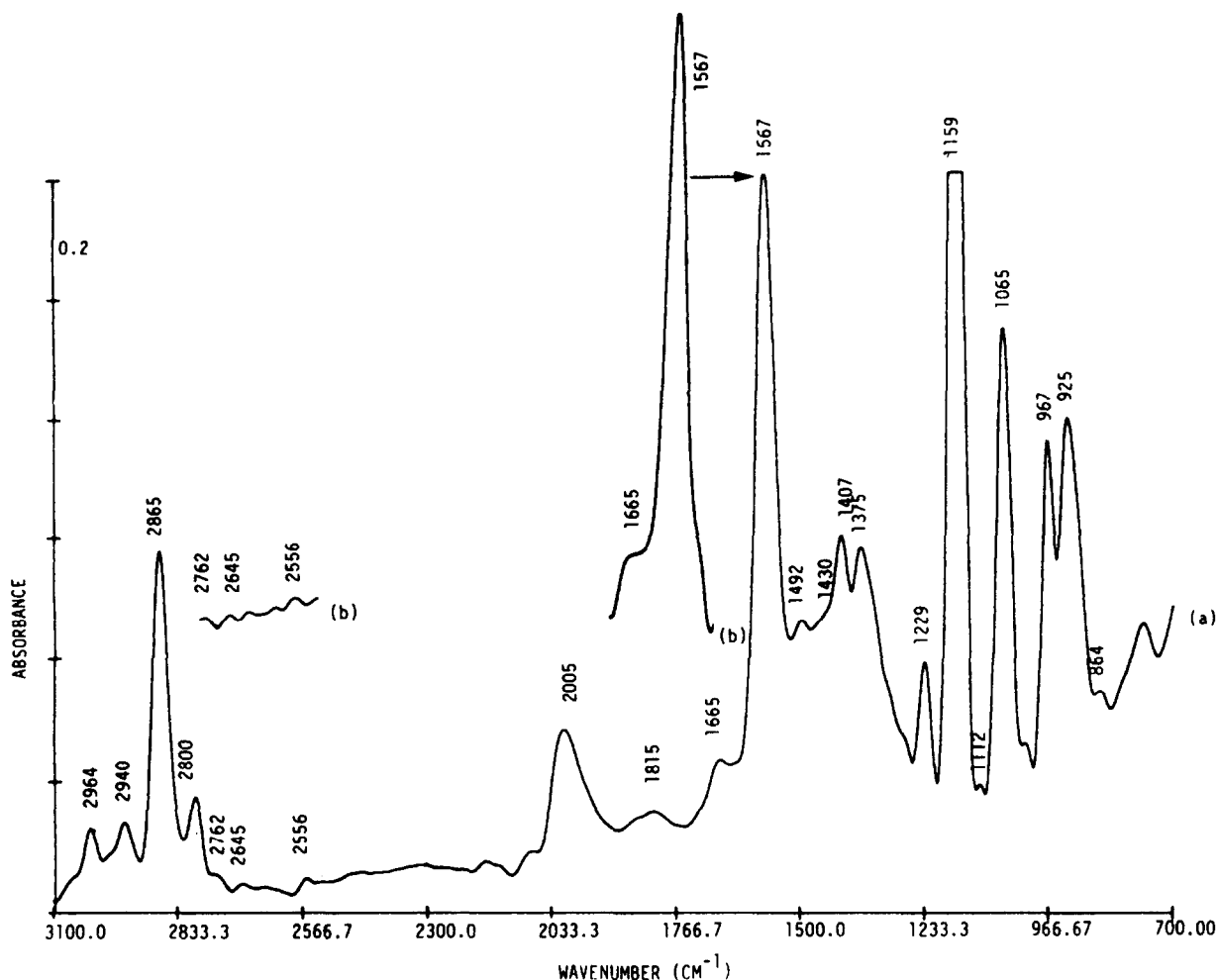


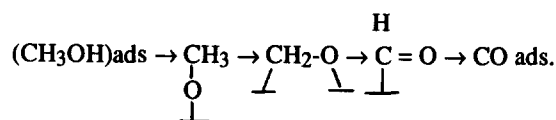
Fig. 8. FTIR spectra: (a) after  $\text{CH}_2\text{O}$  adsorption and heating to  $120^\circ\text{C}$  on  $\text{Rh}/\text{Pr}_6\text{O}_{11}$ . (b) difference spectra between  $120^\circ\text{C}$  and  $60^\circ\text{C}$  after  $\text{CH}_2\text{O}$  on  $\text{Rh}/\text{Pr}_6\text{O}_{11}$ .

oxygen end of the species with a cation. This interaction results in a decrease of the frequency of the  $\nu\text{C}=\text{O}$  vibration of the formyl species. Further neutral formyl entities with higher  $\nu\text{C}=\text{O}$  frequencies ( $1630\text{--}1640\text{ cm}^{-1}$  and even at  $1660\text{ cm}^{-1}$ ) have been prepared [52–54]. Van der Lee et al., [55] and van der Lee and Ponc [56] have shown that the formation of methanol is related to the amount of positively charged rhodium as extracted by acetylacetonate for rhodium catalysts. Formyl species can be stabilized by a positive charge on the metal [57–59]. A positive charge on the metal would give less back-donation, the carbene nature proposed by Gladysz [60] would diminish and the  $\nu\text{C}=\text{O}$  frequency would appear

at a higher frequency. This would also explain the stability of this species to higher temperature  $400\text{ K}$  as compared to  $280\text{ K}$  as observed by Saussey et al., [27]. An  $\eta^1(\text{C})$  formyl species (VII) is therefore proposed to give rise to the band at  $1665\text{ cm}^{-1}$ .

#### 4. Conclusion

From our results the following scheme can be written for methanol decomposition to  $\text{CO}$  on the rhodium containing catalysts.



The presence of an  $\eta^2(\text{CHO})$  species as proposed by Anton et al., [35] for formaldehyde adsorption on Ru cannot be excluded. However it could not be observed in our conditions. The observed formyl species are not very stable and appear only as a transient entity during heating up of methanol or formaldehyde. It is decomposed at temperature higher than 120°C. It can also only be observed on the promoted catalysts. In previous studies [8–15], it has been shown that the promoters can affect the carbon monoxide adsorption. A C and O coordinated species is present on the promoted catalysts. It is known that such an adsorption mode might favour the CO insertion [8,20–22]. In the present work it is also evidenced that a formyl species is stabilized in presence of the promoters. It is therefore proposed that the role of the promoter is to suppress the sites for methane formation [4], to create new sites for CO adsorption [8–15] and to stabilize the acyl (formyl and acetyl) species. No oxygenated species other than methoxy entities are observed on the unpromoted Rh/SiO<sub>2</sub> catalyst, which produces only hydrocarbons in the CO + H<sub>2</sub> reaction.

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