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# Participation of linear methoxy species bonded to Ti<sup>4+</sup> sites in the methanol carbonylation catalyzed by TiO<sub>2</sub>-supported rhodium: An infrared investigation

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#### 1. Introduction

The carbonylation of methanol is the most effective catalytic route for the production of acetic acid and methyl acetate. BASF and Monsanto were pioneers in the design of robust and profitable industrial processes for methanol carbonylation with cobalt and rhodium catalysts, respectively [1–3]. Both processes involve the use of methyl iodide as cocatalyst. The BASF process uses a cobalt carbonyl complex (*i.e.*, [CoH(CO)<sub>4</sub>]) as catalyst and occurs at relatively high pressure (680 bar) and temperature (250 °C), whereas the Monsanto process uses a rhodium carbonyl complex (*i.e.*,  $[Rh(CO)_2I_2]^-$ ) as catalyst and the reaction occurs at moderate pressure (30-60 bar) and temperature (150-200 °C), achieving higher methanol conversion than that obtained by the BASF process [3,4]. The advantages of the Monsanto process have motivated increasing research on the mechanistic aspects of the methanol carbonylation catalyzed by rhodium [5,6]. An accepted catalytic cycle representing the Monsanto process is shown in Fig. 1.

It is widely accepted that the rate determining step for the reaction consists of the oxidative addition of  $CH_3I$  to  $Rh(CO)_2I_2^-$  to give  $RhCH_3(CO)_2I_3^-$  (Fig. 1). Then, CO insertion into the Rh-methyl bond occurs to give a Rh-acetyl complex, which after CO addition and reductive elimination produces  $CH_3COI$  and regenerates the  $Rh(CO)_2I_2^-$  complex (Fig. 1). Hydrolysis of  $CH_3COI$  gives acetic acid and HI, which reacts with methanol to produce water and regenerate the  $CH_3I$  promoter (Fig. 1). Evidence of the various intermediate

#### ABSTRACT

TiO<sub>2</sub>-supported rhodium samples synthesized from the  $Rh_6(CO)_{16}$  complex were catalytically active and selective for the gas-phase methanol carbonylation at 140 °C and atmospheric pressure in the presence of methyl iodide as promoter. Infrared (IR) spectra recorded during catalysis allowed the identification of molecularly adsorbed methanol, together with linear, doubly, and triply-bridged surface methoxy species on Ti<sup>4+</sup> sites of the support. IR bands characteristic of rhodium complexes that might be regarded as reaction intermediates were also observed, in addition to bands assigned to surface acetate species attributed to the formation of methyl acetate. Our results reveal that only linear methoxy species on Ti<sup>4+</sup> sites react with flowing CO in the presence of CH<sub>3</sub>I to give methyl acetate, whereas bridged methoxy species and molecularly adsorbed methanol are only spectators in methanol carbonylation.

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Rh complexes comes from X-ray crystallography, nuclear magnetic resonance (NMR) and infrared (IR) spectroscopic studies [3,5,6].

Because recovery of the catalyst in the homogeneous process is typically complex and expensive, there have been various attempts to synthesize solid catalysts for methanol carbonylation by stabilizing rhodium complexes on polymers, metal oxides and zeolites [7–10]. Haynes et al. [8] anchored a  $[Rh(CO)_2I_2]^-$  complex on a polymer support and tested the resulting catalyst for methanol carbonylation. They characterized the catalyst under reaction conditions by IR spectroscopy and identified rhodium complexes during catalysis that are analogous to the intermediates found in the homogeneous process (Fig. 1). The authors concluded that the methanol carbonylation reaction proceeds by the same sequence of organometallic reactions for both the homogeneous and the heterogeneous processes.

For the homogeneous process, it is widely accepted that methanol does not coordinate to rhodium atoms during the reaction, but it is only involved in the cycle to regenerate  $CH_3I$  (Fig. 1). Nevertheless, the participation of methanol during the reaction catalyzed by supported rhodium has not been described.

Because methanol is a simple molecule with vibration modes that are sensitive to the nature of its interactions with solid surfaces, its adsorption on metal oxides has been widely investigated by IR spectroscopy [11–25]. It has been observed that methanol can be adsorbed both molecularly and dissociatively on metal oxides, including TiO<sub>2</sub> [11–16], ZrO<sub>2</sub> [17,18], Al<sub>2</sub>O<sub>3</sub> [19,20], and others [21–25]. In some cases, it has been possible to determine which of the methanol-derived surface species participate as intermediates in some chemical reactions [12,26]. For example, Wu et al. [12] found that linear methoxy species bonded to TiO<sub>2</sub> have a

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Fig. 1. Catalytic cycle representing the Monsanto process for methanol carbonylation [3].

higher photo-oxidation rate than bridged methoxy species to give CO<sub>2</sub>. Similarly, Rousseau et al. [26] used IR spectroscopy to investigate the total oxidation of methanol catalyzed by CeO<sub>2</sub>-supported gold catalysts. They found that only linear and doubly-bridged methoxy species bonded to Ce<sup>4+</sup> cations participated in the catalysis, whereas doubly-bridged Ce<sup>4+</sup> methoxy species having an oxygen vacancy in the neighborhood were only spectators.

In this work, we report the methanol carbonylation to give methyl acetate catalyzed by  $TiO_2$ -supported rhodium samples prepared from  $Rh_6(CO)_{16}$ . We used  $TiO_2$  as support because the adsorption of methanol on its surface is well established in the literature [11–16], with IR spectra being sensitive to the identification of various types of alcohol-derived surface species. Here we focused on investigating the reactions of methanol-derived surface species with CO by IR spectroscopy. Our results show the presence of various surface methoxy species bonded to  $Ti^{4+}$  sites during catalysis, and demonstrate that only linear methoxy species react to give the carbonylation product.

#### 2. Experimental

#### 2.1. Synthesis of TiO<sub>2</sub>-supported rhodium samples

The syntheses and sample transfers were performed in absence of air and moisture with a N<sub>2</sub>-filled glove box (Labconco 5070). Samples of TiO<sub>2</sub>-supported rhodium containing 2 wt% Rh were prepared by slurrying Rh<sub>6</sub>(CO)<sub>16</sub> (Sigma-Aldrich) in *n*-pentane with TiO<sub>2</sub> powder (Evonik, P25; approximately 30% rutile and 70% anatase) that had been partially dehydroxylated under vacuum at 400 °C. The surface area of the TiO<sub>2</sub> support was 50 m<sup>2</sup> g<sup>-1</sup>. The slurry was stirred for 24 h and the solvent removed by evacuation (pressure < 10<sup>-3</sup> Torr) for 12 h. The resultant TiO<sub>2</sub>-supported rhodium sample was stored in the glove box.

### 2.2. Transmission electron microscopy characterizing TiO<sub>2</sub>-supported rhodium samples

Samples were characterized by transmission electron microscopy (TEM) on a Jeol JEM-2100F HRTEM operated at 200 kV. Each powder sample was dispersed and placed on a holey

carbon film grid. Samples were analyzed in both bright field and dark field imaging modes.

### 2.3. IR spectra characterizing TiO<sub>2</sub>-supported rhodium samples during methanol carbonylation

Samples of the bare  $TiO_2$  support and  $TiO_2$ -supported rhodium were loaded into an IR cell that was closed and isolated with two standard three-way valves. IR spectra were recorded in the diffuse reflectance Fourier transform (DRIFT) mode with a Nicolet FTIR 6700 spectrometer equipped with a SpectraTech Collector<sup>TM</sup> attachment fitted with a high-temperature and high pressure environmental chamber. Spectra were recorded by coadding 128 scans with a resolution of  $4 \text{ cm}^{-1}$ . KBr powder was normally used as a reference material. Difference IR spectra of the adsorbed species were obtained by absorption subtraction of the cell and catalyst background spectra using the installed software.

The samples were characterized by IR spectroscopy during methanol carbonylation. In one type of experiment, IR spectra were recorded as each sample (*ca.* 25 mg) was treated in a flowing mixture of methanol ( $P_{CH_3I} = 108.96$  Torr), methyl iodide ( $P_{CH_3I} = 108.96$  Torr), CO ( $P_{CO} = 52.43$  Torr) and He (total flow rate 20 ml (NTP) min<sup>-1</sup> at 760 Torr) at 140 °C for 90 min. In another type of experiment, the TiO<sub>2</sub>-supported rhodium sample was exposed to flowing methanol at 140 °C for 5 min and then it was evacuated with He for 1 h. IR spectra were then recorded as the sample was treated in a continuous flow of a mixture of CO and He ( $P_{CO} = 76$  Torr, total flow rate 20 ml (NTP) min<sup>-1</sup> at 760 Torr) and as intermittent pulses of CH<sub>3</sub>I (*ca.* 20 µL) were injected to the cell each 10 min at 140 °C.

### 2.4. Mass spectra characterizing the effluent gases from the flow reactor/DRIFT cell

Mass spectra of the effluent gases from the flow reactor/DRIFT cell during methanol carbonylation were measured with an on-line Pfeiffer OmniStar<sup>TM</sup> mass spectrometer running in multi-ion monitoring mode. In the experiments, the changes in the signal intensities of the main fragments of methanol (m/e=31), CO (m/e=28), methyl acetate (m/e=43, 74), acetic acid (m/e=43, 45), dimethyl ether (m/e=45, 46) and CO<sub>2</sub> (m/e=44)were recorded as the bare TiO<sub>2</sub> support and the TiO<sub>2</sub>-supported



Fig. 2. Transmission electron micrograph characterizing a  ${\rm TiO}_2\mbox{-supported}$  Rh sample.

rhodium sample were treated in a flowing mixture of methanol ( $P_{CH_3OH} = 126.66$  Torr), methyl iodide ( $P_{CH_3I} = 108.96$  Torr), CO ( $P_{CO} = 52.43$  Torr) and He (total flow rate 20 ml (NTP) min<sup>-1</sup> at 760 Torr) as the temperature was ramped from 25 to 400 °C. All signals are reported relative to that of the He carrier gas at m/e = 4 to remove any effects of pressure fluctuations.

#### 3. Results and discussion

#### 3.1. Characterization of TiO<sub>2</sub>-supported rhodium samples

After impregnation of the rhodium precursor on the  $TiO_2$  powder, the resultant solid was gray color. A transmission electron micrograph characterizing a  $TiO_2$ -supported rhodium sample is shown in Fig. 2. The results indicate the presence of well-dispersed small rhodium particles with an average diameter of 5.4 nm.

IR spectra in the C–O stretching ( $\nu_{CO}$ ) region characterizing the pure Rh<sub>6</sub>(CO)<sub>16</sub> precursor, the bare support and the TiO<sub>2</sub>-supported rhodium sample are shown in Fig. 3. The IR spectrum characterizing Rh<sub>6</sub>(CO)<sub>16</sub> includes three intense  $\nu_{CO}$  bands at 2074, 2023 and 1801 cm<sup>-1</sup> (Fig. 3a). The bands at 2074 and 2023 cm<sup>-1</sup> have been assigned to the symmetric and asymmetric  $\nu_{CO}$  vibrations of terminal carbonyls bonded to rhodium, respectively; whereas the band at 1801 cm<sup>-1</sup> is assigned to the asymmetric  $\nu_{CO}$  vibration of bridged carbonyls attached to three rhodium atoms [27].

The IR spectrum characterizing the TiO<sub>2</sub>-supported rhodium sample (Fig. 3b) includes bands at 2088 and 2019 cm<sup>-1</sup>, which can be assigned to the symmetric and asymmetric  $v_{CO}$  vibrations of two terminal carbonyls bonded to a Rh<sup>I</sup> atom [28-30]. Because these  $v_{CO}$  bands are quite different from those observed in the IR spectrum characterizing the pure precursor (Fig. 3a), we conclude that Rh<sub>6</sub>(CO)<sub>16</sub> reacted with the TiO<sub>2</sub> surface during the synthesis of the sample. IR spectra in the O–H stretching ( $v_{OH}$ ) region comparing the bare support and our TiO<sub>2</sub>-supported rhodium sample (Fig. 3, inset) are in agreement with this conclusion, showing that a band at 3686 cm<sup>-1</sup>, assigned to isolated hydroxyl groups on the TiO<sub>2</sub> surface [11,13,31], appeared with lower intensity in the spectra characterizing the TiO<sub>2</sub>-supported rhodium sample than in that characterizing the bare support. This observation indicates that the  $Rh_6(CO)_{16}$  complex reacted with surface hydroxyl groups of TiO<sub>2</sub>, leading to the fragmentation of the precursor on the support to give



**Fig. 3.**  $\nu_{CO}$  IR spectra characterizing (a) Rh<sub>6</sub>(CO)<sub>16</sub> diluted in KBr, (b) TiO<sub>2</sub>-supported rhodium and (c) TiO<sub>2</sub> calcined at 400 °C. Inset:  $\nu_{OH}$  IR spectra characterizing (b) the TiO<sub>2</sub>-supported Rh sample and (c) the bare support.

rhodium species represented as  $Rh^{I}(CO)_{2}$  and schematized in Fig. 4 [32–40]. Our results indicate that the rhodium complex might have also reacted with adsorbed water, as evidenced by the decrease in the intensity of the band at  $1630 \, \text{cm}^{-1}$  upon adsorption of the  $Rh_{6}(CO)_{16}$  complex on TiO<sub>2</sub> (Fig. 3). Our proposal is consistent with that of Smith et al., [38] who reported that the octahedron frame of  $Rh_{6}(CO)_{16}$  was fragmented when this complex reacted with OH groups or adsorbed water on the surfaces of alumina and magnesia to give oxidized rhodium species. Others have also reported similar results [39,41] including the possible reactions of  $Rh_{6}(CO)_{16}$  with hydroxyl groups on metal oxides.

To test our hypothesis of the reaction of  $Rh_6(CO)_{16}$  with surface hydroxyl groups on TiO2, we performed titration experiments with HNO<sub>3</sub> of surface hydroxyl groups on both the bare support and the supported rhodium sample [42]. The results (Supplementary Data) indicate that the total amount of surface hydroxyl groups on the supported rhodium sample was lower than that on the sample of the bare support. These results confirm our proposal that some surface hydroxyl groups reacted with the  $Rh_6(CO)_{16}$  complex during the synthesis of the TiO<sub>2</sub>-supported rhodium sample. Although the titration experiments are in agreement with our IR data, we caution that it is not possible to make accurate quantitative statements regarding the exact amount of  $Rh_6(CO)_{16}$  that reacted with surface hydroxyl groups because of the presence of water on the surface of the samples, as evidenced by the band at  $1630 \text{ cm}^{-1}$  (Fig. 3). It is possible that the Rh precursor also reacted with surface water, as others have proposed [38] and as our own data suggest, as evidenced by the decrease in the intensity of the 1630-cm<sup>-1</sup> band upon adsorption of  $Rh_6(CO)_{16}$  on the TiO<sub>2</sub> support (Fig. 3).





Fig. 5. Changes in the intensity of the mass spectral signals of the effluent gases from the flow reactor when the TiO2-supported Rh sample was treated in the flowing mixture of CH<sub>3</sub>OH, CO, CH<sub>3</sub>I and He at increasing temperature. (•) Methyl acetate (m/e = 74) and  $(\bigcirc)$  dimethyl ether (m/e = 46).

#### 3.2. Methanol carbonylation catalyzed by TiO<sub>2</sub>-supported Rh

Mass spectra characterizing the effluent gases from the flow reactor that contained a sample of TiO<sub>2</sub>-supported rhodium as it was treated in a flowing mixture of methanol, CO, CH<sub>3</sub>I and He at increasing temperature are shown in Fig. 5. The results show the formation of methyl acetate starting at approximately 80 °C, as evidenced by the increase in the intensity of the signal of the fragment at m/e = 74 (Fig. 5). The intensity of the mass fragment of methyl acetate increased rapidly from 80 °C until it reached a maximum value at approximately 140 °C. Then, it remained nearly constant from 140 to 170 °C, and it finally decreased from that temperature until the set point (400 °C) was reached. As the intensity of the mass fragment of methyl acetate decreased above 170 °C, dimethyl ether started to form, as evidenced by the rapid increase in the intensity of the signal of the mass fragment at m/e = 46 (Fig. 5). The formation of dimethyl ether increased with increasing temperature until the set point was reached.

These results indicate that the TiO<sub>2</sub>-supported rhodium sample was active towards the carbonylation of methanol to give methyl acetate. The catalyst was selective in the temperature range between 100 and 170°C under the reaction conditions used in this work. At higher temperatures, the formation of dimethyl ether occurred probably by the dehydration of methanol, as others have proposed [43,44].

When the same experiment was done in the presence of the bare TiO<sub>2</sub> support, no formation of methyl acetate was observed and only dimethyl ether was produced (Supplementary Data). These results confirm that the presence of rhodium is necessary for the catalyst to be active for the methanol carbonylation.

#### 3.3. Surface species formed during methanol carbonylation catalyzed by TiO<sub>2</sub>-supported rhodium at 140°C

In order to identify surface species formed during catalysis, we recorded IR spectra of a TiO<sub>2</sub>-supported rhodium sample as it was treated in a flowing reactor/DRIFT cell with the flowing mixture of CH<sub>3</sub>OH, CO, CH<sub>3</sub>I and He at 140 °C during 90 min.

The results (Fig. 6) show the appearance of a band at  $2974 \, \mathrm{cm}^{-1}$ , assigned to the asymmetric C–H stretching ( $v_{CH}$ ) mode of gasphase methanol [45], and the evolution of various IR bands characteristic of both, molecularly and dissociatively adsorbed methanol on the surface of the catalyst. The formation of those surface species upon adsorption of methanol on various metal

#### Table 1

Observed frequencies/cm<sup>-1</sup> and band assignments of main surface species formed as samples of the bare support and TiO2-supported Rh were exposed to a flowing mixture of CH<sub>3</sub>OH, CO, CH<sub>3</sub>I and He.<sup>a</sup>

Samples treated in reactive flowing mixture		Assignment	Refs.
Rh/TiO <sub>2</sub>	TiO <sub>2</sub>		
2974 2942 2922 2865 2838 2820 1510 1441 1437 1262 <sup>c</sup>	2974 2940 2920 2872 2838 2819 1437 1262 <sup>c</sup>	$\begin{array}{l} \nu_{a\ CH}, CH_{3}OH \ gas-phase \\ \nu_{a\ CH}, CH_{3}OH_{(ads)} \\ \nu_{a\ CH}, CH_{3}O_{(ads)} \\ 2\delta_{CH3}, CH_{3}O_{(ads)} \\ \nu_{s\ CH}, CH_{3}O_{(ads)} \\ \nu_{s\ CH}, CH_{3}O_{(ads)} \\ \nu_{s\ CO}, CH_{3}COO_{(ads)}^{b} \\ \nu_{s\ CO}, CH_{3}COO_{(ads)}^{b} \\ \delta_{CH}, CH_{3}O_{(ads)} \end{array}$	[45] [11-14] [11-14] [13] [11-14] [11-14] [12] [12] [13,16]
1235° 1138 1119 1056 1035 1013 2063 1988 1731	1235° 1155 1125 1057 1036 1012	$\begin{array}{l} \rho_{\text{CH3}}, \text{CH}_3\text{O}_{(ads)} \text{ linear} \\ \nu_{\text{OC}}, \text{CH}_3\text{O}_{(ads)} \text{ linear} \\ \nu_{\text{OC}}, \text{CH}_3\text{OH}_{(ads)} \\ \nu_{\text{OC}}, \text{CH}_3\text{O}_{(ads)} \text{ doubly-bridged} \\ \nu_{\text{OC}}, \text{CH}_3\text{O}_{(ads)} \text{ triply-bridged} \\ \nu_{\text{CO}}, \\ \nu_{\text{CO}}, \\ \nu_{\text{CO}}, \\ \nu_{\text{CO}} \end{array}$	[12,13] [12,13] [13] [13] [13] [7,8,10] [7,8,10] [8,10]
Notation.			

<sup>a</sup> Reaction conditions:  $P_{\rm CH_3\,OH} = 126.66$  Torr,  $P_{\rm CH_{2}I} = 108.96$  Torr,  $P_{CO} = 52.43$  Torr, catalyst weight = 25 mg, reaction temperature = 140 °C, reaction time = 90 min.

<sup>b</sup> Bands at 1510 and 1449 cm<sup>-1</sup> were observed when a sample of the bare TiO<sub>2</sub> support was exposed to flowing methyl acetate at 140 °C.

<sup>c</sup> Bands at 1261 and 1238 cm<sup>-1</sup> were observed when CH<sub>3</sub>I was adsorbed on KBr powder.

 $v_{CO}$  vibration of a Rh-acetyl complex. (ads).- adsorbed.

oxides (e.g., TiO<sub>2</sub> [11–16], ZrO<sub>2</sub> [17,18], CeO<sub>2</sub> [21]) has been widely reported. Details regarding the assignment of the bands observed in this work are discussed in the following paragraph and summarized in Table 1.

The bands observed at 2942, 2838 and  $1056 \text{ cm}^{-1}$  (Fig. 6A and B) can be assigned to the symmetric  $v_{CH}$ , asymmetric  $v_{CH}$  and  $v_{CO}$ vibration modes of molecularly adsorbed methanol on TiO<sub>2</sub>, respectively [12,13]. The bands at 2922 and  $2820 \text{ cm}^{-1}$  can be assigned to the symmetric and asymmetric  $v_{CH}$  vibrations of methoxy species bonded to  $Ti^{4+}$  sites [12,13], and the band at 2866 cm<sup>-1</sup> can be assigned to the overtone of the  $\delta_{CH3}$  deformation mode in Fermi resonance with  $v_{CH3}$  vibrations of methoxy species (Fig. 6A) [13]. The results indicate the presence of three types of surface methoxy species bonded to Ti<sup>4+</sup> during the experiment, as evidenced by the appearance of bands at 1138, 1119, 1035 and 1013 cm<sup>-1</sup> (Fig. 6B). The bands at 1138 and  $1119 \text{ cm}^{-1}$  can be assigned to the  $-CH_3$ rocking and the  $v_{OC}$  modes of linear methoxy species bonded to  $Ti^{4+}$  sites, respectively [12,13,23]. The band at 1437 cm<sup>-1</sup> is assigned to  $\delta_{CH3}$  mode of methoxy species [13,16] and the bands at 1035 and 1013 cm<sup>-1</sup> can be assigned to the  $v_{CO}$  vibrations of doubly and triply-bridged methoxy species on Ti<sup>4+</sup> sites, respectively [13]. In summary, these results show that methanol was adsorbed both molecularly and dissociatively on the surface of the TiO<sub>2</sub>-supported rhodium sample. Specifically, three types of surface methoxy species on the support were observed: (a) linear, (b) doubly- and (c) triply-bridged. Bolstering the assignment of these bands to methanol-derived species bonded to TiO<sub>2</sub>, IR spectra characterizing the bare support as it was exposed to the reactive mixture at 140 °C show the same bands as those observed when the experiment was done with the TiO<sub>2</sub>-supported rhodium sample (Supplementary Data). A schematic representation of the various types of methoxy species bonded to the support is shown in Fig. 7. The formation of methoxy species on various metal oxides, including TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub> after cleavage of the O–H bond of



**Fig. 6.** Evolution of IR spectra characterizing the TiO<sub>2</sub>-supported Rh sample as it functioned as catalyst for methanol carbonylation at 140 °C. (A)  $\nu_{CH}$  region, (B) 1600–950 cm<sup>-1</sup> region and (C)  $\nu_{C0}$  region. Reaction conditions:  $P_{CH_3OH} = 126.66$  Torr,  $P_{CH_3I} = 108.96$  Torr,  $P_{C0} = 52.43$  Torr. Total flow rate 20 ml (NTP) min<sup>-1</sup>.



Fig. 7. Schematic representation of (a) linear, (b) doubly and (c) triply-bridged methoxy species bonded on Ti<sup>4+</sup> sites.

methanol has been widely reported [12,17,21]. It has been established that the presence of doubly and triply-bonded methoxy species is caused by bonding of the surface species at defect sites with oxygen vacancies on metal oxides [12,23].

The IR bands observed at 1262 and 1235 cm<sup>-1</sup> (Fig. 6B) can be attributed to vibrations of CH<sub>3</sub>I, as they also appeared in IR spectra characterizing a sample of KBr impregnated with CH<sub>3</sub>I (Table 1).

Fig. 6C shows  $v_{CO}$  IR spectra characterizing the TiO<sub>2</sub>-supported rhodium sample during the same catalysis experiment at 140°C. The results show the initial appearance (after 2 min time on stream (TOS)) of bands at 2088 and 2015 cm<sup>-1</sup>. These bands can be assigned to the symmetric and asymmetric  $v_{CO}$  vibrations of two terminal carbonyls bonded to a Rh<sup>I</sup> atom [28-30]. These bands shifted to lower frequencies with increasing TOS, until they were observed at 2063 and 1988 cm<sup>-1</sup>. Similar  $\nu_{CO}$  band-shifts have been observed during methanol carbonylation catalyzed by zeolite-supported rhodium [10] and by organorhodium complexes in solution [5]. The shift in the frequencies of the  $v_{CO}$  bands is consistent with the reaction between the initially present rhodium dicarbonyls and CH<sub>3</sub>I (most probably by oxidative addition), because the presence of iodine ligands bonded to the rhodium causes an additional electron-donating effect, which lowers the frequencies of the  $v_{CO}$ bands [10,46].

It is generally agreed that the oxidative addition of CH<sub>3</sub>I to the rhodium dicarbonyls is followed by the insertion of CO to the Rhmethyl bond, leading to Rh-acetyl species [3,5,7]. Our results are consistent with that proposal, showing the appearance of a broad band centered at  $1731 \text{ cm}^{-1}$  (Fig. 6C), characteristic of the  $\nu_{CO}$  stretching mode of Rh-acetyl species [8,10].

In addition to the bands described previously, bands at 1441 and 1510 cm<sup>-1</sup> appeared almost instantly when the TiO<sub>2</sub>-supported rhodium sample was treated with the reactive flowing mixture (Fig. 6B). Because those bands were not observed when the experiment was done with the bare support (Table 1 and Supplementary Data), one could hypothesize that they correspond to vibration modes of a product formed on the surface of the catalyst. To assign those bands, IR spectra were measured after the bare TiO<sub>2</sub> support had been exposed to methyl acetate at 140°C, followed by evacuation in flowing He for 60 min. The results (Table 1 and Supplementary Data) show the appearance of bands at 1449 and 1510 cm<sup>-1</sup>. The frequencies of these bands are very similar to those of the bands observed as the TiO<sub>2</sub>-supported rhodium sample was used as catalyst for methanol carbonylation at 140 °C (Fig. 6B). Therefore, we assign the bands at 1441 and 1510 cm<sup>-1</sup> to the symmetric and asymmetric  $v_{COO}$  vibrations of surface acetate species. Indeed, Wu et al. [12] assigned bands at 1535 and 1453 cm<sup>-1</sup> to acetate species bonded to Ti<sup>4+</sup> sites of TiO<sub>2</sub>. Therefore, our results show evidence of methyl acetate adsorbed on the surface of the catalyst. This carbonylation product might form by the reaction between methanol and surface Rh-acetyl complexes. The question that arises is which of the various methanol-derived surface species reacted with the Rh-acetyl complex to give methyl acetate.

## 3.4. Evidence of the participation of linear methoxy species bonded to $Ti^{4+}$ in the carbonylation of methanol catalyzed by $TiO_2$ -supported rhodium

Although the results shown in Fig. 6 allow to distinguish between various methanol-derived surface species bonded to the surface of the catalyst, it is not possible to determine from those data which surface species participated in the catalysis, because the TiO<sub>2</sub>-supported rhodium sample was continuously in contact with the reactants in gas-phase and the intensities of all IR bands characteristic of adsorbed methanol, linear and bridged methoxy species remained nearly constant during the experiment. Thus, we performed an experiment in which surface species derived from



**Fig. 8.** IR subtraction spectra characterizing a sample of  $TiO_2$ -supported rhodium in flowing He at 140 °C after it had been exposed to methanol adsorption at 140 °C for 5 min.

methanol were first stabilized on the surface of a TiO<sub>2</sub>-supported rhodium sample at 140 °C. Then, the reactions of those species were monitored by IR spectroscopy in the presence of flowing CO and as intermittent pulses of CH<sub>3</sub>I (*ca.* 20  $\mu$ L) were admitted to the flow reactor/DRIFTS cell.

Fig. 8 shows IR spectra characterizing the TiO<sub>2</sub>-supported rhodium sample in flowing He at 140 °C after methanol had been adsorbed on its surface. The results show the presence of molecularly adsorbed methanol, linear, doubly and triply-bridged methoxy species, as evidenced by the appearance of bands at 1142, 1119, 1051, 1038 and 1008 cm<sup>-1</sup>. Bands characteristic of surface formate species also appeared in the spectra at 1555, 1357 and 1376 cm<sup>-1</sup> (Fig. 8). The bands at 1357 and 1555 cm<sup>-1</sup> are assigned to the symmetric and asymmetric  $\nu_{COO}$  vibrations of adsorbed formate species, respectively [23,47]; whereas the band at 1376 cm<sup>-1</sup> is assigned to their  $\delta_{CH}$  vibrations [23,47]. Surface formate species might have been formed by decomposition of methanol on the TiO<sub>2</sub> support [12,14,26,47,48].

Fig. 9 shows the evolution of IR spectra measured at  $140 \,^{\circ}$ C as the TiO<sub>2</sub>-supported Rh sample with adsorbed methanol was treated in flowing CO and in the presence of intermittent pulses of CH<sub>3</sub>I. The results indicate that the introduction of flowing CO did not cause significant changes on the intensities of the various bands. However, once the first CH<sub>3</sub>I pulse was admitted to the cell, bands



**Fig. 9.** IR subtraction spectra as a function of TOS in the 1600–980 cm<sup>-1</sup> region characterizing the TiO<sub>2</sub>-supported rhodium sample that had been exposed to methanol adsorption as it was treated in flowing CO (10% CO in He) and with intermittent pulses of CH<sub>3</sub>I at 20, 30, 40 and 50 min TOS at 140 °C.



**Fig. 10.** Correlation between the intensities of the IR bands characteristic of surface acetate species (1447 cm<sup>-1</sup>, filled circles), triply-bridged methoxy (1008 cm<sup>-1</sup>, filled squares) and linear methoxy species (1142 cm<sup>-1</sup>, open circles) as a function of TOS characterizing the TiO<sub>2</sub>-supported rhodium sample that had been exposed to methanol adsorption as it was treated in flowing CO (10% CO in He) and with intermittent pulses of CH<sub>3</sub>I.

at 1262 and 1236 cm<sup>-1</sup>, characteristic of CH<sub>3</sub>I appeared (Fig. 9), and the bands at 1119 and 1142 cm<sup>-1</sup>, attributed to the  $\nu_{CO}$  and the –CH<sub>3</sub> rocking modes of linear methoxy species bonded to Ti<sup>4+</sup> decreased in intensity (Fig. 9). The results also show the appearance of bands at 1447 and 1509 cm<sup>-1</sup> (Fig. 9), which are assigned to the symmetric and asymmetric  $\nu_{COO}$  vibrations of surface acetate species [12]. These results indicate that linear methoxy species bonded to Ti<sup>4+</sup> sites are involved in the formation of methyl acetate.

In contrast, the data show that the bands characteristic of molecularly adsorbed methanol  $(1051 \text{ cm}^{-1})$  and brigded methoxy species bonded to Ti<sup>4+</sup> (1038 and 1008 cm<sup>-1</sup>) did not change in intensity when the CH<sub>3</sub>I pulses were admitted to the flow reactor/DRIFT cell (Fig. 9). Therefore, we conclude that only linear methoxy species bonded to Ti<sup>4+</sup> sites participated in the formation of methyl acetate, whereas the other alcohol-derived surface species were only spectators [49].

Fig. 10 shows the dependence between the intensities of the IR bands at 1142, 1447 and 1008 cm<sup>-1</sup> as a function of TOS during the experiment. It is clearly observed that the decrease in the intensity of the band at 1142 cm<sup>-1</sup>, characteristic of linear methoxy species bonded to  $Ti^{4+}$ , correlates well with the increase in the intensity of the band at 1447 cm<sup>-1</sup>, characteristic of surface acetate species. Thus, our conclusion that methyl acetate was formed by the carbonylation of linear methoxy species bonded to  $Ti^{4+}$  sites is bolstered. Again, because the intensity of the band at 1008 cm<sup>-1</sup>, characteristic of bridged methoxy species did not change during the experiment, we conclude that those species did not participate in the reaction.

Our results, showing that only one specific methanol-derived surface species bonded to the support participated in the methanol carbonylation are analogous to those of Rousseau et al. [26] for the aerobic oxidation of methanol catalyzed by CeO<sub>2</sub>-supported gold particles. The authors found that methanol adsorption led to the formation of three types of methoxy species which were identified by IR spectroscopy, and their results show that the linear and doubly-bridged methoxy species bonded to Ce<sup>4+</sup> are intermediates in the formation of CO<sub>2</sub>, while doubly-bridged methoxy species with an oxygen vacancy in the neighborhood are spectators. Similarly, Bronkema et al. [50] investigated the selective methanol oxidation over TiO<sub>2</sub>-supported vanadium to give formaldehyde. They found three types of species derived from methanol adsorption: (a) methanol molecularly adsorbed, (b) Ti–OCH<sub>3</sub>/Ti–OH

and (c) V–OCH<sub>3</sub>/Ti–OH species. Their results suggest that the V–OCH<sub>3</sub>/Ti–OH pairs are the reactive species to give formaldehyde at low temperatures in presence or in absence of O<sub>2</sub> [50]. Given the bifunctional character of the catalysts used in the aforementioned examples and in our own work, it is suggested that supports capable of stabilizing specific alcohol-derived surface species might confer particular catalytic properties to supported metal catalysts.

There are at least two possible routes to explain the formation of methyl acetate involving the participation of linear methoxy species bonded on  $Ti^{4+}$  sites. One possibility is the nucleophilic attack of surface linear methoxy species on the Rh-acetyl complex. Another possibility is from the reaction between the CH<sub>3</sub>COI (produced by the reductive elimination of the Rh-acetyl complex) and surface linear methoxy species. Although our results demonstrate that linear methoxy species bonded to  $Ti^{4+}$  participate in the catalysis, we do not have enough information to determine the exact manner by which they react with other surface intermediates. Therefore, more data are needed before proposing a detailed reaction mechanism for the carbonylation of methanol catalyzed by our samples.

#### 4. Conclusions

In summary, we used IR spectroscopy to monitor surface species formed on  $TiO_2$ -supported rhodium catalysts during methanol carbonylation. Our results, showing the formation of Rh-acetyl species, indicate that the reaction route with our samples is analogous to that of the Monsanto process, with two separate sites for the activation of CO and methanol. While CO is activated on rhodium centers, our data show that methanol is activated on the support, with evidence of various methanol-derived species during catalysis. Our results demonstrate that only linear methoxy species bonded to  $Ti^{4+}$  sites participated in the methanol carbonylation to give methyl acetate. These results have important implications on the design of solid bifunctional catalysts for methanol carbonylation, as they suggest that the ability of the support to stabilize linear methoxy species might be crucial to determine the activity and selectivity of supported rhodium catalysts.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.03.020.

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