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Participation of linear methoxy species bonded to Ti^{4+} sites in the methanol carbonylation catalyzed by TiO_2-supported rhodium: An infrared investigation

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ABSTRACT

TiO_2-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^{4+} 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^{4+} sites react with flowing CO in the presence of CH_3I to give methyl acetate, whereas bridged methoxy species and molecularly adsorbed methanol are only spectators in methanol carbonylation.

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.*, $[CoH(CO)_4]$) 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 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_2 [11–16], ZrO_2 [17,18], Al_2O_3 [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_2 have a

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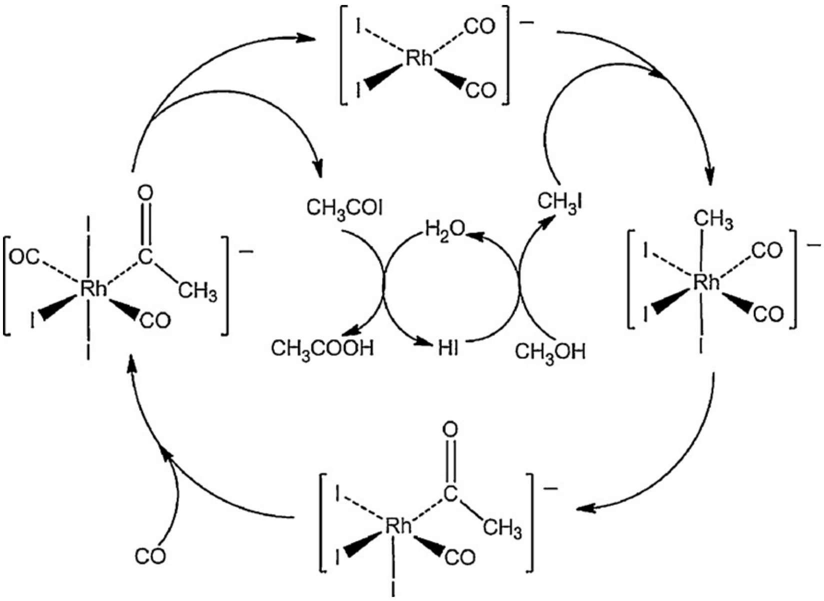

Fig. 1. Catalytic cycle representing the Monsanto process for methanol carbonylation [3].

higher photo-oxidation rate than bridged methoxy species to give CO_2. Similarly, Rousseau et al. [26] used IR spectroscopy to investigate the total oxidation of methanol catalyzed by CeO_2-supported gold catalysts. They found that only linear and doubly-bridged methoxy species bonded to Ce^{4+} cations participated in the catalysis, whereas doubly-bridged Ce^{4+} 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_2-supported rhodium samples

The syntheses and sample transfers were performed in absence of air and moisture with a N_2-filled glove box (Labconco 5070). Samples of TiO_2-supported rhodium containing 2 wt% Rh were prepared by slurrying $Rh_6(CO)_{16}$ (Sigma-Aldrich) in *n*-pentane with TiO_2 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_2 support was $50\,m^2\,g^{-1}$. The slurry was stirred for 24 h and the solvent removed by evacuation (pressure < 10^{-3} Torr) for 12 h. The resultant TiO_2-supported rhodium sample was stored in the glove box.

2.2. Transmission electron microscopy characterizing TiO_2-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_2-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™ attachment fitted with a high-temperature and high pressure environmental chamber. Spectra were recorded by coadding 128 scans with a resolution of $4\,cm^{-1}$. 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^{-1} at 760 Torr) at 140 °C for 90 min. In another type of experiment, the TiO_2-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^{-1} at 760 Torr) and as intermittent pulses of CH_3I (*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™ 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_2 ($m/e = 44$) were recorded as the bare TiO_2 support and the TiO_2-supported