

In situ FT-IR studies on the CO₂ hydrogenation over the SiO₂-supported RhM (M = Cr, Mo, W) complex catalysts

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Abstract

The in situ FT-IR spectra were used to study the CO₂ hydrogenation reactions over the SiO₂-supported heterobinuclear metal complex catalysts, RhM (M = Cr, Mo, W). The bands, which correspond to the formate species adsorbed on the catalysts, were observed. During the hydrogenation reactions, the adsorbed linear and bridged bridging CO were not observed. The experimental results suggest that for the CO₂ and CO hydrogenation reactions over the same catalysts, their catalytic active intermediate species and the reaction mechanisms should be different. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: CO₂ hydrogenation; In situ FT-IR; Bimetal complex catalyst

1. Introduction

The hydrogenation of CO₂ to valuable chemicals has received much interest in the recent years. The Cu–ZnO based catalysts are well known to be active for the methanol synthesis through the hydrogenation of CO or CO₂. The Cu-formate species on surface are regarded as the intermediates of the conversion from CO₂ to methanol [1,2]. However, the reaction mechanisms of the active species on the Cu based catalysts are still not clear. Until now, the supported noble bimetal catalysts for the CO₂ hydrogenation to methanol have not been intensively studied yet. We reported the experimental results about the SiO₂-supported heterobinuclear metal complex catalysts, (dppe) Rh(μ -CO) M(CO)₃ (M = Cr, Mo, W; dppe = Ph₂P(CH₂)₂PPh₂) [3], (**I**). The complex

catalysts exhibit high activity and selectivity for the methanol synthesis from CO + H₂ [4] and CO₂ + H₂ [5,6].

The present paper reports the in situ FT-IR results of the species adsorbed on the RhM/SiO₂ catalysts during the CO₂ hydrogenation reactions.

2. Experimental

2.1. The preparation of the catalysts

The catalysts were prepared using the impregnation method. The complexes (**I**) were used as the catalyst precursors. Prior to impregnation, silica was evacuated at 673 K for 2 h to remove physically adsorbed water, and then an appropriate amount of THF solution of (**I**) was poured into the silica. After the impregnation process was completed, the catalysts were dried under vacuum at room temperature.

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2.2. The measurement of in situ IR spectra

The in situ IR spectra were measured using an IR stainless steel reactor cell with a CaF_2 window. The catalysts, pressed into a 10 mm diameter disk, were placed in the cell, which was used as a reactor. The spectra were recorded using a Perkin-Elmer FT-IR 2000 spectrometer with a resolution of 2 cm^{-1} . The pressure of the CO_2 and H_2 atmosphere was kept at 0.1 MPa with a constant flow-rate ratio ($\text{H}_2/\text{CO}_2 = 3:1$). The reaction temperature was increased to a certain temperature under vacuum and was kept for 15 min. The CO_2 and H_2 gases were passed through the reactor cell at this reaction temperature for 15 min, and at the same time the in situ FT-IR spectra were recorded under the CO_2 hydrogenation condition.

3. Results and discussion

Figs. 1–3 show the in situ FT-IR spectra of the 3 wt.% RhM/SiO₂ catalysts during the CO_2 hydrogenation reaction temperatures.

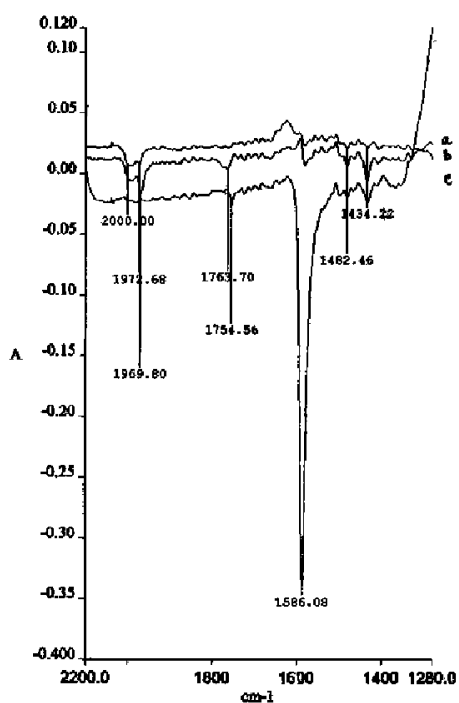


Fig. 1. In situ IR spectra of Rh-Cr/SiO₂ catalyst at various temperature in $\text{CO}_2 + \text{H}_2$ flow: (a) 413; (b) 473; (c) 533 K.

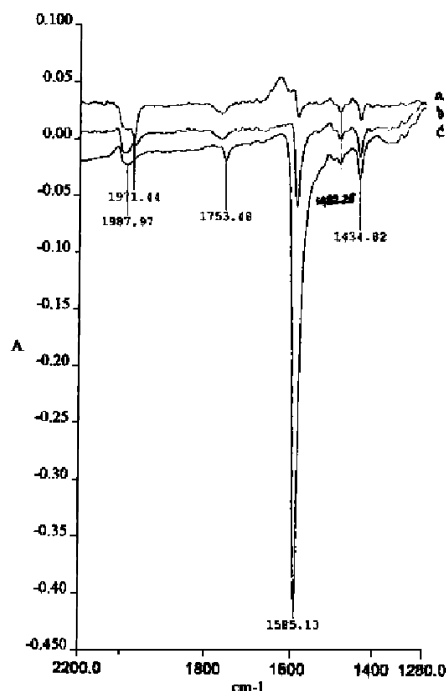


Fig. 2. In situ IR spectra of Rh-Mo/SiO₂ catalyst at various temperature in $\text{CO}_2 + \text{H}_2$ flow: (a) 413; (b) 493; (c) 533 K.

As shown in Fig. 1, on RhCr/SiO₂, the bands at 2000 , 1992 cm^{-1} (terminal CO) and 1763 cm^{-1} (bridging CO), which are attributed to co-ordinated CO of the original complex, decrease evidently and even disappear (for terminal CO) when the reaction temperature is increased from 413 to 513 K. The bands at 1482 and 1434 cm^{-1} still remain and the bands are attributed to co-ordinated PPh_3 of the original complex. The bands at 2360 and 2337 cm^{-1} , which are attributed to CO_2 in gas phase, are too strong to be canceled. At the same time, a new strong sharp band appears at 1586 cm^{-1} and its intensity increases evidently with increasing the reaction temperature from 413 to 533 K. At 1313 cm^{-1} appear some weak bands, which can be assigned to the stretching frequency of the formate species adsorbed on Rh of RhCr. Similar bands were previously reported, which were ascribed to the formate species adsorbed on Cu or Rh during the CO_2 hydrogenation reaction; e.g. the bands at 2933 , 2858 , 1591 and 1353 cm^{-1} for Cu/SiO₂ [7]; at 1548 cm^{-1} for Cu/SiO₂ [8]; at 2956 , 2883 , 1560 , 1351 cm^{-1} for Cu/TiO₂ [7]; at 1585 cm^{-1} for

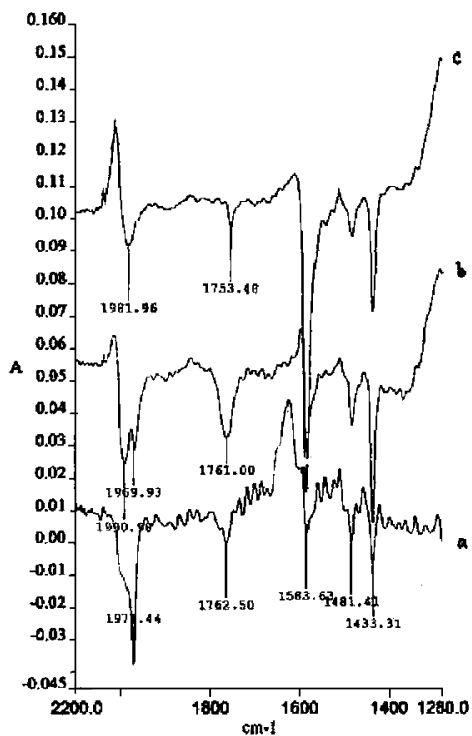


Fig. 3. In situ IR spectra of Rh-W/SiO₂ catalyst at various temperature in CO₂ + H₂ flow: (a) 413; (b) 493; (c) 533 K.

Cu(Zn)/SiO₂; at 1595, 1380 cm⁻¹ for Cu/ZnO/Al₂O₃ [9]; at 1568, 1373 cm⁻¹ for CuO/TiO₂ [10]; and at 1511, 1378 cm⁻¹ for Rh-Li/SiO₂ [11], etc. Recently, Bettahar et al. reported that there are three types of formate species adsorbed Zn/Al₂O₃: the bands at 2881, 2744, 1595, 1375 cm⁻¹; at 1650, 1320 cm⁻¹; at 2895, 2767, 1590, 1390, 1370 cm⁻¹; and a formate specie adsorbed on Cu at 2825, 2847, 2692, 1352 cm⁻¹ during the CO₂ hydrogenation reaction over the Cu–Zn Al₂O₄ catalyst [12]. Therefore, these formate species adsorbed on Rh or RhM can be regarded as an intermediate of the methanol synthesis from the CO₂ hydrogenation reaction. The intensity of the band at 1586 cm⁻¹ increases with increasing the reaction temperature. It is reasonable taking into account that the catalytic activity increases with increasing the reaction temperature [5,6].

Similarly, as shown in Figs. 2 and 3, on RhMo/SiO₂ and RhW/SiO₂, the bands, which are attributed to co-ordinated CO of the original complexes, also decrease when the reaction temperature is increased from

413 to 533 K. The band, attributed to co-ordinated bridging CO, shifts to a lower wave number (from 1763 to 1753 cm⁻¹). At the same time, the intensities of the bands ascribed to the formate species adsorbed on Rh of RhM also increase when the reaction temperature is increased, and the same weak band at 1313 cm⁻¹ also appears. The bands at 1481, 1434 cm⁻¹, which are attributed to co-ordinated PPh₃ of the original complexes, still remained. It indicates that the RhM/SiO₂ catalysts are still stable at 533 K.

The FT-IR spectra of the CO₂ hydrogenation reactions on the RhM (M = Cr, Mo and W)/SiO₂ catalysts at the same reaction temperature are shown in Fig. 4 (493 K) and Fig. 5 (533 K). As shown in Fig. 4, all the bands, which are attributed to co-ordinated terminal CO at 1991, 1968 cm⁻¹ and bridging CO at 1763 cm⁻¹, still remained with proper intensities. The bands at 1584 cm⁻¹, attributed to the formate species adsorbed on Rh of RhM, become stronger. The intensity of the band for RhMo/SiO₂ is stronger than that for RhCr/SiO₂ or RhW/SiO₂. All the bands at 1481 and 1435 cm⁻¹, attributed to co-ordinated

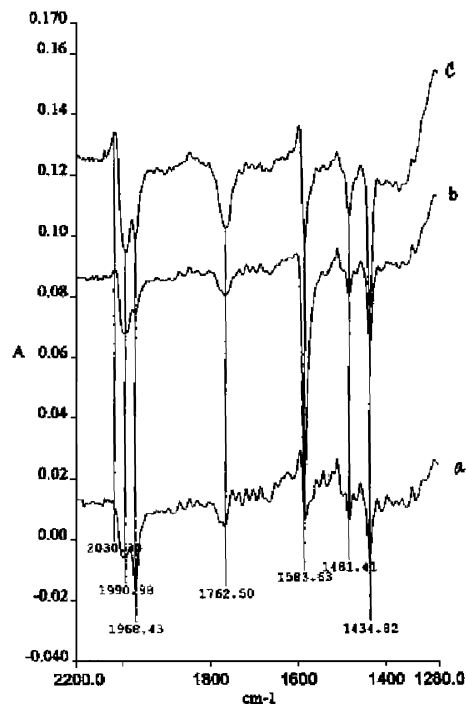


Fig. 4. In situ IR spectra of three catalysts at 493 K in CO₂ + H₂ flow: (a) Rh-Cr/SiO₂; (b) Rh-Mo/SiO₂; (c) Rh-W/SiO₂.

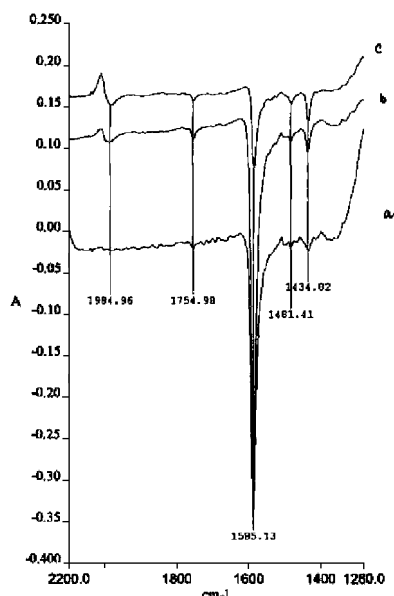


Fig. 5. In situ IR spectra of three catalysts at 533 K in $\text{CO}_2 + \text{H}_2$ flow: (a) Rh-Cr/SiO₂; (b) Rh-Mo/SiO₂; (c) Rh-W/SiO₂.

PPh_3 , still remained with proper intensities. Fig. 5 shows that the intensities of the bands, attributed to co-ordinated CO, obviously decrease and even disappear (for RhCr/SiO₂). However, the bands, attributed to co-ordinated bridging CO, shift to 1755 cm^{-1} . The bands attributed to the formate species adsorbed on Rh of RhM become stronger than those at 493 K. The result indicates that the formate species adsorbed on Rh of RhM are catalytically active for the CO_2 hydrogenation reaction, which produces methanol. The hydrogenation process of the formate species is probably the rate-determining step. The in situ FT-IR spectra of the SiO₂-supported complex catalysts exhibit notable difference from those of the SiO₂-supported Rh catalyst during the CO_2 hydrogenation reaction. The latter show the strong bands at 2040 and 1806 cm^{-1} , which are assigned to the linear and bridged CO species adsorbed on Rh [11].

These results are obviously different from the result of the CO hydrogenation over the same catalysts previously reported. For the spectra of the CO hydrogenation, co-ordinated bridging CO disappear firstly, and then co-ordinated terminal CO disappear. Some new bands appear at 2058 1997 and 2004 cm^{-1} for Rh-Cr/SiO₂, RhMo/SiO₂, and RhW/SiO₂, respectively. They are attributed to the linear CO species

adsorbed on Rh, but the band attributed to the adsorbed bridged CO species [13] does not appear. However, for the CO_2 hydrogenation reaction, the bands attributed to the adsorbed linear and bridged CO species do not appear. The bands at 1589 cm^{-1} , ascribed to the formyl species adsorbed on Rh for all the RhM/SiO₂ catalysts during the CO hydrogenation reaction, are weak and broad. However, the bands at 1585 cm^{-1} , ascribed to the formate species adsorbed on Rh for RhM/SiO₂ catalysts during the CO_2 hydrogenation reaction, are strong and sharp. The results indicate that the mechanisms of the CO and CO_2 hydrogenation reactions over the same RhM/SiO₂ catalysts should be different. The following mechanism of the CO_2 hydrogenation reaction over the RhM/SiO₂ catalysts is suggested. The CO_2 gas molecules are readily adsorbed by the catalysts, and the adsorbed CO_2 species on the catalytic site are rapidly converted to the formate species adsorbed on Rh or RhM under the reaction conditions. The formate species are hydrogenated to methanol, and the process is probably a rate-determining step. Therefore, the formate species adsorbed on Rh or RhM can be regarded as a major intermediate for the methanol synthesis from the CO_2 hydrogenation. The CO molecules produced in the CO_2 hydrogenation should result from the reverse water gas shift reaction.

4. Conclusions

In situ FT-IR was used to study the methanol synthesis reaction from the CO_2 hydrogenation over the RhM/SiO₂ catalysts. Some special formate species with an OCO asymmetric band at 1586 cm^{-1} is observed. The formate species are probably bound to Rh or RhM, and are active intermediates.

The comparison between the in situ FT-IR results of CO_2/H_2 and CO/H_2 under the same reaction conditions shows that the produced surface species for the two reaction systems are essentially different. Under CO/H_2 atmosphere, no adsorbed formate species can be observed.

Acknowledgements

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