

# In situ FT-IR study on CO<sub>2</sub> hydrogenation over SiO<sub>2</sub>-supported PtM (M = Cr, Mo, W) complex catalysts

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## Abstract

The in situ FT-IR spectra were used to study the CO<sub>2</sub> hydrogenation reaction over the SiO<sub>2</sub>-supported heterobinuclear metal complex catalysts, PtM (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 bridging CO was not observed. The experimental results suggest that for the CO<sub>2</sub> and CO hydrogenation reaction over the same catalysts, their catalytic active intermediate species and the reaction mechanisms should be different. © 2001 Published by Elsevier Science B.V.

*Keywords:* CO<sub>2</sub> hydrogenation; In situ FT-IR; Bimetal complex catalyst

## 1. Introduction

The hydrogenation of CO<sub>2</sub> to valuable chemicals has received much attention in recent years. The Cu-ZnO-based catalysts are well known to be active for the methanol synthesis through the hydrogenation of CO or CO<sub>2</sub>. The Cu-formate species on surface are regarded as the intermediate of the conversion from CO<sub>2</sub> to methanol [1,2]. However, the reaction mechanism and the active species on the Cu-based catalysts are still not clear. Until now, the supported noble bimetal catalysts for CO<sub>2</sub> hydrogenation to methanol have not been intensively studied yet. We reported the experimental results about the SiO<sub>2</sub>-supported heterobinuclear metal complex catalysts, (PPh<sub>3</sub>)HPt(μ-PPh<sub>2</sub>)(μ-CO)M(CO)<sub>4</sub> (M = Cr, Mo, W) [3], (I). The complex catalysts exhibit high activity and selectivity for methanol synthesis from

CO + H<sub>2</sub> [4] and CO<sub>2</sub> + H<sub>2</sub> [5–7]. The present paper reports the in situ FT-IR results of the adsorbed species on the PtM/SiO<sub>2</sub> catalysts during CO<sub>2</sub> hydrogenation reaction.

## 2. Experimental

### 2.1. The preparation of the catalysts

The catalysts were prepared using the impregnation method. The complex (I) was used as the catalyst precursor. Prior impregnation, the silica was evacuated at 693 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 impregnation process was completed, the catalysts were dried under vacuum at room temperature. For comparison, a Pt/SiO<sub>2</sub> catalyst derived from trans-Pt(H)(PPh<sub>3</sub>)<sub>2</sub> [8] complex was prepared by the same means.

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## 2.2. The measurement of in situ IR spectra

The in situ IR spectra were measured using a stainless steel reactor cell with a  $\text{CaF}_2$  window. The catalysts were pressed into a disk (10 mm diameter) and were placed in the reactor cell, which was used as a reactor. The spectra were recorded using a Perkin-Elmer FT-IR 2000 spectrometer with a resolution of  $2\text{ cm}^{-1}$ . The pressure of reactants 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 reaction temperature under vacuum and was kept for 15 min, the reactants were passed through the reactor cell at this reaction temperature, and continued 15 min, at the same time, in situ FT-IR spectra were recorded under the  $\text{CO}_2$  hydrogenation condition.

## 3. Results and discussion

Figs. 1–4 show the in situ FT-IR spectra for the 3 wt.% PtM/SiO<sub>2</sub> and Pt/SiO<sub>2</sub> catalysts during the  $\text{CO}_2$  hydrogenation reaction at various reaction temperatures, respectively. As shown in Fig. 1, on the

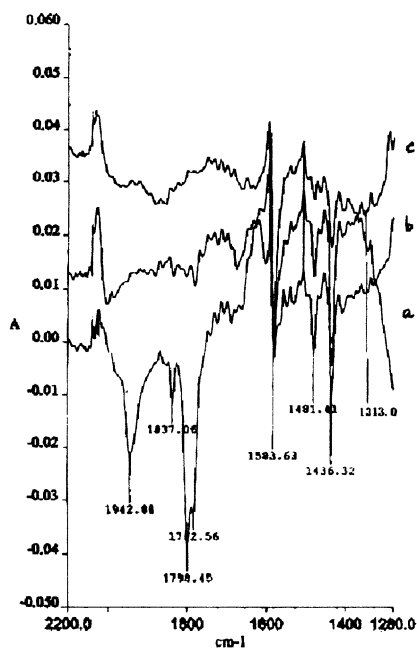


Fig. 1. In situ infrared spectra of PtCr/SiO<sub>2</sub> catalyst at various temperatures in  $\text{CO}_2 + \text{H}_2$  flow: (a) 413 K; (b) 473 K; (c) 513 K.

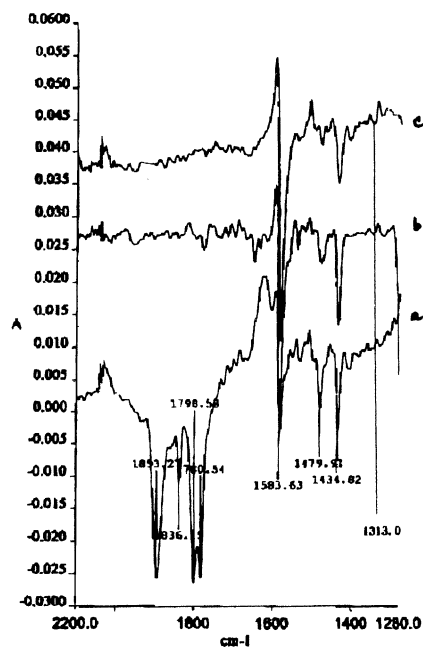


Fig. 2. In situ infrared spectra of PtMo/SiO<sub>2</sub> catalyst at various temperatures in  $\text{CO}_2 + \text{H}_2$  flow: (a) 413 K; (b) 473 K; (c) 513 K.

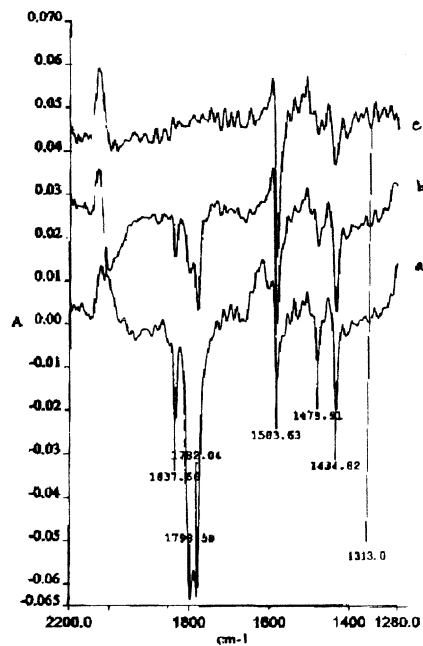


Fig. 3. In situ infrared spectra of PtW/SiO<sub>2</sub> catalyst at various temperatures in  $\text{CO}_2 + \text{H}_2$  flow: (a) 413 K; (b) 473 K; (c) 513 K.

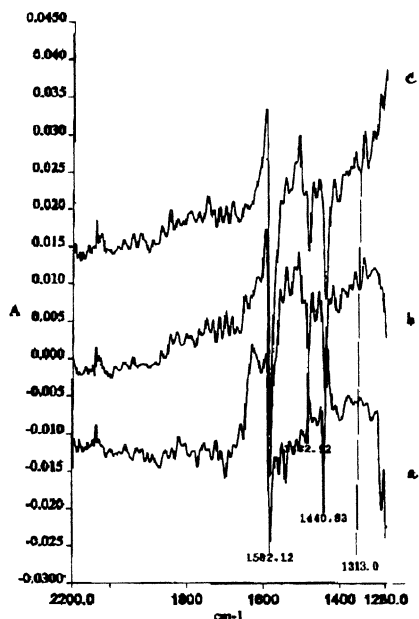


Fig. 4. In situ infrared spectra of Pt/SiO<sub>2</sub> catalyst at various temperatures in CO<sub>2</sub> + H<sub>2</sub> flow: (a) 413 K; (b) 473 K; (c) 513 K.

PtCr/SiO<sub>2</sub> catalyst, the bands attributed to the coordinated CO of original complex at 1942, 1837 cm<sup>-1</sup> (terminal CO) and at 1798, 1782 cm<sup>-1</sup> (bridging CO) decreased and even disappeared when the reaction temperature was increased from 413 to 513 K. The bands at 1481 and 1436 cm<sup>-1</sup>, which are attributed to the coordinated PPh<sub>3</sub> of original complex, still remained. The bands at 2360 and 2337 cm<sup>-1</sup>, which are attributed to gas-phase CO<sub>2</sub>, were too strong to cancel. At the same time, a new strong incisive band at 1583 cm<sup>-1</sup> and a new weak band at 1313 cm<sup>-1</sup> appeared. These bands could be assigned to the stretching frequency of formate species adsorbed on Pt or PtM. Similar bands were previously reported, which were ascribed to the formate species adsorbed on Cu or Rh during the CO<sub>2</sub> hydrogenation reaction, e.g. the bands at 2933, 2858, 1591 and 1353 cm<sup>-1</sup> for Cu/SiO<sub>2</sub> [9], at 1548 cm<sup>-1</sup> for Cu/SiO<sub>2</sub> [10], at 2956, 2882, 1560 and 1351 cm<sup>-1</sup> for Cu/TiO<sub>2</sub> [9], at 1585 cm<sup>-1</sup> (IRAS) for Cu(Zn)/SiO<sub>2</sub>, at 1595 and 1380 cm<sup>-1</sup> for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> [11], at 1568 and 1373 cm<sup>-1</sup> for CuO/TiO<sub>2</sub> [12], at 1511 and 1378 cm<sup>-1</sup> for Rh-Li/SiO<sub>2</sub> [13], etc. Recently, Bettahar et al. reported that there are three types of formate

species adsorbed on Zn/Al<sub>2</sub>O<sub>3</sub>, the bands at 2882, 2774, 1595 and 1375 cm<sup>-1</sup>, at 1650 and 1320 cm<sup>-1</sup>, at 2895, 2767, 1590, 1390 and 1390 cm<sup>-1</sup>, and a formate species adsorbed on Cu at 2925, 2847, 2692 and 1352 cm<sup>-1</sup> during the CO<sub>2</sub> hydrogenation reaction over Cu-ZnAl<sub>2</sub>O<sub>4</sub> catalyst [14]. Therefore, the formate species adsorbed on Pt of PtM can be regarded as an intermediate of methanol synthesis from CO<sub>2</sub> hydrogenation reaction. The intensity of the band at 1583 cm<sup>-1</sup> increases with increase of the reaction temperature from 413 to 513 K. It is reasonable taking into account that the catalytic activity increases with increased reaction temperature [5,6].

Similarly, as shown in Figs. 2 and 3, on PtMo/SiO<sub>2</sub> and PtW/SiO<sub>2</sub>, the bands, which are attributed to coordinated CO of original complexes, also decrease and even disappear when the reaction temperature is increased from 413 to 513 K. At the same time, a new strong incisive band at 1583 cm<sup>-1</sup> and a weak band at 1313 cm<sup>-1</sup> appear, which can be assigned to stretching frequency of formate species adsorbed on Pt of PtMo and PtW. The intensity of the bands also increases with increase in the reaction temperature from 413 to 533 K.

As comparison, as shown in Fig. 4, on Pt/SiO<sub>2</sub>, during CO<sub>2</sub> hydrogenation reaction, a new strong incisive band at 1582 cm<sup>-1</sup> appears, it could be ascribed to the formate species adsorbed on Pt, its intensity also increases with increase in the reaction temperature. The result is identical, as the Pt is active site of PtM/SiO<sub>2</sub> catalysts for CO<sub>2</sub> hydrogenation reaction. For comparing, the spectra of CO<sub>2</sub> hydrogenation on PtM/SiO<sub>2</sub> and Pt/SiO<sub>2</sub> at the same reaction temperature, given in Fig. 5 (at 473 K) and Fig. 6 (at 513 K). As shown in Fig. 5, the bands attributed to the coordinated terminal and bridging CO of original complexes obviously decrease, particularly for that of PtM/SiO<sub>2</sub> almost disappeared, moreover the terminal CO firstly decreased and disappeared. At the same time, the strong bands at 1583 cm<sup>-1</sup> appear for four catalysts, and the weak bands at 1313 cm<sup>-1</sup> also appear. As shown in Fig. 6, the bands ascribed to the coordinated CO of original complexes all disappeared, while the intensity of bands at 1583 cm<sup>-1</sup>, ascribed to the formate species adsorbed on Pt of PtM, still remained very strong and that at 1313 cm<sup>-1</sup> also remained. The results suggest that the hydrogenation reaction of formate species is not a fast step, and

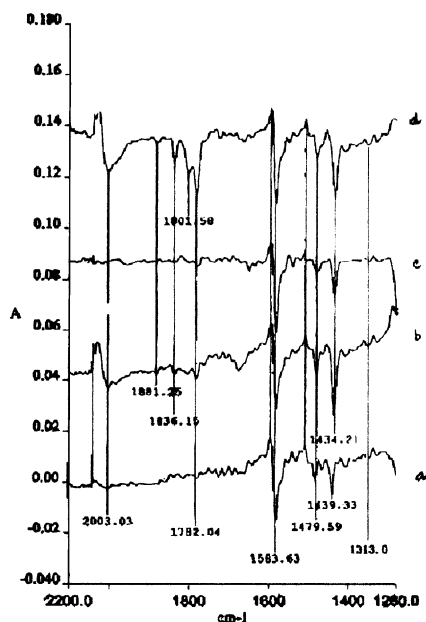


Fig. 5. In situ infrared spectra of four catalysts at 473 K in  $\text{CO}_2 + \text{H}_2$  flow: (a) Pt/SiO<sub>2</sub>; (b) Pt/SiO<sub>2</sub>; (c) PtMo/SiO<sub>2</sub>; (d) PtW/SiO<sub>2</sub>.

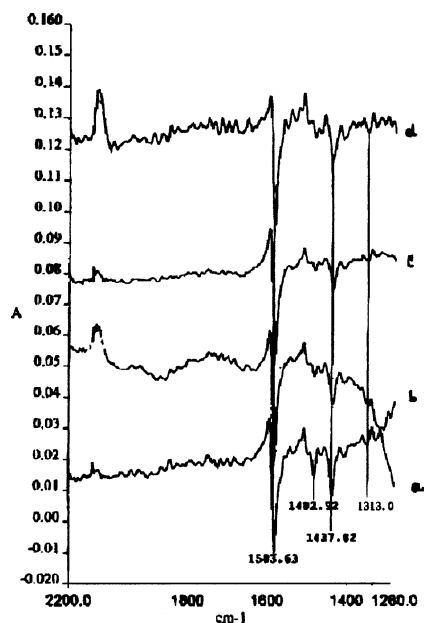


Fig. 6. In situ infrared spectra of four catalysts at 513 K in  $\text{CO}_2 + \text{H}_2$  flow: (a) Pt/SiO<sub>2</sub>; (b) PtCr/SiO<sub>2</sub>; (c) PtMo/SiO<sub>2</sub>; (d) PtW/SiO<sub>2</sub>.

probably is a rate-determining step for  $\text{CO}_2$  hydrogenation to methanol.

These results are obviously different from the results of CO hydrogenation reaction over the same catalysts previously reported. For the spectra of the CO hydrogenation reaction, both bands of adsorbed linear CO (at  $2057\text{ cm}^{-1}$  for PtCr/SiO<sub>2</sub>,  $2040\text{ cm}^{-1}$  for PtMo/SiO<sub>2</sub>,  $2060\text{ cm}^{-1}$  for PtW/SiO<sub>2</sub>) and adsorbed bridged CO (at  $1860\text{ cm}^{-1}$  for PtCr/SiO<sub>2</sub> and PtMo/SiO<sub>2</sub>, at  $1877\text{ cm}^{-1}$  for PtW/SiO<sub>2</sub>) on Pt appear at a temperature range of 463–533 K [15]. However, for the  $\text{CO}_2$  hydrogenation reaction, the bands attributed to the adsorbed linear and bridged CO did not appear. Very small bands at  $2003\text{ cm}^{-1}$  can be ascribed to the adsorbed linear CO, which is an active species for ascribed hydrogenation reaction of gas-phase CO, which is produced by the reverse water gas shift reaction. The bands attributed to the formyl species adsorbed on PtM (at  $1621\text{ cm}^{-1}$  for PtCr/SiO<sub>2</sub>,  $1627\text{ cm}^{-1}$  for PtMo/SiO<sub>2</sub>,  $1600\text{ cm}^{-1}$  for PtW/SiO<sub>2</sub>) during CO hydrogenation reaction are weak and broad, while the bands attributed to the formate species adsorbed on PtM (all at  $1583\text{ cm}^{-1}$ ) are strong and sharp. The results indicate that there are differences in the mechanism between CO and  $\text{CO}_2$  hydrogenation reactions over the same PtM/SiO<sub>2</sub> catalysts. The following mechanism of the hydrogenation reaction over the PtM/SiO<sub>2</sub> catalysts is suggested. The molecules of  $\text{CO}_2$  gas are readily adsorbed by the PtM/SiO<sub>2</sub> catalysts, and the adsorbed  $\text{CO}_2$  species on the catalytic site are rapidly converted to formate species adsorbed on Pt of PtM under reaction condition. The formate species are hydrogenated to methanol, and the process is probably a rate-determining step. Therefore, the formate species adsorbed on Pt of PtM can be regarded as a major intermediate for the methanol synthesis from the  $\text{CO}_2$  hydrogenation. The CO molecules produced in the  $\text{CO}_2$  hydrogenation should result from the reverse water gas shift reaction.

#### 4. Conclusion

In situ FT-IR was used to study the methanol synthesis reaction from the  $\text{CO}_2$  hydrogenation over PtM/SiO<sub>2</sub> catalysts. Some special formate species with an OCO asymmetric band at  $1583\text{ cm}^{-1}$  were

observed, which were probably bound to Pt, and were active intermediates. The comparison between the in situ FT-IR results of CO<sub>2</sub>/H<sub>2</sub> and CO/H<sub>2</sub> under the same reaction conditions shows that the produced surface species for the two reaction systems are essentially different. Under CO/H<sub>2</sub> atmosphere, no adsorbed formate species can be observed.

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