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NOTE

Selective formation of formaldehyde from carbon dioxide and hydrogen over $PtCu/SiO_2$[†]

Dong-Keun Lee,* Dul-Sun Kim and Sung-Woo Kim‡
Department of Chemical Engineering, Research Institute of Environmental Protection, Gyeongsang National University, Kajwa-dong 900, Chinju, Kyongnam 660-701, Korea

CO_2 hydrogenation was carried out at 423 K and 600 KPa with $PtCu/SiO_2$ catalyst. Formaldehyde rather than methanol was mainly produced, and platinum is believed to play an important role in the selective production of formaldehyde from CO_2 hydrogenation. The optimum atomic ratio of Pt/Cu in the $PtCu/SiO_2$ catalyst for the selective production of formaldehyde was 0.03. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: $PtCu/SiO_2$; Cu/SiO_2; formaldehyde; CO_2 hydrogenation; Pt/Cu ratio

1 INTRODUCTION

The increase of CO_2 in the atmosphere is believed to be the cause of the serious global warming problem. Great efforts and considerable attention have recently been given to the transformation of CO_2 through catalytic reaction. Catalytic hydrogenation of CO_2 has some advantages compared with other countermeasures, such as CO_2 deposit and disposal. Catalytic hydrogenation can fix or convert CO_2 very quickly. In addition to the reduction of CO_2 emission into the atmosphere, it can produce valuable chemicals from emitted and useless CO_2.

Various kinds of chemical have proved to be produced effectively by the CO_2 hydrogenation process. One of the most extensively studied chemicals was methanol.[1–4] CO_2 could also be catalytically converted into carboxylic acids such as formic acid[5,6] and acetic acid.[7,8] Other chemicals from CO_2 hydrogenation include ethanol[9] and higher alcohols,[10,11] methyl amines,[12] hydrocarbons[13,14] and methyl *tert*-butyl ether.[15]

In the present work catalytic hydrogenation of CO_2 was carried out to produce formaldehyde selectively with $PtCu/SiO_2$.

2 EXPERIMENTAL

$PtCu/SiO_2$ and Cu/SiO_2 samples were prepared by impregnating copper and platinum on the surface of SiO_2. The weight loading of Copper was 5% and the atomic ratio of Pt/Cu was in the range of 0.01–0.1. The prepared sample was dried and calcined in a furnace at 723 K for 16 h. The calcined catalyst was then reduced with hydrogen at 523 K for 24 h.

IR spectra were recorded with a Bruker IFS66 FTIR spectrometer with a resolution 2–4 cm^{-1}. About 50 mg of the catalyst was pressed into a wafer and the wafer was placed inside the IR cell designed by the method of Hicks et al.[16]

3 RESULTS AND DISCUSSION

Figures 1 and 2 show the results of temperature-programmed surface reaction (TPSR) on the Cu/SiO_2 and $PtCu/SiO_2$ catalysts that had been exposed to CO_2 for 2 h at 600 KPa and 300 K. TPSR experiments were carried out in flow of hydrogen with programmed heating up to 650 K at a rate of 10 K min^{-1}. One of the most outstanding differences between the TPSR spectra is the production of formaldehyde. No detectable amounts of formaldehyde could be observed on the Cu/SiO_2 (Fig.

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* Correspondence to: Dong-Keun Lee, Department of Chemical Engineering, Gyeongsang National University, Kajwa-dong 900, Chinju, Kyongnam 660-701, Korea.
‡ Present address: Sam Hyup Resource Development Co., Ltd, Korea.

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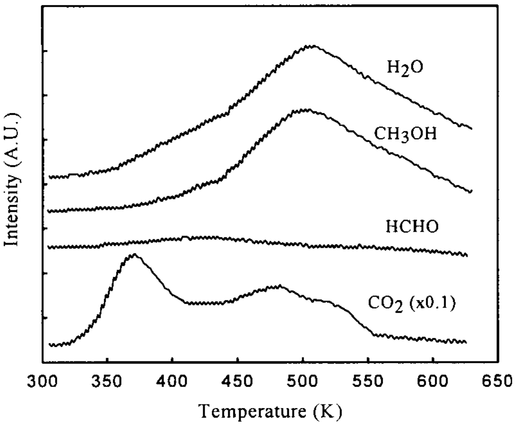

Figure 1 TPSR spectra taken after the exposure of the Cu/SiO$_2$ to CO$_2$ for 2 h at 600 KPa and 300 K (hydrogen flow rate = 60 cm^3 min^{-1}, 0.5 g catalyst).

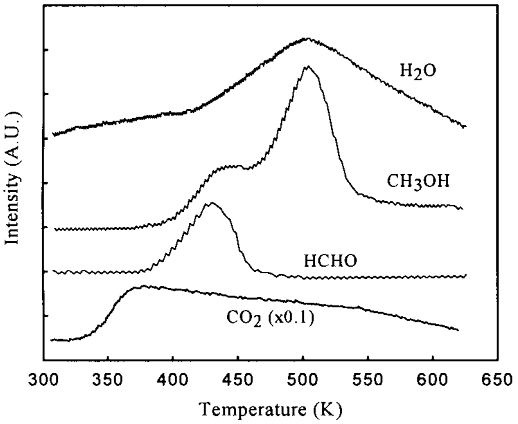

Figure 2 TPSR spectra taken after the exposure of the PtCu/SiO$_2$ (Pt/Cu = 0.03) to CO$_2$ for 2 h at 600 KPa and 300 K (hydrogen flow rate = 60 cm^3 min^{-1}, 0.5 g catalyst).

1), while on the PtCu/SiO$_2$ formaldehyde was produced in a significant amount at around 423 K (Fig. 2). The results in Figs 1 and 2 indicate that platinum must have participated in the production of formaldehyde.

On the basis of the result in Fig. 2, CO$_2$ hydrogenation was carried out at 423 K with the PtCu/SiO$_2$ catalyst, and the results are summarized in Table 1. As the ratio of H$_2$/CO$_2$ increased, the relative rate of methanol formation decreased, and the formation of formaldehyde became more prevalent. This implies that the relative concentration of surface hydrogen on the catalyst might play an important role in the selective production of formaldehyde. When the CO$_2$ hydrogenation had been carried out over Cu/SiO$_2$ catalyst in flows of H$_2$/CO$_2$ (20/1) mixture, the rate of methanol formation was 0.84 × 10^{-4} mol min^{-1} per gram of catalyst, but the formation of formadehyde had been negligible. Burch and coworkers[17–19] studied the synergistic effects between copper and ZnO on the CO$_2$ hydrogenation, and they proposed that hydrogen was spilled over and stored on ZnO phase during the reaction, which promoted the hydrogenation process. In the case of the PtCu/SiO$_2$ catalyst, hydrogen seems to be adsorbed on the surface of platinum and the adsorbed hydrogen is then believed to migrate onto the surface of copper that might be located in the vicinity of platinum. The migrated surface hydrogen will promote the hydrogenation of CO$_2$ to produce formaldehyde.

Table 1 Summarized results of CO$_2$ hydrogenation on the PtCu/SiO$_2$ (Pt/Cu = 0.03) at 423 K and 600 KPa

	Formation rate (10^{-4} mole min^{-1} per gram catalyst)	
H$_2$/CO$_2$	Methanol	Formaldehyde
3	0.80	0.21
4	0.85	0.34
5	0.82	0.40
7	0.66	0.44
20	0.20	0.87

The rates of formaldehyde formation were measured on a series of the PtCu/SiO$_2$ catalysts

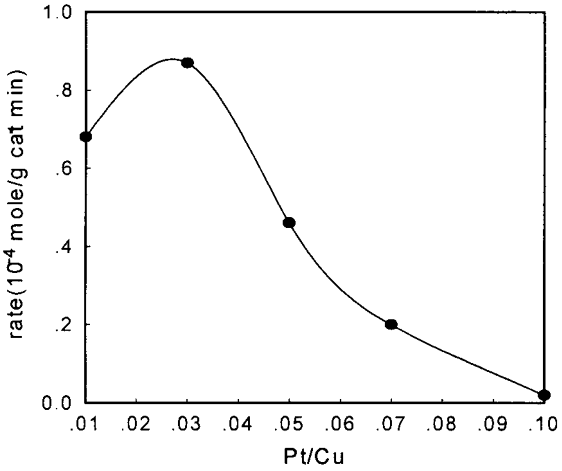

Figure 3 Effects of Pt/Cu atomic ratio on the rate of formaldehyde formation (H$_2$/CO$_2$ = 20, 423 K, 600 KPa).

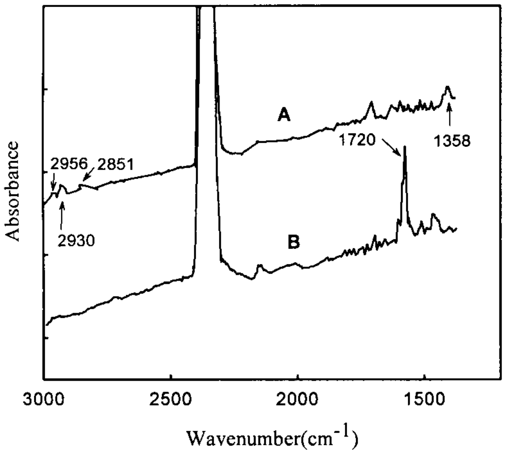

Figure 4 FTIR spectra taken during the CO_2 hydrogenation with the Cu/SiO_2 (A) and the PtCu/SiO_2 (Pt/Cu = 0.03) (B) at 600 KPa and 423 K (H_2/CO_2 = 20).

prepared by varying the atomic ratio of Pt/Cu from 0.01 to 0.1. As shown in Fig. 3, it was apparent that the presence of platinum promoted the formation of formaldehyde and the optimum atomic ratio of Pt/Cu was 0.03.

IR spectra (Fig. 4) were taken after the exposure of the Cu/SiO_2 and PtCu/SiO_2 (Pt/Cu = 0.03) to a H_2/CO_2 (20/1) mixture for 30 min at 600 KPa and 423 K. On Cu/SiO_2 the methanol was detected and ascribed to the shoulder at 2956 cm^{-1}min.[20–22] Bidentate copper formate groups were observed by C—H stretching at 2851 cm^{-1} and 2930 cm^{-1}, and by O—C—O bending at 1358 cm^{-1}.

The IR spectra of the PtCu/SiO_2 were greatly different. No detectable methanol and bidentate formate peaks could be observed, but a new peak was found at 1720 cm^{-1} that was characterized as the adsorbed formaldehyde on copper by the C—O stretching band.[20,23] A number of studies in the literature have proposed that the hydrogenation of copper formate is the rate-determining step in CO_2 hydrogenation. The absence of copper formate indicates that the formate was transformed into formaldehyde and methanol very quickly by the promotion of platinum.

4 CONCLUSIONS

PtCu/SiO_2 catalyst could hydrogenate CO_2 selectively into formaldehyde at 423 K and 600 KPa. Hydrogen seemed to be adsorbed on the surface of platinum and the adsorbed hydrogen was then believed to migrate onto the surface of copper. The migrated surface hydrogen promoted the selective hydrogenation of CO_2 to produce formaldehyde. The optimum atomic ratio of Pt/Cu for the selective formation of formaldehyde was 0.03. No detectable surface intermediates except the adsorbed formaldehyde were observed during the CO_2 hydrogenation.

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