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JOURNAL OF ELECTRON SPECTROSCOPY and Related Phenomena

Journal of Electron Spectroscopy and Related Phenomena 144-147 (2005) 373-376

www.elsevier.com/locate/elspec

In situ EXAFS studies of copper on ZrO₂ during catalytic hydrogenation of CO₂

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Available online 11 March 2005

Abstract

Speciation of copper on ZrO₂ during the catalytic hydrogenation of CO₂ has been studied by in situ extended X-ray absorption fine structural (EXAFS) spectroscopy in the present work. The EXAFS data indicated that about 3.1 nearest oxygen atoms surrounded the Cu atoms with a Cu–O bond distance of 1.95 Å in the calcined Cu/ZrO₂ catalyst. Reduction of the catalyst in hydrogen at 573 K led to a formation of Cu–Cu (2.56 Å) bonds with a coordination number (CN) of 5.6. Mainly CO and CH₃OH were generated in the hydrogenation of CO₂ catalyzed by the reduced Cu/ZrO₂ catalyst at 673 K. About 76% of the Cu(0) species was oxidized to Cu(I) (27%) and Cu(II) (49%) on ZrO₂ during the catalytic hydrogenation process.

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Keywords: CO2; Hydrogenation; ZrO2; XANES; EXAFS

1. Introduction

Hydrogenation of CO₂ to generate valuable chemicals has been widely investigated from the viewpoint of reducing the global warming effect caused by the CO₂ emission. It is also of great interest from the aspect of use of carbon source from CO₂ for the synthesis of oxygenates and hydrocarbons [1]. In the near future, due to the rapid decline of petroleum reserves, the use of CO₂ as C₁ building blocks in the organic synthesis would be environmentally and economically attractive. The amount of CO_2 to be fixed that way is very small compared to the huge amount of CO_2 produced by burning fossil fuels. However, the industrial use of CO_2 as a feedstock has so far been limited by its inherent thermodynamic stability. In the past decade, considerable researches have been investigated to develop methods of activating CO₂ for subsequent chemical transformation [2]. Processes for synthesis of methanol from syngas catalyzed by Cu/ZnO/Al₂O₃ have been well established in an industrial

process [3]. However, they have been suffered a very poor activity for the hydrogenation of CO_2 [4].

Generally, catalyst preparation procedures such as impregnation, ion exchange, deposition precipitation and coprecipitation may influence the catalytic behavior [3]. Various metal oxides have been used as support materials for hydrogenation of CO₂. ZrO_2 is of great interest in catalysis because of its mechanical and thermal stability, high specific surface area, and semiconductor properties. ZrO_2 has been found to maintain a good long-term stability in catalytic hydrogenation of CO₂ [5]. ZrO_2 -supported copper catalysts are very active with a high selectivity for methanol synthesis [6]. However, nature of the catalyst in the CO₂ hydrogenation process has not been extensively studied.

X-ray absorption near edge structural (XANES) and extended X-ray absorption fine structural (EXAFS) spectroscopies are very useful in identification of elements with a different environment, degree of aggregation, or location [7]. By EXAFS, we found that copper oxides (in ZSM-5 or ZSM-48) involved in the catalytic decomposition of NO [8] and oxidation of chlorophenols in supercritical water [9]. These speciation data was very useful in revealing the structure of

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^{0368-2048/\$ –} see front matter @ 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.elspec.2005.01.281

active species in the catalysis process. Thus, the main objective of the present work was to investigate the speciation of copper on ZrO_2 in the catalytic hydrogenation of CO_2 by EXAFS. An in situ EXAFS cell was used in the experiments.

2. Experimental

The 5 wt.% Cu/ZrO₂ catalyst was prepared by impregnation of copper (Cu(CH₃COO)₂) onto ZrO₂ (Prochemistry Co. Ltd. (GR, 99.9%)). The Cu/ZrO₂ catalyst was dried at 378 K for 16 h and calcined at 823 K for 8 h. About 0.5 g of the Cu/ZrO₂ catalyst was activated by reduction in 10% H₂/He gas (flow rate = 40 mL/min) at 573 K for 4 h. Hydrogenation of CO₂ was conducted at 423–923 K in the flowing H₂/CO₂ gas with a molar ratio of 4/1. Product gases were analyzed by gas chromatography and on-line FTIR spectroscopy. Infrared spectra were recorded on a Diglab FT-IR spectrometer (FTS-40) with fully computerized data storage and data handling capability. For all spectra reported, a 64-scan data accumulation was carried out at a resolution of 4 cm⁻¹.

In the temperature programmed reduction (TPR) experiments, the calcined Cu/ZrO₂ catalyst was reduced in 10% H_2/He with a heating rate of 10 K min⁻¹. A thermogravimetric analyzer (SDT 2960 simultaneous TGA-DTA) was used to monitor the weight change of the catalyst in the reduction process.

The X-ray absorption spectroscopic study for the catalytic hydrogenation of CO₂ on Cu/ZrO₂ was conducted in an in situ EXAFS cell [8]. The EXAFS spectra of the catalyst were collected on the Wiggler beamline at the Taiwan Synchrotron Radiation Research Center. The electron storage ring provided energy of 1.3 GeV (current of 80-200 mA). A Si(111) double-crystal monochromator was used for selection of energy with an energy resolution of 1.9×10^{-4} (eV/eV). The absorption spectra were collected in ion chambers that filled with helium gas. Beam energy was calibrated by the adsorption edge of Cu foil at an energy of 8980 eV. The standard deviation calculated from the averaged spectra was used to estimate the statistical noise and error associated with each structural parameter. Samples were measured in the transmission mode. Each EXAFS spectrum was recorded at least twice.

The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 8.0 programs [7]. The isolated EXAFS data was normalized to the edge jump and converted to the wavenumber scale. The Fourier transform was performed on k^2 -weighted EXAFS oscillations in the range of 3.5–12.5 Å⁻¹. XANES spectra of standard samples such as Cu₂O, CuO, and Cu foil were also measured on the Wiggler beamline. Semiquantitative analyses of the edge spectra were conducted by the least-square fitting of linear combinations of standard spectra to the spectrum of the sample. The height and area of the near-edge band in a copper spectrum were quantitatively proportional to the amount of copper species.



Fig. 1. Temperature programmed reduction of the calcined Cu/ZrO₂ catalyst in 10% H_2 /He at a heating rate of 10 K min⁻¹.

3. Results and discussion

Fig. 1 shows the temperature programed reduction of the calcined Cu/ZrO₂ catalyst in the flowing H₂/He gas at 323–837 K. A fast reduction of CuO on ZrO₂ was observed at 573 K. In addition, the observation of essentially little reduction of CuO on ZrO₂ at >600 K suggests a rather little interaction between CuO and the support ZrO₂.

Catalytic hydrogenation of CO_2 was conducted at 423–923 K. The temperature dependence for hydrogenation of CO_2 on the reduced Cu/ZrO₂ catalyst is shown in Fig. 2. It is clear that hydrogenation of CO_2 was enhanced by Cu/ZrO₂ at >673 K. Yields of CO and CH₃OH from the hydrogenation of CO_2 also increased as the reaction temperature increased and subsequently reached 28 and 22%, respectively, at 923 K.

For further understanding the nature of the active copper species on ZrO_2 , X-ray absorption spectra of the catalyst were



Fig. 2. Temperature dependence for the composition of product gases: (a) CO_2 , (b) CO, and (c) CH_3OH in the catalytic hydrogenation of CO_2 on Cu/ZrO_2 .



Fig. 3. In situ XANES spectra of (a) calcined, (b) reduced Cu/ZrO₂ catalysts, and (c) the catalyst that was measured during CO₂ hydrogenation at 673 K. The component fits of the spectrum (c) are also shown in (d).

determined. The in situ XANES spectra of the Cu/ZrO₂ catalyst in the calcined and reduced states and during the hydrogenation of CO₂ at 673 K are shown in Fig. 3. The pre-edge XANES spectra of the calcined Cu/ZrO₂ catalyst exhibited a very weak absorbance feature for the 1s-to-3d transition (8975–8980 eV) which is forbidden by the selection rule in the case of perfect octahedral symmetry [8,9]. A shoulder at 8984–8988 eV and an intense feature at about 8995–9002 eV were attributed to the 1s-to-4p transition that indicated the existence of Cu(II) species. The XANES spectra of the reduced Cu/ZrO₂ catalyst was very similar to that of the Cu foil. The metallic copper is, in general, very active for catalytic hydrogenation of CO₂ [10]. The pre-edge band at 8981–8984 eV may be due to the dipole-allowed 1s-to-4p transition of Cu(I) that might be formed via oxidation of copper by CO₂.

The XANES spectra were also expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range of 8960–9040 eV. XANES spectra of standard samples such as CuO, Cu₂O and Cu foil were measured on the Wiggler beamline. The fit of the XANES spectra during the hydrogenation of CO₂ on ZrO₂ at 673 K is shown in Fig. 3(d). It was found that about 76% of the Cu(0) species was oxidized to Cu(I) (27%) and Cu(II) (49%) on ZrO₂ in the catalytic hydrogenation of CO₂ to yield CO and CH₃OH.

The in situ EXAFS spectra were also recorded and analyzed in the *k* range of $3.5-12.5 \text{ Å}^{-1}$. An over 99% reliability

Table 1	
EXAFS data of the Cu/ZrO ₂ catalysts	

	Shell	<i>R</i> (Å)	CN	σ^2 (Å ²)
Oxidized Cu/ZrO ₂	Cu—O	1.95	3.1	0.003
Reduced Cu/ZrO ₂	Cu-Cu	2.56	5.6	0.004
	CuCu	3.57	10.7	0.006
Cu/ZrO2 ^a	Cu—O	1.91	1.9	0.004
	Cu—Cu	2.51	5.4	0.003

R: bond distance; CN: coordination number; σ^2 : Debye–Waller factor. ^a The in situ EXAFS spectra of the catalyst were measured during the catalytic hydrogenation of CO₂ at 673 K.

of the EXAFS data fitting for copper on ZrO₂ was obtained. In Table 1, the calcined Cu/ZrO₂ catalyst has a Cu–O bond distance of 1.95 Å with a coordination number (CN) of 3.1. In the second shells, the bond distance of Cu-(O)-Cu was 2.90 Å with a CN of 12.6. Reduction of the catalyst led to a formation of mainly metallic copper with an averaged Cu-Cu bond distance of 2.56 Å. The CN of copper in the reduced catalyst was 5.6 approximately. However, hydrogenation of CO2 on the reduced Cu/ZrO2 catalyst at 673 K might cause the oxidation of the metallic copper (Cu(0)) to Cu₂O (Cu(I)) or CuO (Cu (II)). The EXAFS data of the used catalyst showed that about 1.9 nearest oxygen atoms surrounding the copper atoms with the Cu-O bond distance of 1.91 Å. Note that the interactions between copper and ZrO₂ was not observed by in situ EXAFS spectroscopy during the hydrogenation process. Evidently, little high-temperature reduction feature was found in the TPR experiments (see Fig. 1).

The possible reaction path for Cu(0) that involved in the hydrogenation of CO₂ with H₂ may be described as follows. The first and second shells Cu–Cu bond distances in the reduced Cu/ZrO₂ catalyst were 2.56 and 3.57 Å, respectively. Stoichiometrically, two moles of CO₂ interacted with the metallic copper and formed Cu(II) and Cu(I) species with yields of CO_(g) and CH₃OH_(g). When oxygen was inserted into the metallic copper in the CO₂ hydrogenation process, the Cu–Cu bond distance was decreased by 0.05 Å and a formation of Cu–O bonding (1.91 Å) was observed. In the presence of excess H₂, the Cu(II) and Cu(I) species was reduced to metallic copper promptly.

4. Conclusions

The EXAFS data indicated that the calcined Cu/ZrO₂ has a Cu–O bond distance of 1.95 Å with about 3.1 nearest oxygen atoms surrounding. Reduction of the catalyst in hydrogen at 573 K led to the formation of Cu–Cu bonds (2.56 Å) with a CN of about 5.6. Mainly CO and CH₃OH were yielded in the hydrogenation of CO₂ catalyzed by Cu/ZrO₂ at 673 K. The XANES spectra shows that Cu(I) was formed via oxidation of Cu(0) by CO₂. About 76% of the Cu(0) species was oxidized to Cu(I) (27%) and Cu(II) (49%) on ZrO₂ in the catalytic hydrogenation of CO₂ to yield CO and CH₃OH.

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