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Methanol synthesis over a Zn-deposited copper model catalyst

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Methanol synthesis by the hydrogenation of CO_2 over Zn-deposited polycrystalline Cu was studied using surface science techniques. The Zn sub-monolayer was oxidized by the reaction mixture during the reaction at 523 K, leading to the formation of ZnO species. The kinetic results definitely showed that the ZnO species on the Cu surface promoted the catalytic activity of methanol formation, where the activity of Cu increased by a factor of 6 at the Zn coverage of 0.17. A volcano-shaped curve was obtained for the correlation between the Zn coverage and the catalytic activity, which was very similar to the correlation curve between the oxygen coverage and the specific activity for methanol formation previously obtained for the Cu powder catalysts. The role of ZnO in Cu/ZnO based catalysts was ascribed to the stabilization of Cu^+ species by the ZnO moieties on the Cu surface.

Keywords: methanol synthesis; copper catalyst; role of ZnO; XPS

1. Introduction

The synthesis of methanol by the hydrogenation of CO (+ CO_2) over Cu/ZnO based catalysts is an important industrial process and one of the most investigated catalytic reactions. Despite a number of mechanistic studies conducted for some decades, there are still controversies concerning the active species of Cu and the role of ZnO promoting the catalytic activity [1]. Evidence that Cu^{n+} is the pivotal catalytic species for methanol formation has been presented based on surface science studies using a Cu(100) model catalyst [2] and XPS studies [3] of the alkali

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promoted Cu catalysts, while some researchers claim that metallic Cu is the active species for methanol synthesis [4,5]. The reason for the synergetic effect between Cu and ZnO was also ambiguous. Formerly, the active species was proposed to be Cu^+ ions dispersed in the ZnO lattice with methanol mainly produced directly from CO [6]. Later, the promotional role of ZnO was explained by a spillover model; that is, ZnO can act as a reservoir for atomic hydrogen which migrates from ZnO to the Cu surface and promotes methanol formation on Cu [7]. On the other hand, the reactivity of Cu particles deposited on the ZnO single-crystal surfaces has been found to be different depending on the surface planes, such as (0001), (000$\bar{1}$), and (10$\bar{1}$0) [8]. It has also been reported that the oxygen-terminated ZnO(0001) surface stabilizes two-dimensional Cu islands with a surface similar to Cu(110), in the presence of CO, in terms of TPD behavior and the satellite structure observed in C 1s and O 1s spectra [9].

Regarding the debated issue concerning the support effect of metal oxides, we have recently reported that the problems of the active species of Cu and the support effect cannot be separately considered, in which report the correlation between the specific activity of methanol formation and the oxygen coverage on Cu for the post-reaction Cu surface was obtained for Cu-based catalysts containing various metal oxides, suggesting that Cu^+ and Cu^0 species are both essential for the methanol formation, and the support effect for any metal oxide contained in the Cu catalysts is generally explained by the correlation curve [10]. Further, the migration of ZnO_x from ZnO particles onto the Cu surface have been observed upon reduction of Cu/ZnO [11] and Cu/ZnO + ZnO/SiO_2 mixtures [12]; thus, it was concluded that Cu^+ is stabilized by the ZnO_x species that migrated from the ZnO particles onto the Cu surface, leading to formation of a Cu^+–O–Zn active site. To prove the proposed ZnO_x promotional model based on our previous results, we attempted to carry out the UHV studies in which methanol synthesis over the Zn-deposited Cu polycrystalline surface was examined using surface science techniques.

2. Experimental

The apparatus used here is basically composed of three chambers: an analysis chamber equipped with X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES), a preparation chamber for changing the sample and for deposition of metallic Zn onto the surface of a Cu polycrystalline sample, and a high pressure flow reactor which allows us to carry out the hydrogenation of CO_2 at 20 atm. The sample can be transferred between the chambers using a transfer rod and a manipulator without exposure to atmosphere. The heater and thermocouple for controlling the sample temperature are attached to the rear side of the sample holder, which are located outside the reaction cell. The products and reactants are analyzed using an on-line gas chromatograph.

The Cu polycrystal (99.9999%) was a square foil (10 mm × 10 mm × 1 mm),

polished with diamond paste to a mirror finish, and mechanically mounted on the sample holder using thin Ni nails. During the course of this investigation, the sample was repolished several times, and the results of the kinetic measurements were reproduced after repolishing. The front sample surface was routinely Ar^+-sputter cleaned at 300 and 723 K subsequently, followed by an anneal at 723 K for $\sim$ 10 min . No catalytic activity for methanol formation was observed without the sample cleaning procedure. After cleaning of the sample, the activity for methanol formation correlated well with Zn coverage reproducibly. Thus, it is safe to conclude that the methanol formation reaction occurs almost entirely on the front surface, and the back surface is passivated by segregated impurities.

After checking the cleanliness of the Cu surface by XPS or AES in the UHV chamber, the sample was transferred to the preparation chamber, where zinc was vapour-deposited on the front surface of the sample by resistively heating a Zn wire (0.27 mm diameter, 99.99%) located $\sim$ 2 cm from the sample. The Zn-deposited Cu sample was characterized by XPS or AES to estimate the coverage of Zn after flashing the sample to 523 K. The sample was then transferred to the evacuated reactor, which was enclosed and pressurized with CO_2 and H_2. After heating the sample near the reaction temperature ($\sim$ 500 K), the reactant was introduced to the reactor, and then the reaction temperature was adjusted to 523 K. The reaction was traced using the gas chromatographs for at least 60 min. The reaction reached a steady state within 30 min, at which the reaction rate was adopted as a kinetic data. No deactivation of the catalyst was observed for 3 h after the steady state was reached. After the reaction, the heating was tuned off, and the reactant mixture was evacuated. The sample still maintained the reaction temperature without heating for $\sim$ 10 min. The post-reaction sample was then analyzed by XPS. Oxygen was always present on the post-reaction surface in the presence of Zn, indicating that Zn was oxidized by the reaction mixture.

The XPS spectra were recorded with Mg Kα radiation at a pass energy of 50 eV, where the full-width at half maximum (FWHM) was 2.1 eV for a Cu 2p peak for the polycrystalline Cu sample. The AES and XPS spectra were collected with detection normal to the surface. The coverage $\Theta = 1$ defined in this study corresponds to the number of Cu surface atoms (1.7×10^{15} atoms/cm^2), which is assumed to be similar to that for Cu(111), 1.77×10^{15} atoms/cm^2. The oxygen coverage on the Cu surface was estimated by XPS assuming that the oxygen coverage (Θ_O) was equal to 0.5 when the clean Cu surface was oxidized by O_2 at 600 K and 5×10^{-5} Torr for 40 s [13]. The Zn coverage was then estimated from the oxygen coverage and the integrated O 1s : Zn $2p_{3/2}$ XPS intensity ratio using their XPS sensitivity factors. In the AES measurements, the O(KVV)/Cu(LVV) peak-to-peak AES ratio for the Cu surface with adsorbed oxygen of $\Theta_O = 0.5$ was 0.13, which was in fair agreement with the literature data [13]. Further, graphitic carbon was observed on the post-reaction surface, whose coverage was estimated to be $\Theta_C = 0.2$ at $\Theta_{Zn} = 0.17$. However, no significant deactivation was observed by the carbon deposition.

3. Results and discussion

We successfully detected methanol in the hydrogenation of CO_2 ($H_2/CO_2 = 3$) on the Zn-deposited Cu surface because of the high pressure of the reactants (18 atm) [14]. Fig. 1 shows the turnover frequencies (TOF) for the methanol formation at 523 K as a function of the Zn coverage on Cu measured by XPS after the reaction. The yield of methanol is on the order of 3×10^{-4}% at a TOF of 2×10^{-2} molecules/s site, which is much less than the equilibrium conversion of 6.2%. It is clearly shown that the TOF increased with Θ_{Zn} below $\Theta_{Zn} = 0.17$, indicating that the Zn species on the Cu surface directly promotes methanol synthesis. The TOF decrease above $\Theta_{Zn} = 0.17$ is probably due to a decrease in the surface area of metallic Cu which dissociates H_2 molecules.

The post-reaction surface analysis by XPS showed the presence of oxygen on the Cu model catalyst. As shown in fig. 2, the amount of oxygen is found to be equal to that of Zn in the range between $\Theta_{Zn} = 0$ and 0.4, indicating the formation of ZnO on the Cu surface during the methanol synthesis reaction. The binding energy of the O 1s peak at 530.7 eV for the post-reaction surface is close to that for the oxygen in a ZnO crystal (530.6 eV) [15], but it is different from that formed on the pure poly-Cu surface (530.0 eV). The Zn $2p_{3/2}$ peak at 1021.7 eV for the post-reaction surface shifted to higher energies by $\sim$ 0.6 eV, compared to that for the initially deposited Zn metals on the clean Cu surface. Further, the Cu $2p_{3/2}$ peak slightly shifted to lower energies by $\sim$ 0.2 eV, indicating Cu^+ formation [16] in the presence of ZnO.

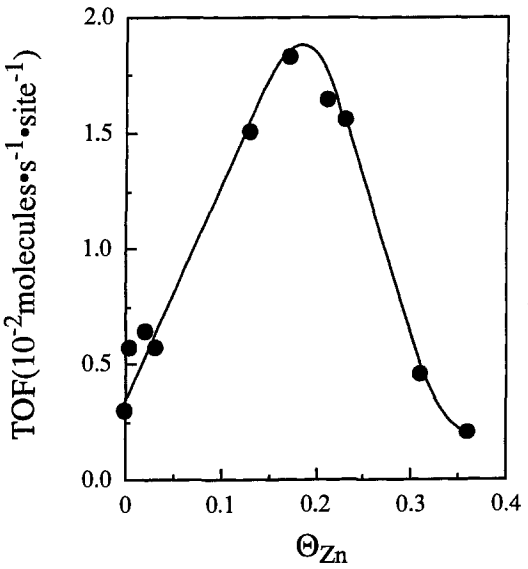

Fig. 1. TOF for methanol formation on the Zn-deposited Cu surface as a function of Zn coverage. The hydrogenation of CO_2 was carried out at 523 K and 18 atm. The Zn coverage was measured after the reaction using XPS.

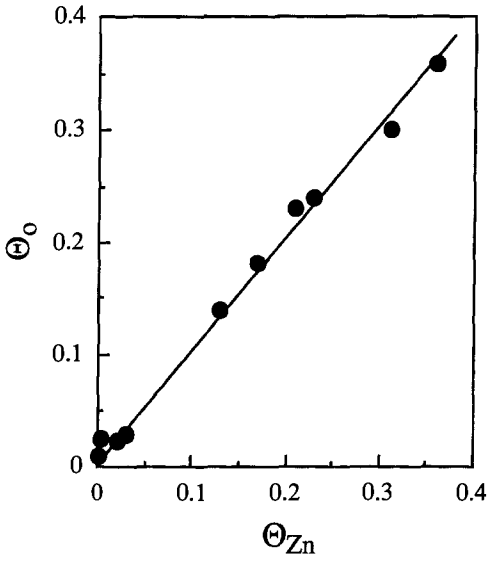

Fig. 2. Oxygen coverage as a function of the Zn coverage for the post-reaction Zn-deposited Cu surfaces.

However, no satellite peak around the Cu $2p_{3/2}$ peak, characteristic for CuO, was observed for the post-reaction surface. It is thus suggested that the oxygen is bound to Zn atoms tightly rather than Cu atoms, leading to the formation of a Cu^+–O–Zn^{n+} ($1 < n < 2$) active species for methanol synthesis. We consider that the amount of oxygen adsorbed on the metallic Cu surface during reaction is very small because oxygen chemisorbed on Cu is readily reduced by H_2.

The volcano-shaped curve shown in fig. 1 is very similar to that of the relation between the specific activity of methanol formation and the oxygen coverage on the post-reaction Cu surfaces previously obtained for the supported Cu catalysts containing various metal oxides, such as Cr_2O_3, Al_2O_3, Ga_2O_3, ZnO, and SiO_2. Among the supported catalysts, the Cu/ZnO/Ga_2O_3 catalyst showed the highest activity with the oxygen coverage $\Theta_O = 0.18$, where the role of the oxygen was considered to stabilize the Cu^+ active species. This is consistent with the present data because the optimum oxygen coverage for methanol formation shown in fig. 1 corresponds to $\Theta_O = 0.17$, where the relation that Θ_{Zn} is equal to Θ_O (fig. 2) is established. The volcano curves obtained for both Zn-deposited Cu model catalysts and supported Cu catalysts are quite important from the following two aspects: firstly, the specific activity of the Cu catalysts for methanol formation is controlled by the amount of Cu^+ and Cu^0 and both species are essential for the methanol formation, and secondly, the support effect for any metal oxide contained in the Cu catalysts is generally explained by the volcano plots, strongly suggesting that the metal oxides play a role in stabilizing the Cu^+ species. Again, the role of Cu^0 is possibly to dissociate H_2 for hydrogenation steps.

To directly compare the TOF obtained in the methanol synthesis over the ZnO/poly-Cu surface with that for the powder Cu/ZnO catalyst, the hydrogenation of CO_2 was carried out at 523 K and 18 atm with small W/F values varying from 3×10^{-5} to 2×10^{-4} g min/cm^3 to get the steady state reaction rate at low conversions, where W and F stand for the catalyst weight (g) and the flow rate (cm^3/min), respectively. For the powder Cu/ZnO catalyst, a TOF of 0.017 molecules/s site at an oxygen coverage of $\Theta = 0.23$ was obtained, which is equal to that for the ZnO/poly-Cu surface, i.e., 0.017 molecules/s site at $\Theta_O = 0.23$. Based on the similarity of the TOF value and the same feature seen in the volcano relation for the powder Cu/ZnO based catalysts and the ZnO/poly-Cu model catalyst, we concluded that both systems have essentially the same catalytic nature, and the role of the ZnO support is to provide ZnO species onto the Cu surface of the Cu particles which directly promote the methanol synthesis by creating active sites, such as Cu^+–O–Zn^{n+} ($1 < n < 2$) species. Note that the TOF for the clean Cu surface (3×10^{-3} molecules/s site) in fig. 1 is comparable to that over Cu(100), 2.7×10^{-4} molecules/s site, for the hydrogenation of CO_2 at a total pressure of 2 atm ($CO_2 : H_2 = 1 : 1$) and 543 K [17] since methanol formation is approximately first order in pressure.

Although some researchers claim that the activity of Cu catalysts is determined only by the surface area of metallic Cu, the present study definitely denies the model of Cu^0 single active sites by showing the promotional effect of ZnO species on Cu in spite of the resulting decrease in surface area of metallic Cu. Furthermore, the ZnO/poly-Cu surface was found to be an excellent model for the supported Cu/ZnO catalysts. Thus, we believe that for powder Cu/ZnO catalysts Cu^+ species exist at the interface between Cu and ZnO particles and/or between Cu and ZnO_x species decorated on the Cu surface. We have previously reported that ZnO_x species migrate upon H_2 high-temperature reduction from ZnO particles to Cu particles, leading to increase of specific activity. The migration of ZnO_x was further observed in a physical mixture of ZnO/SiO_2 and Cu/SiO_2 [3].

More detailed data will be presented elsewhere.

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