Catalysis Letters 35 (1995) 297–302

Methanol synthesis by the hydrogenation of CO_2 over Zn-deposited Cu(111) and Cu(110) surfaces

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Received 13 June 1995; accepted 18 August 1995

The hydrogenation of CO_2 over Zn-deposited Cu(111) and Cu(110) surfaces was performed at 523 K and 18 atm using a high pressure flow reactor combined with XPS apparatus. It was shown that the ZnO_x species formed on Cu(111) during reaction directly promoted the methanol synthesis. However, no such promotional effect of the Zn was observed for methanol formation on Cu(110). Thus, Zn on Cu(111) acts as a promoter, while Zn on Cu(110) acts as a poison. The activation energy and the turnover frequency are in fairly good agreement with those obtained for Cu/ZnO powder catalysts.

Keywords: methanol synthesis; Cu(111); Cu(110); Zn deposition

1. Introduction

The activity and selectivity of catalysts are well-known to be modified by the addition of trace amounts of secondary elements such as alkali metals. The resulting increase in activity has been explained as electronic and ensemble effects [1,2]. However, the exact nature of these effects is still ambiguous because of the complexity of the catalytic reaction mechanism and the surface structure of the catalysts. On the other hand, some surface science approaches have succeeded in examining the structural nature of the alkali promoter for catalytic reactions at an atomic level. For example, Strongin and Somorjai have shown that the potassium on Fe(100) and Fe(111) significantly increases the rate of ammonia synthesis, although the potassium adsorbed on inactive Fe(110) has no promotional effect on ammonia synthesis [3]. Thus, it is a very interesting problem of just how the structure of additives on the surface influences the promotional effect of catalytic reactions.

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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. There has been much controversy concerning the role of ZnO and it has not yet been fully understood [4]. Recently, we have investigated the role of ZnO on Cu catalysts using both a powder catalyst and poly and single crystalline model catalysts [5–7], and have found that the ZnO_x on the Cu surface directly promotes the methanol synthesis by creating new active sites such as Cu^+–O–Zn species. In this communication, we report the effect of Zn deposited on Cu(111) and Cu(110) surfaces on the catalytic activity for methanol formation using surface science techniques. Our major results showed that the effect of Zn on methanol formation strongly depended on the structure of the Cu substrate.

2. Experimental

The ultra-high vacuum apparatus used in this work has been described elsewhere [6,7]. Briefly, it is composed of an analysis chamber equipped with XPS and AES, a preparation chamber for changing samples and for deposition of Zn on the surface of Cu single crystalline samples, and a high pressure flow reactor. The reactor allows the samples to be exposed to reaction gases at pressures up to 30 atm, from which the sample is transferred to the analysis chamber without exposure to atmosphere. The sample was cleaned by Ar ion sputtering and characterized by XPS and AES in the UHV chamber. Zn was then vapor-deposited on the front surface, which was characterized by XPS and AES to estimate the coverage of Zn. The XPS spectra were recorded with Mg Kα radiation at a pass energy of 20 eV. The oxygen coverage on the Cu surface was estimated by XPS assuming that saturated oxygen coverage (Θ_O) was equal to 0.5 when clean Cu(111) was oxidized by up to 10^5L of O_2 at 300 K. In the XPS measurements, the O 1s/Cu $2p_{3/2}$ integrated intensity ratio was 0.013 for the Cu(111) surface with saturated oxygen. The Zn coverage was then estimated from oxygen coverage and the integrated O 1s : Zn $2p_{3/2}$ XPS intensity ratio using XPS sensitivity factors. After the sample was transferred to the reactor, the hydrogenation of CO_2 was performed at a constant pressure of 18 atm and a fixed gas composition of $CO_2 : H_2 = 1 : 3$. The total feed-rate measured at the end of the flow line (1 atm) by a film flow meter was 100 cm^3/min. The reaction products were analyzed using on-line gas chromatographs. The reaction reached a steady state within 30 min, at which the reaction rate was adopted. No deactivation of the catalyst was observed for 3 h after steady state was reached. The reaction without the Cu samples was also performed after each regular reaction test. The stainless steal walls of the reactor were found to show some activity for methanol formation, methanation reaction, and the reverse water–gas shift reaction in the blank test, i.e., reaction without the Cu sample, although the reaction walls and the sample holder were coated with Au (1 μm)/Cr (2 μm), which lessened the catalytic activity as well as carbon deposition significantly. The activity of the reactor walls for methanol formation was estimated to be 10–15% for that of the clean Cu sample over a temperature range of 523–573 K. In each kinetic measurement for the methanol synthesis, the blank tests were carried out to eliminate contributions of the catalytic activity of the materials except for the Cu sample. After the reaction, the sample was cooled to 373 K and immediately the reactant gases were evacuated. The post-reaction surface was then evaluated by XPS analysis, where the coverage of $\Theta = 1$ corresponds to the number of Cu surface atoms, which is 1.77×10^{15} and 1.082×10^{15} atoms/cm^2 for Cu(111) and Cu(110), respectively. The activity of the Zn-deposited Cu surfaces was evaluated using the turnover frequency (TOF) defined as a number of product molecules formed on a Cu atom per second (molecules/site s).

3. Results and discussion

The hydrogenation of CO_2 over the Zn-deposited Cu(111) and Cu(110) surfaces was carried out at 523 K and 18 atm with varying Zn coverage (Θ_{Zn}) estimated by XPS analysis after the reaction. Fig. 1 shows the turnover frequency (TOF) for methanol formation by the hydrogenation of CO_2 and that for CO formation by the reverse water–gas shift (RWGS) reaction as a function of the Θ_{Zn}. Because the deposited Zn is oxidized to ZnO_x species on the Cu surface during the reaction, the Zn in Θ_{Zn} is due to the ZnO_x species. It is shown that the TOF for methanol formation over the Cu(111) surface increased with the Zn coverage below $\Theta_{Zn} = 0.19$ and decreased above $\Theta_{Zn} = 0.2$. The optimum TOF obtained at $\Theta_{Zn} = 0.2$ was about 13 times greater than that for the clean Cu(111) surface. No activity for methanol formation was observed above $\Theta_{Zn} = 0.5$. These results clearly indicated that the ZnO_x species on the Cu surface directly promoted the methanol synthesis in the range of $0 < \Theta_{Zn} < 0.3$. The apparent activation energies for methanol formation over clean Cu(111) and Zn/Cu(111) were 73.6 ± 6.9 kJ mol^{-1} and 83.7 ± 3.9 kJ mol^{-1}, respectively, which are close to those of the powder Cu/ZnO (50/50) catalyst (69.3 ± 3.6 kJ mol^{-1}) and ZnO_x/poly-Cu catalyst ($\Theta_{Zn} = 0.17$, 76.3 ± 4.0 kJ mol^{-1}) [7]. Thus, the deposition of Zn leads to the creation of new active sites without varying the activation energy. It is also indicated that the ZnO_x on Cu(111) could be regarded as a model catalyst for the methanol synthesis over Cu/ZnO catalysts.

Strikingly, the catalytic property of the deposited Zn on Cu(110) was different from that for Cu(111). Although the clean Cu(110) surface was three times more active for methanol formation than the clean Cu(111) surface, the activity of Zn-deposited Cu(110) monotonously decreased with increasing Θ_{Zn}. Thus, no promotional effect of Zn on TOF for methanol formation was observed for Cu(110). It is quite interesting that the promotional effect of the deposited Zn for the methanol synthesis strongly depends on the structure of the Cu substrates.

The RWGS reaction also occurred on the Zn-deposited Cu(111) and Cu(110)

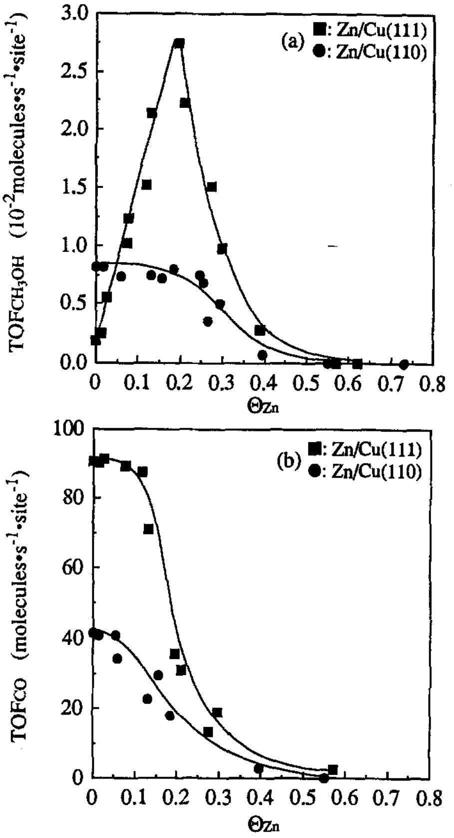

Fig. 1. Turnover frequency for methanol formation (a) and CO formation (b) at 523 K as a function of the Zn coverage (θ_{Zn}) on the Zn/Cu(111) and Zn/Cu(110) model catalysts. The Zn coverage was measured after the reaction using XPS.

surfaces [8] as shown in fig. 1. The clean Cu(111) was more active than the clean Cu(110) by a factor of 2.3. It should be noted that no promotional effect of ZnO_x species on the RWGS reaction was observed for both Cu(111) and Cu(110). The TOF for CO formation started to decrease at $\theta_{Zn} = 0.10$, and reached zero at $\theta_{Zn} = 0.5$. It is known that CO formation by RWGS reaction mainly occurs over metallic Cu. Thus, the results indicate that the deactivation of CO formation with increasing θ_{Zn} is due to covering the surface Cu atoms with the deposited Zn. In spite of the decrease in the number of surface Cu atoms, methanol formation over Cu(111) was promoted by the deposited Zn. This indicates that the increase in the methanol synthesis activity upon dosing with Zn is not due to an increase in the surface area of metallic Cu.

The Zn-deposited Cu(111) and Cu(110) surfaces before and after the reaction were analyzed by XPS. Fig. 2a shows the Zn $2p_{3/2}$ spectra of the surfaces with a Zn coverage of $\theta_{Zn} = 0.15$. On Cu(111), the peak at 1021.1 eV for the initially depos-

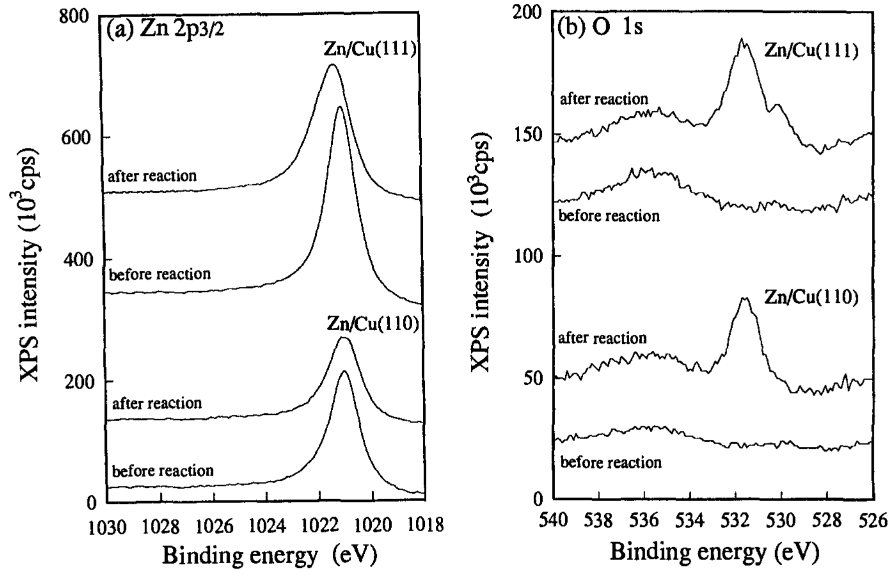

Fig. 2. XPS spectra of Zn $2p_{3/2}$ (a) and O 1s (b) for the surfaces of Zn/Cu(111) and Zn/Cu(110) model catalysts ($\theta_{Zn} = 0.15$) before and after reaction.

ited Zn atoms shifted to 1021.4 eV for the post-reaction surface. Because the Zn $2p_{3/2}$ peak at 1021.1 eV was assigned to Zn metal atoms [9], the peak shift was attributable to the oxidation of Zn atoms [10]. Accompanied by the peak shift, the full-width at half maximum (FWHM) of the Zn $2p_{3/2}$ peak increased from 1.3 to 1.7 eV, indicating the partial oxidation of Zn on the Cu(111) surface during the methanol synthesis reaction. However, the amount of Zn was the same before and after the reaction. As for Cu(110), the feature seen in the Zn $2p_{3/2}$ peak was slightly different from that for the Cu(111) surface. That is, no shift in the Zn $2p_{3/2}$ peak was observed before and after the reaction. Thus, the deposited Zn on Cu(110) was not easily oxidized to ZnO_x during the methanol synthesis reaction. In this sense, there is a small difference in the chemical state of the deposited Zn between Cu(111) and Cu(110).

Fig. 2b shows the O 1s spectra of the surfaces with a Zn coverage of $\theta_{Zn} = 0.15$. On Cu(111), the O 1s peaks at 530.4 and 531.7 eV seen in the spectra for the post-reaction surface were assigned to the oxygen bound to Zn atoms [11,12] and formate species formed as the reaction intermediate [13], respectively. The O/Zn and O/Cu XPS ratios were 0.136 and 0.038, respectively, where the oxygen signal is for the sum of formate-oxygen and ZnO_x-oxygen. Here, the x in the ZnO_x was estimated as 0.15 based on the area of the O 1s peak at 530.4 eV. Thus, the amount of Zn atoms oxidized during the methanol synthesis reaction was small. However, the degree of oxidation increased with increasing Zn coverage. On the other hand, for Cu(110), the only peak seen was at 531.7 eV in the O 1s spectrum for the post-reaction surface with no peak at 530.4 eV which is characteristic for oxygen in a

ZnO crystal. The O/Zn and O/Cu XPS ratios were 0.226 and 0.038, respectively, where the oxygen signal is for formate-oxygen.

The results in this work clearly indicate that the deposited Zn with a special structure on Cu surfaces promotes the methanol synthesis over Cu catalysts. That is, Zn on Cu(111) acts as a promoter, while Zn on Cu(110) acts as a poison. No such effects of Zn on a Cu surface have ever been reported in surface science studies and powder catalysts studies. Recent STM results showed the formation of adsorbed Zn islands on the Cu(111) surface [8]. More detailed data will be presented elsewhere.

Acknowledgement

This work was partly supported by the New Energy and Industrial Technology Development Organization.

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