Active sites for methanol synthesis on a Zn/Cu(100) catalyst

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Abstract

The active sites for methanol synthesis on a Zn/Cu(100) catalyst are clarified using the dipped adcluster model (DAM) combined with ab initio HF and MP2 calculations. In comparison with that on a Cu(100) catalyst studied previously, it is shown that the Cu–Zn site provides an easier reaction pathway for the rate-limiting step; the energy barriers are all lower and the dioxomethylene intermediate is more stable than that at the Cu–Cu site on a Cu(100) catalyst. The present results prove that the Cu–Zn site is the active site which cooperates with the Cu–Cu site to catalyze methanol synthesis. Electron transfer is the important factor in affecting the reactivity of the catalysts. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The hydrogenation of CO_2 to methanol on a Cu-based catalyst has been the subject of numerous investigations [1]. Currently, most attention has been directed at clarifying the reaction mechanism and the nature of the active site on the catalyst [2–17]. In order to answer some of these questions, a series of investigations has been performed for methanol synthesis using model catalysts such as Cu(100) [5–8], Cu(110) [10], Cu(111) and Zn vapor-deposited copper surfaces [11–13]. The advantage of the model system is that it can give fundamental insight in methanol synthesis as compared with the behavior of real Cu/ZnO catalyst.

Chorkendorff and co-workers have shown that methanol can be synthesized from H_2 and CO_2 on a clean Cu(100) surface [6–8]. Methanol is also synthesized from CO_2/H_2 mixtures on a clean polycrystalline Cu foil and Cu(110) single-crystal surface [9,10]. These authors suggested that the active site for methanol synthesis on real Cu/ZnO catalysts is metallic Cu. Recently, Nakamura and co-workers carried out a series of studies for methanol synthesis on Zn-deposited copper single-crystal samples [11–13]. They found that, when the Zn coverage is ~ 0.2, the Zn-deposited Cu(111) surface is highly reactive and promotes methanol synthesis by an order of magnitude. The turnover frequency of methanol with the model catalyst agreed with that measured on real Cu/ZnO catalyst under the same reaction conditions [12]. The Cu–Zn is supposed to be the active site for methanol synthesis [12,13]. Very recently, Morikawa et al. [18] reported a DFT periodic slab model study, in which an adsorbed Zn

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state on a model Zn/Cu(111) surface was suggested as a step towards understanding the role of Zn.

In a previous study [19], we reported a theoretical study on the reaction mechanism of the hydrogenation of CO_2 to methanol on a Cu(100) catalyst. It was shown that formate, dioxomethylene, formaldehyde, and methoxy are the main intermediates, and that hydrogenation of adsorbed formate to formaldehyde is the rate-limiting step in methanol synthesis. In this Letter, we report our studies for the active site in methanol synthesis by examining the reaction mechanism of the rate-limiting step on a Zn/Cu(100) catalyst.

The calculational methods are the same as that used previously [19], i.e., the dipped adcluster model

Fig. 1. Two-layer model clusters used in this study: (A) $Cu_8(6,2)$ cluster with the atoms 1–6 in the first layer, and 7 and 8 in the second layer; and (B) $Cu_7Zn_1(6,2)$ cluster with Zn at the bridge position of the first layer.

(DAM) [20–22] combined with ab initio Hartree–Fock (HF) and second-order Møller–Plesset (MP2) methods. The former $Cu_8(6,2)$ DAM cluster (Fig. 1A) is replaced by a Cu_7Zn_1 DAM cluster (Fig. 1B) to model the Zn/Cu(100) alloy catalyst. This cluster can model the Cu–Zn bridge site reasonably and has almost the same size as the $Cu_8(6,2)$ cluster; therefore, the results on a Zn/Cu(100) catalyst can be compared reasonably with those on a Cu(100) catalyst. The surface coverage of Zn is 0.167 in the Cu_7Zn_1 cluster model, which may correspond to the experimental value of 0.20 for the highly reactive Zn/Cu(111) surface [12]. Other details of the calculations are described elsewhere [19,23].

2. Results and discussion

In the previous study [19], the rate-limiting step in methanol synthesis from CO_2 and H_2 on Cu(100) surface is identified to be the hydrogenation of adsorbed formate to formaldehyde. Fig. 2 shows the energy diagrams of this step on a Zn/Cu(100) alloy catalyst in comparison with that on a clean Cu(100) catalyst. The energy diagrams are composed of two elementary steps: the hydrogenation of formate to dioxomethylene (step 1) and the hydrogenation of dioxomethylene to formaldehyde (step 2). The Cu–Cu site of the Cu(100) catalyst and the Cu–Zn site of the Zn/Cu(100) catalyst are responsible for these reaction steps, and the reaction mechanisms are essentially the same on both catalysts.

The differences between the two energy diagrams are evident. On a Cu(100) catalyst, the activation energy of step 1 is calculated to be 23 kcal/mol, and the formation of dioxomethylene is endothermic by 17.1 kcal/mol. The next step (step 2) has an activation energy of 17 kcal/mol. The experimental activation energy for the hydrogenation of formate on a Cu(100) surface was reported to be 19.6 kcal/mol [8]. The relatively large energy barriers in steps 1 and 2 and an unstable dioxomethylene intermediate at the Cu–Cu site indicate a slow reaction path, and explain the low activity of the clean Cu(100) catalyst. On the other hand, on a Zn/Cu(100) catalyst, the activation energy of step 1 is calculated to be 8.5 kcal/mol, and it is exothermic by 2.7 kcal/mol. The
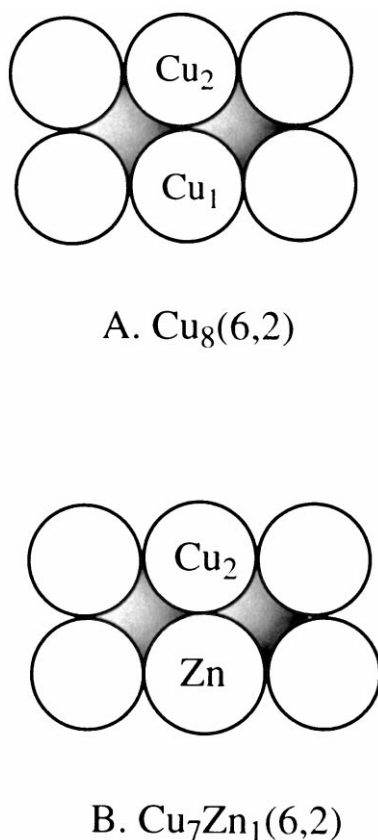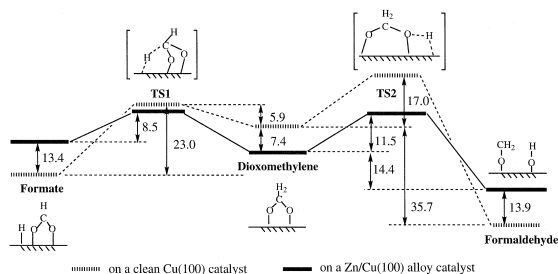
Fig. 2. Energy diagram of the hydrogenation of formate to formaldehyde on a model Zn/Cu(100) alloy catalyst (solid line) in comparison with that on a model Cu(100) clean catalyst (dashed line). Energies are in kcal/mol.

dioxomethylene intermediate formed at the Cu–Zn site is 7.4 kcal/mol more stable than that at the Cu–Cu site. It can be supposed that if formate adsorbs at the Cu–Zn site, the reaction leading to dioxomethylene would be much faster than that at the Cu–Cu site. The activation energy of step 2 at the Cu–Zn site is 11.5 kcal/mol, which is again lower than the 17 kcal/mol for the same reaction at the Cu–Cu site. All these results indicate that the Cu–Zn site on a Zn/Cu(100) catalyst cooperates with the Cu–Cu site to make the reaction easier and works as the active site for the hydrogenation of formate to formaldehyde, the rate-limiting step in methanol synthesis.

Another interesting feature of the results is that the formate and the formaldehyde species adsorbed at the Cu–Zn site are calculated to be less stable than that at the Cu–Cu site. Since the adsorbates prefer to occupy the most stable site on the surface, most of them will be adsorbed at the Cu–Cu site. The Cu–Cu site should play an important role in formate formation and in the reaction process of formaldehyde to methanol product. Indeed, these reaction steps are previously calculated to proceed much more easily than the rate-limiting step on a clean Cu(100) catalyst [19]. Formate can be easily formed at the Cu–Cu site and has been confirmed to be an intermediate in methanol synthesis by various studies [2–13]. It was also shown that the Cu–Cu site is active for hydrogen dissociation on the catalyst surface [1,3]. Therefore, the Cu–Cu site is very important for methanol synthesis [5–10].

The above results provide a clearly understandable reaction mechanism for methanol synthesis on Zn-deposited copper catalysts. CO_2 reacts with hydrogen on the catalyst to produce the adsorbed formate intermediate. Formate adsorbed at the Cu–Cu site can be hydrogenated into dioxomethylene with a relatively higher activation energy. On the Zn-deposited copper catalyst, the Cu–Zn alloy sites are formed by substitution of Zn atoms with the Cu surface atoms, as confirmed by the experimental STM images [24]. Since the dioxomethylene intermediate at the Cu–Zn site is more stable and reactive than that on the Cu–Cu site, formate on the Cu–Cu site will migrate onto the Cu–Zn site and is hydrogenated into dioxomethylene via a lower transition state. The hydrogenation of dioxomethylene to formaldehyde will proceed mainly at the Cu–Zn site because of the existence of a low-energy path. The formaldehyde product at the Cu–Zn site will then migrate back to the Cu–Cu site due to its higher stability. As a result, both the Cu–Zn and Cu–Cu sites are important and they cooperate with each other to realize high reactivity in methanol synthesis. The Cu–Zn site provides an active site for the rate-limiting step and hence enhances the activity of the catalyst. As pointed out previously [19], a key to enhance the overall reactivity in methanol synthesis is to design the catalyst which stabilizes the dioxomethylene intermediate and works to lower the energy barrier in the hydrogenation of formate. The Cu–Zn site on the Zn-deposited copper catalyst plays such a role and explains the high reactivity reported experimentally [11–13].

The electronic origin of the higher reactivity of Zn/Cu(100) catalyst as compared to Cu(100) catalyst is explained from the difference in the electronic properties of Zn and Cu. Since all the adsorbates are electron-withdrawing species, the charge transfer ability of the catalyst appears to be the main factor in affecting the reactivity. The Zn atom of the Zn/Cu(100) catalyst shows a different electronic state from the Cu atoms: though Cu is in a neutral metallic state, the Zn atom is almost in the ionic Zn^+ state. Therefore, Zn acts as an electron source and modifies the electronic properties of the catalyst to realize a larger charge-transfer ability. Table 1 shows that in the rate-limiting step, the adsorbates have larger negative charges on the Zn–Cu site than on the Cu–Cu site. This confirms that the Zn-deposited copper catalyst has larger charge-transfer ability.

Table 1

Mulliken charges of the adsorbates on the Cu–Cu and Zn–Cu sites of the Cu(100) and Zn/Cu(100) DAM clusters

State	Cu–Cu site			Zn–Cu site		
	adsorbates	Cu_1	Cu_2	adsorbates	Zn	Cu_2
Cluster[a]		+0.02	+0.02		+0.31	−0.11
Formate	−0.53	+0.12	+0.12	−0.53	+0.61	+0.04
TS1	−0.84	+0.14	+0.14	−0.94	+0.66	+0.06
Dioxomethylene	−1.00	+0.29	+0.11	−1.32	+1.12	+0.20
TS2	−0.78	+0.48	+0.18	−1.04	+1.12	+0.19
Formaldehyde	−1.16	+0.34	+0.19	−1.16	+0.81	+0.20

[a] $Cu_8(100)$ and $Zn/Cu_7(100)$ neutral clusters.

Such an effect becomes significant in the reaction steps and affects the reactivity of the catalysts towards methanol synthesis. The fact that the promoter modifies the electronic properties of the metal surface and hence affects the reactivity has been reported for the reactions of S_2 and O_2 with metallic Cu and Cu/ZnO by Rodriguez and co-workers [25,26]. It is also noteworthy that, in the rate-limiting reaction step, the O–Zn bond distance is calculated to be shorter than the O–Cu bond distance. The O–Zn interaction is then stronger than the O–Cu interaction, another difference of the Zn/Cu(100) catalyst in comparison with the Cu(100) catalyst. More details about the geometries and the electronic properties of the reaction species will be described elsewhere [23].

The present theoretical results support the proposal of Nakamura and co-workers [11–13] that the Cu–Zn site is an active site which cooperates with the Cu–Cu site to catalyze methanol synthesis. However, they attributed the role of Zn to be stabilization of the formate on the Cu–Zn site [12,27]. This is in contrast with our theoretical results which indicate that the formate is less stable at the Cu–Zn site. The reason for this difference is not clear at present. From the calculated energy diagrams shown in Fig. 2, two significant roles of Zn are apparent: one is to stabilize the dioxomethylene intermediate on the Cu–Zn site, and the other is to lower the activation energies both in the hydrogenation of formate and in the hydrogenation of dioxomethylene. The latter effect is more important in determining the reactivity of the catalyst surface.

The promotive effect of Zn was reported to be small on the Zn/Cu(100) and Zn/Cu(110) catalysts [13], but significant on the Zn/Cu(111) catalyst, and the Zn/Cu(111) catalyst has the largest reaction rate [13]. The results on the Zn/Cu(111) catalyst can be easily understood: since Cu(111) is the most inactive surface and a clean Cu(111) surface alone cannot catalyze methanol synthesis, the promotive effect on this surface should be most significant. From the view point of the surface structure, Cu(100) is more similar to Cu(111) than to Cu(110), so that the promotive effect of Zn for Cu(100) may also be evident but smaller than that for Cu(111).

Finally, the above results may provide a clue for catalyst design. Since both Cu–Zn and Cu–Cu sites are very important in methanol synthesis, and the Cu–Zn site mainly works to enhance the reaction of the rate-limiting step and the Cu–Cu site mainly responds for other reaction steps, the key point in catalyst design is to realize highly dispersed Cu–Zn and Cu–Cu sites, the latter site should be more abundant than the former one. It has been shown that the Zn–Zn site, which may be formed at high Zn coverage on the surface, plays no role in methanol synthesis [23]. Therefore, an active catalyst should have Zn atoms in a highly dispersed state. The reactivity of the catalysts may be very sensitive to the coverage of Zn on the surface [12,13], and further work is necessary for a deeper understanding.

3. Conclusions

In this study, we have clarified the role of the active site of Zn/Cu catalyst for methanol synthesis by studying the reaction mechanism of the hydro-

genation of formate to formaldehyde on a model Zn/Cu(100) catalyst using the dipped adcluster model combined with ab initio theoretical methods, and compared this with previous results on a clean Cu(100) surface.

The effect of Zn on a Zn/Cu(100) catalyst is to modify the rate-limiting step of the reaction and the roles are two-fold: one is to lower the activation energies of the hydrogenation reactions of formate and dioxomethylene, and the other is to stabilize the dioxomethylene intermediate at the Cu–Zn site. The role of the Cu–Zn site is then to enhance the reactivity of the adsorbed formate and dioxomethylene species, and so act as an active site in methanol synthesis.

The formate and formaldehyde species at the Cu–Cu site are more stable than that at the Cu–Zn site. Except for the rate-limiting step, other reaction steps relevant to methanol synthesis may proceed mainly on the Cu–Cu site. Therefore, for overall methanol synthesis both Cu–Zn and Cu–Cu sites are important and cooperate for smooth overall progress of the series of the reactions.

Electron transfer is an important key feature in this catalytic reaction process. All the adsorbates are anionic on the surface, and the role of Zn is to modify the electronic properties of the Zn/Cu(100) catalyst so as to realize larger electron transfer. This is the main factor which is responsible for the high reactivity of the formate and dioxomethylene on a Zn/Cu(100) catalyst.

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