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Catalysis Today 36 (1997) 39–44

CATALYSIS TODAY

A theoretical study for methanol synthesis by CO_2 hydrogenation

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Abstract

Ab initio MO calculations were carried out using the density functional method for the reaction intermediate of methanol synthesis by CO_2 hydrogenation. The energy change of the bridging-formate due to changing the Cu–Cu interatomic distance showed that the formate intermediate was formed at the neighboring Cu atoms and no significant difference was found in the stability of the copper crystal surface. The stability of the methanol synthesis intermediates with the atomic charge of Cu was also calculated. The stability of the formate and the formaldehyde intermediates increased as the total charge increased. The stability of the methoxy species was almost constant between a total charge of 0 to +0.4. There seems to be an appropriate value for the charge of the surface copper. On the other hand, the reverse water–gas shift reaction producing carbon monoxide occurred on the metallic copper. The calculation of the total atomic charge distributions on Cu/CuO and Cu/ZnO clusters showed that the cationic copper was located only on the boundary of Cu and the oxide. The number of active sites increased as much as the degree of dispersion of Cu and the oxide, and a high-performance catalyst is expected to be designed in such a manner.

Keywords: Ab initio MO calculations; CO_2 hydrogenation; Methanol synthesis; Cu/ZnO catalyst

1. Introduction

The methanol synthesis from CO_2 and H_2 has received considerable attention in recent years because of the global warming problem. It has been shown that Cu/ZnO catalysts are highly effective for this reaction. However, there is still much controversy about the nature of the active components and the mechanism of reaction that takes place on them. Recent advances in computer technology and the methodology of computer chemistry have enabled a significant advance in our understanding of one of the most basic chemical processes; elementary chemical reaction. In the previous paper [1], the authors have tried to calculated probable intermediates on the active components of the Cu/ZnO catalyst by ab initio molecular orbital calculations. It was found that the methanol synthesis proceeded mainly on the Cu^+ site as in Scheme 1.

First, CO_2 is linearly adsorbed on the Cu^+ site. The H atom, which is probably adsorbed on the metallic copper, attacks the C atom of the adsorbed CO_2 and a formate intermediate is formed. Then, H atoms attack the C and the O atoms of the formate species, and the C–O bond is broken simultaneously. A formaldehyde-type intermediate is formed on the Cu^+ site. The H^- on Zn, which is adsorbed on ZnO as a result of the heterogeneous dissociation of H_2, attacks

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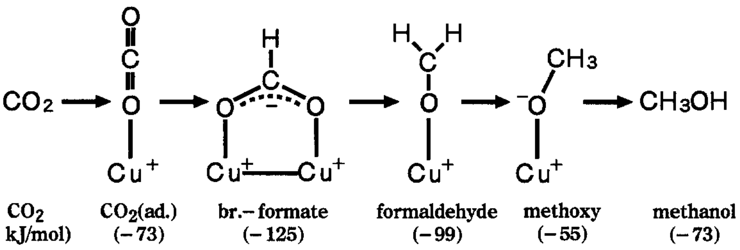
PII S0920-5861(96)00194-0



Scheme 1. CO_2 hydrogenation mechanism on Cu/ZnO catalyst proposed by ab initio MO calculations. The values in parentheses are relative energies in kJ/mol.

the C atom of the formaldehyde-type species, and a methoxy intermediate is formed. Furthermore, the H^+ on the O atom of ZnO attacks the O atom of the methoxide, and finally, methanol is produced. All the relative energies of these intermediates were lower than that of the reactant system. Moreover, the required energies of each elementary step were under 44 kJ/mol, and this route seems to proceed with ease.

In this paper, the authors have tried to elucidate the stability of reaction intermediates for different crystal surfaces of copper and different charges of reaction site. Furthermore, the authors have calculated the atomic charge distributions of Cu/CuO and Cu/ZnO model surfaces for the purpose of high-performance catalyst design.

2. Method of calculations

The CPU power of computers and the methodology of computer chemistry have rapidly advanced in recent years. However, it is still difficult to study theoretically the reaction mechanism on heterogeneous surfaces including metals or metal oxides by the first principle quantum chemistry because of the complexity of reaction mechanisms and difficulty of surface modeling. For this reason, we have to divide the catalytic reaction into two parts, the mechanism of reaction on the reaction site which should be as small as possible and the electronic state of the model clusters to lower the activation energy of the reaction and to promote the objective reaction.

A number of reaction intermediates can be considered for CO_2 hydrogenation, and several sites are possible on the Cu/ZnO surface. In the our previous paper [1], the authors have considered twenty intermediate species and tried to identify them by ab initio MO calculations, using the Gaussian 92 program (1992, Gaussian, Inc.). It was found that the bridging-formate, formaldehyde, and methoxy intermediates were important for the methanol synthesis. In this paper, the authors have tried to calculate the stability of these intermediates and the charge distributions of Cu/CuO and Cu/ZnO clusters using the density functional method.

All calculations were performed by a local method using VWN (Vosko–Wilk–Nusair) functionals [2]. The authors used a DNP basis set, which is a double-numerical quality basis set with polarization functions. The mesh, which controls the selection of mesh points for numerical integration, was FINE and LMAXs, which specify the maximum angular momentum of the multipolar fitting functions, were 3 for C, O, and Cu, and 2 for H. The 1s, 2s, and 2p orbitals for Cu, and the 1s orbitals for C and O were treated as frozen core orbitals and were removed from the molecular orbital expansions and also from the self-consistent procedures. The program used for the calculations was D-Mol Ver. 2.2 (1992, Biosym Technologies Inc., San Diego) with the HP-9000/735 and 755 workstations.

3. Results and discussion

There are various surfaces on copper crystals. For example, the Cu atom on (111) surface adjoins six surface atoms and three atoms in the inner layer. The interatomic distance of Cu is 2.56Å for the neighboring atoms. The Cu atom on (100) surface adjoins four surface atoms at a distance of 2.56Å and the second nearest neighboring atoms are located 3.26Å from the atom at the center. The bridging-formate intermediate links two Cu atoms and the stability can change as a function of the Cu–Cu interatomic distance, to clarify the stability of the bridging-formate species as a different copper surface, the distance between the Cu–Cu atoms was fixed at 2.0–3.6Å and other geometrical parameters were optimized. Fig. 1 shows the fully optimized geometry of the bridging-formate intermediate. The Cu–Cu distance was 2.490Å, which was slightly shorter than that of the metallic copper (111) surface. Fig. 2 shows the structural change due to changing the Cu–Cu interatomic distance. As the Cu–Cu distance increased from 2.0Å to 3.6Å, the Cu–O distance decreased slightly from 1.86Å to 1.81Å. The C–O and the C–H distances and the OCO angle did not change largely, and there was no drastic change in the geometry. The energy change due to changing the geometry is shown in Fig. 3. In this figure, the relative energy means the energy relative to the energy of r(Cu–Cu) = 2.560Å.

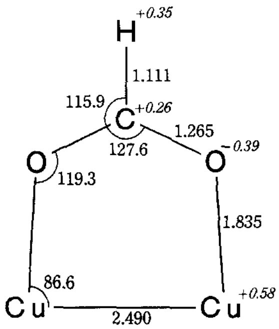


Fig. 1. Full-optimized geometry of bridging-formate intermediate. Bond distances are in angstroms and angles in degrees. Italic values are total atomic charges.

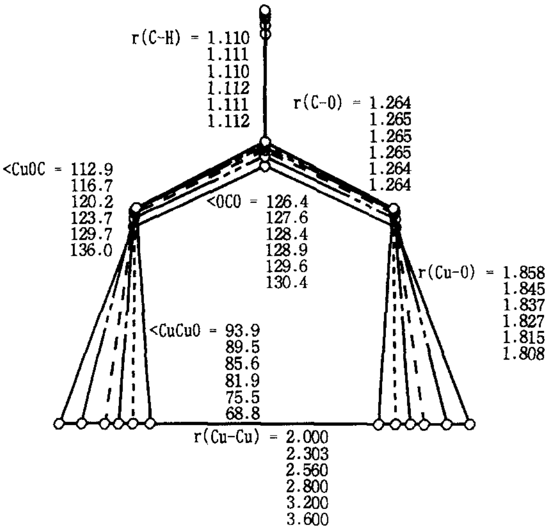


Fig. 2. Geometry change of bridging-formate intermediate due to changing Cu–Cu interatomic distance.

The diatomic cation, Cu_2^+, was the most stable at r(Cu–Cu) = 2.303Å and became less stable by increasing r(Cu–Cu). The r(Cu–Cu) of the most stable formate intermediate was 2.490Å, which was the bond distance of the full-optimized geometry. It was more stable than that of r(Cu–Cu) = 2.560Å by 0.3 kJ/mol; however, the stability of the intermediate did not change very much compared with the change of the Cu_2^+. That is to say, the bridging-formate intermediate was formed at the neighboring Cu atoms and there was no significant difference in the stability of copper crystal surfaces.

The optimized geometries of the formaldehyde and the methoxy intermediates associated with methanol synthesis are shown in Fig. 4, together with the optimized geometries of the carboxyl and the formyl intermediates, which seemed to be associated with the reverse water–gas shift reaction. To clarify where on the copper surface these intermediates and the formate intermediate were easily formed, the authors tried to optimize the geometries by changing the total charge from 0 to +1 and calculated the energies. Because the formate intermediate contains two Cu atoms, the total charge was changed from 0 to +2. In order to neglect the energy

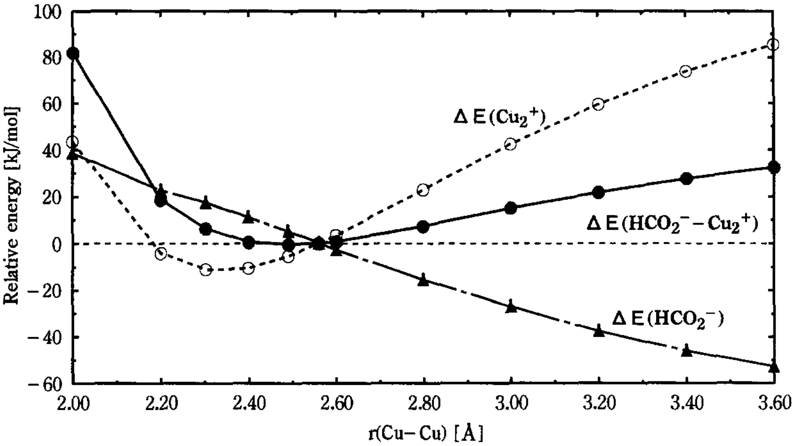


Fig. 3. Relative energy change of bridging-formate intermediate due to changing Cu–Cu interatomic distance.

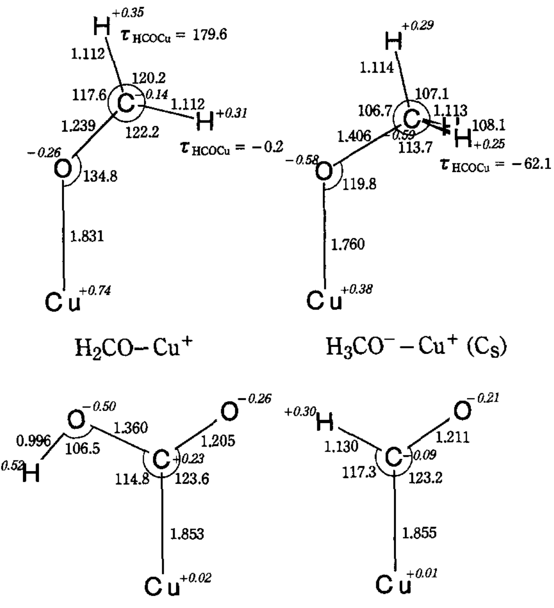
change of the copper, the relative energies were defined as follows:

$$\Delta E = \left[E(\mathrm{HCO_2 - Cu_2^{2n+}}) - \mathrm{E}(\mathrm{HCO_2 - Cu_2^{2+}})\right] - \left[E(\mathrm{Cu_2^{2n+}}) - E(\mathrm{Cu_2^{2+}})\right],$$

for the formate intermediate and

$$\Delta E = \left[E(\mathrm{CH_xO - Cu^{n+}}) - E(\mathrm{CH_xO - Cu^{+}})\right] - \left[E(\mathrm{Cu^{n+}}) - E(\mathrm{Cu^{+}})\right],$$

for the other intermediates. The relative energies of the intermediates as a function of the total charge are shown in Fig. 5. The stability of the formate (HCO_2) and the formaldehyde (H_2CO) intermediates increased as the total charge, n, increased. It suggested that these species were easily formed on cationic copper. The stability of the methoxy (H_3CO) intermediate was almost constant between $n = 0$ and $+0.4$ at a value of -13 kJ/mol. This species became slightly unstable by increasing n. There seemed to be an appropriate value for the charge of surface copper. It was not inconsistent with the experimental results [3], in which a maximum activity of the methanol production was obtained at an oxygen coverage of 0.18. The carboxyl (HOOC) and the formyl (OHC) intermediates, which seem to be associated with the reverse water–gas shift reaction producing carbon monoxide, became unstable by increasing the total charge. When $n = 0$, the relative energies of the carboxyl and the formyl intermediates were -48.5 and -17.6 kJ/mol, respectively. These intermediates were more stable on the metallic copper than on the cationic copper and it seems that the reverse water–gas shift reaction occurred on the metallic copper. This result is consistent with Cambell's experimental result [4].



$H_2CO–Cu^+$ $H_3CO^-–Cu^+$ (C_S)

$HOOC–Cu^0$ (C_S) $OHC–Cu^0$ (C_S)

Fig. 4. Optimized geometries of formaldehyde, methoxy, carboxyl, and formyl intermediates. Bond distances are in angstroms and angles in degrees. Dihedral angles, τ, are defined as positive clockwise. Italic values are total atomic charges.

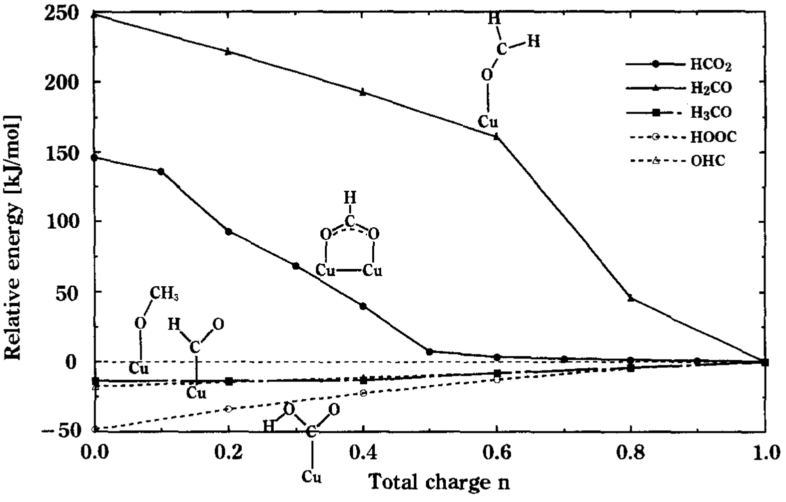
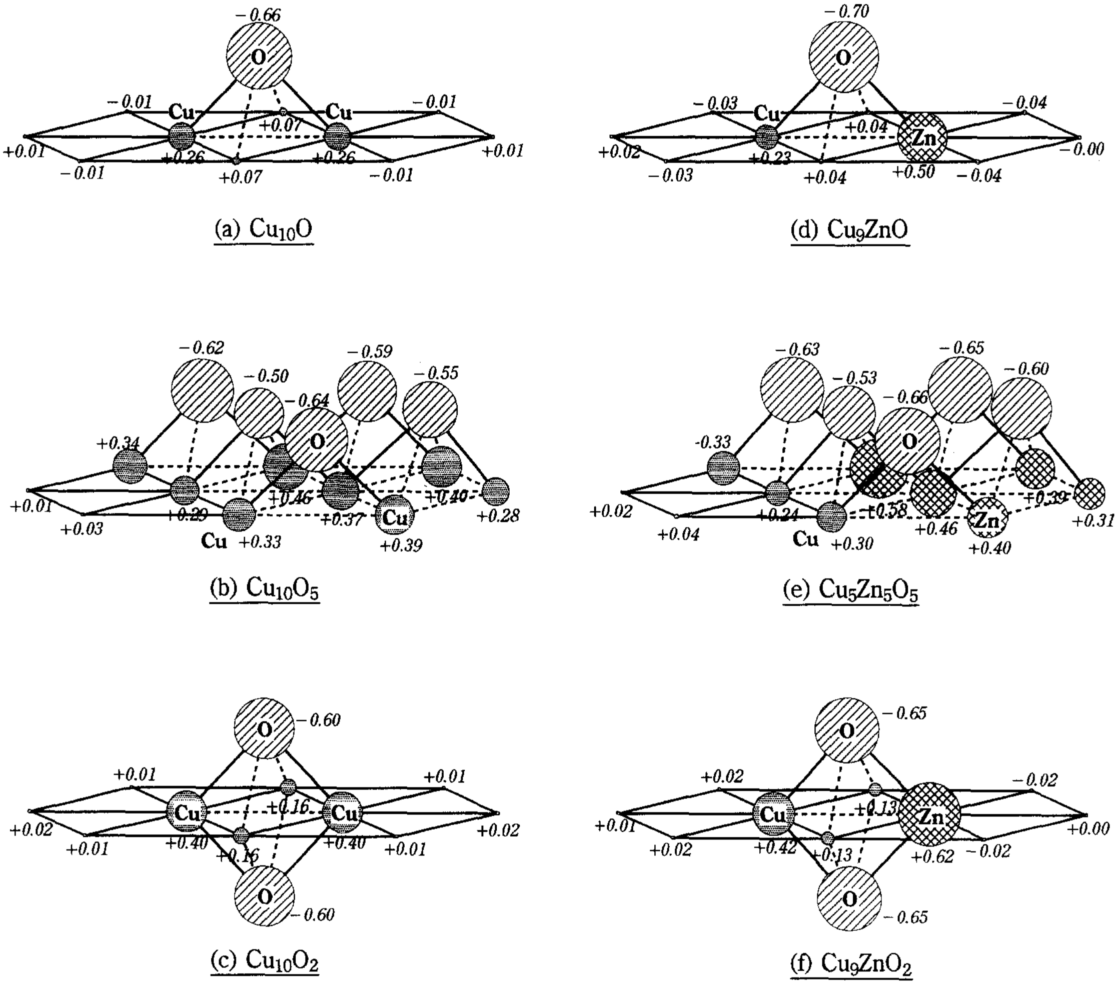


Fig. 5. The stability of reaction intermediates as a function of total charges.



(a) $Cu_{10}O$

(d) Cu_9ZnO

(b) $Cu_{10}O_5$

(e) $Cu_5Zn_5O_5$

(c) $Cu_{10}O_2$

(f) Cu_9ZnO_2

Fig. 6. Total atomic charge distributions on Cu/CuO and Cu/ZnO clusters.

The formate and the formaldehyde intermediates were more stable because of the large positive total charge and the methoxy intermediate was stable between $n = 0$ and $+0.4$. Because these intermediates seemed to be associated with methanol synthesis, the charge of copper was appropriate at about $+0.4$. Furthermore, the CO production by the reverse water–gas shift reaction seemed to occur on metallic copper, and an appropriate charge of copper seemed to enhance the production rate and the selectivity for methanol. In order to ascertain which site had an appropriate charge, the authors calculated the atomic charge distributions of Cu/CuO and Cu/ZnO cluster models. The atomic charge distributions are shown in Fig. 6. First, ten copper atoms were located in a monolayer with a close-packed structure and one oxygen atom was added to this Cu_{10} layer (a). In this process, ten Cu atoms were fixed and only the location of the O atom was optimized. The two Cu–O bond lengths were both 1.784Å and the two Cu · · · O lengths were both 2.540Å. Only the Cu atom bonded to the O atom had a positive charge of $+0.26$ and the other Cu atoms were almost neutral. Furthermore, four more oxygen atoms were introduced into this cluster, which is a model of Cu_5–$(CuO)_5$. The charge of oxygen atoms was $-0.5 \sim -0.6$ and that of the copper atoms of the CuO was $+0.3 \sim +0.5$. In the Cu_5, only a half of the Cu atoms, i.e., those on the boundary of Cu–CuO, had a positive charge of about $+0.3$ and the other Cu atoms were metallic. Two oxygen atoms were added to the Cu_{10} layer on both sides (c). The Cu atoms bonded to the oxygen atoms had a positive charge of $+0.40$ and the Cu atoms weakly bonded to the oxygen atoms were slightly cationic, $+0.16$. The other Cu atoms which were not linked to the oxygen atoms were neutral. The total atomic charge distributions of these three Cu/CuO clusters showed that only the Cu atoms in the narrow region of Cu/CuO boundary were cationic. The CuO was exchanged with ZnO and the charge distributions were calculated in the same manner (d) ~ (f). Similarly the Cu atoms adjacent to ZnO had a positive charge of $+0.2 \sim +0.4$ and the other Cu atoms were metallic.

The formate and the formaldehyde intermediates were more stable, having a large positive charge, and the methoxy intermediate was stable between 0 and $+0.4$. The methanol synthesis seemed to occur on the boundary of Cu and CuO or ZnO. The number of active sites increased in the same degree as the dispersion of Cu and oxides, and a high-performance catalyst is expected to be designed in such a manner. No difference between Cu/CuO and Cu/ZnO have not been found; however, the dynamic stability of the catalyst surface will have to be studied with larger models.

Acknowledgements

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

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