

Why Is Formate Synthesis Insensitive to Copper Surface Structures?

Guichang Wang,[†] Yoshitada Morikawa,^{‡,§} Taketoshi Matsumoto,[⊥] and Junji Nakamura^{*,#}

Department of Chemistry, and Center of Theoretical Chemistry Study, Nankai University, Tianjin, 300071, P. R. China, The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Osaka, 567-0047, Japan, Research Institute for Computational Sciences (RICS), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki, 305-8568 Japan, Institute for Molecular Science, Nishigonaka 38, Myodaiji, Okazaki 444-8585, Aichi, Japan, and Institute of Materials Science, University of Tsukuba, Tennoudai 1-1-1, Tsukuba, Ibaraki 305-8573, Japan

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Experiments have revealed that formate synthesis from carbon dioxide and hydrogen is structure insensitive to copper catalyst surfaces, while the reverse formate decomposition reaction is structure sensitive. The present ab initio density functional theory (DFT) calculations show that the reaction of CO₂ with surface atomic hydrogen initially leads to the formation of unstable monodentate formate, which has similar adsorption energies on Cu(111), Cu(100), and Cu(110). The structure of the transition state is similar to that of monodentate formate. It is also shown that gaseous CO₂ is directly reacted with surface hydrogen, as suggested by previous experiments. The position of the similar transition state and the direct reaction mechanism well explain the similar energetic pathways, that is, the structure insensitivity.

Usually the kinetics of catalytic or surface reactions at metal surfaces depends on the surface structure. However, in some cases, the reaction rates stay the same regardless of the surface structure, and these are called “structure-insensitive reactions”.¹ Without detailed kinetic analysis or theoretical study, it is very difficult to understand why reactions are structure insensitive. It has been experimentally observed that the synthesis of formate from CO₂ and H₂ (CO₂ + 1/2 H₂ → HCOO_a) is structure insensitive to copper surfaces, while the reverse reaction of formate decomposition is structure sensitive.² That is, the reaction rates for formate synthesis and the activation energies are very similar among Cu(110), Cu(100), and Cu(111), while the reverse reaction of formate decomposition on copper shows different activation energies. The question is why the forward reaction is structure insensitive, while the backward reaction is structure sensitive. Concerning the question, we found a unique kinetic feature. That is, the hydrogen pressure dependence of the initial rate of formate synthesis, r , is as follows:

$$r = kP_{\text{H}_2}^{1/2}P_{\text{CO}_2}/(1 + k'P_{\text{H}_2}^{1/2})$$

where k and k' are rate constants, and P_{H_2} and P_{CO_2} are the pressures of H₂ and CO₂, respectively.² The denominator (1 + $k'P_{\text{H}_2}^{1/2}$) is the hindrance factor for adsorption of H₂ and CO₂ by major surface species of atomic hydrogen. The first order in

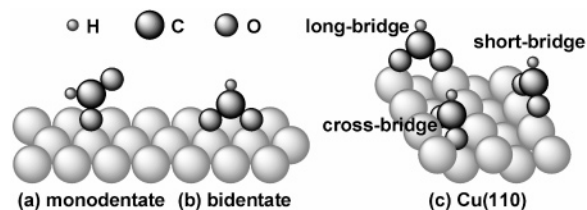


Figure 1. Side view of the structure of HCOO in (a) monodentate form and (b) bidentate form. (c) Possible adsorption sites of the bidentate HCOO onto the Cu (110) surface.

the denominator means that an increase in H₂ pressure (or hydrogen coverage) hinders H₂ adsorption, but does not hinder the adsorption of CO₂, suggesting that CO₂ reacts directly with a surface hydrogen atom without passing through the adsorption state of CO₂ on Cu. If this is correct, the mechanism can be an Eley–Rideal (E–R) type, in which gaseous CO₂ reacts with hydrogen atoms. This may be responsible for the observed structure insensitivity of formate synthesis. The purpose of the present study using ab initio density functional theory (DFT) calculations is to clarify the reason for the structure insensitivity of the formate synthesis as well as to clarify the possibility of the proposed mechanism of the direct reaction of CO₂ with surface hydrogen.

Formate species adsorbed on copper surfaces have two different adsorption forms, monodentate and bidentate, as shown in Figure 1a,b. In bidentate formate, both oxygen atoms are bound to copper atoms, whereas, in the monodentate form, only one oxygen atom is bound to the copper. There are three different sites for the adsorption of the bidentate formate, as shown in Figure 1c, which are designated as short-bridge, cross-bridge, and long-bridge sites.

* Corresponding author. Tel./Fax: +81-29-853-5279. E-mail: nakamura@ims.tsukuba.ac.jp.

[†] Nankai University.

[‡] Osaka University.

[§] National Institute of Advanced Industrial Science and Technology (AIST).

[⊥] Institute for Molecular Science.

[#] University of Tsukuba.

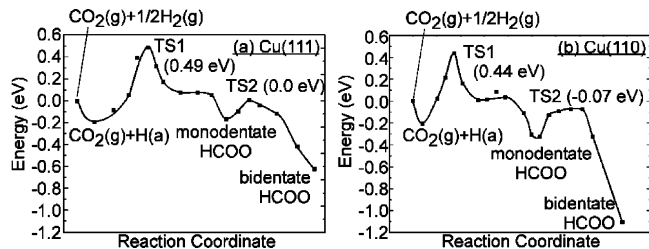


Figure 2. Reaction coordinates for HCOO synthesis and decomposition on (a) a Cu(111) surface and (b) a Cu(110) surface, respectively.

We first calculated adsorption energies for the bidentate formate adsorbed on three different sites and for the monodentate formate on Cu(110), Cu(100), and Cu(111). In agreement with previous experimental³ and cluster model⁴ works, present slab calculations show that a bidentate structure is preferred. Relative adsorption energies for bidentate formate on the three Cu surfaces decrease in the order (110), 1.20 eV > (100), 0.93 eV > (111), 0.69 eV. A significant surface structure effect is thus observed for the adsorption energy of bidentate formate. The monodentate formate is found to be the most unstable, with a low adsorption energy that does not differ much between the three surfaces.

After confirming that the calculated adsorption energies of formate agree with the experimental data as described above, detailed reaction path calculations for formate synthesis on Cu(111) and Cu(110) were carried out in order to examine the structure insensitivity. Figure 2 shows the energy diagram for the formate synthesis on Cu(111) and Cu(110), where a CO₂ molecule approaches the adsorbed hydrogen and reacts with it directly, that is, an E-R-type mechanism. The apparent activation energy of the formate synthesis corresponds to the barrier from the CO_{2,g} and H_a states to the transition state (TS1) in Figure 2. That is because, at the experimental reaction condition of 323–353 K under atmospheric pressure, the steady-state hydrogen coverage is estimated to be close to saturation, while the CO₂ coverage was negligibly small due to its small adsorption energy.² The activation energy for the decomposition of bidentate formate can also be obtained from the difference between TS1 and the bidentate formate state. The calculated activation energies for the formate synthesis, E_{syn} , 0.69 eV on Cu(111) and 0.64 eV on Cu(110), are in agreement with those obtained experimentally, 0.58 eV on Cu(111) and 0.62 eV on Cu(110).² The calculated results thus reproduced the structure-insensitive character of the formate synthesis. For the decomposition of bidentate formate, the calculated activation energies, E_{dec} , of 0.97 eV on Cu(111) and 1.44 eV on Cu(110) are close to the experimental data of 1.12 eV on Cu(111) and 1.50 eV on Cu(110).² The calculated results clearly reproduce the experimental results in which the activation energies of formate decomposition are significantly different between Cu(111) and Cu(110), that is, they exhibit a structure-sensitive character.

The adsorption energies of bidentate formate on Cu(111), Cu(100), and Cu(110) were also estimated from experimental data, $E_{\text{dec}} - E_{\text{syn}} + E_{\text{H}}$, and these are close to those obtained by the present DFT calculations, but not to those obtained by the cluster calculations (Table 1). The overall agreement between the calculated and experimental results for the adsorption energy as well as the activation energy gives assurance that detailed analysis of the reaction path using DFT calculations is reliable.

The present DFT calculations thus reproduce the *structure-insensitive* and *structure-sensitive* features of the synthesis and decomposition of bidentate formate, respectively. We then examined why the structure sensitivity is different between the

TABLE 1: Comparison of Experimental and Theoretical Formate Adsorption Energies on Cu Surfaces

copper	adsorption energy of Bi-HCOO (eV)		
	expt [2] ($E_{\text{dec}} - E_{\text{syn}} + E_{\text{H}}$) ^a	this work	cluster model ^b
Cu(111)	0.74	0.69	0.34
Cu(100)	1.22	0.93	1.12
Cu(110)	1.08	1.20	1.77

^a E_{dec} and E_{syn} are the apparent activation energies for the formate decomposition and the formate synthesis, respectively. ^b From ref 5.

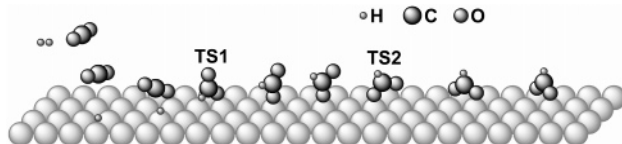


Figure 3. Calculated snapshot of structural changes of intermediates in the conversion of CO_{2,g} + H_{2,g} to bidentate formate on Cu(111).

forward and backward reactions for the synthesis of bidentate formate. Figure 2 reveals that the energy change from CO_{2,g} + 1/2 H_{2,g} to monodentate formate through TS1 is similar for Cu(111) and Cu(110), indicating that the forward and backward reactions from CO_{2,g} + 1/2 H_{2,g} to monodentate formate are structure insensitive in terms of activation energy. On the other hand, the conversion of bidentate formate to monodentate formate is structure sensitive because of the significant difference in the adsorption energies of bidentate formate between Cu(111) and Cu(110). The synthesis and decomposition of bidentate formate on Cu(111) thus consists of a structure-insensitive process through TS1 and a structure sensitive process through TS2. The present study thus indicates that the bidentate formate is not formed directly from CO_{2,g} + 1/2 H_{2,g}, but rather via monodentate formate. Accordingly, the strange feature of the observed different structure sensitivity for the forward and backward reactions is ascribed to the presence of unstable monodentate formate. Monodentate formate has been detected on Cu(110) by IRAS at 200 K, and this converts to bidentate formate at 300 K.⁶

The next question is why the formate synthesis is structure insensitive. Figure 3 shows a calculated snapshot for the structural changes of the intermediates during the conversion of CO_{2,g} + H_a to bidentate formate. Note that the reaction takes place via the E-R type mechanism, and the snapshot is obtained with the calculation results shown in Figure 2. To explain the structure insensitivity, it needs to be determined why overcoming the energy barrier from the CO_{2,g} + H_a state to TS1 (Figure 2) is structure insensitive. While climbing the barrier to TS1, the carbon atom located in the center of the CO₂ molecule directly attacks a hydrogen atom on a Cu site, while one of the oxygen atoms in the CO₂ attaches to the nearest neighboring Cu atom (Figure 3). The distance to the nearest neighboring Cu atoms is identical on Cu(111), Cu(100), and Cu(110). The orientation of the CO₂ approaching the hydrogen atom, or climbing the barrier, is thus independent of the copper surface structure. Also, it is important that the position of TS1 is identical on any copper surface. The structure of TS1 is similar to that of monodentate formate with adsorption energies independent of copper surface structures, giving an identical energy potential at TS1. It is concluded that the structure insensitivity of the formate synthesis is ascribed to (i) the direct reaction of CO₂ with atomic hydrogen and (ii) a transition state that is similar to the monodentate formate in molecular structure.

The E–R-type mechanism can be a nonadiabatic process, in which the translational or vibrational energy of CO₂ is used to overcome the transition barrier without losing energy by being trapped in the adsorbed state of CO₂ and being equilibrated to the surface temperature. Because the energy level of the lowest unoccupied molecular orbital (LUMO) in CO₂ molecules decreases upon bending the O–C–O axis,⁷ charge transfer from hydrogen to the LUMO may take place by vibrational excitation of CO₂, as suggested by the organometallic chemistry in the synthesis of monodentate formate from CO₂ and the Cu–H of a CuH(PH₃)₂ complex.⁸ Bending of the O–C–O axis is also seen in TS1 in Figure 3.

In summary, the DFT-GGA calculations reproduce the structure-insensitive and structure-sensitive features of formate synthesis and formate decomposition, respectively. The structure insensitivity is ascribed to (i) the direct reaction of CO₂ with atomic hydrogen, in which a CO₂ molecule reacts directly with adsorbed hydrogen without first requiring adsorption of CO₂ and (ii) a transition state similar to the monodentate formate in molecular structure. The two factors are independent of the copper surface structure, giving a structure-insensitive energetic pathway from CO_{2,g} + 1/2 H_{2,g} to monodentate formate.

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Supporting Information Available: Calculation procedure and adsorption energy of formate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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