Catalytic Reactions on a Metal Oxide Single Crystal: Switchover of the Reaction Paths in Formic Acid Decomposition on TiO₂(110)

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Chemistry on well-defined surfaces of metal oxides has recently attracted attention in surface science and catalysis communities. It has been demonstrated that local coordination environments around cations control the reactions of formates[1] and acetates[2] on faceted TiO₂(001) surfaces. Previous studies, however, have been focused on characterization of adsorbates and their non-catalytic reactions under vacuum. Few pioneering works examined catalysis over metal oxide single crystals.[3,4] We have studied here the catalytic decomposition reaction of formic acid on a TiO₂(110) surface in a steady state, to provide better understanding of the traditional acid–base concept in light of the microscopic structure of reaction sites. The acid–base property is one of the most important characteristics of metal oxides in view of their catalytic application for industry. The selectivity in the decomposition reaction of formic acid has been used to scale the acid–base character: dehydration to CO and D₂O over acidic oxides and dehydrogenation to CO₂ and D₂ over basic oxides.[5]

A TiO₂(110) surface exposed to formic acid exhibited a (2 × 1) LEED pattern at 300 K.[6] The results of XPS and UPS revealed that formates ordered on the (2 × 1) surface:[7]

$$DCOOD(g) + O_s \rightarrow DCOO(a) + O_sD(a) \quad (1)$$

where O_s is an oxygen atom of the substrate. Figure 1 illustrates a model of the (2 × 1) formate overlayer, where all the exposed Ti⁴⁺ cations are coordinated by bridge formates. The ridges of oxygen atoms on TiO₂(110) are able to arrange the formates in rows along the [001] direction.

A pressure jump method was adopted to measure the rate of the catalytic reaction in a steady state. When the crystal maintained at a reaction temperature is inserted into a narrow stream of DCOOD down a capillary doser, reaction starts on the surface to give a jump in product pressure. The jump height correspond to the formation rate of products. The contribution of sample holding materials is to be canceled.

Four products, CO, D₂O, CO₂, and D₂, were detected above 450 K. Figure 2 shows typical Arrhenius plots of the rates in turnover frequency (TOF),[8] r_{CO}, r_{D_2O}, r_{CO_2}, and r_{D_2}, at 1×10^{-3} and 5×10^{-5} Pa of DCOOD. The dehydration rates, r_{CO} and r_{D_2O}, were balanced and increased with temperature to saturated values. The saturation temperature shifted higher with increasing pressure. The activation energy was determined to be 120 ± 10 kJ/mol in the linear region. These results reproduce those on TiO₂ powder catalysts.[9]

On the other hand, TDS results showed that the formates on TiO₂(110) decomposed at 570 K under vacuum to give reaction-limited peaks of CO, D₂O, CO₂, D₂, and DCOOD (CO:D₂O:
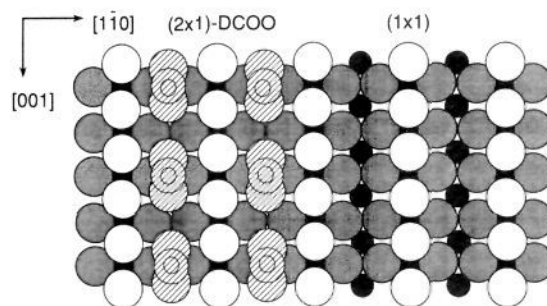
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Figure 1. Models for the TiO₂(110) (1 × 1) and the TiO₂(110) (2 × 1) DCOO surfaces. Open and shaded circles, O²⁻; filled circles, Ti⁴⁺; hatched circles, bridge formate. Hydroxyl groups are not shown.
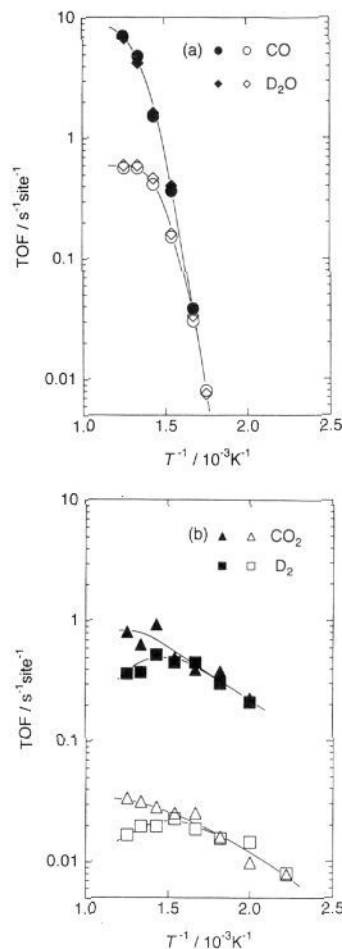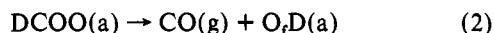

Figure 2. Rates for the formation of (a) CO and D₂O and (b) CO₂ and D₂ in catalytic decomposition of formic acid on TiO₂(110) at different DCOOD pressures; filled symbols at 1×10^{-3} Pa, open symbols at 5×10^{-5} Pa.

CO₂:D₂:DCOOD = 16:5:11:6:7). This event obeyed first-order kinetics, indicating that the decomposition is a unimolecular reaction of formate. The activation energy and the preexponential factor for the decomposition step were determined to be 120 ± 10 kJ/mol and $2 \times 10^{9 \pm 1}$ s⁻¹, respectively, by changing the heating rate between 0.5 and 4 K/s in a series of TDS measurements. The activation energy observed by TDS agrees with that for the steady-state dehydration reaction. We thus conclude that the catalytic dehydration reaction proceeds by the unimolecular decomposition of surface formate.
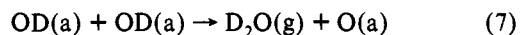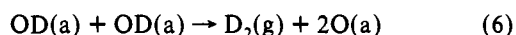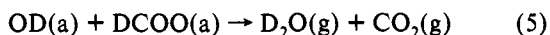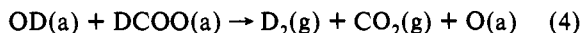
Here, the rate-limiting step of the catalytic unimolecular decomposition must preferentially yield CO and hydroxyl group,

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$$DCOO(a) \rightarrow CO(g) + O_fD(a) \qquad (2)$$

where O_f represents an oxygen atom of formate origin. If CO_2 and D_2 were also direct products of step **2**, then r_{CO_2} and r_{D_2} would increase with reaction temperature with an activation energy idential to that for the dehydration. This is not the case. The origin of D_2O, CO_2, D_2, and DCOOD observed in TDS is likely addressed to successive reactions tirggered by the liberated O_fD,

$$OD(a) + DCOO(a) \rightarrow DCOOD(g) + O(a) \qquad (3)$$

$$OD(a) + DCOO(a) \rightarrow D_2(g) + CO_2(g) + O(a) \qquad (4)$$

$$OD(a) + DCOO(a) \rightarrow D_2O(g) + CO_2(g) \qquad (5)$$

$$OD(a) + OD(a) \rightarrow D_2(g) + 2O(a) \qquad (6)$$

$$OD(a) + OD(a) \rightarrow D_2O(g) + O(a) \qquad (7)$$

In the steady states, $O_sD(a)$ is continually provided by step **1** to react with the $O_fD(a)$,

$$O_sD(a) + O_fD(a) \rightarrow D_2O(g) + O_s \qquad (8)$$
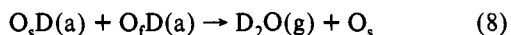
Thus, the three steps **1**, **2**, and **8** compose a catalytic dehydration cycle. When **1** and **8** are fast enough, the cycle selectively works. With increasing reaction temperature, step **2** becomes so fast that the overall rate is controlled by a short supply of DCOOD. Indeed, a positive order of 0.8 ± 0.2 with respect to DCOOD pressure (10^{-3}–10^{-6} Pa) was observed on the saturated rates of the dehydration.

The catalytic dehydrogenation path was also found on $TiO_2(110)$, as shown in Figure 2b. The activation energy was determined to be 15 ± 5 kJ/mol below 650 K. Note that the dehydrogenation rates deviated from straight lines at elevated temperatures. The negative deviations are ascribed to the decreasing coverage of formates, where step **2** is so fast that the coverage goes down with temperature. The dehydrogenation reaction is thus suggested to proceed through the surface formates. One may point out that r_{CO_2} was not balanced with r_{D_2} in the deviated region. The oxidative dehydrogenation reaction coupled to the reduction of the substrate,

$$DCOOD + O_s \rightarrow CO_2 + D_2O \qquad (9)$$
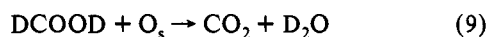
could be responsible for the excess production of CO_2 at the high temperatures.

A reaction order of 0.9 ± 0.1 was observed on r_{D_2} and r_{CO_2} with respect to DCOOD pressure at 600 K, at which temperature formates nearly covered the surface. This strongly suggests that the DCOOD molecule physisorbed or in the gas phase also participates in the dehydrogenation process. Thereby, we propose a bimolecular reaction of a formate and a DCOOD molecule for the catalytic dehydrogenation:

$$DCOO(a) + DCOOD(g/a) \rightarrow$$
$$D_2(g) + CO_2(g) + DCOO(a) \qquad (10)$$
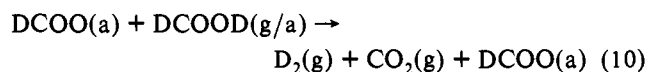
where the acidic D atom of the $DCOOD(g/a)$ molecule reacts with the D atom of $DCOO(a)$. A numerical simulation based on the competitive process of **10** and the dehydration cycle reproduced the observed kinetics.[7] The participation of the DCOOD molecule promotes a new reaction path, in contrast to the break of a C–O bond in the unimolecular dehydration step **2**. A bimolecular reaction of a formate with an impinging molecule was proposed in the dehydrogenation of formate on polycrystalline ZnO and MgO.[10] In the water–gas shift reaction on MgO,[11] ZnO,[12] and CeO_2[13,14] catalysts, the reactivities of formate intermediates are drastically affected by coadsorbed water to yield dehydrogenated products.

$TiO_2(110)$ favors the dehydrogenation below 600 K, contrasting to previous reports on TiO_2 powder catalysts.[5] The participation of a DCOOD molecule switches the reaction path of a formate from dehydration to dehydrogenation, accompanied by a decrease in activation energy. The reason why the bimolecular dehydrogenation has not been observed on the powder catalysts could be related to the structure-sensitive character of the reaction and/ or the more condensed formate adlayers in high-pressure conditions. Further studies on other surfaces and other oxides will help us to address this point. The observed switchover of the reaction paths indicates that the microscopic mechanism at working surfaces controls the acid–base catalysis of metal oxides besides the simple intrinsic acid–base character at static surfaces.

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