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The Mechanism for the Selective Oxidation of CO Enhanced by H_2O on a Novel PROC Catalyst

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Abstract Preferential oxidation (PROX) reaction of CO in H_2 catalyzed by a new catalyst of $FeO_x/Pt/TiO_2$ (Fe: Pt: TiO_2 = 100: 1: 100) was studied by dynamic in-situ DRIFT-IR spectroscopy. The oxidation of CO is markedly enhanced by H_2 and H_2O, and the enhancement by H_2/D_2 and H_2O/D_2O takes a common hydrogen isotope. Dynamics of DRIFT-IR spectroscopy suggests that the oxidation of CO with O_2 in the absence of H_2 proceeds via bicarbonate intermediate. In contrast, rapid oxidation of CO in the presence of H_2 proceeds via HCOO intermediate and the subsequent oxidation of HCOO by the reaction with OH, that is, CO + OH→ HCOO and HCOO + OH → CO_2 + H_2O. The latter reaction is a rate determining step being responsible for a common hydrogen isotope effect by H_2/D_2 and H_2O/D_2O.

Keywords Mechanism of CO oxidation reaction · Novel PROX catalyst · $FeO_x/Pt/TiO_2$ · Dynamics of in-situ IR spectroscopy · H_2O promoted oxidation of CO · Intermediates, formate and bicarbonate · Rate determining step · Hydrogen isotope effect

1 Introduction

Preferential oxidation (PROX) of CO in H_2 is an important process to produce CO free hydrogen gas for hydrogen fuel cell. On the other hand, highly selective oxidation of CO in excess H_2 is undoubtedly a curious phenomenon if we consider the selectivity by traditional kinetics, because CO adsorbs stronger than H_2 on metallic catalysts and the oxidation of H_2 is far more rapid than that of CO. Therefore, the mechanism of the PROX reaction will make clear a valuable insight into the selectivity behind the heterogeneous catalysis. It is known that Ru and Au supported on oxide are a high performance PROX catalyst, but it is not obvious whether this is intrinsic property of Ru and Au or a kinetic phenomenon. In addition, when the oxidation of CO is enhanced by H_2O, the reaction is often discussed by relating to the shift reaction CO + H_2O → H_2 + CO_2 [1]. The mechanism shift reaction has been explained by nucleophilic attack of H_2O to coordinated CO and the oxidation is catalyzed by a redox cycle of central metal ion with the reduction of H^+ to H_2 [2]. In previous paper, we developed a new PROX catalyst, $FeO_x/Pt/TiO_2$, on which the oxidation of CO is markedly accelerated by adding H_2 and/or H_2O at 60 °C, but no water gas shift reaction occurs even at 80 °C.

It should be mentioned that the activity and the selectivity for the oxidation of CO in H_2 on a 1 wt% Pt loaded on a FeO_x/TiO_2 (FeO_x is ca. 100 wt% in Fe) are similar to that on the Pt catalysts supported on TiO_2, Al_2O_3 and CeO_2. However, when a 1 wt% Pt/TiO_2 is covered with 130–140 wt% FeO_x (ca. 100 wt% in Fe), the activity and the selectivity for the PROX reaction of CO are dramatically improved as referred the reaction at 60 °C in Fig. 1(a) and (b) [3]. Therefore, we could say the $FeO_x/Pt/TiO_2$ is a new PROX catalyst being active at low temperature. It is evident that the enhancement by H_2 and/or H_2O is responsible for high performance of this new PROX catalyst, that is, ca. 18–20% conversion of CO in absence of H_2 is elevated to ca. 90–100% by adding H_2 or H_2O at 60 °C

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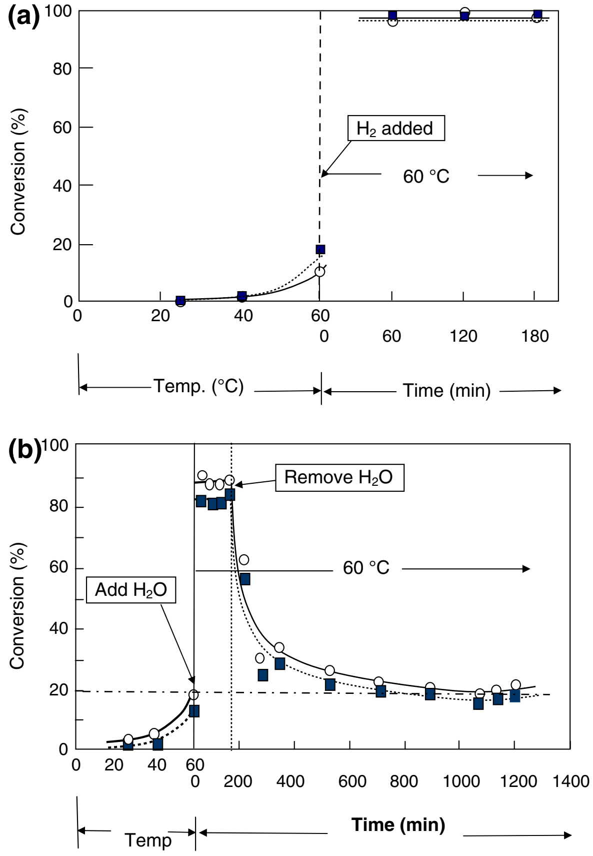


Fig. 1 Oxidation of CO on the $FeO_x/Pt/TiO_2$ catalyst (1.5 g) enhanced by H_2 **(a)** (20 ml/min) and H_2O **(b)**. Total flow rate of 100 ml/min was attained by a mixture of **(a)** 5% CO/N_2 (60 ml/min) + O_2 (1.5 ml/min) + N_2 (38.5 ml/min), and **(b)** 5% CO/N_2 (60 ml/min) + O_2 (1.5 ml/min) + H_2 (20 ml/min) + N_2 (18.5 ml/min). ■ CO conversion, ○ O_2 conversion

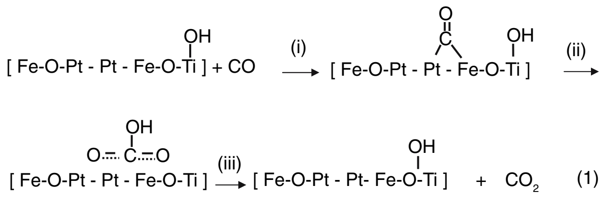
[4]. We also found that the enhancement of CO conversion by H_2/D_2 and H_2O/D_2O takes a common hydrogen isotope effect of ca. 1.4 at 60 °C [5]. These results strongly suggest that H_2O molecule contributes to the oxidation reaction of CO and hydrogen is involved at the rate determining step on the $FeO_x/Pt/TiO_2$ catalyst. It should be pointed out once again that no shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, occurs on this catalyst at 80 °C. Taking these facts into account, the reaction mechanism was deduced from the dynamic spectroscopy of intermediates taking place by adding or removing CO and/or H_2.

2 Experimental

The spectra were measured using a Nexus 670 (Thermo Nicolet) in-situ diffuse reflection chamber with a high sensitivity MCT detector by a resolution of 4 cm^{-1}. After pretreatment of the catalyst ($FeO_x/Pt/TiO_2$) at 350 °C in pure nitrogen, a steady state DRIFT IR spectrum was obtained by exposing the catalyst to the flow of a desired mixture of reactant gases at 60 °C. A total flow rate of 240 ml/min of ($CO + O_2 + H_2 + N_2$) was composed 120 ml/min of 10% CO in N_2, 6 ml/min of O_2, and 40 ml/min of H_2 with a balanced gas of N_2 (74 ml/min), and that of ($CO + O_2 + N_2$) was composed of 120 ml/min of 10% CO in N_2, 6 ml/min of O_2, and 114 ml/min of a balanced N_2. The dynamics of intermediates were deduced by the in-situ IR spectrum obtained by stopping the CO flow of ($CO + O_2 + N_2$) or ($CO + O_2 + H_2 + N_2$). The enhancement effect of the reaction by H_2 was studied by adding H_2 to ($CO + O_2 + N_2$) or by removing H_2 from ($CO + O_2 + H_2 + N_2$). Subtraction of the steady-state DRIFT spectrum from the flow of ($CO + O_2 + N_2$) or ($CO + O_2 + H_2 + N_2$) yielded the dynamic change of the surface species in response to the addition or removal of CO in the presence or absence of H_2.

3 Results and Discussion

If IR detectable species are the intermediate of the oxidation of CO, their intensity should be decreased by stopping the CO in a flow of either ($CO + O_2 + N_2$) or ($CO + O_2 + H_2 + N_2$). Figure 2(a) shows the change of the DRIFT-IR spectrum by stopping CO at 60 °C in the absence of H_2. When the CO of ($CO + O_2 + N_2$) was stopped, negative peaks were grown at 1,836 cm^{-1}, 1,824 cm^{-1}, 1,632 cm^{-1}, 1,396 cm^{-1}, and 1,292 cm^{-1}. These peaks reflect the decrease of adsorbed species by removing CO from the gas phase. Negative bands at 1,836 cm^{-1} and 1,824 cm^{-1} are the decrease of bridge-adsorbed CO by the reaction with O_2, where the two bands may be the CO on Pt–Pt and Pt–Fe sites, respectively [6]. The other three peaks at 1,632 cm^{-1}, 1,396 cm^{-1} and 1,293 cm^{-1} are temporarily assigned as a bicarbonate intermediate according to references [7–9]. It is an interesting fact that the negative growth of the bicarbonate peaks accompanies with the positive growth of the OH peaks at 3,691 cm^{-1} and 3,697 cm^{-1}. The surface may have a constant amount of OH species even in the absence of H_2. Therefore, if a part of these OH species steadily contribute to the formation of bicarbonate species during the oxidation of CO with O_2, decrease of the bicarbonate species by stopping CO will make increase surface OH species according to **step (iii)** in Eq. 1.



$$[\text{Fe-O-Pt-Pt-Fe-O-}\overset{\text{OH}}{\text{Ti}}] + \text{CO} \xrightarrow{(i)} [\text{Fe-O-Pt-}\overset{\text{O=C}}{\text{Pt}}\text{-Fe-O-}\overset{\text{OH}}{\text{Ti}}] \xrightarrow{(ii)} [\text{Fe-O-Pt-Pt-Fe-O-}\overset{\overset{\text{OH}}{\text{O=C=O}}}{\text{Ti}}] \xrightarrow{(iii)} [\text{Fe-O-Pt-Pt-Fe-O-}\overset{\text{OH}}{\text{Ti}}] + CO_2 \quad (1)$$

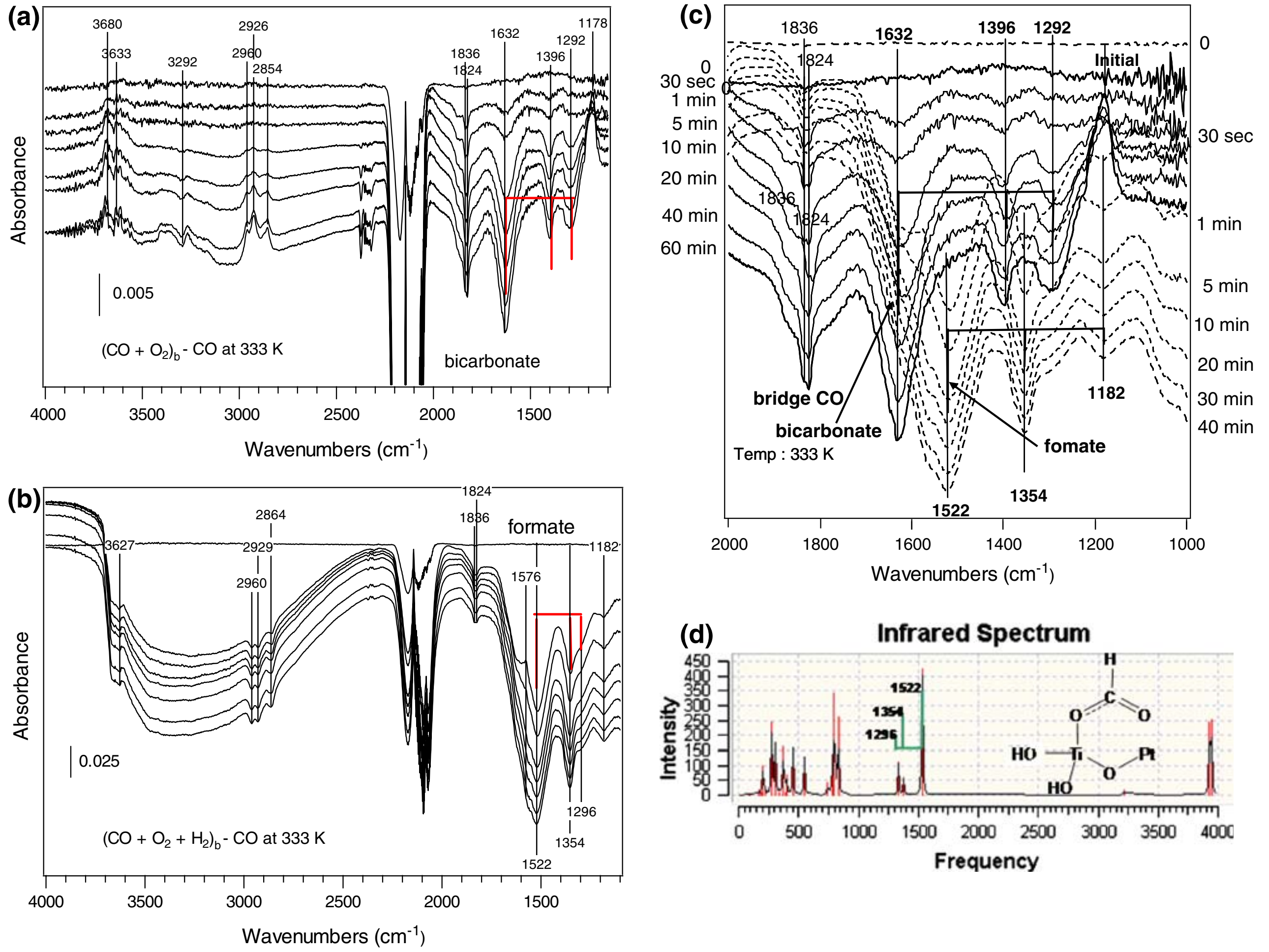


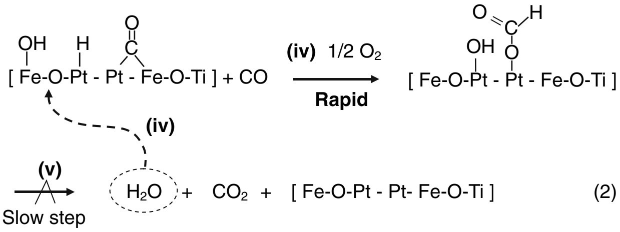
Fig. 2 (**a**) Dynamics of the in-situ DRIFT-IR spectrum of a FeO$_x$/Pt/TiO$_2$ catalyst at 60 °C when the CO in a flow of (CO + O$_2$) was stopped. Negative growth of the spectrum assignable to bicarbonate was recorded at 0 (initial), 30 sec, 1, 5, 10, 20, 40, 60 min after the stop of CO. (**b**) Dynamics of the in-situ DRIFT-IR spectrum of a FeO$_x$/Pt/TiO$_2$ catalyst at 60 °C when the CO in the flow of (CO + O$_2$ + H$_2$) was stopped**.** Negative growth of the spectrum assignable to formate was recorded at 0 (initial), 30 sec, 1, 5, 10, 20, 30, 40 min after the stop of CO. (**c**) Spectra **a** of bicarbonate and **b** of fomate were put on together. (**d**) Calculation of formate was performed for a model using B3LYP + LANL2DZ method

In contrast, when the CO in a flow of (CO + O$_2$ + H$_2$) was stopped, negatively grown bands were different from the bicarbonate peaks as shown in Fig. 2(b). That is, the bridge-adsorbed CO peaks at 1,836 cm^{-1} and 1,824 cm^{-1} are the same, but the peaks at 1,522 cm^{-1}, 1,354 cm^{-1} and 1,296 cm^{-1} (shoulder) are undoubtedly different from the bicarbonate peaks. In addition, the decreasing rate of these peaks is very rapid to accomplish within 1 min. These bands observed in the presence of H$_2$ are very similar to the formate spectrum observed during the oxidation of formaldehyde (H$_2$CO) at 1,522 cm^{-1} (υ_{as}) and 1,354 cm^{-1} (υ_s) on the Pt/TiO$_2$ catalyst (the same TiO$_2$ used in here) [10] and the peaks given by the adsorption of HCOOH on a Pt/TiO$_2$ [9]. By putting spectrum (a) to spectrum (b) in Fig. 2(c), it is evident that the oxidation of CO proceeds via different intermediates in the presence of H$_2$. That is, the bridge-adsorbed CO rapidly changes to HCOO in the presence of H$_2$ or H$_2$O, and is followed by a rapid decomposition as discussed below.

The peaks of formate depend on its conformation on metal or oxide, but the characteristics peaks of mono- or bi-dentate are similar on various systems [11–13]. We performed a simple calculation for a model shown in Fig. 2(d) by using B3LYP + LANL2DZ method [14]. The calculation gives characteristic peaks at 1,300 (υ_s), 1,369 and 1,485 cm^{-1}(υ_{as}), which may correspond to the experimental peaks at 1,354 cm^{-1} (υ_s) and 1,522 cm^{-1} (υ_{as}), but their agreement is not so good. One impressive result of the dynamic in-situ IR spectroscopy is that the negative growth of formate peaks accompanies negative growth of broad OH bands at 3,000–3,600 cm^{-1} and C–H vibration bands at 2,870–2,960 cm^{-1} as shown in Fig. 2(b). This fact indicates that the OH species contribute to the decomposition of HCOO intermediates into CO_2 and H_2O. The amount of intermediate species detected during catalysis depends on the dynamic balance of the formation of intermediate and its forward reaction. When the CO is removed from a steady flow of ($CO + O_2 + H_2$), the bridge-adsorbed CO completely disappeared within a 30 s as shown in Fig. 2(b). In contrast, the negative growth of the bridge-adsorbed CO as well as of the bicarbonate in the absence of H_2 are slow as shown in Fig. 2(a), which takes more than 10 min. Very rapid decrease of the adsorbed CO may be schematically described by step (iv) in Eq. 2, that is, the bridge-adsorbed CO reacts very rapidly with Fe–OH^- and the produced HCOO subsequently reacts with Pt–OH to decompose into CO_2 and H_2O according to step (v). It is known that formic acid is formed by the reaction of CO with $Ca(OH)_2$ or NaOH. Therefore, we could say that the step (v) is a thermodynamically feasible reaction.

The dynamics of the spectroscopy taking place by stopping gas phase CO shown in Fig. 2(b) represents the simultaneous decrease of the broad band at 3,000–3,600 cm^{-1} and the HCOO bands with time. This fact reveals that the HCOO undergoes oxidative decomposition by the reaction with OH on Pt surface as is described by the **step (v)**, which is the rate determining slow step being responsible for the hydrogen isotope effect. In addition, an interesting point is that the local hydrophilic property is directly influenced by the interaction with adsorbed species.

Accordingly, we could say that H_2O molecule promotes the reaction as a molecular catalyst, where a small amount of H_2O is steadily provided by the oxidation of H_2 In other words, highly selective oxidation of CO is attained by repeated formation of HCOO according to Eq. 2.



$$[\mathrm{Fe\text{-}}\overset{\mathrm{OH}}{\mathrm{O}}\mathrm{\text{-}}\overset{\mathrm{H}}{\mathrm{Pt}}\mathrm{\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Pt\text{-}Fe\text{-}O\text{-}Ti}] + \mathrm{CO} \xrightarrow[\textbf{Rapid}]{\textbf{(iv)}\ 1/2\ O_2} [\mathrm{Fe\text{-}O\text{-}}\overset{\mathrm{OH}}{\mathrm{Pt}}\mathrm{\text{-}}\overset{\overset{\mathrm{O{=}C\text{-}H}}{|}}{\overset{\mathrm{O}}{\mathrm{Pt}}}\mathrm{\text{-}Fe\text{-}O\text{-}Ti}]$$

$$\xrightarrow[\text{Slow step}]{\textbf{(v)}} H_2O + CO_2 + [\mathrm{Fe\text{-}O\text{-}Pt\text{-}Pt\text{-}Fe\text{-}O\text{-}Ti}] \quad (2)$$

As indicated above, the amount of HCOO depends on the dynamic balance of the formation and decomposition of HCOO intermediate. Therefore, the amount of HCOO should be influenced not only by CO but also by H_2 (or H_2O). In a flow of ($CO + O_2$), a trace amount of H_2O is hard to remove so that a small amount of HCOO necessarily exists on the catalyst during reaction. When H_2 is added to a flow of ($CO + O_2$), a small amount of HCOO on the surface is quickly decomposed within 1 min as shown by the dotted spectrum (a) in Fig. 3 by reacting with OH formed on the Pt, because the formation of $HCOO^-$ is behind by the slow increase of Fe–OH^-. In contrast, when H_2 is removed from a flow of ($CO + O_2 + H_2$), the decomposition of HCOO (vi) is suppressed, but the reaction of CO with Fe–OH^- does not stop immediately because enough amount of Fe–OH^- exists on the surface. As a result, the HCOO is increased instead of decreased as shown in Fig. 3(b).

4 Conclusion

One important conclusion is that we cannot gain insight into the activity and selectivity without clarifying the reaction mechanism, although the catalytic activity and/or the selectivity of supported metal catalysts are so often

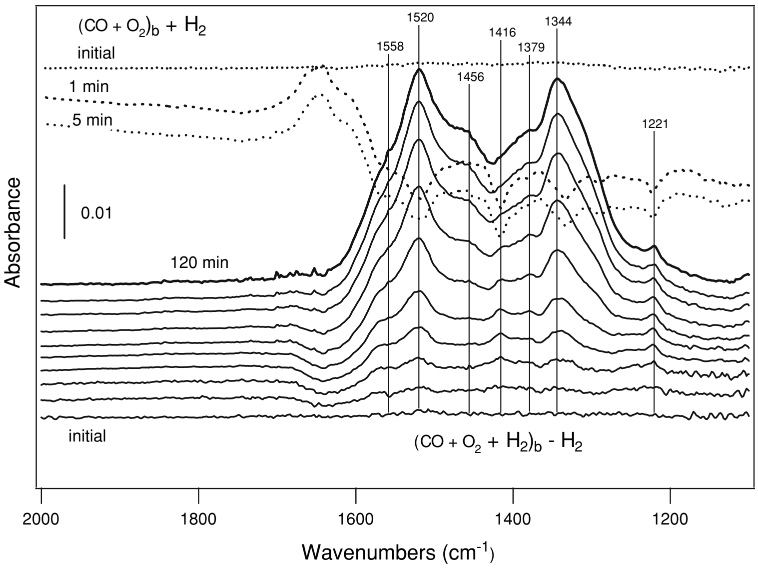


Fig. 3 Dynamics of the in-situ DRIFT-IR spectrum taking place by the addition of H_2 to a flow of ($CO + O_2$) or by the remove of H_2 form a flow of ($CO + H_2 + O_2$) at 60 °C

discussed in relation to the particle size. The oxidation of CO via HCOO intermediate is responsible for the PROX reaction of CO on the $FeO_x/Pt/TiO_2$ catalyst, but it is undoubtedly different form the shift reaction. It is also shown that the subsequent oxidative decomposition of HCOO with OH is the rate determining step, so that H_2/D_2 and H_2O/D_2O give a common hydrogen isotope effect. The role of FeO_x is still unsolved big puzzle, but I could say that one vital role of FeO_x is the formation of bridged CO adsorption sites, which may be Pt–Fe sites. Similar role was observed on a Au/TiO_2 by loading a large amount of FeO_x, where a poorly active Au/TiO_2 catalyst with large Au particles changes to a superior active catalyst by loading a large amount of FeO_x, and the adsorption of bridge-adsorbed CO on Au–Fe sites was confirmed by in-situ IR spectroscopy [15]. Such unexpected restructuring or new site formation by FeO_x was supported quite recently by the calculation for the FeO_x–Pt–TiO_2 system [16]. Finally, it should be pointed out that the collision of reactant molecules from gas phase to Pt or Au particles should be markedly lowered by loading with a large amount of FeO_x, but the reaction rate is markedly enhanced. We could say that this is a typical common feature of heterogeneous system observed on the crystal habit, enzyme reaction, sticking probability, and heterogeneous reaction, that is, it is caused by the efficient delivery of molecules or atoms by rapid migration over the inactive surface area to active sites. This important ignored problem will be discussed in a next paper.

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