CrossMark
click for updatesCite this: *RSC Adv.*, 2015, 5, 949

Catalytic oxidation of CO on metals involving an ionic process in the presence of H₂O: the role of promoting materials

Ken-Ichi Tanaka,^{*a} Hong He^a and Youzhu Yuan^b

A new catalytic oxidation of CO involving an ionic process in the presence of H₂O is proposed on a Pt-catalyst with specific promoting materials (co-catalysts). Oxidation of CO is very slow at room temperature on ordinary Pt-catalysts such as Pt/SiO₂, Pt/Al₂O₃, Pt/TiO₂, Pt/Graphite, and Pt/carbon nano-tube (CNT), and H₂ or H₂O have no effect on the reaction. However, in the presence of specific co-catalysts, the oxidation of CO is markedly enhanced by H₂ or H₂O, so that highly selective preferential oxidation (PROX) of CO in H₂ is attained. The role that co-catalysts play in the oxidation of CO enhanced by H₂ or H₂O was clarified by the experiments with Pt supported on CNT and carbon nano-fiber (CNF) that had Ni–MgO and FeO_x at their one terminal end, respectively. Oxidation of CO was markedly enhanced by H₂ on the Pt/CNT and Pt/CNF, but no enhancement was observed on the Pt/CNT-p and Pt/CNF-p, where the CNT-p and CNF-p were purified by removing Ni–MgO and FeO_x. Similar enhancement of the oxidation of CO by H₂ or H₂O was observed on FeO_x/Pt/TiO₂ and FeO_x/Au/TiO₂, although no enhancement was observed on the Pt/TiO₂ and Au/TiO₂ catalysts. The *in situ* DRIFT spectra of the FeO_x/Pt/TiO₂ catalyst (Fe : TiO₂ : Pt = ca. 100 : 100 : 1) during reaction in a flow of (CO + O₂ + H₂) suggested the rate-determining slow step was HCOO(a) + OH(a) → CO₂ + H₂O. The oxidation of CO enhanced by H₂O/D₂O and H₂/D₂ showed a common hydrogen isotope effect of $r_H/r_D = 1.4\text{--}1.5$. The highly selective oxidation of CO in H₂ on the Pt/CNT and Pt/CNF catalysts strongly suggests efficient transport of ionic intermediates from Ni–MgO or FeO_x to Pt over the hydrophobic CNT and CNF surface according to the local potential gradient. According to this mechanism, selectivity in the preferential oxidation of CO in H₂ is defined by the turnover number of a H₂O molecule forming CO₂ during its residence time on the catalyst, which is essentially different from the selectivity based on competitive adsorption and/or reaction. The role of the H₂O molecule is as a kind of messenger molecule or a molecular catalyst to promote the reaction on the surface expressed by the equation $n(\text{CO} + 1/2\text{O}_2) + \text{H}_2\text{O} \rightarrow n\text{CO}_2 + \text{H}_2\text{O}$. In this mechanism, the selectivity is given by $n/(n + 1)$. Curious phenomena previously observed in the PROX reaction of CO in H₂ on various catalysts are well explained by the mechanism including an ionic process proposed in this paper.

Received 8th August 2014
Accepted 20th November 2014

DOI: 10.1039/c4ra08349k

www.rsc.org/advances

1. Introduction

Catalytic oxidation of CO on metals, especially on Pt, has been studied as a model of catalysis involving the reaction of adsorbed CO(a) with adsorbed O(a) or activated lattice oxygen. However, this reaction that appears simple is not so simple, as will be demonstrated in this review. The adsorption of CO on metals has been widely studied, both experimentally and theoretically. For example, it was shown that the adsorption

bond of CO on metals was influenced by local electron density on the metal surface as experimentally demonstrated by King *et al.*¹ on a K⁺/Ni(100) film (~200 nm thick) by detecting radiating heat accompanying the adsorption of 50 ns pulses of 10¹² molecules of CO, which was in good agreement with the bonding model given by Blyholder.² The lack of activity of Au surface for the oxidation of CO was well explained theoretically by the model, given that it has no ability to adsorb CO. In contrast to this accepted knowledge, the unusual catalytic activity of Au particles, dependent on the particle size and support oxide used, was found by Haruta *et al.*^{3,4} That is, inactive Au particles change to an extremely active catalyst for the oxidation of CO at a crucial particle size ca. 3 nm. Haruta hypothesized that the active perimeter of the particles played a role in their activity in the reaction of adsorbed CO.⁵ However, the activation of Au particles smaller than a critical size of ca. 3

^aResearch Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: ezz01606@nifty.com

^bState Key Laboratory of Physical Chemistry of Solid Surfaces and National Engineering Laboratory for Green Chemical Productions of Alcohols-Ethers-Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

nm is difficult to explain simply by the perimeter length. In relation to this phenomenon, Goodman hypothesized the activity to be by a quantum effect,⁶ but later, Chen and Goodman showed the importance of the stability of specific materials.⁷

On the other hand, it is well known that the lattice oxygen becomes labile at the perimeter on Rh/Ce_{0.5}Zr_{0.5}O₂, Pt-Rh/CeO₂, and Pt-Rh/CeO₂-ZrO₂.^{8,9} Bollinger and Vannice¹⁰ performed an interesting experiment by depositing TiO₂ on highly pure inactive Au powder (10 μm), and observed the activation of the Au particles for the oxidation of CO at 313 K. They postulated the formation of active sites at the Au-TiO₂ interface. Farrauto *et al.*¹¹ found activation of a 5 wt% Pt/γ-Al₂O₃ catalyst for the selective oxidation of CO in H₂ on addition of FeO_x and they proposed that a change in the electronic properties of the Pt particles caused by FeO_x was responsible for the activity rather than the activation of the lattice oxygen of FeO_x, although they observed no change in the IR spectrum of the CO adsorbed on Pt. So far, the oxidation mechanism of CO on metals has been explained based on the reaction of adsorbed CO(a) with adsorbed O(a) or labile lattice oxygen. Adsorption of CO on 1 wt% Pt/TiO₂ as well as on 1 wt% Au/TiO₂ is markedly influenced by the FeO_x deposited on them as shown in Fig. 1, and the oxidation of CO on FeO_x/Pt/TiO₂ and FeO_x/Au/TiO₂ is markedly enhanced by H₂O and/or H₂. However, the rate-determining step of the oxidation of CO enhanced by H₂O on the FeO_x/Pt/TiO₂ catalyst is neither the adsorption nor the subsequent reaction of the adsorbed CO, as discussed in this review. This fact suggests that the bonding form of adsorbed CO(a) may have no direct effect on the activity, but the adsorption ability should be indispensable.

So far, the oxidation of CO in H₂ (in the presence of H₂O) has been explained by the competitive reaction of CO(a) and H(a) with adsorbed oxygen or active lattice oxygen, but Daniells *et al.*³⁶ proposed a new reaction mechanism of CO *via* hydroxyl-carbonyl intermediates on an Au/Fe₂O₃ catalyst. Tanaka *et al.*^{12–16} found unusual catalytic activity with Pt/TiO₂ and Au/

TiO₂ covered with a large amount of FeO_x (*ca.* 100 wt% in Fe) for the oxidation of CO in the presence of H₂, that is, H₂O. So far no one has observed CO adsorbed on the Au catalyst, but an IR peak appearing at 1803 cm⁻¹ on the FeO_x/Au/TiO₂, assignable to bridge-bonded CO, was observed when 1 wt% Au/TiO₂ was covered with a large amount of FeO_x as shown in Fig. 1.^{13,16} Interestingly, the bridge bonded CO was also markedly increased on the Pt/TiO₂ catalyst after addition of a large amount of FeO_x, but the peak at 1629 cm⁻¹ derives from a foreign species not related to the oxidation of CO, as deduced from a DRIFT spectroscopic study illustrated in Fig. 5. As will be described in more detail, adsorption of CO is very rapid compared to other elementary steps during the oxidation of CO.

To put it simply, the low temperature oxidation of CO is enhanced by H₂O on FeO_x/Pt/TiO₂, and is different from the oxidation with O₂ without H₂ on FeO_x/Pt/TiO₂ and in the presence of H₂ on Pt/TiO₂. In fact, the *in situ* IR spectroscopy suggested the rate-determining reaction of HCOO(a) + OH(a) → CO₂ + H₂O on the FeO_x/Pt/TiO₂ catalyst. Based on the dynamics of the *in situ* DRIFT spectroscopy, a mechanism involving an ionic process in which ions are formed on the FeO_x and are rapidly transported onto the Pt is strongly suggested, and the rate determining reaction mentioned above takes place on the Pt.^{13,14,16} The role of promoting materials in this oxidation of CO was proved more conclusively on Pt/CNT (carbon nano-tubes having Ni-MgO at the terminal end) and on the Pt/CNF (carbon nano-fibres having FeO_x at the terminal end). If Ni-MgO and FeO_x were removed from CNT (CNT-p) and CNF (CNF-p) by purification procedure, the oxidation of CO enhanced by H₂O on Pt stopped. An important fact is that the Pt particles are completely separated from Ni-MgO_x or FeO_x on the Pt/CNT and Pt/CNF catalysts, but the promoting materials and H₂O are indispensable for this new catalytic oxidation of CO.

Fukuoka *et al.*¹⁷ reported curious activity of Pt-nano-rods (3 nm × several hundred nm) for the selective oxidation of CO in H₂ depending on their location, either inside of SiO₂-nano-tubes or on the external surface of SiO₂-nano-tubes as shown in Fig. 10, which was explained by the existence of a specific electronic state in the Pt-nano-rods in the SiO₂-nano-tubes for the oxidation of CO(a) with O(a). Yuan *et al.*^{18,19} observed the effect of the crystalline shape of the CeO₂ support in Au/CeO₂ catalysts on their activity and selectivity for the oxidation of CO in H₂. These phenomena are difficult to understand based on the mechanism premising the reaction of adsorbed CO(a) with adsorbed O(a) or lattice oxygen without considering the indispensable contribution of H₂O, that is, a new oxidation mechanism of CO *via* an ionic process may take place, as presented in this paper. If the oxidation of CO proceeds by a new mechanism, as proposed in this review, the definition of the selectivity for the preferential oxidation of CO in H₂ should be different from that of the traditional mechanism based on the competitive reaction of CO and H₂. A meaningful definition of the selectivity in the preferential oxidation of CO in H₂ is given by the turn-over number “*n*” of one H₂O molecule forming a CO₂ molecule as described by the equation $n(\text{CO} + 1/2\text{O}_2) + \text{H}_2\text{O} \rightarrow n\text{CO}_2 + \text{H}_2\text{O}$, in the residence time of the H₂O molecule on the

Fig. 1 Bridge-bonded CO peak (1844–1792 cm⁻¹) on 1 wt% Pt/TiO₂ and 1 wt% Au/TiO₂ is markedly increased on the FeO_x/Pt/TiO₂ and FeO_x/Au/TiO₂ surfaces at 40 °C. The peaks at 2172 and 2118 cm⁻¹ are gas-phase CO.^{13,16}

catalyst, that is, H_2O is a kind of messenger molecule or a molecular catalyst on the surface.

Many investigators have studied the activation or passivation effects of oxide layers deposited on metals. A well-known phenomenon is the growth of a passive oxide layer on precious metals by reduction, which was named the SMSI (strong metal support interaction) effect by Tauster *et al.*²⁰ In this case an inactive TiO_{2-x} layer is formed in a reducing atmosphere over precious metals supported on TiO_2 . Using STM, Netzer *et al.*²¹ demonstrated the wetting growth of an oxide layer on a metal with a V_2O_3 layer on a $\text{Pd}(111)$ surface. Formation of active oxide layers on metals was also observed. Discontinuous changes in the activity of an oxide layer depending on its thickness were first observed by Lambert *et al.*²² for CeO_2 deposited on a $\text{Pt}(111)$ surface. One monolayer of CeO_2 on the $\text{Pt}(111)$ surface is inactive for the adsorption of CO as well as for the oxidation of CO; however, deposition of more than two monolayers of CeO_2 abruptly gives superior activity in the oxidation of CO. Similar activation depending on the number of layers was observed for FeO_x deposited on a $\text{Pt}(111)$ surface by Shaikhutdinov *et al.*,²³ that is, the structural change of the FeO_x layers causes a change in the reactivity of the lattice oxygen. It is worth noting that the lattice activation was observed without H_2O , and it is extremely interesting to consider the effect of H_2O on the activation of lattice oxygen in order to understand the new catalytic oxidation of CO enhanced by H_2O .

2. Co-catalysts for the oxidation of CO enhanced by H_2O

Catalytic oxidation of CO with O_2 on Pt has been explained as a model of the reaction of adsorbed species depending on the coverage of CO(a) and O(a). In fact, all adsorbed CO(a) and O(a) on the Pt surface appear to contribute to the catalytic reaction as Golchet and White²⁴ demonstrated on a Pt foil by changing the ratio of O_2 to CO pressure at 180–212 °C, which is apparent uniformity by rapid diffusion of adsorbed species. It is also known that the oxidation of CO on Pt catalysts is very slow at temperatures lower than 80 °C because of the strong adsorption of CO, but the PROX reaction of CO in H_2 is catalyzed on Pt with specific promoting materials even at room temperature. So far, the role of co-catalysts has been explained as weakening the adsorption of CO on Pt or improving reactivity of CO and/or O(a) on Pt or of lattice oxygen of the support or promoting materials. As pointed out in this paper, the role of co-catalysts is difficult to understand based on these traditional explanations. We confirmed that the role of promoting materials is to provide a new reaction path for the oxidation of CO in the presence of H_2O by using CNT and CNF with promoting materials only at their one terminal end. Yoshida *et al.*²⁵ were the first to successfully observe the growing process of multi-wall CNT from a nano-size Fe_3C particle by heating in C_2H_2 by *in situ* TEM, and it was shown that the nano-size catalyst surface was covered with graphene first, and expelled a multi-wall CNT, so that the size of the multi-wall CNT was decided by the size of the

Fe_3C particle. As the left TEM image of Fig. 2(a) shows, the width of CNT prepared by the Ni-MgO catalyst is narrower than the particle remaining at the terminal end of the CNT. This fact may indicate that the size of the active Ni catalyst (probably nickel carbide) is smaller than the particle size of Ni-MgO remaining at the terminal end of CNT. The Pt-particles are clearly smaller than the width of the CNT, and they are completely separated from the Ni-MgO or FeO_x localized at the terminal end of the CNT. However, the Ni-MgO or FeO_x at the terminal end of CNT is indispensable for the catalytic oxidation of CO enhanced by H_2O on Pt/CNT and Pt/CNF catalysts. As shown in Fig. 2(a), a highly selective oxidation of CO took place in excess H_2 at room temperature on the Pt/CNT catalyst. In contrast, if the Ni-MgO was removed from the CNT by purification (CNT-p), low temperature oxidation of CO in H_2 was no longer catalyzed on the Pt/CNT-p catalyst.^{12,26} This result proves that the Ni-MgO is indispensable for the selective oxidation of CO in H_2 , but it is not necessary for it to be in contact with the Pt particles. One should be reminded that the Pt/CNT and Pt/CNT-p showed almost equal low activity for the oxidation of CO with O_2 in the absence of H_2 . Taking these results into account, the hydrogen isotope effect for the oxidation of CO by H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$ was studied, and it was confirmed that H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$ gave equal hydrogen isotope effects for the oxidation of CO. Accordingly, we can conclude that H_2O is the molecule responsible for the PROX of CO in H_2 .

As shown in Fig. 2(a), nearly 100% conversion of CO was attained at a flow of 100 mL min^{-1} of $(\text{CO} + \text{H}_2 + \text{O}_2 + \text{N}_2)$ ($\text{CO} : \text{O}_2 : \text{H}_2 = 1 : 1 : 28$) over 15 wt% Pt/CNT (the amount of Pt was equivalent to 0.8 g of 0.75 wt% Pt/ TiO_2).²⁷ If the Ni-MgO was removed from the CNT by chemical purification (CNT-p), the Pt/CNT-p lost the activity for the oxidation of CO in H_2 (H_2O in practice) as shown in Fig. 2(a). The essential role of Ni-MgO as a co-catalyst for the oxidation of CO enhanced by H_2 (H_2O in practice) was confirmed by using graphite, that is, the oxidation of CO in H_2 on Pt/Graphite and Pt/Graphite with Ni-MgO.²⁷ As shown in Fig. 2(c), Pt/Graphite was not active for the oxidation of CO at temperatures lower than 120 °C, but Pt supported on Ni-MgO-doped graphite was highly active in the temperature range of 40–120 °C. From these results, we can confidently conclude that Ni-MgO and FeO_x are indispensable materials in the oxidation of CO enhanced by H_2 , actually by H_2O , but the Pt-particles and Ni-MgO and FeO_x do not need to be in contact with one another on the surface. To realize the rapid oxidation of CO enhanced by H_2O on Pt/CNT and Pt/CNF, the rapid transport of intermediate species is necessary between the Ni-MgO and Pt-particles over the nano-tubes. This transport mechanism on the surface is crucial to understanding the oxidation mechanism of CO promoted by H_2O .

To more strictly confirm the contribution of the co-catalysts separated from the Pt, the reaction was performed using CNF (VGCF-X; $\phi 15 \text{ nm} \times 4 \text{ }\mu\text{mL}$ of Showa Denko Co.), which were prepared using a ferrocene catalyst in the gas phase. The FeO_x remaining at the terminal end of the CNF was completely removed by heating the fibers at 2900 °C (CNF-p). Three lots of CNF, VGCF; $\phi 150 \text{ nm} \times 8 \text{ }\mu\text{mL}$, VGCF-H; $\phi 150 \text{ nm} \times 6 \text{ }\mu\text{mL}$, and VGCF-S; $\phi 80 \text{ nm} \times 10 \text{ }\mu\text{mL}$, were used. As shown in Fig. 2(b), the

Fig. 2 (a) TEM images of CNT, Pt/CNT, and Pt/CNT-p, and the activity and selectivity of Pt/CNT and Pt/CNT-p for the PROX reaction of CO in H₂. Conversion of CO (solid) and O₂ (open) attained in a flow of 100 mL min⁻¹ of (CO/O₂/H₂ = 1.5/1.5/42.0 mL min⁻¹) with a balance of N₂ on 15 wt% Pt/CNT and 15 wt% Pt/CNT-p (0.8 g). (b) Conversion of CO attained in a flow of (CO/O₂/H₂/N₂) = 3.0/1.5/20.0/78.5 (mL min⁻¹) on 5 wt% Pt/CNF (VGCF-X) (●), 5 wt% Pt/CNT-p (○), 5 wt% Pt/VGCF (▲), 5 wt% Pt/VGCF-S (◇). (c) Conversion of CO (solid) and O₂ (open) attained in a flow of (CO/O₂/H₂/N₂) = 3.0/1.5/20/75.5 (mL min⁻¹) on 15 wt% Pt/Graphite (0.8 g) (○, ●) and 5 wt% Pt/Graphite doped with 5 wt% of Ni-MgO (□, ■). PROX reaction of CO on Pt/Graphite and Pt/(Graphite + Ni-MgO).^{12,26}

Pt/CNF (VGCF-X) catalyst was very active for the PROX reaction of CO in H₂, and nearly 100% selective oxidation of CO (CO/O₂ = 2/1) was attained in a flow of CO (3.0 mL min⁻¹) + O₂ (1.5 mL min⁻¹) + H₂ (20.0 mL min⁻¹) + N₂ (78.5 mL min⁻¹) at temperatures lower than 80 °C. As expected, the Pt-catalyst supported on the CNF-p having no FeO_x (Pt/VGCF, Pt/VGCF-H and Pt/VGCF-S) had very poor catalytic activity for the oxidation of CO at temperatures lower than 100 °C. Although Ni-MgO and FeO_x are separated from the Pt particles on the CNT and CNF, these promoting materials are indispensable in the catalytic oxidation of CO on Pt enhanced by H₂O. Accordingly, the total mechanism for the oxidation of CO promoted by H₂O is accomplished by the effective transport of the intermediates between Ni-MgO or FeO_x and Pt particles.²⁸

A similar promoting effect of H₂ and H₂O on the oxidation of CO was observed on Pt/TiO₂ overlaid with a large amount of FeO_x.¹³⁻¹⁶ As shown in Fig. 3(a), the oxidation of CO was not enhanced by H₂O (or H₂) on a 1 wt% Pt/TiO₂ catalyst, but was markedly enhanced on the FeO_x/Pt/TiO₂ catalyst at 60 °C by H₂ and H₂O as shown in Fig. 3(b) and (c),^{13,15} where the FeO_x/Pt/TiO₂ was prepared by overlaying a large amount of FeO_x (ca. 100 wt% in Fe) on the 1 wt% Pt/TiO₂. If H₂ or H₂O were removed from the gas phase, the oxidation of CO was quickly suppressed as shown in Fig. 3(c).

These results strongly suggest that the role of H₂O is not the activation of the Pt or FeO_x, but provides a new catalytic oxidation reaction of CO(a) as discussed in detail below. It is worth noting that the Pt/TiO₂ and FeO_x/Pt/TiO₂ used here have almost equal activity for the oxidation of CO with O₂ at 60 °C in the absence of H₂ or H₂O, that is, the H₂O molecule enhances the oxidation of CO only on the FeO_x/Pt/TiO₂ surface but not on the Pt/TiO₂, although their activity for the oxidation of CO in the absence of H₂ or H₂O is almost equal at temperatures higher than 100 °C. Therefore, the role of H₂O molecules in reaction (ii) in eqn (1) is like a messenger molecule or a molecular catalyst.

Since Langmuir's work in 1921,²⁹ the catalytic oxidation of CO with O₂ on Pt catalysts has been explained by the mechanism of reaction (i), that is, the reaction of adsorbed CO(a) with adsorbed O(a) or labile lattice oxygen. As mentioned above, Golchet and White²⁴ showed that all adsorbed CO(a) and O(a) on the Pt-foil during reaction depended on the ratio of P(O₂)/P(CO), and all adsorbed species contribute to the oxidation reaction at 180 °C and 212 °C, but steady state adsorption on the Pt surface during catalysis depended on the ratio of P(O₂)/P(CO). One should be reminded that this result does not mean homogeneous activity of the Pt surface and/or homogeneous reactivity of the adsorbed CO(a) and O(a) species, because rapid surface diffusion of adsorbed species smears the heterogeneity of the Pt surface and the reactivity of the adsorbed species.

When the oxidation of CO and H₂ proceeds independently on Pt surface as premised in the L-H mechanism, the two species neither enhance nor inhibit oxidation of the other, rather the reaction of CO and H₂ is controlled by the

Fig. 3 (a) The oxidation of CO with O₂ on a 1 wt% Pt/TiO₂ catalyst is not enhanced by H₂O at 60 °C. (b) The oxidation of CO in a flow of [CO (3 mL min⁻¹) + O₂ (1.5 mL min⁻¹) + N₂ (95.5 mL min⁻¹)] on a FeO_x/Pt/TiO₂ catalyst is markedly enhanced by H₂ (15.0 mL min⁻¹) at 60 °C. (c) Enhancement of the oxidation of CO by H₂O on FeO_x/Pt/TiO₂ is reversible at 60 °C.¹³

competitive mechanism of the adsorption and reaction of CO(a) and H(a). Therefore, if the activity of a Pt catalyst is changed by some additives or support materials, this should be explained as the result of a change in CO(a) or O(a) caused by the change of Pt or by the formation of active lattice oxygen. However, the role of the support or promoting materials in catalysis is not so simple as is rationalized by the reactivity of adsorbed species or lattice oxygen. To illustrate this point, here we take up the results of Korotkikh and Farrauto *et al.*¹¹ in experiments on the Pt/γ-Al₂O₃ and FeO_x/Pt/γ-Al₂O₃ catalysts. The activity of Pt/γ-Al₂O₃ for the oxidation of CO in H₂ was markedly improved by the addition of FeO_x, but the IR spectrum of CO adsorbed on FeO_x/Pt/γ-Al₂O₃ showed no difference compared to that of CO on Pt/γ-Al₂O₃. They explained the activation of the FeO_x/Pt/γ-

Al₂O₃ catalyst as a synergy effect of Pt and FeO_x, that is, as they premised the reaction of adsorbed CO with adsorbed oxygen or lattice oxygen, and the difference of the activity between Pt/γ-Al₂O₃ and FeO_x/Pt/γ-Al₂O₃ was explained by the term synergy effect, but the physical or chemical meaning of the synergy effect was not made clear.

In contrast to the CO adsorbed on Pt/γ-Al₂O₃ and FeO_x/Pt/γ-Al₂O₃, the CO adsorbed on FeO_x/Pt/TiO₂ was entirely different from that on the Pt/TiO₂. That is, linearly bonded CO(a) becomes predominant on the Pt/TiO₂ catalyst but bridge-bonded CO(a) (1809 cm⁻¹) is the main adsorbed species on the FeO_x/Pt/TiO₂ catalyst. Furthermore, the oxidation of CO was markedly enhanced by H₂ on the FeO_x/Pt/TiO₂ catalyst as shown in Fig. 3(b) and (c), but the reaction on the Pt/TiO₂ catalyst was not enhanced by H₂ as shown in Fig. 3(a).^{13,14} It should be emphasized that the bonding of CO is different on FeO_x/Pt/TiO₂ and Pt/TiO₂, but we could not realize the difference in apparent reactivity for the two forms of CO, bridge-bonded CO and linearly bonded CO, in the catalytic oxidation of CO enhanced by H₂ or H₂O on FeO_x/Pt/TiO₂. This fact convinces us that the rate-determining step of the oxidation of CO enhanced by H₂O on the FeO_x/Pt/TiO₂ catalyst is not the oxidation of adsorbed CO(a) with adsorbed O(a) or lattice oxygen. As argued in this paper, the oxidation of CO enhanced by H₂O, reaction (ii), is a new oxidation reaction *via* intermediates [X_i(a)] in eqn (1). In fact, the oxidation of CO enhanced by H₂/D₂ showed an equal hydrogen isotope effect of $r_{\text{H}}/r_{\text{D}} = 1.4\text{--}1.5$ on FeO_x/Pt/TiO₂ and Pt/CNT as well as on Au/CeO₂ and FeO_x/Au/TiO₂ catalysts, which is equal to the isotope effect when enhanced by H₂O/D₂O,^{14,18,30} which indicates that the H₂O molecule is responsible for the enhancement in either case. To understand the oxidation mechanism of CO promoted by H₂O, it is essential to deduce the rate-determining slow step and to identify the intermediates [X_i], as discussed in the following section.

3. Intermediates and rate-determining slow step

When a catalytic reaction proceeds at a steady-state, chemical potentials and the amounts of the intermediates can be illustrated by a series-connected water tank model shown in Fig. 4 as illustrated by Tamaru.³¹

In situ DRIFT spectra attained on a FeO_x/Pt/TiO₂ catalyst in a flow of (CO + O₂ + N₂) and (CO + H₂ + O₂ + N₂) at 60 °C are shown in Fig. 5(a) and (b) in blue. CO(a) peaks of almost equal intensity were observed in a flow of (CO + O₂ + N₂) and (CO + O₂ + H₂ + N₂) on FeO_x/Pt/TiO₂, although the reaction rates were quite different, as shown in Fig. 3(a) and (b). When the CO was removed from a flow of (CO + O₂ + H₂ + N₂), the IR peaks for CO(a) were very quickly erased as shown in Fig. 5(b), but the decrease in the CO(a) was very slow in the absence of H₂ as shown in Fig. 5(a). As it is known that the desorption of CO(a) on Pt is very slow at room temperature, the rapid decrease of the CO(a) is caused by its rapid reaction in the presence of H₂, that is, in the presence of H₂O. Therefore, the adsorption of CO, step (i), is very rapid, and the adsorption of CO on the FeO_x/Pt/TiO₂

Fig. 4 A series-connected water tank model showing the chemical potential of intermediates (ξ_1) and (ξ_2) in a steady-state reaction of (A) to (B).³¹ The model shows a case when step (iii) is the rate-determining step.

Fig. 5 Time-resolved *in situ* DRIFT spectra of CO(a) attained on a FeO_x/Pt/TiO₂ catalyst at 60 °C. (a) CO was removed from (CO + O₂ + N₂); (b) CO was removed from (CO + H₂ + O₂ + N₂). A series of spectra were recorded at time intervals: (1) is immediately after the removal of CO, and (2)–(6) are 5, 10, 15, 20, 30, and 45 min after CO removal.^{28,30}

catalyst may be nearly a dynamic saturation in (CO + O₂) or (CO + O₂ + H₂). If step (ii) is the rate-determining slow step, (ξ_1), that is, CO(a) is detectable but (ξ_2) may be lower than the detectable level in steady-state reaction. If step (iii) is the rate-determining slow step, both (ξ_1) and (ξ_2) may be detectable on a steady-state catalyst surface. Therefore, our goal is to detect intermediate (ξ_2) on a steady-state catalyst during the oxidation reaction of CO, as will be discussed below.

In situ DRIFT spectra include every species existing on the catalyst surface. Therefore, the spectrum responsible for the reaction intermediates must be extracted from the spectrum. One promising way to do this is to extract the part of the spectrum that changes on abrupt removal of CO from the reactant gas. In this procedure, the spectrum attained on a steady-state catalyst is subtracted as a background, and the spectra that change with time during the reaction are extracted. In this way, the change in the spectrum with time caused by removing CO from the reactant gas was extracted. If step (iii) in eqn (2) is the rate-determining slow step, the intermediates of (ξ_1) and (ξ_2) are nearly in dynamic equilibrium in the steady-state reaction. As mentioned above, the oxidation of CO

enhanced by H₂ or H₂O exhibits an equal hydrogen isotope effect of $r_{\text{H}}/r_{\text{D}} = 1.4\text{--}1.5$ for H₂/D₂ and H₂O/D₂O, which suggests that H₂O is responsible for the oxidation of CO enhanced by H₂.^{28,30} The isotope effect is caused by either the kinetic isotope effect given by the rate constant ($k_{\text{H}} > k_{\text{D}}$) or the thermodynamic pre-equilibration of the intermediates (concentration) proceeding with the rate-determining step ($k_{\text{H}}/k_{\text{D}}$).

Time-resolved DRIFT spectra obtained by removing CO from a steady flow of (CO + H₂ + O₂) are shown in Fig. 6, which reflect the decrease of intermediates from the FeO_x/Pt/TiO₂ catalyst due to the reaction, that is, the spectra correspond to the decrease of (ξ_1) and (ξ_2) in eqn (2) by the reaction. Large negative peaks at 2172 and 2119 cm⁻¹ are due to gas phase CO decreased by the removal. At the same time, linearly-bonded CO(a) (2065, 2067 cm⁻¹) and bridge-bonded CO(a) (1836 cm⁻¹), ξ_1 , are rapidly decreased by changing to (ξ_2) on the FeO_x/Pt/TiO₂ catalyst by the reaction. That is, ξ_1 CO(a) is very rapidly changed to (ξ_2) in eqn (2) because the desorption of CO is very slow. Intermediates (ξ_2) are also decreased with time by the reaction, which is observed as the growth of large negative peaks at 1522, 1354 and 1296 cm⁻¹ and a large broad band from 3000–3800 cm⁻¹ centred at ca. 3400 cm⁻¹ in Fig. 8.^{28,30} Large negative peaks at 1522 and 1354 cm⁻¹ with a shoulder at 1296 cm⁻¹ are assignable as HCOO⁻(a), and the broad band from 3000–3800 cm⁻¹ centred at 3400 cm⁻¹ is assigned as the highly reactive OH(a). These two are the key intermediates (ξ_2) in eqn (2). The most remarkable features are the broad band centred at 3400 cm⁻¹ assigned as OH, and the rapid growth of large negative peaks with time.

It is worth noting that the large broad band assigned as OH was rapidly decreased from the surface by the reaction, but the characteristic scissors mode of adsorbed H₂O at 1650 cm⁻¹ was not observed. This fact indicates that the amount of H₂O on the catalyst changed little on removal of gas phase CO, although H₂O formation should be increased by removing CO from

Fig. 6 Time-resolved *in situ* DRIFT attained by removing CO from a flow of (CO + H₂ + O₂ + N₂) at 60 °C. The spectra were obtained at the 30 s, 1 min, 5 min, 10 min, 20 min, 30 min, and 40 min. after the removal of CO.^{28,30}

(CO + H₂ + O₂). The lack of an increase or decrease in the scissors mode of adsorbed H₂O (1650 cm⁻¹) indicates that neither the increase nor the decrease of adsorbed H₂O occurs on removal of gas phase CO. This fact indicated saturation of the catalyst surface with H₂O(a) in the steady-state reaction of (CO + H₂ + O₂). Taking these results into account, the broad band centred at 3400 cm⁻¹ is not adsorbed H₂O(a) but the reactive OH(a) species, which undergo reaction with HCOO(a) at the rate-determining step as described by step (iii) in eqn (2).^{13,26} In fact, the HCOO(a) and OH(a) peaks at 1522 and 3355 cm⁻¹ (negative growth of the peaks) rapidly decreased at the same rate, as shown in Fig. 7(b).

If the reaction of HCOO(a) with OH(a) on the Pt surface is the rate-determining slow step as deduced, the concept for the selectivity of preferential oxidation of CO in H₂ should be different from the traditional selectivity based on the competitive reaction of adsorbed CO(a) and H(a) with O(a). As was proved above, even if Pt particles are not in contact with the Ni-MgO or FeO_x on the CNT or CNF, the oxidation of CO expressed by reaction (ii) in eqn (1) occurs on the Pt, where the role of H₂O is like a molecular catalyst working on the surface. Taking this mechanism into account, the selectivity for the preferential oxidation of CO in H₂ is given by the turn-over number "n" of H₂O molecules, that is, a meaningful selectivity is the formation of "n" CO₂ molecules by one H₂O molecule in a steady-state reaction. According to this definition, if one H₂O molecule produces 10 molecules of CO₂ during its stay on the catalyst surface, the selectivity for oxidation of CO in H₂ (H₂O is formed by the oxidation of H₂) becomes 91% (10/11). An interesting question is why the oxidation of CO is enhanced by H₂O on hydrophobic Pt/CNT and Pt/CNF surfaces. Surface diffusion or surface transport of adsorbed species is essential in order to explain various phenomena taking place on the surfaces including catalysis, but its embodiment is quite difficult. One interesting example is the reduction of pale yellow WO₃ powder with H₂ in the presence of Pt/Al₂O₃ as shown by Boudart *et al.*³² They showed that well-evacuated WO₃ did not change its colour to blue in H₂ even when mixed with Pt/Al₂O₃ powder. However, if a small amount of H₂O or alcohols was added to the H₂, pale yellow WO₃ was readily changed to blue H_xWO₃ by H₂ at 50 °C, and the efficiency of the promoting molecules depends on their proton affinity. Taking these results into account, the role of H₂O was explained by an ionic process on the surface, that is, adsorbed H(a) on Pt is ionized in the presence of H₂O, H(a) + H₂O → H₃O⁺ + e, and H₃O⁺ diffuses over the surface and reacts on the WO₃ with an electron transported through the bulk to form blue H_xWO₃, which is described as WO₃ + H₃O⁺ + e → H_xWO₃ + H₂O. In this case, H₂O is an indispensable molecule for forming the H₃O⁺ ion on the Pt surface, and the H₃O⁺ ion is transported to WO₃. This process is quite interesting in considering the role of Ni-MgO and FeO_x on the Pt/CNT and Pt/CNF catalysts.

From the dynamics of the DRIFT spectroscopy, the reaction of HCOO(a) with OH(a) was deduced as the rate-determining slow step of the oxidation of CO enhanced by H₂O on the FeO_x/Pt/TiO₂ catalyst. One question regards the mechanism for the rapid formation of the HCOO intermediate on the FeO_x/Pt/

Fig. 7 (a) Change of *in situ* DRIFT spectra of the FeO_x/Pt/TiO₂ catalyst with time when CO was removed from the gas phase in the presence of H₂ (blue) and in the absence of H₂ (red). (b) Decrease of HCOO(a) (1522 cm⁻¹) and OH (at 3355 cm⁻¹) (solid lines) with time attained by removing gas phase CO in the presence of H₂. Broken line indicates slow decrease of bicarbonate peak (1632 cm⁻¹) with time.

TiO₂ catalyst. The formation of HCOOH by the reaction of CO with Ca(OH)₂ is known as a long-established industrial process. Therefore, a question is where the HCOO⁻ is formed, either on the FeO_x or Pt surface by the reaction of CO with OH⁻ ion. One important result was obtained in Fig. 5(b), that is, the CO(a) adsorbed on Pt of the FeO_x/Pt/TiO₂ was very quickly erased by the reaction in the presence of H₂. This fact strongly suggests rapid transport of OH⁻ ion from FeO_x to Pt surface, and reacts with adsorbed CO on the Pt to form HCOO(a) + electron (e). The released electron reacts with H₃O⁺ to form highly reactive OH(a) on the Pt, and the reaction of OH(a) with HCOO(a) is preponderant over the ordinary reaction of CO(a) with O(a) on Pt catalysts at low temperature. An overall reaction mechanism is schematically described in Fig. 8.

Local potential gradient on the dual functional catalyst and the oxidation of CO on it enhanced by H₂O

It is evident that the oxidation of CO taking place in the presence of H₂O on FeO_x/Pt/TiO₂, Pt/CNT, and Pt/CNF catalysts is a new oxidation reaction of CO *via* ionic intermediates such as HCOO⁻. To accomplish this mechanism, effective transport of ionic intermediates from FeO_x to the Pt surface over the support surface is indispensable. The local potential gradient formed on the surface with heterogeneous local charge between FeO_x and the Pt particles may be the driving force for efficient transport of ions such as OH⁻ and H₃O⁺. As will be discussed below, the ratio of OH⁻/H⁺ ions on Ni-MgO or FeO_x and Pt is the origin of the local potential gradient between the FeO_x or Ni-MgO and Pt, keeping overall charge neutrality on the support. If we consider hydrated metal ions in aqueous solution, the ionization equilibrium is given by the balance of proton activity of the hydrated H₂O molecules of the metal ion and aqueous solution as described by eqn (3).

Local Potential Gradient on the Dual Functional Catalyst and the Oxidation of CO on it Enhanced by H₂O

Fig. 8 Oxidation mechanism of CO enhanced by H₂O via ionic process. The upper illustration shows potential gradient between Pt and FeO_x made by the population of H⁺ and OH[−] ions, and OH[−] ion transport from FeO_x to Pt and HCOO[−] is formed by the reaction with CO. The lower part describes the steady reaction mechanism on the dual functional catalyst with FeO_x and Pt. Selectivity for the preferential oxidation of CO in H₂ is given by $n/(n + 1)$, where “ n ” is the number of CO₂ molecules produced by repeated contribution of one H₂O molecule staying on the catalyst.

It has been considered that the pK_a of metal ions with different valence (α) cannot be compared on a universal scale. However, a universal equation (i) of eqn (5) was derived for metal ions in aqueous solution by defining “the electronegativity of metal ions (χ_α)” given by eqn (4).³³

The electronegativity of metal ions (χ_α) is defined by eqn (4), as briefly explained next. An original concept of the electronegativity was given empirically for the elements to understand the bond strength between hetero-atoms, $A_2 + B_2 \rightarrow 2A-B$, by Pauling. A similar concept was derived theoretically by Mulliken in an equation $\chi_0 = (I + A)/2$, where “ I ” is the ionization energy of a neutral M^0 to M^{+1} ion and “ A ” is the electron affinity of a neutral element defined as the formation energy of M^{-1} ion from M^0 . If the ionization energy of metal ions can be expressed by a quadratic equation with respect to charge, Mulliken's equation $(I + A)/2$ is the tangent of the ionization energy curve (a kind of chemical potential of electron) of neutral elements at charge zero as pointed out by Iczkowski *et al.*³⁴ This idea was extended to metal ions ($M^{\alpha+}$) by Tanaka *et al.*³³ as the concept of electronegativity of metal ions (χ_i) according to eqn (4).

$$\left. \begin{aligned} I &= \sum I_\alpha = a\alpha + b\alpha^2 + \chi_\alpha^3 + \dots \approx a\alpha + b\alpha^2 \\ \chi_\alpha &= \partial \sum I_\alpha / \partial \alpha \approx (1 + 2\alpha)\chi_0 \end{aligned} \right\} \quad (4)$$

where χ_0 is the electronegativity of neutral metal atoms expressed by the Pauling electronegativity scale. As shown in Fig. 9(a) and (b), the proton activity of hydrated metal ions ($M^{\alpha+}$) is well expressed by the electronegativity of metal ions (χ_α) in formula (i) of eqn (5).

$$\left. \begin{aligned} \text{(i) } pK_a &= 20(1 - \chi_\alpha/14) \\ \text{(ii) ZPC} &= 16.8(1 - \chi_\alpha/22) \end{aligned} \right\} \quad (5)$$

If a metal oxide is immersed in aqueous solution, the hydrated oxide is ionized to create proton activity in equilibrium with that of the aqueous solution, which is described by the equation $[\text{Oxide}(\text{H}_2\text{O})_n + \text{H}_2\text{O} \leftrightarrow \text{Oxide}(\text{H}_2\text{O})_{n-1}(\text{OH})^- + \text{H}_3\text{O}^+]$. As a result, the hydrated oxide has charge depending on the proton activity of the hydrated surface with respect to that of the aqueous solution. When the proton activity (pH) of the solution becomes equal to that of the hydrated oxide surface, the charge over the hydrated oxide becomes neutral (zero charge), which is referred to as the zero point of charge (ZPC). Therefore, the proton activity of the hydrated oxide surfaces is expressed by the ZPC of the oxides, and it was shown that the ZPC of the oxide surface can be expressed by a linear relation with respect to the electronegativity of the metal ions (χ_α) as shown in Fig. 9(b), which is expressed by equation (ii) in eqn (5).

As was deduced, the FeO_x/Pt/TiO₂ surface during the oxidation of CO in the presence of H₂ is saturated with H₂O, because the *in situ* IR spectrum showed neither an increase nor a decrease of the scissors peak of adsorbed H₂O when the CO in gas phase was removed. If the FeO_x surface is saturated with H₂O molecules during reaction, an ionization equilibrium may be established on the catalyst surface. Taking account of the

Fig. 9 (a) Ionization constant (pK_a) of aqueous metal ions in water at 25 °C depending on the electronegativity of $+\alpha$ valence ion (χ_α). (b) The pH of water providing ZPC of oxide surfaces plotted against the electronegativity of ions.^{33,35}

proton activity of the hydrated FeO_x and Pt surface, excess negative charge on FeO_x creates an equilibrium distribution of ions, $\text{OH}^-/\text{H}^+ > 1$. To maintain the overall neutrality of the surface, the distribution of ions creates a local potential gradient, δ^+ and δ^- , as shown schematically in Fig. 8. The local potential gradient between the FeO_x and Pt is responsible for the rapid and efficient transport of OH^- ions from FeO_x onto Pt.

Unusually selective oxidation of CO in H_2 has been reported on several catalysts, but it is difficult to rationalize by the traditional mechanism based on the reaction of adsorbed CO(a) with adsorbed O(a) or lattice oxygen. If we consider the ionic process such as deduced in this section, previously observed unusual activity and selectivity in the oxidation of CO in H_2 are well rationalized as discussed in the next section.

4. Unusual effect of H_2O molecule on catalytic oxidation of CO

Fukuoka *et al.*¹⁷ reported curious activity of Pt-nano-rods (3 nm $\times$ several hundred nm) in the oxidation of CO in H_2 depending on their location, either inside of SiO_2 -nano-tubes or on the external surface of SiO_2 -nano-tubes. As shown in Fig. 10, ca. 100% conversion of CO ($\text{CO}/\text{O}_2 = 1$) was attained at ca. 80 °C by flowing a mixture of ($\text{CO} : \text{O}_2 : \text{H}_2 : \text{N}_2$) (1 : 1 : 93 : 5 vol.%) at 1200 h^{-1} GHSV through the Pt-nano-rods prepared inside of SiO_2 -nano-tubes. In contrast, the Pt-nano-particles supported on the external surface of SiO_2 -nano-tubes showed very low activity at temperatures lower than 100 °C, which was almost equal to the activity of ordinary Pt/ SiO_2 and Pt/ Al_2O_3 catalysts as shown in Fig. 10. This unusual catalytic activity of the Pt-nano-rods inside the SiO_2 -nano-tubes in the oxidation of CO was explained by formation of a specific state of Pt inside the SiO_2 -nano-tubes, that is, the Pt undergoes specific activation for the oxidation of adsorbed CO(a) with O(a) , but they did not consider the effect of H_2O . As the Pt nano-rod only exists inside the SiO_2 -nano-tubes, H_2O and CO_2 are only formed inside of the SiO_2 -nano-tubes, and the molecules produced inside SiO_2 -nano-tubes are effused out through the 3 nm exit of the SiO_2 -nano-tubes. The effusion rate is known to be in inverse proportion to the square root of the molecular weight.

Fig. 10 Model of nano-tube silica and conversion of CO in the PROX reaction in excess H_2 . Conversion of CO on Pt-rods supported within SiO_2 -nano-tubes (○) and on the external surface of SiO_2 -nano-tubes (●) in a flow of ($\text{CO} : \text{O}_2 : \text{H}_2 : \text{N}_2 = 1 : 1 : 93 : 5$ vol.%) at GHSV = 1200 h^{-1} over 100 mg catalyst (5 wt% Pt). Reference activities of Pt/ SiO_2 (▲) and Pt/ Al_2O_3 (+) are indicated with a broken line.¹⁷

In effusion of free CO_2 and H_2O molecules through a pin-hole, the ratio is $\text{H}_2\text{O} : \text{CO} : \text{O}_2 : \text{CO}_2 = 1 : 3.0 : 3.7 : 4.0 : 4.7$. Accordingly, the gas phase inside the SiO_2 -nano-tubes should be considerably different from that outside the SiO_2 nano-tubes. In particular, H_2O molecules will stay for a far longer time on the inner surface of the SiO_2 -nano-tubes by wetting the hydrophilic SiO_2 surface and clustering with hydrogen bonds. In contrast, in the case of Pt supported on the outer surface of SiO_2 nano-tubes, H_2O is formed on the outer surface. In a steady flow of reactant gas, the H_2O pressure is far lower than that inside of the Pt/ SiO_2 nano-tubes. Therefore, if the oxidation of CO is enhanced by H_2O on Pt/ SiO_2 , it will prevail over ordinary oxidation of CO(a) with O(a) on the Pt held inside SiO_2 nano-tubes at low temperature. That is, the observed result is explainable without assuming a curious state of Pt. If we measure an *in situ* IR spectrum during the reaction of CO in H_2 , we could find the difference of the oxidation mechanism of CO on Pt-nano-rod on the outer surface of SiO_2 -nano-tubes and on the inside SiO_2 -nano-tubes.

When the catalyst activity of metals is changed by the support oxide or additives, the activity is explained by the change of active area on metals or active lattice oxygen, but the same reaction mechanism is usually premised. A typical example is the SMSI effect. However, in the case of $\text{FeO}_x/\text{Pt}/\text{TiO}_2$, if a Pt/ TiO_2 catalyst was overlaid with a large amount of FeO_x , the activity for the oxidation of CO in H_2 was markedly improved by the addition of FeO_x as shown in Fig. 3, and in the case of Pt/CNT and Pt/CNT-p, the activity is markedly improved in the presence of Ni-MgO separated from the Pt on CNT. These results strongly indicate the new functional role of additives.

To understand these phenomena, the ionic processes were deduced in the catalytic oxidation of CO enhanced by H_2O on the Pt-catalysts with specific promoting materials and on $\text{FeO}_x/\text{Au}/\text{TiO}_2$ catalyst.¹⁶ Tanaka *et al.*¹⁶ showed that large Au particles supported on TiO_2 are inactive for the oxidation of CO, but they change to being an active catalyst for the oxidation of CO in the presence of H_2O after being loaded with a large amount of FeO_x . Bollinger and Vannice¹⁰ also reported an interesting activation of highly pure Au powder (10 μm) for the oxidation of CO at 40 °C by adding TiO_2 , and Daniells *et al.*³⁶ suggested the formation of hydroxyl-carbonyl intermediates on an $\text{Au}/\text{Fe}_2\text{O}_3$ catalyst.

Recently, Yuan *et al.*^{18,19} found an interesting phenomenon whereby the performance of Au/CeO_2 catalysts depended on the crystalline shapes of the CeO_2 , that is, the selectivity for the oxidation of CO in H_2 depended on the crystalline shapes in the order polyhedral $\approx$ rods > cubes, although O_2 consumption in ($\text{H}_2 + \text{CO} + \text{O}_2$) showed little influence by the CeO_2 morphology. They found differences in the ratio of Au^+ and Au^{3+} ions depending on the CeO_2 crystal shapes such that $(\text{Au}^+ + \text{Au}^{3+})/(\text{Au}^0 + \text{Au}^+ + \text{Au}^{3+}) = 25.3 : 46.0 : 61.5$ (%) for (cube) : (polyhedron) : (rod). It is known that the selectivity for the oxidation of CO depends on the $(\text{Au}^+ : \text{Au}^{3+})$ ratio but that it has little effect on the total consumption of O_2 (activity). It is a noteworthy fact that the oxidation of CO enhanced by H_2/D_2 showed an equal hydrogen isotope effect of $r_{\text{H}}/r_{\text{D}} = 1.44$ on the three Au/CeO_2 catalysts with different crystalline morphologies of CeO_2 .¹⁹ These results suggest that the oxidation of CO on the

Au/CeO₂ catalyst may proceed *via* an ionic process, and the reaction is given by reaction (ii) of eqn (1), and that the selectivity is given by the turn-over number of H₂O molecules on the Au/CeO₂ surface, which takes on a larger “*n*” value on CeO₂ surfaces with larger (Au⁺ + Au³⁺)/(Au⁰ + Au⁺ + Au³⁺) values.

Lastly, it should be mentioned that adsorbed HCOO(a) species are very often observed on various catalysts in the oxidation reaction of organic molecules as well as in the water gas shift reaction, but this does not mean similar catalysis, because a catalytic reaction is accomplished by combining all elementary processes required for the catalysis on the surface, that is, similarity of one intermediate does not mean the similarity of catalysis. The Horiuti–Polanyi mechanism is a typical example of confusion, in which the isomerization and the hydrogenation of olefins were premised as occurring by the same catalysis *via* common alkyl intermediates. However, it was proved that the active sites promoting the hydrogenation of olefins were clearly different from the sites for the isomerization of olefins, although both reactions proceed *via* alkyl intermediates.³⁷ From this view point, the water gas shift reaction is undoubtedly different from the irreversible oxidation of CO with O₂ enhanced by H₂O, reaction (ii) in eqn (1), even if HCOO(a) intermediates are observed in both reactions.

5. Conclusions

(1) A new catalytic oxidation of CO enhanced by H₂O *via* an ionic process: oxidation of CO with O₂ on Pt and Au with specific promoting materials is markedly enhanced by H₂O, which involves ionic processes, and the rate-determining slow step is the reaction of HCOO(a) + OH → CO₂ + H₂O on Pt. The role of H₂O is as a kind of molecular catalyst messenger molecule on the surface as expressed by reaction (ii) in eqn (1): CO + 1/2O₂ + H₂O → CO₂ + H₂O.

(2) Function of co-catalysts: the co-catalysts are indispensable for the oxidation of CO on Pt promoted by H₂O, but Pt and promoting materials do not need to be in contact with one another. It was proved by the Pt supported on CNT and CNT-p, where the CNT has Ni–MgO at its terminal end but the CNT-p has no Ni–MgO. The Pt/CNT-p had no activity for the oxidation of CO enhanced by H₂O, but the Pt/CNT was extremely active in the presence of H₂O although the Pt and Ni–MgO are separated one from another on the CNT.

(3) A new concept for the selectivity of preferential oxidation of CO in H₂: selectivity for the preferential oxidation of CO in H₂ is given by $n/(n+1)$, where “*n*” is the number of CO₂ molecules produced by the repeated contribution of one H₂O molecule according to the equation CO + 1/2O₂ + H₂O → [X_i(a)] → CO₂ + H₂O, where H₂O is produced by the oxidation of H₂. The “*n*” is the turn-over number of one H₂O molecule to *n*CO₂ molecules before it leaves the catalyst.

Acknowledgements

We acknowledge the financial support from the MOST of China (2011CBA00508) and the National Natural Science Found for Creative Research Groups of China (51221892), and thank Mrs

Qingcai Feng of the Research Center for Eco-Environmental Sciences of the Chinese Academy of Sciences for her help in accomplishing this review. K.-I. Tanaka acknowledges Mr Mitsushi Umino, the President of Astech Co., for his support of the research.

Notes and references

- 1 N. Al-Sarraf, J. T. Stuckless and D. A. King, *Nature*, 1992, **360**, 243.
- 2 G. Blyholder, *J. Phys. Chem.*, 1964, **68**, 2772.
- 3 M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301.
- 4 M. Date, M. Okumura, S. Tsubota and M. Haruta, *Angew. Chem., Int. Ed.*, 2004, **43**, 2129.
- 5 M. Haruta, *Catal. Today*, 1997, **36**, 153.
- 6 M. Valden, X. Lai and D. W. Goodman, *Science*, 1998, **281**, 1647.
- 7 M. S. Chen and D. W. Goodman, *Science*, 2004, **306**, 252.
- 8 G. Vlaic, P. Fornasiero, S. Geremia, J. Kaspar and M. Grazianj, *J. Catal.*, 1997, **168**, 386.
- 9 Y. Zhang, S. Anderson and M. Muhammed, *Appl. Catal., B*, 1995, **6**, 325.
- 10 M. A. Bollinger and M. A. Vannice, *Appl. Catal., B*, 1996, **8**, 417.
- 11 O. Korotkikh and R. Farrauto, *Catal. Today*, 2000, **62**, 249.
- 12 K.-I. Tanaka, M. Shou, H. B. Zhang, Y. Z. Yuan, T. Hagiwara, A. Fukuoka, J. Nakamura and D. L. Lu, *Catal. Lett.*, 2008, **126**, 89.
- 13 K.-I. Tanaka, M. Shou, H. He and X. Y. Shi, *Catal. Lett.*, 2006, **110**, 185.
- 14 K.-I. Tanaka, M. Shou, H. He, X. Y. Shi and X. L. Zhang, *J. Phys. Chem. C*, 2009, **113**, 12427.
- 15 M. Shou, K.-I. Tanaka, K. Yoshioka, Y. Moro-oka and S. Nagano, *Catal. Today*, 2004, **90**, 255.
- 16 M. Shou, H. Takekawa, D. Y. Ju, T. Hagiwara, D. L. Lu and K.-I. Tanaka, *Catal. Lett.*, 2006, **108**, 119.
- 17 A. Fukuoka and M. Ichikawa, *Top. Catal.*, 2006, **40**, 103.
- 18 G. Q. Yi, Z. N. Xu, G. C. Guo, K.-I. Tanaka and Y. Z. Yuan, *Chem. Phys. Lett.*, 2009, **479**, 128.
- 19 G. Q. Yi, H. W. Yang, B. D. Li, H. Q. Lin, K.-I. Tanaka and Y. Z. Yuan, *Catal. Today*, 2010, **157**, 83.
- 20 S. J. Tauster, S. C. Fung and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170.
- 21 S. Surnev, J. Schoiswohl, G. Kresse, M. G. Ramsey and F. P. Netzer, *Phys. Rev. Lett.*, 2002, **89**, 246101.
- 22 C. Hardacre, R. M. Ormerod and R. M. Lambert, *J. Phys. Chem.*, 1994, **98**, 10901.
- 23 Y.-N. Sun, Z.-H. Qin, M. Lewandowski, E. Carrasco, M. Sterrer, S. Shaikhutdinov and H.-J. Freund, *J. Catal.*, 2009, **266**, 359.
- 24 A. Golchet and J. M. White, *J. Catal.*, 1978, **53**, 266.
- 25 H. Yoshida, S. Takeda, T. Uchiyama, H. Kohno and Y. Honnma, *Nano Lett.*, 2008, **8**, 2082.
- 26 K.-I. Tanaka, M. Shou and Y. Z. Yuan, *J. Phys. Chem. C*, 2010, **114**, 16917.

Review

- 27 K.-I. Tanaka, H. He, M. Shou and X. Y. Shi, *Catal. Today*, 2011, **175**, 467.
- 28 X. Y. Shi, K.-I. Tanaka, H. He, M. Shou, W. Xu and X. Zhang, *Catal. Lett.*, 2008, **120**, 210.
- 29 I. Langmuir, *Trans. Faraday Soc.*, 1921, **17**, 607.
- 30 M. Show and K.-I. Tanaka, *Catal. Lett.*, 2006, **111**, 115.
- 31 K. Tamaru, *Dynamic Heterogeneous Catalysis*, Acad. Press Inc., London, 1978.
- 32 R. B. Levy and M. Boudart, *J. Catal.*, 1974, **32**, 364.
- 33 K.-I. Tanaka and A. Ozaki, *J. Catal.*, 1976, **8**, 1.
- 34 R. P. Iczkowski and J. L. Magrave, *J. Am. Chem. Soc.*, 1962, **83**, 3547.
- 35 K.-I. Tanaka, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3887.
- 36 S. T. Daniells, M. Makkee and J. A. Moulijn, *Catal. Lett.*, 2005, **100**, 39.
- 37 K.-I. Tanaka, *Adv. Catal.*, 1985, **33**, 99.