RSC Advances

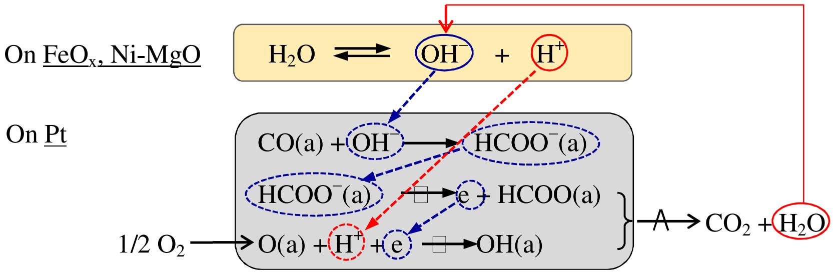
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Graphical and textual abstract

Catalytic oxidation of CO on metals involving ionic process in the presence of H_2O: The role of promoting materials

Ken-ichi Tanaka,* Hong He and Youzhu Yuan



A new catalytic oxidation of CO enhanced by H_2O *via* an ionic process: Oxidation of CO with O_2 on Pt and Au with specific promoting materials is markedly enhanced by H_2O, which involves ionic processes, and the rate-determining slow step is the reaction of HCOO(a) + OH → CO_2 + H_2O on Pt. The role of H_2O is as a kind of molecular catalyst messenger molecule on the surface.

Journal Name RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Catalytic oxidation of CO on metals involving ionic process in the presence of H_2O: The role of promoting materials

Ken-ichi Tanaka,[a*] Hong He[b] and Youzhu Yuan[c]

A new catalytic oxidation of CO involving ionic process in the presence of H_2O is proposed on Pt-catalyst with specific promoting materials (co-catalysts). Oxidation of CO is very slow at room temperature on ordinary Pt-catalysts such as Pt/SiO_2, Pt/Al_2O_3, Pt/TiO_2, Pt/Graphite, Pt/carbon nano-tube (CNT), and H_2 or H_2O gives no effect on the reaction. However, in the presence of specific co-catalysts, the oxidation of CO is markedly enhanced by H_2 or H_2O, so that highly selective preferential oxidation (PROX) of CO in H_2 is attained. The role of co-catalysts plays in the oxidation of CO enhanced by H_2 or H_2O 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 H_2 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 enhanced the oxidation of CO by H_2 or H_2O was observed on the $FeO_x/Pt/TiO_2$ and $FeO_x/Au/TiO_2$, although no enhancement was observed on the Pt/TiO_2 and Au/TiO_2 catalysts. The *in-situ* DRIFT spectra of the $FeO_x/Pt/TiO_2$ catalyst (Fe : TiO_2 : Pt = *ca.* 100 : 100 : 1) during reaction in a flow of ($CO + O_2 + H_2$) suggested the rate-determining slow step was $HCOO(a) + OH(a) \rightarrow CO_2 + H_2O$. The oxidation of CO enhanced by H_2O/D_2O and H_2/D_2 showed a common hydrogen isotope effect of $r_H/r_D = 1.4-1.5$. The highly selective oxidation of CO in H_2 on the Pt/CNT and Pt/CNF catalysts strongly suggests efficient transport of ionic intermediates from the 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 H_2 is defined by the turnover number of a H_2O molecule forming CO_2 during its time of residence on the catalyst, which is essentially different from the selectivity based on competitive adsorption and/or reaction. The role of H_2O molecule is as a kind of messenger molecule or a molecular catalyst to promote the reaction on the surface expressed by the equation $n(CO + 1/2\ O_2) + H_2O \rightarrow n\ CO_2 + H_2O$. In this mechanism, the selectivity is given by $\mathbf{n}/(\mathbf{n+1})$. Curious phenomena previously observed in the PROX reaction of CO in H_2 on various catalysts are well explained by the mechanism including ionic process proposed in this paper.

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 10^{12} 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, giving that have no ability to adsorb CO. In contrast to this accepted knowledge, 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 nm is difficult to explain simply by the perimeter length. In relation to this phenomenon, Goodman hypothesized the activity 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 $Rh/Ce_{0.5}Zr_{0.5}O_2$, $Pt\text{-}Rh/CeO_2$, and $Pt\text{-}Rh/CeO_2\text{-}ZrO_2$.[8,9] Bollinger and Vannice[10] performed an interesting experiment by depositing TiO_2 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 $Au\text{-}TiO_2$ interface. Farraut et al.[11] found activation of a 5 wt.% $Pt/\gamma\text{-}Al_2O_3$ catalyst for the selective oxidation of CO in H_2 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/TiO_2 as well as on 1 wt.% Au/TiO_2 is markedly influenced by the FeO_x deposited on them as shown in Fig. 1, and the oxidation of CO on $FeO_x/Pt/TiO_2$ and $FeO_x/Au/TiO_2$ is markedly enhanced by H_2O and/or H_2. However, the rate-determining step of the oxidation of CO enhanced by H_2O on the $FeO_x/Pt/TiO_2$ catalyst is neither the adsorption nor the subsequent reaction of 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 H_2 (in the presence of H_2O) has been explained by the competitive reaction of CO(a) and H(a) with adsorbed oxygen or active lattice oxygen, but Daniells et al.[12] proposed a new reaction mechanism of CO *via* hydroxyl-carbonyl intermediates on an Au/Fe_2O_3 catalyst. Tanaka et al.[13–16] found unusual catalytic activity with Pt/TiO_2 and Au/TiO_2 covered with a large amount of FeO_x (*ca.* 100 wt.% in Fe) for the oxidation of CO in the presence of H_2, that is, H_2O. So far no one observed CO adsorbed on the Au catalyst, but an IR peak appearing at 1803 cm^{-1} on the $FeO_x/Au/TiO_2$, assignable to bridge-bonded CO, was observed when 1 wt.% Au/TiO_2 was covered with large amount of FeO_x as shown in Fig. 1.[13,16] Interestingly, the bridge bonded CO was also markedly increased on the Pt/TiO_2 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 in simply, the low temperature oxidation of CO is enhanced by H_2O on $FeO_x/Pt/TiO_2$, and is different from the oxidation with O_2 without H_2 on $FeO_x/Pt/TiO_2$ and in the presence of H_2 on Pt/TiO_2. In fact, the *in-situ* IR spectroscopy suggested the rate-determining reaction of $HCOO(a) + OH(a) \rightarrow CO_2 + H_2O$ on the $FeO_x/Pt/TiO_2$ catalyst. Based on the dynamics of the *in-situ* DRIFT spectroscopy, a mechanism involving 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 H_2O on Pt stopped. An important fact is that the Pt particle are completely separated from $Ni\text{-}MgO_x$ or FeO_x on the Pt/CNT and Pt/CNF catalysts, but the promoting materials and H_2O are indispensable for this new catalytic oxidation of CO.

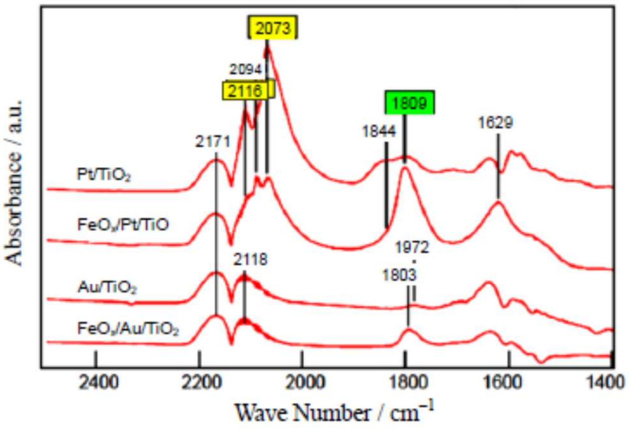


Fig. 1 Bridge-bonded CO peak (1844–1792 cm^{-1}) on 1 wt.% Pt/TiO_2 and 1 wt.% Au/TiO_2 is markedly increased on the $FeO_x/Pt/TiO_2$ and $FeO_x/Au/TiO_2$ surfaces at 40 °C. The peaks at 2172 and 2118 cm^{-1} are gas-phase CO.[13,16]

Fukuoka et al.[17] reported curious activity of Pt-nano-rods (3 nm × several hundred nm) for the selective 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, which was explained by the existence of a specific electronic state in the Pt-nano-rods in the SiO_2-nano-tubes for the oxidation of CO(a) with O(a). Yuan et al[18,19] observed the effect of the crystalline shape of CeO_2 support in Au/CeO_2 catalysts on their activity and selectivity in the oxidation of CO in H_2. 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 H_2O, 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 H_2 should be different from that of the traditional mechanism based on the competitive reaction of CO and H_2. A meaningful definition of the selectivity in the preferential oxidation of CO in H_2 is given by the turn-over number "**n**" of one H_2O molecule forming CO_2 molecule as described by the equation $n(CO + 1/2\ O_2) + H_2O \rightarrow n\ CO_2 + H_2O$, in the residence time of the H_2O molecule on the 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 $TiO_{2\text{-}x}$ 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 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 was first observed by Lambert et al.[22] for CeO_2 deposited on a Pt(111) surface. One monolayer of CeO_2 on the 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 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 worthy of note 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.

1. 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 White[24] 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 ºC 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 have been explained as weakening the adsorbed CO on Pt or improving the adsorption of O(a) or proving active lattice oxygen from 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 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 having promoting materials only at their one terminal end. Yoshida et al.[25] was the first to successfully observe 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 narrow 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 necessarily for it to be in contact with 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 H_2O/D_2O was studied, and it was confirmed that H_2/D_2 and H_2O/D_2O gave an 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.

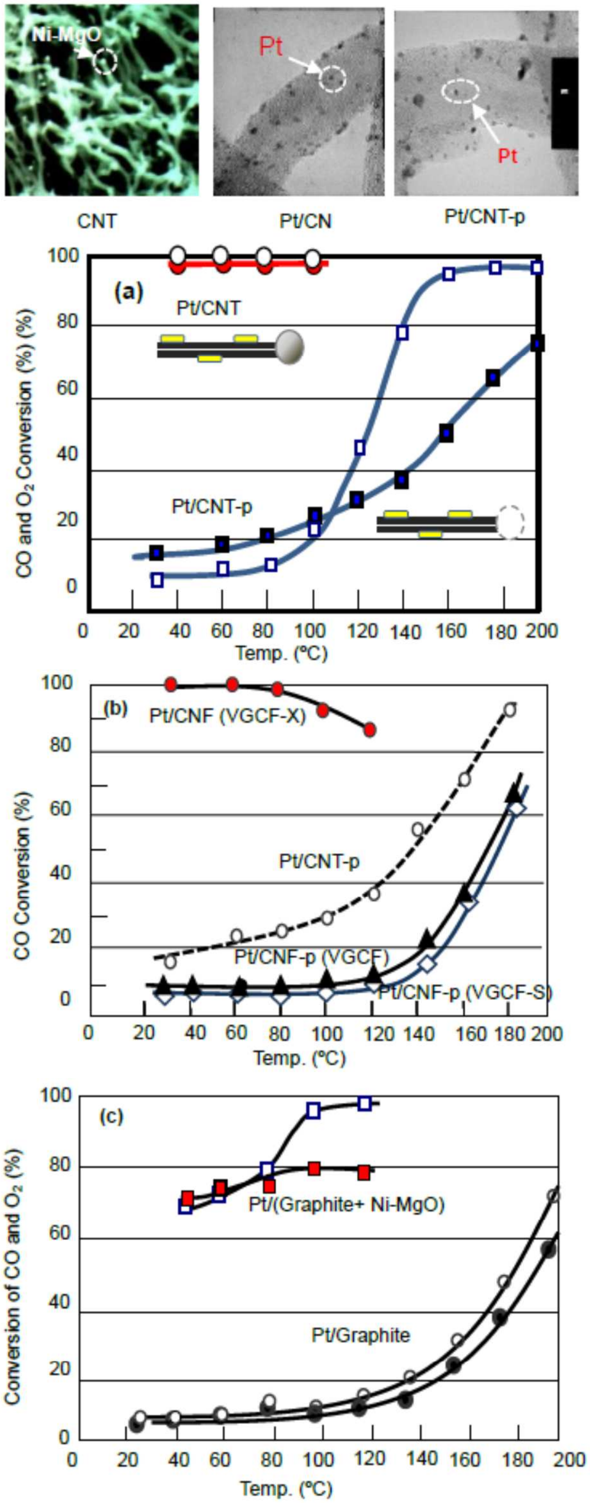


Fig. 2 **(a)** TEM images of CNT, Pt/CNT, and Pt/CNT-p, and the activity and selectivity of Pt/CNT and Pt/CNT-p for the PROX reaction of CO in H_2. Conversion of CO (solid) and O_2 (open) attained in a flow of 100 mL/min of ($CO/O_2/H_2$ = 1.5/1.5/42.0 mL/min) with a balance of N_2 on 15 wt.% Pt/CNT and 15 wt.% Pt/CNT-p (0.8 gr).
(b) Conversion of CO attained in a flow of ($CO/O_2/H_2/N_2$) = 3.0/1.5/20.0/78.5 (mL/min) on 5 wt.% Pt/CNF (VGCF-X) (●) and 5 wt.% Pt/CNT-p (○), 5 wt.% Pt/VGCF (▲), 5 wt.% Pt/VGCF-S(◇).

(c) Conversion of CO (solid) and O_2 (open) attained in a flow of (CO / O_2/ H_2 / N_2) = 3.0 / 1.5 / 20 /75.5 (mL/min) 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]

As shown in Fig. 2(a), nearly 100 % conversion of CO was attained in a flow at 100 mL/min of (CO + H_2 + O_2 + N_2) (CO : O_2 : 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 ºC. 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 understand 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; ϕ15 nm × 4 μmL of Showa Denko Co.), which were prepared using 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 ºC (CNF-p). Three lots of CNF, VGCF; ϕ150 nm × 8 μmL, VGCF-H; ϕ150 nm × 6 μmL, and VGCF-S; ϕ80 nm × 10 μmL, were used. As shown in Fig. 2(b), the Pt/CNF (VGCF-X) catalyst was very active for the PROX reaction of CO in H_2, and nearly 100% selective oxidation of CO (CO/O_2 = 2/1) was attained in a flow of CO (3.0 mL/min) + O_2 (1.5 mL/min) + H_2 (20.0 mL/min) + N_2 (78.5 mL/min) 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 ºC. 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 H_2O. Accordingly, the total mechanism for the oxidation of CO promoted by H_2O is accomplished by the effective transport of the intermediates between Ni-MgO or FeO_x and Pt particles.[28]

A similar promoting effect of H_2 and H_2O on the oxidation of CO was observed on Pt/TiO_2 overlaid with a large amount of FeO_x.[13–16] As shown in Fig. 3(a), the oxidation of CO was not enhanced by H_2O (or H_2) on a 1 wt.% Pt/TiO_2 catalyst, but was markedly enhanced on the FeO_x/Pt/TiO_2 catalyst at 60 ºCby H_2 and H_2O as shown in Fig. 3(b) and (c),[13,15] where the FeO_x/Pt/TiO_2 was prepared by overlaying a large amount of FeO_x (*ca*. 100 wt.% in Fe) on the 1 wt.% Pt/TiO_2. If H_2 or H_2O was 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 H_2O is not the activation of the Pt or FeO_x, but provides a new catalytic oxidation reaction of CO(a) as is discussed in detail below. It is worthy of note that the Pt/TiO_2 and FeO_x/Pt/TiO_2 used here have almost equal activity for the oxidation of CO with O_2 at 60 ºC in the absence of H_2 or H_2O, that is, the H_2O molecule enhances the oxidation of CO only on the FeO_x/Pt/TiO_2 surface but not on the Pt/TiO_2, although their activity for the oxidation of CO in the absence of H_2 or H_2O is almost equal at temperature higher than 100 C. Therefore, the role of H_2O molecules in **reaction-(ii)** in **eq. (1)** is like a messenger molecule or a molecular catalyst.

$$\left.\begin{array}{ll}\textbf{(i)} & CO + 1/2\ O_2 \rightarrow [CO(a) + O(a)] \rightarrow CO_2 \\ \textbf{(ii)} & CO + 1/2\ O_2 + H_2O \rightarrow [\mathbf{X_i(a)}] \rightarrow CO_2 + H_2O\end{array}\right\} \textbf{eq. (1)}$$

Since Langmuir's work in 1921,[29] the catalytic oxidation of CO with O_2 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 White[24] showed that all adsorbed CO(a) and O(a) on the Pt-foil during reaction depended on the ratio of P(O_2)/P(CO), and all adsorbed species contribute to the oxidation reaction at 180 ºC and 212 °C, but steady state adsorption on the Pt surface during catalysis depended on the ratio of P(O_2)/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 reactivity of the adsorbed species.

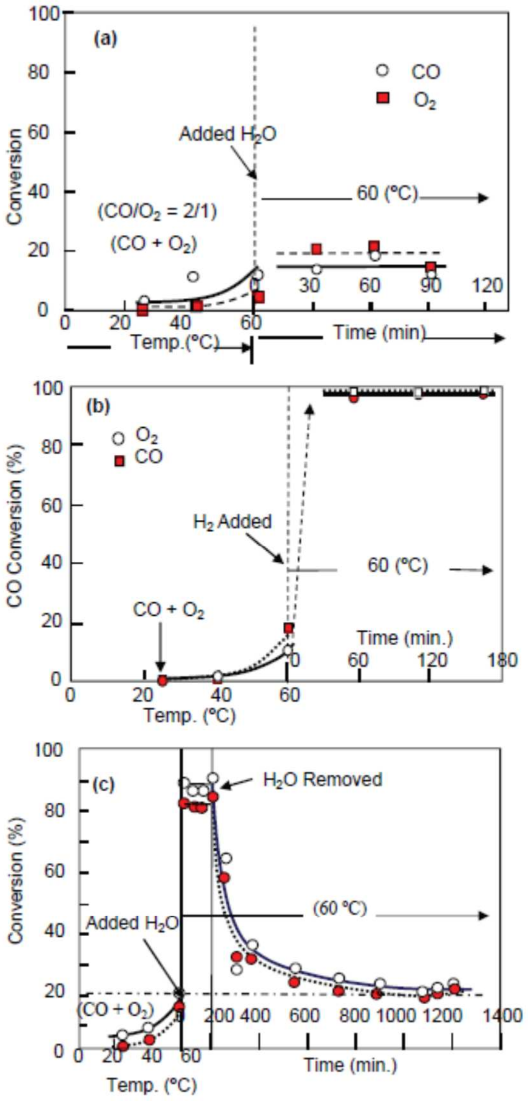


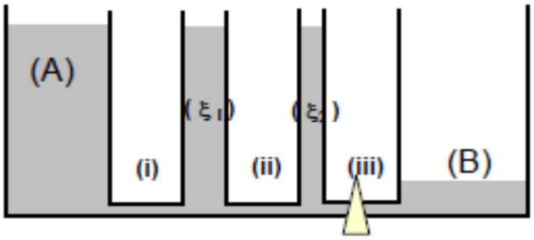
Fig. 3 **(a)** The oxidation of CO with O_2 on a 1 wt.% Pt/TiO_2 catalyst takes no enhancement of H_2O at 60 ºC; **(b)** The oxidation of CO in a flow of [CO (3 mL/min) + O_2 (1.5 mL/mi) + N_2 (95.5 mL/min)] on a $FeO_x/Pt/TiO_2$ catalyst takes remarked enhancement by H_2 (15.0 mL/min) at 60 ºC; **(c)** Enhancement of the oxidation of CO by H_2O on $FeO_x/Pt/TiO_2$ is reversible at 60 ºC.[13]

When the oxidation of CO and H_2 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 H_2 is controlled by the competitive mechanism of the adsorption and reaction of CO(a) and H(a). Therefore, if the activity of a Pt catalyst would be changed by some additives or support materials, this should be explained as the results 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 reactivity of adsorbed species or lattice oxygen. To illustrate this point, here we take up the result of Korotkikh and Farrauto et al.[11] in experiments on the $Pt/\gamma\text{-}Al_2O_3$ and $FeO_x/Pt/\gamma\text{-}Al_2O_3$ catalysts. The activity of $Pt/\gamma\text{-}Al_2O_3$ for the oxidation of CO in H_2 was markedly improved by the addition of FeOx, but the IR spectrum of CO adsorbed on $FeO_x/Pt/\gamma\text{-}Al_2O_3$ showed no difference compared to that of CO on $Pt/\gamma\text{-}Al_2O_3$. They explained the activation of the $FeO_x/Pt/\gamma\text{-}Al_2O_3$ 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 $Pt/\gamma\text{-}Al_2O_3$ and $FeO_x/Pt/\gamma\text{-}Al_2O_3$ 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 $Pt/\gamma\text{-}Al_2O_3$ and $FeO_x/Pt/\gamma\text{-}Al_2O_3$, the CO adsorbed on $FeO_x/Pt/TiO_2$ was entirely different from that on the Pt/TiO_2. That is, linearly bonded CO(a) becomes predominant on the Pt/TiO_2 catalyst but bridge-bonded CO(a) (1809 cm^{-1}) is the main adsorbed species on the $FeO_x/Pt/TiO_2$ catalyst. Furthermore, the oxidation of CO was markedly enhanced by H_2 on the $FeO_x/Pt/TiO_2$ catalyst as shown in Fig. 3(b) and (c), but the reaction on the Pt/TiO_2 catalyst was not enhanced by H_2 as shown in Fig. 3(a).[13,14] It should be emphasized that the bonding of CO is different on $FeO_x/Pt/TiO_2$ and Pt/TiO_2, 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 H_2 or H_2O on $FeO_x/Pt/TiO_2$. This fact convinces us that the rate-determining step of the oxidation of CO enhanced by H_2O on the $FeO_x/Pt/TiO_2$ 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 H_2O, **reaction-(ii)**, is a new oxidation reaction via intermediates [$\mathbf{X_i(a)}$] in **eq. (1)**. In fact, the oxidation of CO enhanced by H_2/D_2 showed an equal hydrogen isotope effect of $r_H/r_D = 1.4\text{–}1.5$ on $FeO_x/Pt/TiO_2$ and Pt/CNT as well as on Au/CeO_2 and $FeO_x/Au/TiO_2$ catalysts, which is equal to the isotope effect when enhanced by H_2O/D_2O, [14,18,30] which indicates that the H_2O molecule is responsible for the enhancement in either case. To understand the oxidation mechanism of CO promoted by H_2O, it is essential to deduce the rate-determining slow step and to identify the intermediates [$\mathbf{X_i}$], as discussed in the following section.

2. Intermediates and rate-determinng slow step

When a catalytic reaction proceeds at a steady-steady, 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]



$$CO(g) \xrightleftharpoons{(i)} (\xi_1) \xrightarrow{(ii)} (\xi_2) \overset{(iii)}{\nrightarrow} CO_2 \qquad \textbf{eq. (2)}$$

Fig. 4 A series-connected water tank model showing 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.

In-situ DRIFT spectra attained on a $FeO_x/Pt/TiO_2$ catalyst in a flow of ($CO + O_2 + N_2$) and ($CO + H_2 + O_2 + N_2$) 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 ($CO + O_2 + N_2$) and ($CO + O_2 + H_2 + N_2$) on $FeO_x/Pt/TiO_2$, although the reaction rates were quite different, as shown in Fig. 3(a) and (b). When the CO was removed from a flow of ($CO + O_2 + H_2 + N_2$), the IR peaks for CO(a) were very quickly erased as shown in Fig. 5(b), but the decrease of the CO(a) were very slow in the absence of H_2 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 H_2, that is, in the presence of H_2O. Therefore, the adsorption of CO, **step (i)**, is very rapid, and the adsorption of CO on the $FeO_x/Pt/TiO_2$ catalyst may be nearly a dynamic saturation in ($CO + O_2$) or ($CO + O_2 + H_2$). 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.

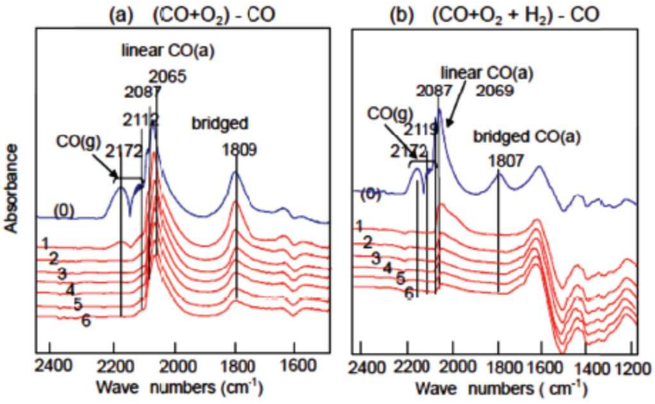


Fig. 5 Time-resolved *in-situ* DRIFT spectra of CO(a) attained on a $FeO_x/Pt/TiO_2$ catalyst at 60 °C. **(a)** CO was removed from ($CO + O_2 + N_2$); **(b)** CO was removed from ($CO + H_2 + O_2 + N_2$). A series of spectra were recorded at time interval: (1) is immediately after the removal of CO, and (2)-(7) are 5, 10, 15, 20, 30, and 45 min after CO removal.[28,30]

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 the removing CO from the reactant gas was extracted. If **step-(iii)** in **eq. (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 H_2 or H_2O exhibits an equal hydrogen isotope effect of r_H/r_D =1.4–1.5 for H_2/D_2 and H_2O/D_2O, which suggests that H_2O is responsible for the oxidation of CO enhanced by H_2.[28,30] The isotope effect is caused by either the kinetic isotope effect given by the rate constant (k_H> k_D) or the thermodynamical pre-equilibration of the intermediates (concentration) proceeding with the rate-determining step (K_H/K_D).

Time-resolved DRIFT spectra obtained by removing CO from a steady flow of ($CO + H_2 + O_2$) are shown in Fig. 6, which reflect the decrease of intermediates from the $FeO_x/Pt/TiO_2$ catalyst due to the reaction, that is, the spectra correspond to the decrease of (ξ_1) and (ξ_2) in **eq. (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 $FeO_x/Pt/TiO_2$ catalyst by the reaction. That is, ξ_1 CO(a) is very rapidly changed to (ξ_2) in **eq. (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 highly reactive OH(a). These two are the key intermediates (ξ_2) in **eq. (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 worthy of note that the large broad band assigned as OH was rapidly decreased from the surface by the reaction, but the characteristic scissors mode of adsorbed H_2O at 1650 cm^{-1} was not observed. This fact indicates that the amount of H_2O on the catalyst changed little on removal of gas phase CO, although H_2O formation should be increased by removing CO from ($CO + H_2 + O_2$). The lack of increase or decrease in the scissors mode of adsorbed H_2O (1650 cm^{-1}) indicates that neither the increase nor the decrease of adsorbed H_2O occurs on removal of gas phase CO. This fact indicated saturation of the catalyst surface with H_2O(a) in the steady-state reaction of ($CO + H_2 + O_2$). Taking these results into account, the broad band centred at 3400 cm^{-1} is not adsorbed H_2O(a) but the reactive OH(a) species, which undergo reaction with HCOO(a) at the rate-determining step as described by **step-(iii)** in **eq. (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).

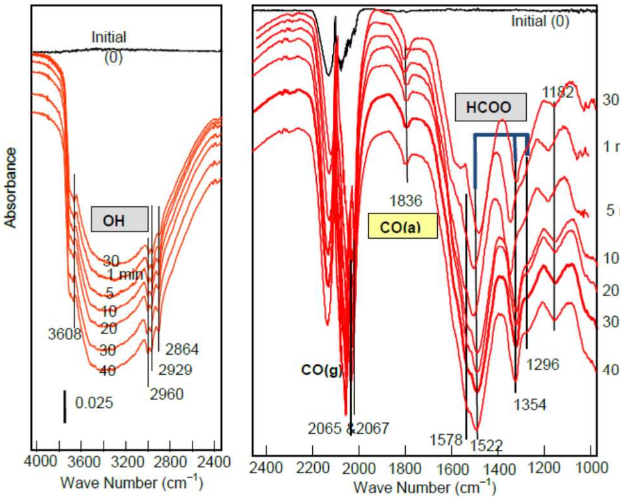


Fig. 6 Time-resolved *in-situ* DRIFT attained by removing CO from a flow of ($CO + H_2 + O_2 + N_2$) at 60 °C. The spectra were obtained at the 30 sec, 1 min, 5 min, 10 min, 20 min, 30 min, and 40 min. after the removal of CO.[28,30]

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 H_2 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 **eq. (1)** occurs on the Pt, where the role of H_2O is like a molecular catalyst working on the surface. Taking this mechanism into account, the selectivity for the preferential oxidation of CO in H_2 is given by the turn-over number "**n**" of H_2O molecules, that is, a meaningful selectivity is the formation of "**n**" CO_2 molecules by one H_2O molecule in steady-state reaction. According to this definition, if one H_2O molecule produces 10 molecules of CO_2 during its stay on the catalyst surface, the selectivity for oxidation of CO in H_2 (H_2O is formed by the oxidation of H_2) becomes 91% (10/11). An interesting question is why the oxidation of CO is enhanced by H_2O 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 WO_3 powder with H_2 in the presence of Pt/Al_2O_3 as shown by Boudart et al.[32] They showed that well-evacuated WO_3 did not change its colour to blue in H_2 even when mixed with Pt/Al_2O_3 powder. However, if a small amount of H_2O or alcohols was added to the H_2, pale yellow WO_3 was readily changed to blue H_xWO_3 by H_2 at 50 ºC, and the efficiency of the promoting molecules depends on their proton affinity. Taking these results into account, the role of H_2O was explained by an ionic process on the surface, that is, adsorbed H(a) on Pt is ionized in the presence of H_2O, $H(a) + H_2O \rightarrow H_3O^+ + e$, and H_3O^+ diffuses over the surface and reacts on the WO_3 with an electron transported through the bulk to form blue H_xWO_3, which is described as $WO_3 + H_3O^+ + e \rightarrow H_xWO_3 + H_2O$. In this case, H_2O is an indispensable molecule to form H_3O^+ ion on the Pt surface, and H_3O^+ ion is transported to WO_3. This process is quite interesting in considering the role of Ni-MgO and FeO_x on the Pt/CNT and Pt/CNF catalysts.

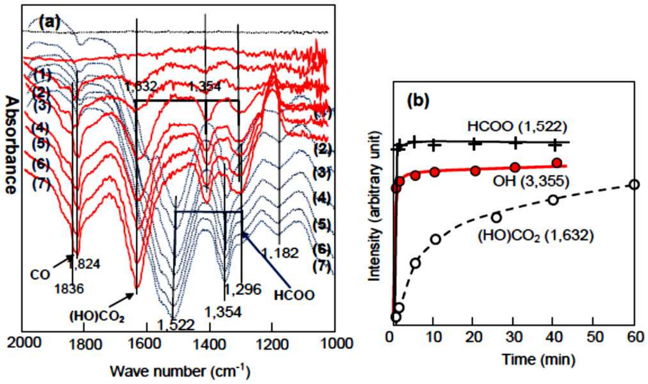


Fig. 7 (a) Change of *in-situ* DRIFT spectra of the $FeO_x/Pt/TiO_2$ catalyst with time when CO was removed from the gas phase in the presence of H_2 (blue) and in the absence of H_2 (red); (b) Decreasing of HCOO(a) (1522 cm^{-1}) and OH (at 3355 cm^{-1}) (solid lines) with time attained by removing gas phase CO in the presence of H_2. Broken line indicates slow decrease of bicarbonate peak (1632 cm^{-1}) with time.

From the dynamics of the DRIFT spectroscopy, reaction of HCOO(a) with OH(a) was deduced as the rate-determining slow step of the oxidation of CO enhanced by H_2O on $FeO_x/Pt/TiO_2$ catalyst. One question regards the mechanism for the rapid formation of the HCOO intermediate on $FeO_x/Pt/TiO_2$ 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 obtined in Fig. 5 (b), that is, the CO(a) adsorbed on Pt of the $FeO_x/Pt/TiO_2$ was very quickly erased by the reaction in the presence of H_2. 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 H_3O^+ 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 Grdient on the Dual Functional Catalyst and the Oxidation of CO on it Enhanced by H_2O

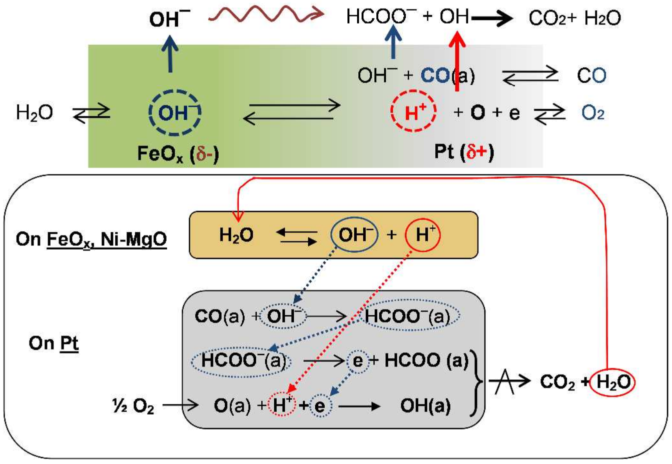


Fig. 8 Oxidation mechanism of CO enhanced by H_2O *via* ionic process. Upper illustration shows potential gradient between Pt and FeO_x made by the population of H^+ and OH^- ions, and OH^- ion transports from FeO_x to Pt and $HCOO^-$ is formed by the reaction with CO. Lower part describes the steady reaction mechanism on the dual functional catalyst with FeO_x and Pt. Selectivity for the preferential oxidation of CO in H_2 is given by **n**/(**n+1**), where "**n**" is the number of CO_2 molecules produced by repeated contribution of one H_2O molecule staying on the catalyst.

It is evident that the oxidation of CO taking place in the presence of H_2O on $FeO_x/Pt/TiO_2$, 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 H_3O^+. 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 H_2O molecules of metal ion and aqueous solution as described by **eq.-(3)**.

$$M(H_2O)_n^{\alpha+} + H_2O \rightleftharpoons M(H_2O)_{n-1}(OH)^{(\alpha-1)+} + H_3O^+ \quad \textbf{eq. (3)}$$

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 **eq. (5)** was derived for metal ions in aqueous solution by defining "the electronegativity of metal ions (χ_α)" given by **eq. (4)**.[33]

The electronegativity of metal ions (χ_α) is defined by **eq. (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, $A_2 + B_2 \rightarrow 2$ A-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 neutral M^0 to M^{+1} ion and "A" is electron affinity of 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.[27] 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 **eq. (4)**.

$$\left.\begin{aligned} I &= \Sigma I_\alpha = a\,\alpha + b\,\alpha^2 + \chi\alpha^3 + ---- \simeq a\,\alpha + b\,\alpha^2 \\ \chi_\alpha &= \partial\Sigma I_\alpha/\partial\alpha \approx (1+2\alpha)\,\chi_o \end{aligned}\right\} \quad \textbf{eq. (4)}$$

where χ_o is the electronegativity of neutral metal atoms expressed by Pauling Electronegativity scale. As shown in Fig. 11 (a), the proton activity of hydrated metal ions ($M^{\alpha+}$) is well expressed by the electronegativity of metal ions (χ_α) in formula-**(i)** of **eq. (5)**.

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

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 [Oxide$(H_2O)_n$ + H_2O ↔ Oxide$(H_2O)_{n-1}(OH)^-$ + H_3O^+]. 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 hydrated oxide surfaces is expressed by the ZPC of oxides, and it was shown that the ZPC of oxide surface can be expressed by a linear relation with respect to the electronegativity of metal ions (χ_α) as shown in Fig. 9(b), which is expressed by **equation-(ii)** in **eq. (5)**.

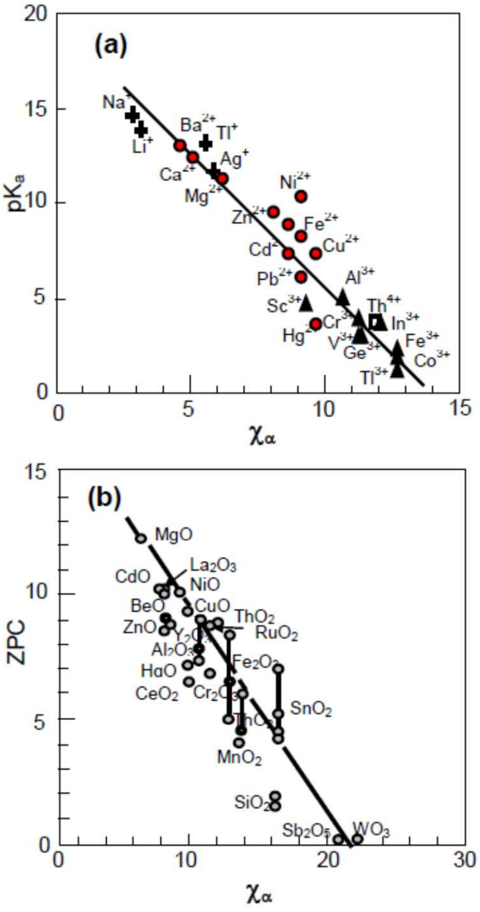


Fig. 9 (a) Ionization constant (pK_a) of aqueous metal ions in water at 25 ºC depending on the electronegativity of +α valence ion (χ_α); (b) The pH of water providing ZPC of oxide surfaces plotted against the electronegativity of ions.[33,35]

As was deduced, the FeO_x/Pt/TiO_2 surface during the oxidation of CO in the presence of H_2 is saturated with H_2O, because the *in-situ* IR spectrum showed neither increase nor decrease of the scissors peak of adsorbed H_2O when the CO in gas phase was removed. If the FeO_x surface is saturated with H_2O molecules during reaction, an ionization equilibrium may be established on the catalyst surface. Taking account of the proton activity of the hydrated FeO_x and Pt surface, excess negative charge on FeO_x creates an equilibrium distribution of ions, $OH^-/H^+ > 1$. To maintain 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 unsual activity and selectivity in the oxidation of CO in H_2 are well rationalized as discussed in the next section.

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

Fukuoka et al.[17] reported curious activity of Pt-nano-rods (3 nm × 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 ($CO/O_2 = 1$) was attained at ca. 80 ºC by flowing a mixture of (CO + O_2 + H_2 + N_2) (1 : 1: 93 : 5 vol %) at 1,200 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 ºC, 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. In effusion of free CO_2 and H_2O molecules through a pin-hole, the ratio is $H_2O : CO : O_2 : CO_2 = 1 : 3.0 : 3.7 : 4.0 : 4.7$. Accordingly, the gas phase inside SiO_2-nano-tubes should be considerably different from that outside the SiO_2 nano-tubes. In particular, H_2O molecules will stay 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 be realize 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.

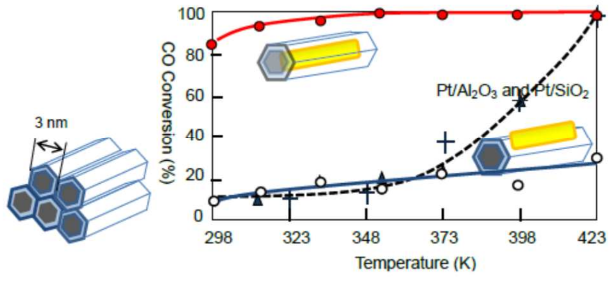


Fig. 10 Model of nano-tube silica and conversion of CO in the PROX reaction in excess H_2. Conversion of CO on Pt-rods supported within SiO_2-nano-tubes (○) and on the external surface of SiO_2-nano-tubes (●) in a flow of ($CO + O_2 + H_2 + N_2 = 1 : 1 : 93 : 5$ vol %) at GHSV = 1,200 h^{-1} over 100 mg catalyst (5 wt.% Pt). Reference activities of Pt/SiO_2 (▲) and Pt/Al_2O_3 (+) are indicated with broken line**.**[17]

When 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 $FeO_x/Pt/TiO_2$, 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 $FeO_x/Au/TiO_2$ 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 loading a large amount of FeO_x. Bollinger and Vannice[10] 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 Au/Fe_2O_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 ≈ rods > cubes, although O_2 consumption in (H_2 + CO + 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 $(Au^+ + Au^{3+})/(Au^0 + Au^+ + Au^{3+})$ = 25.3 : 46.0 : 61.5 (%) for (cube) : (polyhedron) : (rod). It is known that the selectivity for the oxidation of CO depends on the $(Au^+ + Au^{3+})$ ratio but that it is 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_H/r_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/CeO_2 catalyst may proceed via an ionic process, and the reaction is given by **reaction-(ii)** of **eq. (1)**, and that the selectivity is given by the turn-over number of H_2O molecules on the Au/CeO_2 surface, which takes on a larger "**n**" value on CeO_2 surfaces with larger $(Au^+ + Au^{3+})/(Au^0 + Au^+ + Au^{3+})$ 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 O_2 enhanced by H_2O, **reaction-(ii)**, even if HCOO(a) intermediates are observed in both reactions.

Conclusions

(1) A new catalytic oxidation of CO enhanced by H_2O *via* an ionic process: Oxidation of CO with O_2 on Pt and Au with specific promoting materials is markedly enhanced by H_2O, which involves ionic processes, and the rate-determining slow step is the reaction of HCOO(a) + OH → $CO_2 + H_2O$ on Pt. The role of H_2O is as a kind of molecular catalyst messenger molecule on the surface as expressed by **reaction (ii)** in **eq. (1)**: $CO + 1/2\, O_2 + H_2O \rightarrow CO_2 + H_2O$.

(2) Function of co-catalysts: The co-catalysts are indispensable for the oxidation of CO on Pt promoted by H_2O, 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 H_2O, but the Pt/CNT was extremely active in the presence of H_2O 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 H_2: Selectivity for the preferential oxidation of CO in H_2 is given by **n/(n+1)**, where "**n**" is number of CO_2 molecules produced by the repeated contribution of one H_2O molecule according to the equation $CO + 1/2\, O_2 + H_2O \rightarrow [\mathbf{X_i(a)}] \rightarrow CO_2 + H_2O$, where H_2O is produced by the oxidation of H_2. The "**n**" is the turn-over number of one H_2O molecule to n CO_2 molecules before it leaves the catalyst.

Acknowledgements:

We acknowledge the financial supports 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

[a] The Research Center for Eco-Environmental Sciences (guest professor), Chinese Academy of Sciences, Beijing 100085, China, and the University of Tokyo (professor emeritus), Japan. e-mail: ezz01606@nifty.com.

[b] The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China.

[c] State 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.

1 N. Al-Sarraf, J.T. Stuckless, and D.A. King, *Nature*, 1992, **360**, 243.
2 G. Blyholder, J. Phys. Chem., 68 (1964) 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: Environ.*, 1995, **6**, 325.
10 M.A. Bollinger and M.A. Vannice, *Appl. Catal. B: Environ.*, 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. Lev. 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.
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.
27 A. Golchet and J.M. White, *J. Catal*., 1978, **53**, 266.
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. Jap.*, 1973, **46**, 3887.
36 S.T. Daniells, M. Makkee, and J. A. Moulijn, *Catal. Lett*., 2005, **100**, 39.
37 K-I. Tanaka, *Adv. in Catal*., 1985, **33**, 99.