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Isotope effect of H_2/D_2 and H_2O/D_2O for the PROX reaction of CO on the FeOx/Pt/TiO_2 catalyst

Masashi Shou and Ken-ichi Tanaka*

Advanced Science Research Laboratory, Saitama Institute of Technology, 1690 Fusaiji, Fukaya, Saitama 369-0293, Japan

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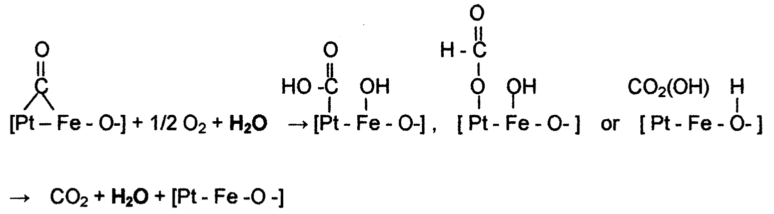
The oxidation reaction of CO with O_2 on the FeOx/Pt/TiO_2 catalyst is markedly enhanced by H_2 and/or H_2O, but no such enhancement occurs on the Pt/TiO_2 catalyst. Isotope effects were studied by H_2/D_2 and H_2O/D_2O on the FeOx/Pt/TiO_2 catalyst, and almost the same magnitude of isotope effect of ca. 1.4 was observed for the enhancement of the CO conversion by H_2/D_2 as well as by H_2O/D_2O at 60 °C. This result suggests that the oxidation of CO with O_2 via such intermediates as formate or bicarbonate in the presence of H_2O, in which H_2O or D_2O acts as a molecular catalyst to promote the oxidation of CO as described below.



KEY WORDS: PROX reaction of CO; Isotope effect of H_2/D_2 and H_2O/D_2O; Molecular catalysis of H_2O; A new PROX catalyst; FeO_X loaded Pt/TiO_2 catalyst.

1. Introduction

Our previous studies discovered a new PROX catalyst (preferential oxidation of CO in H_2) by loading a large amount of FeO_x on supported Pt catalysts [1, 2, 3]. The oxidation of CO on this catalyst is markedly enhanced by adding H_2 and/or H_2O [4]. By loading a large amount of FeO_x on a Pt/TiO_2, the activity is extraordinarily enhanced even though the Pt content is effectively reduced by more than a half. It is tacitly assumed that the reaction on supported metal catalyst takes place only on the metal particles. Therefore, the activity is normalized by dispersion or by assuming specific active sites such as the perimeter. However, the precise role of the support remains a puzzle. A good example is the activity of supported Au catalyst. Haruta et al. [5, 6] showed the size dependent activity of Au particles in the oxidation of CO, and they explained the size effect by the contribution of specific sites located at the perimeter. In contrast, Chen and Goodman [7] recently claimed that a specific array of bi-layer Au atoms on TiO_2 is responsible for the activity; and the size as well as the perimeter are not essential for the activity. We also showed that a low activity 1 wt.% Au/TiO_2 catalyst becomes a superior active catalyst by loading a large amount of FeO_x [8], which is very similar to the activation of 1 wt.% Pt/TiO_2 catalyst by loading a large amount of FeO_x.

The catalysis has been generally explained by the adsorption and followed reaction of the adsorbed molecules. In the case of highly dispersed supported metal catalyst, transportation of molecules and/or intermediates over the support is indispensable to provide molecules to the active site. However, this important role of the support has not been taken into account. Imagine a Pt particle on a support having "Crain Bottle" like curvature (or Riemann Curvature), the whole molecules diffusing over the bottle can reach to the Pt particle. In this case, the apparent sticking probability on the Pt particle depends on the transferable area of the precursor molecules over the support. Why the site-specific enzyme to DNA works so efficiently. Recently it was proved that site-specific DNA-binding proteins undergoes one dimensional transfer along the DNA chain to their working target site [9]. Enhancement of catalytic activity of Pt particles embedded in meso-porous SiO_2 tube [10] is perhaps caused by a similar mechanism of

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*To whom correspondence should be addressed.
E-mail: ktanaka@sit.ac.jp

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two dimensional transportation of reactant molecules to Pt particles. We have pointed out that the transportation of molecules and/or intermediates to active sites requires some times such molecule as H_2O as discussed in our previous paper [4], that is, the oxidation of CO with O_2 on the FeOx/Pt/TiO_2 is markedly enhanced by H_2 and/or H_2O. To confirm the mechanism of this promoting effect of H_2 and/or H_2O, the isotope effects of H_2/D_2 and H_2O/D_2O on the oxidation of CO with O_2 were studies in this paper.

2. Experimental

1 wt.% Pt/TiO_2 (Pt/TiO_2) was prepared by immersing TiO_2 in a solution of $PtCl_4$. After the evaporation of water, the catalysts were dried at 140°C and then calcinated in air at 400°C. The calcinated Pt/TiO_2 was suspended in a solution of $Fe(NO_3)_3$ containing the desired amount Fe ion, and all Fe ion was loaded on the Pt/TiO_2 by vaporization of water. The catalyst was then calcined again in air at 400°C. 100 wt.% FeO_x/Pt/TiO_2 means the weight of Fe is almost equal to that of TiO_2 (Pt/Fe - 1/350 in atom ratio). The reaction was carried out by mounting 1.5 g of catalyst in a fixed-bed flow reactor. Reactant gas was flowed at 100 ml/min of a mixture of 5% CO/N_2 (60 ml/min), O_2 (1.5 ml/min), and H_2 (20 ml/min) with a balance gas of N_2 (18.5 ml/min), where the total flow rate (100 ml/min) was adjusted by a balance gas of N_2 flow. It was confirmed that steady activity is attained by flowing the reactant gas for more than 30 min at each reaction temperature. The isotope effect of H_2 and D_2 for the oxidation of CO was obtained by switching the H_2 flow (20 ml/min) to D_2 flow (20 ml/min). The isotope effect of H_2O and D_2O on the steady conversion of CO was measured by flowing N_2 (40 ml/min) through H_2O or D_2O tank kept at room temperature (the vapor pressure was difficult to measure but it may be about 24 Torr (about 3% in N_2) at 25°C. The reaction for studying the isotope effect was carried out at 60°C at which a steady state conversion is attainable.

3. Results and Discussion

DRFT-IR (Diffuse Reflectance Fourier Transform IR) spectroscopy showed that the main adsorbed form on the FeO_x/Pt/TiO_2 catalyst is the bridge bonded CO [2, 3, 8], which is quite different from the linearly adsorbed CO on a 5% Pt/Al_2O_3 added a small amount of Fe-oxide reported by Korotkikh and Parrauto [11, 12] and Sakamoto et al [13]. In addition, the oxidation of CO with O_2 on the FeOx/Pt/TiO_2 catalyst is markedly accelerated in the presence of H_2 and/or H_2O, but no such enhancement occurs on the Pt/TiO_2 catalyst. For example, the CO conversion of ca. 20% at 60°C in flow of (CO + O_2 + N_2) is elevated to ca. 100% conversion of O_2 and ca. 90% selectivity for CO (CO/O_2 = 2/1) in the presence of H_2, and is elevated to ca. 85% of O_2 conversion by adding moisture [4]. That is, the promoting effect of H_2 or H_2O is responsible for the superior activity of the FeOx/Pt/TiO_2 catalyst. It should be pointed out that no shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, was detected by adding H_2O moisture to a flow of CO at 60°C as shown in Fig. 1.

In-situ DRFT-IR studies of the FeO_x/Pt/TiO_2 catalyst showed that the reaction of bridge bonded CO with O_2 is faster than that of linearly bonded CO on the FeO_x/Pt/TiO_2 in the absence of H_2. Furthermore, not only the reaction of bridge bonded CO but the linearly bonded CO with O_2 are tremendously enhanced by adding H_2. That is, the IR peaks of adsorbed CO were completely erased in the first IR scanning (within 2 min) at 60°C in the presence of H_2 when the flow of CO is stopped. When the flow of CO is maintained, the bridge bonded CO as well as the linearly bonded CO species are detectable during the reaction of CO with O_2 in the presence of H_2 even though the oxidation of adsorbed CO is markedly accelerated in the presence of H_2. These results imply that the adsorption of CO takes place more rapidly than the reaction of adsorbed CO in the presence of H_2 and/or H_2O. The oxidation of CO with O_2 is enhanced by H_2 and/or H_2O but they do not appear in the over-all reaction of $CO + 1/2O_2 \rightarrow CO_2$. If H_2 directly contributes to the oxidation reaction of CO with O_2, the PROX reaction of CO cannot be attained because the oxidation of CO and H_2 will take place in a constant ratio. Therefore, we speculate that H_2O molecule may contribute to promote the oxidation of CO. We may remind an analogous example of the oxidation of ethylene to acetaldehyde by $PdCl_2$ (Wacher reaction),$C_2H_4 + 1/2O_2 \rightarrow CH_3CHO$, in which hydroxyl ethyl intermediate is formed by reacting adsorbed ethylene with OH anion [14].

$$(C_2H_4)PdCl_2(H_2O) + H_2O[(C_2H_4)PdCl_2(OH)]^- + H_3O^+ \rightarrow [HO-CH_2CH_2-PdCl] + HCl + H_2O, \text{ and}$$
$$[HO\text{-}CH_2CH_2-PdCl] \rightarrow CH_3CHO + Pd + HCl.$$

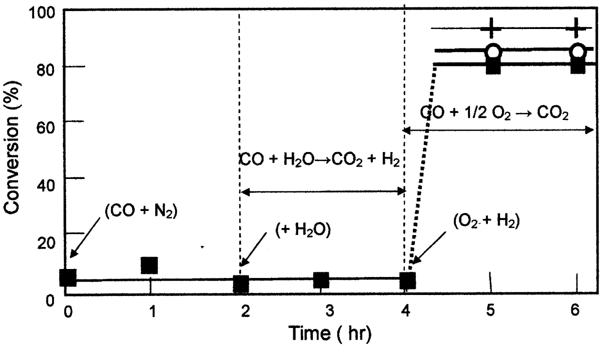


Figure 1. After flowing (100 ml/min) of 3% CO in N_2 for 2 hours at 60°C, H_2O was introduced in the N_2flow. No shift reaction occurs by adding H_2O, but the oxidation of CO occurs by adding O_2 with H_2O.

In over-all equation, H_2O does not appear, but the oxidation of ethylene in H_2O or in D_2O gives a large isotope effect (4.05). The isotope effect is explained by the ionization (dissociation) constant of H_2O and D_2O coordinated to Pd ion. Taking the reaction mechanism and the isotope effect on the oxidation of ethylene into account, the hydrogen isotope effect on the oxidation of CO on the FeOx/Pt/TiO_2 catalyst is of considerable interest.

A steady conversion of CO was attained by flowing a mixture of CO (3 ml/min) + O_2 (1.5 ml/min) + N_2 (95.5 ml/min) for 4 hours over the FeOx/Pt/TiO_2 catalyst at 60°C. Subsequently, D_2 (20 ml/min) was added to the reactant gas with the total flow rate being kept at 100 ml/min by reducing the N_2 flow to 75.5 ml/min. As shown in Fig. 2, the conversion of CO is enhanced by the addition of D_2, but the conversion gradually decreased to ca. 60% in 3 hours. When the D_2 flow was switched to H_2 flow (20 ml/min) after 3 hr, the CO conversion increases from 60% to 76% as shown in Fig. 2. When the H_2 flow is stopped (and N_2 flow is increased to 95.5 ml/min), the conversion of CO goes down finally to ca. 40%. These results show a clear isotope effect of H_2/D_2 for the oxidation of CO with O_2. It should be pointed out that the conversion is gradually lowered to 16% in a flow of CO + O_2 + N_2 after 4 hours, but the conversion of CO just after the stop of H_2 flow is 40%, which is higher than the initial conversion. We speculate that a small amount of H_2O remaining on the catalyst or in the reactor system may enhance the activity for a few minutes after the stop of H_2. A similar observation was made when D_2 was switched to H_2 flow, the conversion did not increase as steeply as noted during the initial addition of H_2. This is presumably because the replacement of D_2O with H_2O is slow on the catalyst. Taking these phenomena into account, the isotope effect of H_2/D_2 on the conversion of CO is computed to be H_2/D_2 = (76–16)/(60–16) = 1.4. If H_2O is indeed responsible for the promoting effect of H_2, the isotope effect of H_2O/D_2O will be 1.4.

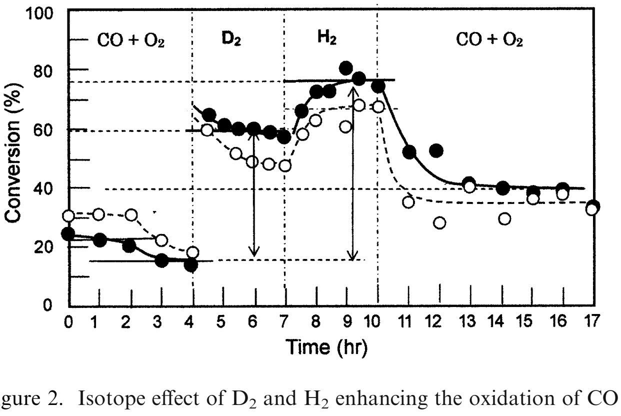


Figure 2. Isotope effect of D_2 and H_2 enhancing the oxidation of CO with O_2 on the FeOx/Pt/TiO_2 catalyst at 60°C CO conversion (●) and O_2 conversion (○). D_2 (20 ml/min) was added at 4 hr of a steady reaction of 3 % CO (3 ml/min) + O_2 (1.5 ml/min) + N_2 (95.5 ml/min), and the D_2 (20 ml/min) was replaced with H_2 flow (20 ml/min) at 7 hr of the reaction. Then, the H_2 flow was stopped at 10 hr. The isotope effect is H_2/D_2 = (76 – 16)/(60 – 16) = 1.4.

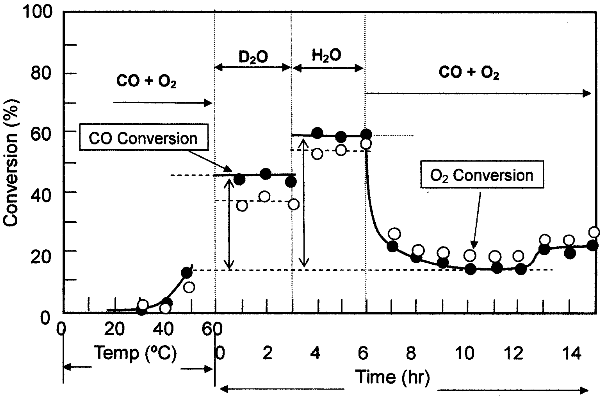
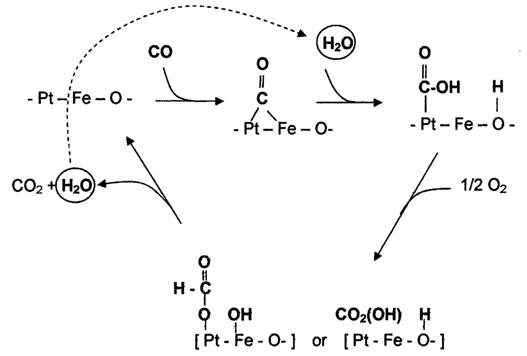


Figure 3. Isotope effect on the oxidation of CO with O_2 enhanced by D_2O and H_2O on the FeOx/Pt/TiO_2 catalyst at 60°C CO conversion (●) and O_2 conversion (○). After a steady conversion was attained at 60°C by flowing CO (3 ml/min) + O_2 (1.5 ml/min) + N_2 (95.5 ml/min), D_2O was introduced into the N_2 flow by bubbling through liquid D_2O at room temperature. After the reaction enhanced by D_2O was run for 3 hours, D_2O was replaced with H_2O. The isotope effect is, $(H_2O)/(D_2O)$ = (60 – 13)/(45 – 13) = 1.4.

In a second set of experiments, the isotope effect of H_2O/D_2O on CO conversion was determined. After a steady conversion of CO (13%) was attained at 60°C by flowing a mixture of {CO (3 ml/min) + O_2 (1.5 ml/min) + N_2 (95.5 ml/min)}, D_2O vapor was added into N_2flow. The conversion was enhanced to 45% by adding D_2O moisture in N_2. When D_2O in N_2 flow was changed to H_2O at 3 hr, the conversion of CO was further elevated from 45% to 60% as shown in Fig. 3. It was also confirmed that the CO conversion was lowered to the original value of 13% when H_2O moisture was removed from the N_2 flow. From these results, the isotope effect of H_2O/D_2O on the conversion of CO is evaluated to be (60 – 13)/(45 – 13) = 1.4, which is very similar to the isotope effect of H_2/D_2. These results suggest that the isotope effect is caused by the contribution of H_2O or D_2O molecule to the oxidation of CO on the FeOx/Pt/TiO_2 catalyst, and support the reaction mechanism proposed in our previous paper [4]. As indicated by the dotted line, the oxidation of CO is promoted by H_2O, in which H_2O acts as a molecular catalyst as indicated by the dotted line.

The oxidation reaction of CO on Au/AI_2O_3, Au/SiO_2, Au/TiO_2, and Au/Fe_2O_3 catalysts is also promoted by H_2O and/or H_2 (4, 15~ 24) Costello et al. [16] recently reported an isotope effect of H_2/D_2 = 1.4 for the oxidation of CO but they observed no isotope effect of H_2O/D_2O on the Au/Al_2O_3 catalyst. They explained that the isotope effect of H_2/D_2 is responsible for the



A mechanism for the PROX reaction of CO on the $FeO_x/Pt/TiO_2$ catalyst

reaction mechanism but due to efficient removal of poisonous carbonate (Au-CO_3) from the active sites.

The hydrogen isotope effect observed in the oxidation of CO on the FeOx/Pt/TiO_2 catalyst in this paper suggests the direct contribution of H_2O molecule to the catalytic oxidation of CO, and H_2O molecule undoubtedly is indispensable for the transportation of reactant molecules and/or intermediates We propose to provide confirmation by spectroscopic studies in the following paper.

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