Isotope effect of H$_2$/D$_2$ and H$_2$O/D$_2$O for the PROX reaction of CO on the FeOx/Pt/TiO$_2$ catalyst

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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$_2$O, but no such enhancement occurs on the Pt/TiO$_2$ catalyst. Isotope effects were studied by H$_2$/D$_2$ and H$_2$O/D$_2$O 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$_2$O/D$_2$O 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$_2$O, in which H$_2$O or D$_2$O 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$_2$O/D$_2$O; Molecular catalysis of H$_2$O; 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$_2$O [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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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 H2O as discussed in our previous paper [4], that is, the oxidation of CO with O2 on the FeOx/Pt/TiO2 is markedly enhanced by H2 and/or H2O. To confirm the mechanism of this promoting effect of H2 and/or H2O, the isotope effects of H2/D2 and H2O/D2O on the oxidation of CO with O2 were studied in this paper.

2. Experimental

1 wt.% Pt/TiO2 (Pt/TiO2) was prepared by immersing TiO2 in a solution of PtCl4. After the evaporation of water, the catalysts were dried at 140°C and then calcinated in air at 400°C. The calcinated Pt/TiO2 was suspended in a solution of Fe(NO3)3 containing the desired amount Fe ion, and all Fe ion was loaded on the Pt/TiO2 by vaporization of water. The catalyst was then calcined again in air at 400°C. 100 wt.% FeOx/Pt/TiO2 means the weight of Fe is almost equal to that of TiO2 (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/N2 (60 ml/min), O2 (1.5 ml/min), and H2 (20 ml/min) with a balance gas of N2 (18.5 ml/min), where the total flow rate (100 ml/min) was adjusted by a balance gas of N2 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 H2 and D2 for the oxidation of CO was obtained by switching the H2 flow (20 ml/min) to D2 flow (20 ml/min). The isotope effect of H2O and D2O on the steady conversion of CO was measured by flowing N2 (40 ml/min) through H2O or D2O tank kept at room temperature (the vapor pressure was difficult to measure but it may be about 24 Torr (about 3% in N2) 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 FeOx/Pt/TiO2 catalyst is the bridge bonded CO [2, 3, 8], which is quite different from the linearly adsorbed CO on a 5% Pt/Al2O3 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 O2 on the FeOx/Pt/TiO2 catalyst is markedly accelerated in the presence of H2 and/or H2O, but no such enhancement occurs on the Pt/TiO2 catalyst. For example, the CO conversion of ca. 20% at 60°C in flow of (CO + O2 + N2) is elevated to ca. 100% conversion of O2 and ca. 90% selectivity for CO (CO/O2 = 2/1) in the presence of H2, and is elevated to ca. 85% of O2 conversion by adding moisture [4]. That is, the promoting effect of H2 or H2O is responsible for the superior activity of the FeOx/Pt/TiO2 catalyst. It should be pointed out that no shift reaction, CO + H2O → CO2 + H2, was detected by adding H2O moisture to a flow of CO at 60°C as shown in Fig. 1.

In-situ DRFT-IR studies of the FeOx/Pt/TiO2 catalyst showed that the reaction of bridge bonded CO with O2 is faster than that of linearly bonded CO on the FeOx/Pt/TiO2 in the absence of H2. Furthermore, not only the reaction of bridge bonded CO but the linearly bonded CO with O2 are tremendously enhanced by adding H2. 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 H2 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 O2 in the presence of H2 even though the oxidation of adsorbed CO is markedly accelerated in the presence of H2. These results imply that the adsorption of CO takes place more rapidly than the reaction of adsorbed CO in the presence of H2 and/or H2O. The oxidation of CO with O2 is enhanced by H2 and/or H2O but they do not appear in the over-all reaction of CO + 1/2O2 → CO2. If H2 directly contributes to the oxidation reaction of CO with O2, the PROX reaction of CO cannot be attained because the oxidation of CO and H2 will take place in a constant ratio. Therefore, we speculate that H2O molecule may contribute to promote the oxidation of CO. We may remind an analogous example of the oxidation of ethylene to acetaldehyde by PdCl2 (Wacker reaction),

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\mathrm{CH2=CH2} + \mathrm{HCl} + \mathrm{H2O} \rightarrow \mathrm{CH3CHO} + \mathrm{H2} + \mathrm{HCl}
\]

\[
\{\mathrm{C2H4}\mathrm{PdCl2(H2O)} + \mathrm{H2O})[\mathrm{C2H4}\mathrm{PdCl2(OH)}]^{-} + \mathrm{H3O}^{+} \rightarrow [\mathrm{HO} - \mathrm{CH2CH2} - \mathrm{PdCl}] + \mathrm{HCl} + \mathrm{H2O}, \text{ and} \]

\[
[\mathrm{HO-CH2CH2-PdCl}] \rightarrow \mathrm{CH3CHO} + \mathrm{Pd} + \mathrm{HCl}
\]

Figure 1. After flowing (100 ml/min) of 3% CO in N2 for 2 hours at 60°C, H2O was introduced in the N2 flow. No shift reaction occurs by adding H2O, but the oxidation of CO occurs by adding O2 with H2O.