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Activation of Pt/TiO_2 catalysts by structural transformation of Pt-sites

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Superior activation of on 1 wt% Pt/TiO_2 catalysts for the oxidation of CO was attained by loading a large amount of Fe-oxide (100 wt%) and TiO_2. *In situ* IR spectra of CO proved that the structural transformation is brought about on the Pt-sites by loading of Fe-oxide, where predominant Pt-sites giving linear CO change to highly reactive bridge CO Pt-sites. In contrast, no transformation of the linear CO sites to the bridge CO sites takes place by loading of TiO_2 but the environment of Pt-sites for linear CO is changed.

KEY WORDS: Pt/TiO_2 catalyst; structural transformation of Pt-sites.

The role of support oxides and promoters changing the activity and/or the selectivity of precious metals is an interesting but unsolved puzzle in heterogeneous catalysis, although it has been empirically explained by dispersion in suitable size particles, formation of active perimeter, and changing the local density of states of metallic particles. Incredible catalytic activity of Au particles is a good example. Haruta et al. [1] showed that Au particle changes superior active catalyst for the oxidation of CO when the particles become smaller than 3 nm. Such active Au particles can be prepared on suitable oxides via $[Au(OH)nC_{14}\text{-}n]$-ion in alkaline solution [2], it is difficult to rationalize the mechanism why the activity is so crucial on the size. Recently, Fu et al. [3] claimed that nano-size metallic Au particles might not contribute to the water-gas shift reaction on an Au/CeO_2–La catalyst, where the non metallic Au ion may be the active site for the water–gas shift reaction, and it is similar on the Pt/CeO_2–La catalyst. In this paper, we proposed a new activation method of Pt-catalyst based on Pt-site restructuring.

As shown in previous paper [4], incredible activation of 1 wt% Pt/Al_2O_3 catalyst is attained by loading a large amount of FeOx (100 wt% in Fe) on it, on which selective oxidation of CO in excess H_2 is brought about in ca. 90% selectivity. We supposed that the activation mechanism by loading FeOx might be different from ordinary synergetic effect such as observed on a 5% Pt/AI_2O_3 catalyst by adding Fe-oxide [5–7]. In this paper, we show the spectroscopic evidence for the reconstruction of Pt-sites induced by Fe-oxide (mainly Fe_2O_3). on 1 wt% Pt/TiO_2 catalyst, which may be responsible for the superior activation of Pt-catalyst.

A 1 wt% Pt/TiO_2 prepared by immersing TiO_2 in a solution of $PtCl_4$ was finally heated in air at 400 °C. Then, the Pt/TiO_2 was dipped in a solution of $Fe(NO_3)_3$, and the whole Fe ion was loaded on the Pt/TiO_2 catalyst. The 100 wt% $FeOx/Pt/TiO_2$ catalyst containing almost equal weight of Fe atom to the 1 wt% Pt/TiO_2 (Fe/Pt≃350) was obtained by heating in air at 400 °C. To make clear the effect of FeOx loaded on the 1 wt% Pt/TiO_2 catalst, TiO_2 was loaded on the Pt/TiO_2 catalyst. A 10 or 50 wt% of TiO_2 was loaded on the Pt/TiO_2 catalyst by immersing 1 wt% Pt/TiO_2 in a titanium hydroxide suspended alkaline solution. Catalytic activity for the oxidation of CO was measured by a fixed-bed flow reactor with 0.06 g catalyst. DRIFT-IR (Diffuse Reflectance IR-Fourier Transform) spectrum was measured by a Nexus 670 (Thermo Nicolet) *in situ* DRIFTS spectrometer equipped with an *in situ* diffuse reflection chamber and a high sensitivity MCT detector. All spectra in this experiment were taken at a resolution of 4 cm^{-1}. Figure 1 shows the FT-IR spectra measured in a flow of N_2 containing 3% CO at 313 K, where the peaks at 2172 cm^{-1} and 2116 cm^{-1} represent the gas phase CO (P and Q branches). The peak at 2172 cm^{-1} was adopted as an intensity reference for the adsorbed CO peaks. It is known that the IR spectrum of CO on the $FeOx/PtTio_2$ is entirely different from that on the Pt/TiO_2 catalyst.

The CO adsorbed on the 1 wt% Pt/TiO_2 takes an intense peak at 2071 cm^{-1} with two shoulders at 2094 and 2060 cm^{-1}, and two weak peaks at 1848 and 1809 cm^{-1} as shown in figure 1a. From the reference data [7–9], the peak at 2071 cm^{-1} and the shoulders at 2094 and 2060 cm^{-1} are assignable to linearly adsorbed

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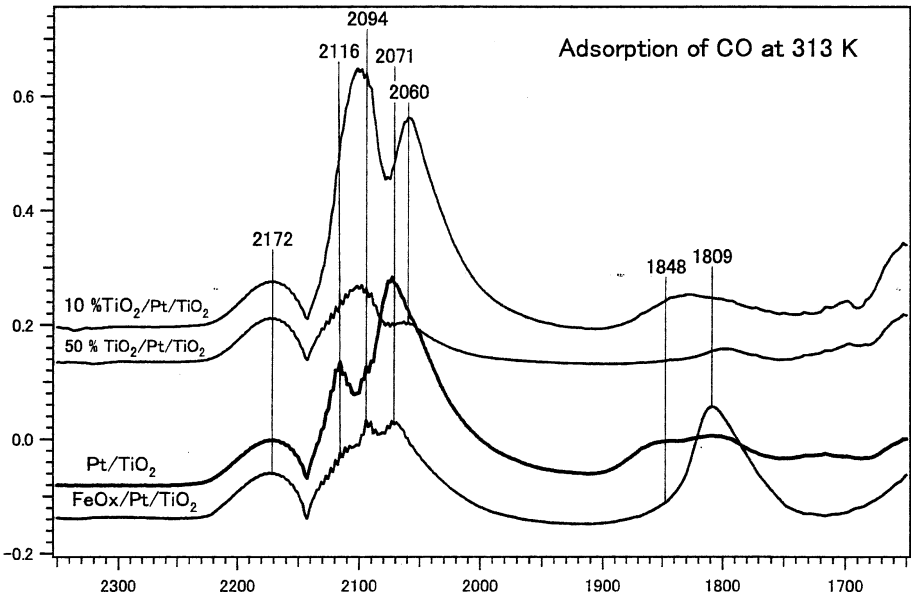

Figure 1. *In situ* IR spectra of CO adsorbed on various catalysts at 313 K. (a) 1 wt% Pt/TiO_2, (b) 100 wt% $FeOx/Pt/TiO_2$, (c) 10 wt% $TiO_2/Pt/TiO_2$, (d) 50 wt% $TiO_2/Pt/TiO_2$.

CO on Pt atoms, where the small peak shift may reflect the adsorption of CO on the Pt-sites with different local density of states. The two peaks at 1848 and 1809 cm^{-1} are the bridge CO, which may be bonded with the pair sites such as Pt–Pt and Pt–Ti.

Adsorption of CO on the $FeOx/Pt/TiO_2$ gave entirely different IR spectrum as shown in figure 1b, where a linear CO at 2071 cm^{-1} was decreased and a bridge CO peak at 1809 cm^{-1} was dramatically increased. This result suggests that the Pt-sites undergo reconstruction by loading Fe-oxide. This result is entirely different from the spectra reported on the Fe-oxide promoted 5 wt% Pt/Al_2O_3 by Liu et al. [6], where only one sharp peak at 2084 cm^{-1} and a weak bridged CO peak at 1820 cm^{-1} appeared on the Pt/Al_2O_3 and the Fe-oxide promoted Pt/Al_2O_3 although the peak height was decreased by paving Pt surface with the Fe-oxide.

The TEM image showed about 2 nm Pt particles on either Pt/Al_2O_3 or Fe-oxide promoted Pt/Al_2O_3. In contrast, Pt particles were hardly identified by the TEM image of our 1 wt% Pt/TiO_2 catalyst although the high resolution gave the lattice image of TiO_2 (not shown here), that is, the Pt is highly dispersed in several atoms, which might be a reason for giving a large peak at 2071 cm^{-1} and the two shoulders for the linearly adsorbed CO on the Pt/TiO_2. However, the TEM image of Pt particles has an ambiguity whether the Pt particle on the TiO_2 has enough layer for the diffraction of electron beam.

It is worthy to note that the peak of linear CO is decreased by loading FeOx but comparable area of the bridge CO peak is grown in figure 1b. This fact suggests that the Pt-sites giving linear CO at 2071 cm^{-1} are transformed to the bridge CO sites by loading FeOx, where the Pt–Fe sites for the adsorption of bridge CO might be formed. It is evident that the bridge CO has higher reactivity than the linear CO on the $FeOx/Pt/TiO_2$ as shown in figure 2. A steady state of adsorption was attained on the $FeOx/Pt/TiO_2$ catalyst by exposing to N_2 containing 3% CO and 1.5% O_2 for 120 min, and then the CO was stopped and N_2 containing 1.5% O_2 was continuously flowed. The gas phase CO peaks at 2173 and 2116 cm^{-1} quickly disappeared from the initial spectrum-(2) by stopping the CO, and the time dependent spectra were attained at 3, 5, 10 and 15 min. The spectra reflect the reaction of adsorbed CO with O_2, and the bridge CO at 1809 cm^{-1} reacts more rapidly than the linear CO, that is, the bridge CO almost disappeared at 15 min although the linear CO at 2065 cm^{-1} was decreased little. From these results, we could expect that the $FeOx/Pt/TiO_2$ will be more active than the Pt/TiO_2. In fact, the oxidation of CO with O_2 takes place far more rapidly on the $FeOx/Pt/TiO_2$ catalyst as shown in figure 3.

To make clear the role of FeOx, TiO_2 was loaded on the Pt/TiO_2. Figure 1c shows the IR spectrum of CO adsorbed on a 10 wt% TiO_2 loaded Pt/TiO_2 catalyst. A main peak of CO on the Pt/TiO_2 at 2071 cm^{-1} was disappeared by loading TiO_2, and the two shoulders at 2060 and 2098 cm^{-1} became the main peaks on the 10 wt% $TiO_2/Pt/TiO_2$. When 50 wt% of TiO_2 was loaded on the Pt/TiO_2 catalyst, however, these peaks at 2060 and 2098 cm^{-1} were suppressed as shown in figure 1d. It should be pointed out that the overlaid TiO_2 on the Pt/TiO_2 gives little effect on the bridged CO, which is remarkable in contrast to the Fe-oxide loaded over the Pt/TiO_2. Taking these facts into account, we deduced that the overlaid TiO_2 modifies merely the circumstance of Pt-sites for linear CO while the Fe-oxide

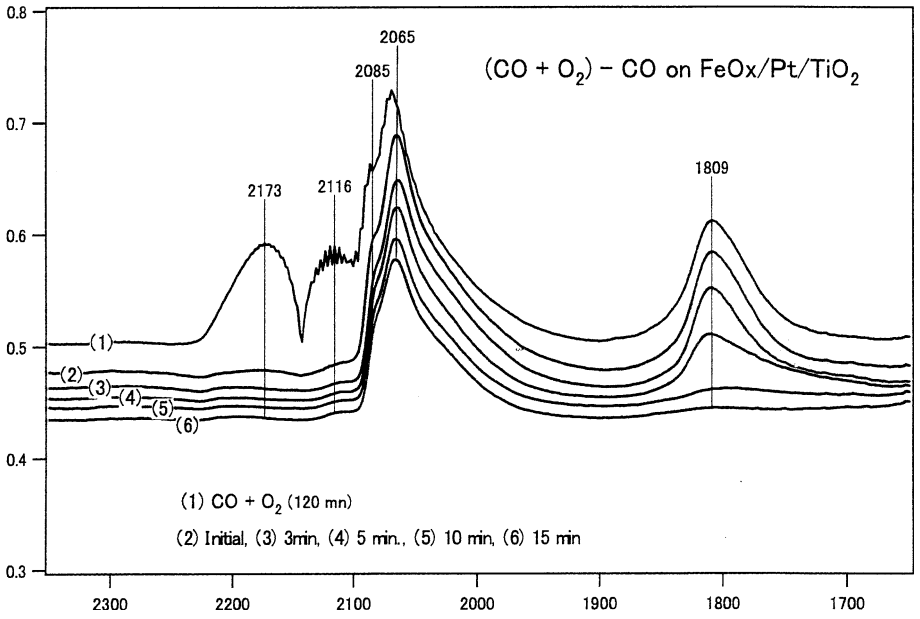

Figure 2. Time dependent *in situ* spectra on 100% FeOx/Pt/TiO_2 : (1) Spectrum exposed to a flow of N_2 containing 3% CO + 1.5% O_2 in N_2 for 120 min at 313 K. Then, CO was removed from the gas phase (spectrum-(2)) and the oxidation adsorbed CO was followed at 3, 5, 10 and 15 min.

transforms the Pt-sites of linear CO into the bridge CO sites (Pt–Fe site). It should be also pointed out that 10% $TiO_2/Pt/TiO_2$ has higher activity than the Pt/TiO_2 and 50% $TiO_2/Pt/TiO_2$ has lower activity than the Pt/TiO_2 as shown in figure 3, which is consistent with the IR spectrum shown in figure 1. That is, the activity is improved by loading TiO_2 but the mechanism is unclear at the present time. We could say that the role of overlaid FeOx and TiO_2 on the activity of 1% Pt/TiO_2 is different from ordinary synergetic effect reported by Liu et al. [6] on the 5% Pt/Al_2O_3, where the activity was improved but IR spectrum was changed little.

We supposed that the Pt–Fe site is formed by loading Fe-oxide, on which the adsorbed CO gives a peak at 1809 cm^{-1} in figure 1b. In conformity with these results, we deduced that the peaks of CO at 1848 and 1809 cm^{-1} in figure 1a are presumed the CO adsorbed on the Pt–Pt and Pt–Ti pair sites on the Pt/TiO_2. A preliminary calculation by the density functional theory gives almost equal wave number for the bridged CO at Pt–Fe site and Pt–Ti site.

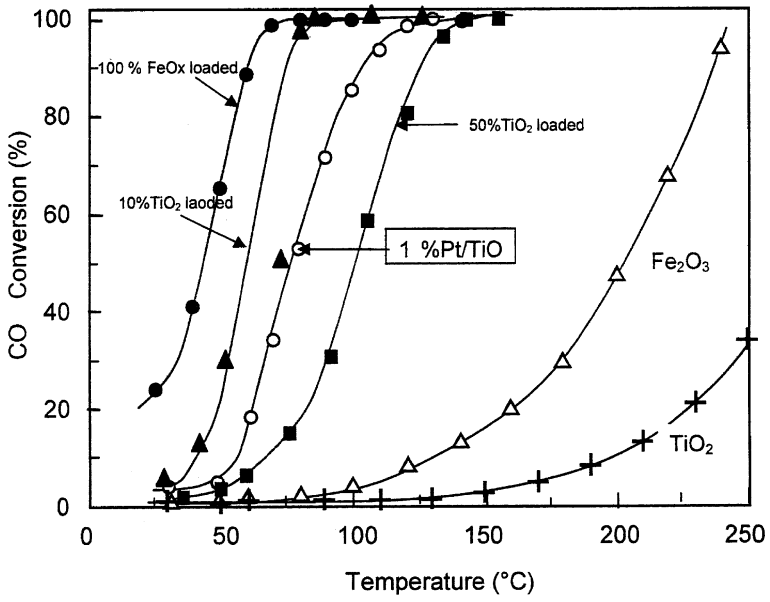

Figure 3. Oxidation of CO over 1 wt% Pt/TiO_2 100% FeOx/Pt/TiO_2, 10% $TiO_2/Pt/TiO_2$ and 50% $TiO_2/Pt/TiO_2$. Conditions: GHSV = 50,000 h^{-1}, 0.8 vol% CO + 10 vol% O_2 in N_2.

We conclude that the overlaid FeOx and TiO_2 on the Pt/TiO_2 make transform the Pt-sites, where the Pt-site for linear CO at 2073 cm^{-1} changes to the Pt–Fe site by Fe-oxide, while the TiO_2 changes the circumstance of the Pt-sites and the CO peaks appear at 2060 and 2098 cm^{-1}. The activity sequence for the oxidation of CO was 100% $FeOx/Pt/TiO_2 > 10\%$ $TiO_2/Pt/TiO_2 > 1$ wt% $Pt/TiO_2 > 50\%$ $TiO_2/Pt/TiO_2$. Finally, it should be pointed out that the activity will be improved by not only the modification of active site but the kinetic enhancement by the support.

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