Development of Pt/ZSM-5 Catalyst with High CO Selectivity for Preferential Oxidation of Carbon Monoxide in a Reformed Gas

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Pt/zeolite catalysts have high CO selectivity for preferential oxidation of CO (PROX). To clarify this reason, characterization of Pt/ZSM-5 catalysts with high and low selectivity was performed. It was found that the catalyst with high selectivity consists of small Pt particles supported in ZSM-5 pores, but another one does of large particles locating outside. Chemical and/or physical molecular sieve effects in ZSM-5 must be responsible to the high selectivity. This concept can be applied to other metal/zeolite systems.

Polymer electrolyte fuel cells (PEFCs) are attracting much attention as power sources applied to electric vehicles and residential co-generation. Hydrogen fuel for PEFCs can easily be obtained by reforming liquid hydrocarbon fuels or natural gas. However, a conventional Pt anode catalyst operating with reformed gases is seriously poisoned by a small amount of carbon monoxide,[1] e.g., the presence of only 10 ppm CO poisons the electrocatalyst, whereas CO content in reformate is about 1% in general.[2] Preferential oxidation of CO (PROX) by adding O_2 in air to reforming gas is one of the convenient processes to lower the CO content to an avoidable level against the poisoning.

In the PROX, an excess O_2 added is also used to oxidize H_2, which leads to loss of the fuel efficiency at PEFC. Accordingly, the PROX catalyst must have a high CO and low H_2 oxidation activity, i.e., high selectivity.

We have investigated Pt catalysts supported on zeolites with different pore sizes for PROX and found that they have higher selectivity than conventional Pt/Al_2O_3 catalyst.[3–6] For the reason, we have pointed out the contribution of certain physical and/or chemical "molecular sieve effects" of zeolite pores. Since H_2 is a very small molecule, it may have a short residence time in zeolite pores. Generally, on the other hand, CO and O_2 exhibit high chemisorption properties in addition to the larger sizes than H_2. Therefore, they must have longer residence times in the pores than H_2 and larger chances of adsorption on Pt clusters supported in zeolite pores, resulting in the selective oxidation of CO more than Pt/Al_2O_3 catalyst. However, there is a counterargument to our explanation, i.e., a difference of the interaction between Pt and zeolite or Al_2O_3 may cause the selectivity improvement.

In the present work, we prepared two kinds of Pt/ZSM-5 catalyst by changing pretreatment temperature. One has high selectivity and the other has low selectivity for PROX. From characterization of them, we will show the importance of "molecular sieve effects" for the high selectivity of Pt/zeolite catalyst at the PROX.

Pt catalysts were supported on ZSM-5 (HSZ-820NAA, TOSOH) by using conventional ion-exchange method.[3–6] Pt loading of Pt/ZSM-5 was determined to be 6 wt %, by ICP analysis. The PROX activity test was carried out in a conventional flow reactor.[3–6] The reaction mixture consisted of 1.0% CO, 0.5% O_2, and H_2 balance. On-line gas chromatograph with TCD was used to measure the catalytic activity. All the data reported here were collected for the steady-states, where carbon balance was achieved under all the reaction conditions. PROX performances of the catalysts were evaluated on CO conversion, O_2 conversion, and selectivity, which was the ratio of O_2 consumption for CO oxidation to total O_2 consumption. Before usage, the catalysts were pretreated at 300 or 500 °C in O_2 flow for 1 h, followed by pretreatment in H_2 flow for 1 h at the same temperature, respectively. The catalysts are denoted as Pt/Z-300 and Pt/Z-500, respectively. To obtain information about physical properties of the catalysts, X-ray diffraction (XRD, Rint-TTR, Rigaku International Corporation) and transmission electron microscope (TEM, HD-2000, Hitachi, Science Systems, Ltd.) observation were performed after the PROX tests.

Figure 1 shows changes of the CO conversion, the O_2 conversion, and selectivity of both catalysts at 200 °C as a function of W/F. W and F are the weight of the catalyst and total flow rate of the reactant gas, respectively. The CO conversion, selectivity and O_2 conversion on Pt/Z-300 increased with increasing W/F. On Pt/Z-500, CO conversion and selectivity also increased with increasing W/F, but they were clearly smaller than those

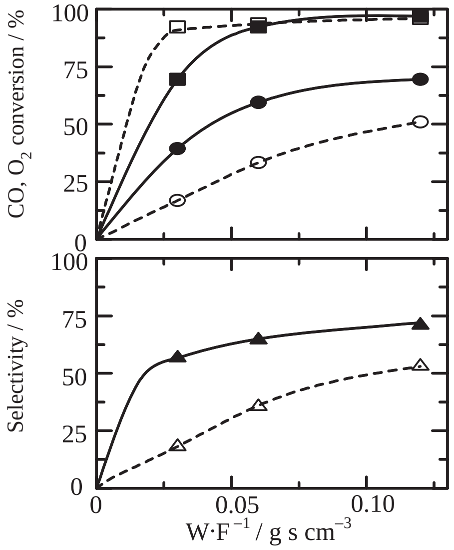

Figure 1. Changes of CO conversion (●,○), O_2 conversion (■,□), and CO selectivity (▲,△) on Pt/Z-300 (full line, closed symbol) and Pt/Z-500 (dotted line, open symbol) at 200 °C as a function of W/F.

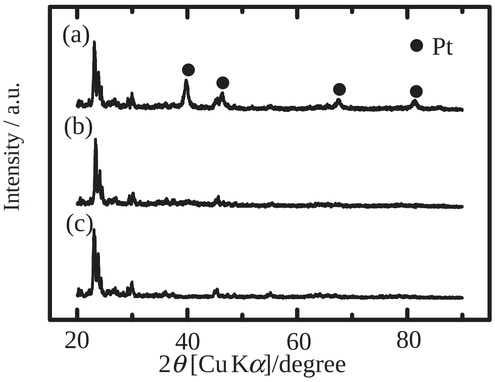

Figure 2. XRD patterns of Pt/ZSM-5 catalysts. (a) Pt/Z-500, (b) Pt/Z-300, and (c) ZSM-5 support.

of Pt/Z-300. On the other hand, O_2 conversion on Pt/Z-500 approached to an almost complete consumption, over 90% even at $W/F = 0.03\,g{\cdot}s{\cdot}cm^{-3}$, resulting in useless combustion of a large amount of H_2 or the low CO selectivity under all the W/F conditions.

To understand the reason why Pt/Z-300 showed such higher CO conversion and selectivity than Pt/Z-500, XRD measurements on the both catalysts after PROX activity tests and on ZSM-5 of their support were performed. The result was shown in Figure 2. Since both catalysts did not show any difference in their diffraction peak positions and intensity between $2\theta = 20$ to $30°$ corresponding to ZSM-5 support, no change in the crystal structure occurred during the pretreatment and PROX tests. At Pt/Z-500, diffraction peaks ascribed to Pt particles were clearly observed, of which average size was estimated to be ca. 11 nm in diameter. On the other hand, no Pt peaks could be observed at Pt/Z-300, indicating a highly dispersed loading of Pt particles below 2 nm in diameter.

Figure 3 shows TEM images observed on test pieces of both Pt supported catalysts prepared by slicing with microtome. On Pt/Z-500 (Figure 3a), many Pt particles with different sizes (> a few nm in diameter) can be observed, although a small number of particles (ca. 1 nm in diameter) are also observed. Because the pore diameter of ZSM-5 is about 0.6 nm,[7] large Pt particles with distributed sizes must exist on outer surfaces of ZSM-5 due to the agglomeration by the free surface diffusion. In Pt/Z-300 (Figure 3b), small particle images of Pt are observed uniformly dispersing with almost the same size (ca. 1 nm in diameter). Such loading state may be obtained by the restriction of the diffusion of ion-exchanged Pt species and the growth of Pt particles due to the limiting space in ZSM-5 cage template. Image sizes of some Pt particles look larger than the pore diameter, but the sizes are not always necessary less than the pore diameter because of such reasons as electron scattering effect by the pore walls or overlapping of particle images. In the same picture, lattice fringe images of ca. 1.0 nm spacing, corresponding to the repeating structure in (111) projection of ZSM-5 cages, are observed. Owing to the particle uniformity and nearly the same sizes between the Pt particles and the spacing, it was conjectured that these monodispersed Pt particles were formed in ZSM-5 pores. Watanabe et al. observed similar image in Pt-Fe/mordenite and concluded that Pt existed in mordenite pores.[8]

As seen above, Pt/Z-300 showed higher CO conversion than

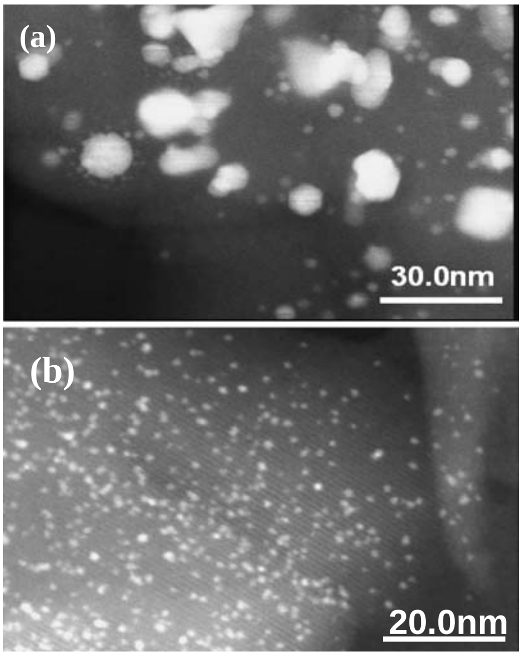

Figure 3. TEM photographs of various Pt/ZSM-5 catalysts. (a) Pt/Z-500, (b) Pt/Z-300.

Pt/Z-500 by 1.5–2 times. This difference is understandable as the difference between their reactive surface areas. However, the superior selectivity at Pt/Z-300 to the latter, i.e., 1.5–3 times higher, is not ascribed to the difference of the surface areas, in other words, the reactive surface area may be large enough to utilize O_2 supplied in the reactant stream even at Pt/Z-500 as shown by the O_2 conversion higher than Pt/Z-300 at $W/F = 0.03\,g{\cdot}s{\cdot}cm^{-3}$. Consequently, the specified reaction spaces in the molecular pores of ZSM-5 must be considered as the essential factor to achieve such a superior CO selectivity at the PROX reaction.

In conclusion, importance of the high dispersion of catalyst particles inside the nano-size pores becomes clear for the improvement of the CO conversion and the selectivity for the PROX reaction. The study on the physical and chemical specificities of such Pt and the alloys for the PROX are going on by us and will be reported elsewhere.

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