High Activity of Pt/$AlPO_4$ Catalyst for Selective Catalytic Reduction of Nitrogen Monoxide by Propene in Excess Oxygen

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The activity of Pt(0.5 wt%)/$AlPO_4$ for C_3H_6-SCR was found to be much higher than that of Pt(0.5 wt%)/Al_2O_3; although the selectivity toward N_2O of both the catalysts were comparable, the maximal conversion of NO to N_2 by Pt(0.5 wt%)/$AlPO_4$ was higher than that by Pt(0.5 wt%)/Al_2O_3, and moreover the temperature window of the former located in lower side than that of the latter. The superiority of Pt(0.5 wt%)/$AlPO_4$ was discussed on the basis of the results of XPS measurements.

The selective catalytic reduction of nitrogen monoxide by hydrocarbons(HC) in excess oxygen (HC-SCR) has attracted a great deal of attention as one of promising deNO$_x$ processes.[1] The HC-SCR was demonstrated over copper ion-exchanged zeolites by Iwamoto et al.[2,3] and Held et al.[4] These findings made a beginning of succeeding research, and by which many effective catalysts such as zeolites, metal oxides, and supported noble metals have been found.[5] Alumina, one of the metal oxides catalysts, is frequently used as a catalyst or catalyst support because of its excellent selectivity toward to N_2 and its durability.[6]

Amorphous aluminum phosphate ($AlPO_4$) has as high surface area as alumina,[7,8] and has also acid sites[7,8] which are considered to be required for HC-SCR catalysts such as alumina.[5] There has, however, been very few report on $AlPO_4$ as a catalyst or catalyst support for HC-SCR.[5–9]

In the present study, therefore, the activity of Pt-loaded $AlPO_4$ for C_3H_6-SCR was examined, and it was found for the first time that Pt-loaded $AlPO_4$ was more active than Pt-loaded Al_2O_3. The reason was also discussed on the basis of XPS studies of the catalysts and their activities for several elementary reactions composing C_3H_6-SCR.

All Pt-loaded catalysts were prepared by impregnating aluminum phosphate ($AlPO_4$), alumina, or silica with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$. The solvent evaporation took place while stirring and in a vacuum (water pump) at 50 °C until the solid seemed dry, followed by drying at 120 °C for 24 h, and heating at 500 °C for 4 h in air. Aluminum phosphate (amorphous, 130 $m^2 \cdot g^{-1}$ after calcination at 500 °C) was prepared by heating an aqueous solution containing a mixture of aluminum nitrate, orthophosphoric acid and urea at 95 °C to form a precipitate, followed by washing, drying at 120 °C for 24 h and calcining at 500 °C for 4 h. Alumina(γ-Al_2O_3, 143 $m^2 \cdot g^{-1}$ after calcination at 800 °C) was prepared by hydrolyzing aluminum triisopropoxide at 5 °C with stirring, followed by drying at 120 °C for 24 h, and calcining in air at 800 °C for 24 h. Silica (JRC-SIO-8, 303 $m^2 \cdot g^{-1}$) was supplied from the Catalysis Society of Japan. The above catalysts were ground to a powder, and then pressed into pellets followed by crushing, sieving (355–500 μm), and calcining at 500 °C for 4 h in air before use.

Catalytic reactions were carried out at temperatures ranging from 200 to 500 °C with a fixed-bed flow reactor by passing a reactant gas mixture at a total flow rate of 80 $mL \cdot min^{-1}$ through a catalyst bed under atmospheric pressure. 0.40 g of a catalyst was packed between quartz-wool plugs in a tubular quartz reactor (6 mm i.d.). The gas mixture contained 1000 or 0 ppm NO, 2.0 or 5.0% O_2, and 1000 or 0 ppm C_3H_6 diluted in helium. The outflow gas was analyzed by gas chromatography using a Molecular Sieve 5A (3 m; separation for N_2, O_2, CO, and NO) and Porapak Q (3 m; separation for CO_2, C_3H_6, and N_2O) columns.

With a Rigaku Denki XPS-7000 spectrometer, X-ray photoelectron spectroscopy (XPS) analyses were performed using a Mg Kα or Al Kα X-ray source operated at 10 kV and 30 mA. The binding energies were corrected by using the value of 285.0 eV for the C 1s level resulting from the contaminated carbon. The reproducibilities of the values thus obtained were within ±0.2 eV.

Figure 1 shows conversions of NO to N_2 and N_2O in C_3H_6-SCR over Pt(0.5 wt%)/$AlPO_4$ and Pt(0.5 wt%)/Al_2O_3. The maximal NO conversion by Pt(0.5 wt%)/$AlPO_4$ was higher than that by Pt(0.5 wt%)/Al_2O_3; moreover, the selectivity toward N_2O of both catalysts was comparable. In addition, the temperature window of the former located at lower side by 100 °C than that of the latter; Pt(0.5 wt%)/$AlPO_4$ is more active than Pt(0.5 wt%)/Al_2O_3 at lower temperatures. Interestingly, with Pt(0.5 wt%)/SiO_2, the temperature of maximum NO conversion was 250 °C, being the same as that of Pt/$AlPO_4$, although its maximum NO conversion was 3% and its conversion to N_2O at 250 °C was 16% (not shown). Figure 2 shows conversions of C_3H_6 to CO_2 in C_3H_6-SCR as well as in the oxidation of

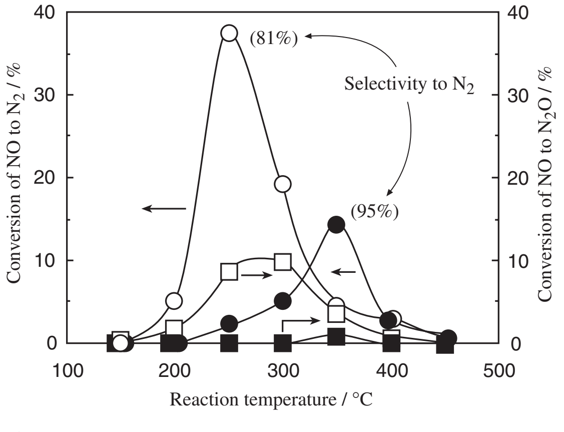

Figure 1. Catalytic activity of Pt(0.5 wt%)/$AlPO_4$ (○, □) and Pt(0.5 wt%)/Al_2O_3 (●, ■) for C_3H_6-SCR.

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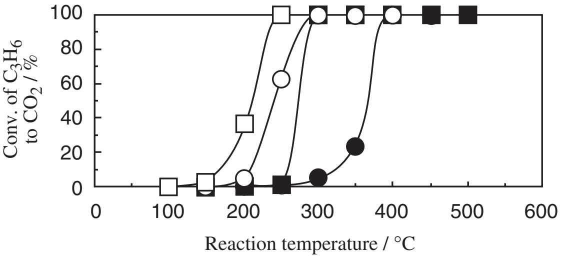

Figure 2. Conversions of C_3H_6 to CO_2 in C_3H_6-SCR (○, ●) and C_3H_6+O_2 (□, ■) reaction over Pt(0.5 wt%)/$AlPO_4$ (○, □) and Pt(0.5 wt%)/Al_2O_3 (●, ■).

C_3H_6 with O_2 over the two catalysts, where conversion to CO was negligible. Pt(0.5 wt%)/$AlPO_4$ had much higher oxidation activity than Pt(0.5 wt%)/Al_2O_3 for both reactions. In addition, curves showing conversion of C_3H_6 to CO_2 in C_3H_6-SCR over both catalysts located at higher temperature side than those of the oxidation of C_3H_6 with O_2, indicating that the presence of NO inhibited the oxidation of C_3H_6 with O_2. Interestingly, the distance between the corresponding pair of the curves of Pt(0.5 wt%)/$AlPO_4$ was narrower than that of Pt(0.5 wt%)/Al_2O_3, indicating that the selectivity of Pt(0.5 wt%)/$AlPO_4$ at a temperature for the NO reduction with C_3H_6 was higher than that of Pt(0.5 wt%)/Al_2O_3. Figure 3 illustrates conversions of NO to NO_2 in the oxidation of NO with O_2, which is known to be closely related to HC-SCR.[10,11] In this reaction also, Pt(0.5 wt%)/$AlPO_4$ is by far superior to Pt(0.5 wt%)/Al_2O_3.

Figure 4 shows XPS Pt4d spectra of Pt/$AlPO_4$, Pt/Al_2O_3, Pt/SiO_2, and Pt wire, where their peak intensities are normalized by using the O1s peak intensities. Any XPS Pt4d spectrum of a Pt-loaded catalyst was corrected by subtracting corresponding background XPS spectrum (i.e. that of a support) from the former spectrum. The results after computer fitting (dotted line) show that the binding energy of Pt4d of Pt(0.5 wt%)/$AlPO_4$ was similar to that of Pt(1 wt%)/SiO_2 and was lower than that of Pt(0.5 wt%)/Al_2O_3 in which there is a strong metal–support interaction.[12] These results indicate that metal–support interaction between Pt and $AlPO_4$ was weak, viz. the Pt is metallic.

It is reported that in C_3H_6-SCR over Pt-loaded catalysts, changing the support from Al_2O_3 to SiO_2 results in temperatures of C_3H_6 light-off and of maximum NO_x conversion, shifting to lower temperatures for samples of comparable metal dispersion.[13] The lower light-off temperature obtained with Pt/SiO_2 compared to Pt/Al_2O_3 has also been reported for hydrocarbon combustion (i.e. in the absence of NO_x) and has been attributed, in the case of Pt/Al_2O_3, to the strong metal–support interaction deactivating the Pt.[12] As the metal–support interaction between Pt and $AlPO_4$ has been also found to be weak, we are considering that metallic Pt of Pt/$AlPO_4$ is responsible for higher $DeNO_x$ activity as follows: The metallic Pt having high oxidation activity results in effective activation of both C_3H_6 and NO, and eventually greater formation of N_2 in C_3H_6-SCR. In addition, fortunately the presence of NO inhibits combustion of C_3H_6 in this reaction system. In conclusion, Pt/$AlPO_4$ is likely to be a more promising catalyst than Pt/Al_2O_3[14,15] for HC-SCR.

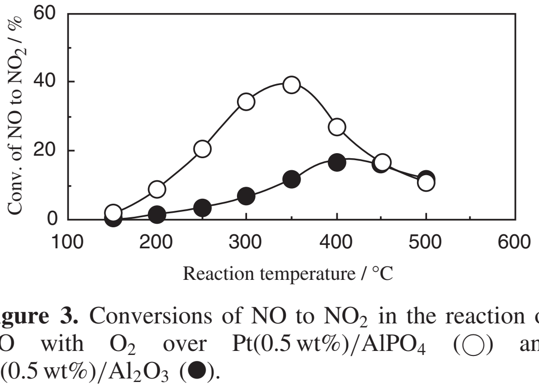

Figure 3. Conversions of NO to NO_2 in the reaction of NO with O_2 over Pt(0.5 wt%)/$AlPO_4$ (○) and Pt(0.5 wt%)/Al_2O_3 (●).

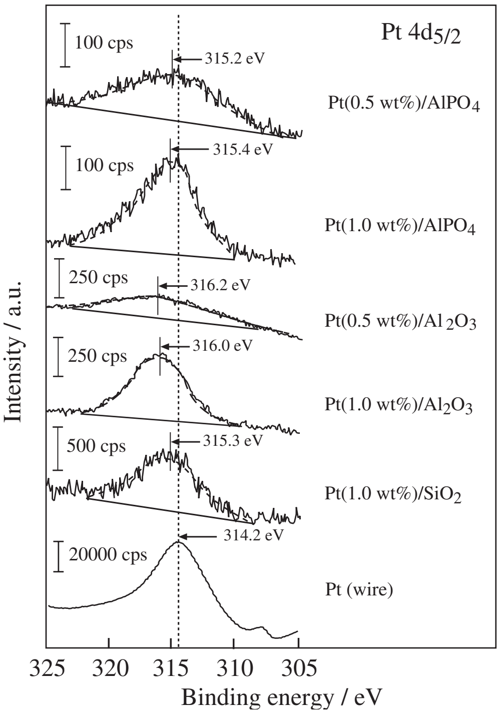

Figure 4. XPS Pt4d spectra of Pt/$AlPO_4$, Pt/Al_2O_3, and Pt/SiO_2.

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