Effect of Pt Precursors on N_2/N_2O Selectivity for Selective Reduction of NO by Hydrocarbon on Supported Pt Catalysts

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Selective catalytic reduction of NO by C_3H_6 has been studied for supported Pt catalysts prepared from organoplatinum complexes and an inorganic platinum salt. N_2/N_2O selectivity is improved by using the organoplatinum complexes as precursors at similar maximum conversions of NOx to N_2 and N_2O for the catalysts tested.

The selective catalytic reduction (SCR) of nitric oxides by hydrocarbons in an oxidizing atmosphere has been widely investigated over various catalysts.[1-4] Among these catalysts supported Pt catalysts have been reported to be the most active for SCR at low temperatures.[5-8] However, there is a drawback that a large amount of NOx is converted to N_2O in using alkane or alkene as a reductant, which is the major component of hydrocarbons in the emissions of diesel and lean-burn gasoline engines. In this study, we have used supported Pt catalysts prepared from organoplatinum complexes and an inorganic platinum salt, and have compared the activity of NO reduction and N_2 selectivity. The obtained Pt particles on the support were characterized by TEM, EXAFS, CO adsorption and XPS, and the relevance of the catalytic performances to the catalyst structures is discussed.

Organoplatinum complexes, $PtMe(OSiPh_3)(cod)$ and PtMe(OPh)(cod) (cod = 1,5-cyclooctadiene), were prepared according to the procedures in our previous paper[9] with some modification. Al_2O_3 (a reference catalyst of the Catalysis Society of Japan, JRC-ALO-2) and SiO_2 (Fuji Silysia Chemical Ltd., CARIACT Q-3) were dried in an oven at 373 K for 24 h followed by evacuation ($<10^{-3}$ Torr) at 473 K for 2 h, which were used as supports. The THF solution of organoplatinum complex was added dropwise to the stirring suspension of the support and THF, and the mixture was stirred for 24 h at room temperature. These operations were carried out under a nitrogen atmosphere to avoid decomposition of the organoplatinum complexes. Hydrogen (1 atm) was introduced into the mixture by bubbling, and the reduction of the Pt complexes was completed in 3 h at room temperature.[9] The mixture was filtered and the resulting solid was dried under vacuum. No Pt complex was remained in the filtered liquid, which was confirmed by NMR and IR. The obtained Pt catalyst was calcined in 10% oxygen/helium flow at 473 K for 1 h and reduced in hydrogen flow at 673 K for 2 h. The Pt loading of the catalyst was 2.0wt%. Another supported Pt catalyst was prepared by the impregnation method using aqueous $Pt(NO_2)_2(NH_3)_2$ solution followed by the treatment in oxygen and hydrogen flow under the same conditions described above. Catalytic activity was tested using a fixed-bed reactor. The gas mixture used was a simulated oxygen-rich exhaust gas, which was composed of 1000 ppm NO, 1000 ppm C_3H_6, 6% O_2, 1200 ppm CO, 10% CO_2, 400 ppm H_2 and 10% H_2O in the balance N_2. Gas hourly space velocity was 200000 h^{-1}. The nitrogen oxides concentrations were monitored by a chemiluminescence analyzer (BCL 101UV, Best Instruments) for NOx (NO + NO_2) and a gas filter correlation analyzer (46H, Best Instruments) for N_2O. EXAFS measurements of the catalysts were performed with a Technos EXAC-820 laboratory EXAFS spectrometer.

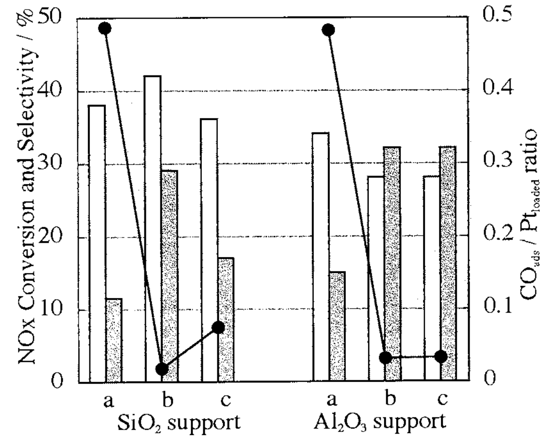

Figure 1. Maximum NOx conversions and N_2 selectivity over Pt/SiO_2 and Pt/Al_2O_3. ☐, Maximum NOx conversion to N_2 and N_2O. ▨, N_2 selectivity at the maximum NOx conversion. ●, CO_{ads} / Pt_{loaded} ratios. The catalysts were prepared by $Pt(NO_2)_2(NH_3)_2$ (a), $PtMe(OSiPh_3)(cod)$ (b), and PtMe(OPh)(cod) (c).

Figure 1 shows the influence of precursors on the maximum NOx conversion and the N_2 selectivity over Pt/SiO_2 and Pt/Al_2O_3 prepared from different Pt precursors. The maximum NOx conversions over all catalysts were obtained at about 498 K. It is apparent that the catalysts prepared from organoplatinum complexes show higher N_2 selectivities than the catalyst prepared from $Pt(NO_2)_2(NH_3)_2$, while there is little difference in the maximum NOx conversions between these catalysts, regardless of the support.

Figure 2 is transmission electron micrographs (TEM) of Pt/SiO_2 catalysts prepared from $PtMe(OSiPh_3)(cod)$ (denoted as $Pt/SiO_2(S)$) and $Pt(NO_2)_2(NH_3)_2$ (denoted as $Pt/SiO_2(N)$). It is interesting to note that the size and dispersion of the Pt particles are greatly different in these two catalysts. For $Pt/SiO_2(S)$, spherical particles of 5-10 nm diameter are clearly observed in the micrograph. On the other hand, the TEM micrograph of $Pt/SiO_2(N)$ indicates that the size of Pt particle is smaller than 3 nm. The dispersions of Pt on these catalysts were estimated by CO adsorption measurements at room temperature. CO/Pt ratios for all catalysts including $Pt/SiO_2(S)$ and $Pt/SiO_2(N)$ obtained from the CO adsorption were shown in Figure 1.

Extended X-ray absorption fine structure (EXAFS) measurements for $Pt/SiO_2(S)$ and $Pt/SiO_2(N)$ were done for Pt L_{III}-edge at room temperature. Figure 3 shows Fourier transforms of k^3-weighted EXAFS function $\chi(k)$. Curve-fitting

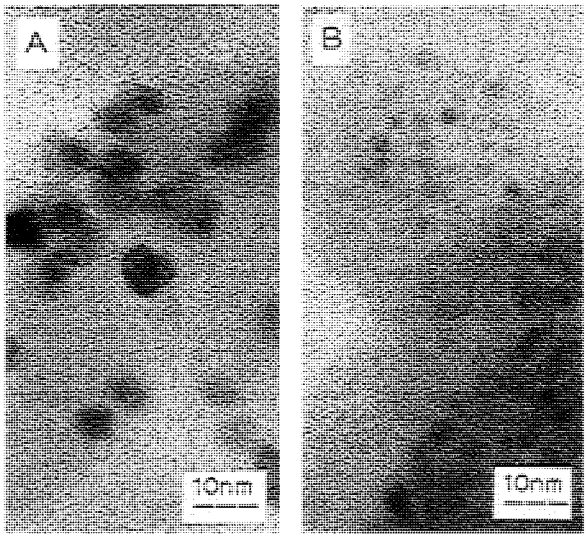

Figure 2. Transmission electron micrograph (1200000 ×), showing the catalyst Pt/SiO$_2$ prepared from (A) PtMe(OSiPh$_3$)(cod) and (B) Pt(NO$_2$)$_2$(NH$_3$)$_2$.

analysis of the main peak in Pt/SiO$_2$(S) revealed that the peak is due to Pt-Pt bond. On the other hand, no characteristic Pt-Pt interaction was observed for Pt/SiO$_2$(N). Thus, the results of EXAFS are consistent with the results of TEM analysis and CO adsorption.

Pt/SiO$_2$(S) and Pt/SiO$_2$(N) were further characterized by X-ray photoelectron spectroscopy (XPS). Pt/SiO$_2$(S) gave peaks located at 70.7 eV (Pt4f$_{7/2}$) and 74.0 eV (Pt4f$_{5/2}$) indicating that the electronic state of Pt in the catalyst is Pt^0. For Pt/SiO$_2$(N) , the peak appeared at 71.0 eV (Pt4f$_{7/2}$) and 74.3 eV (Pt4f$_{5/2}$) showing the presence of oxidized Pt. Recently, we have reported that the highly dispersed Pt on Pt•B/YPO$_4$ gave a binding energy higher than that of aggregated Pt on Pt/YPO$_4$.[10,11] Therefore, the difference of binding energy of Pt between Pt/SiO$_2$(S) and Pt/SiO$_2$(N) could be explained in terms of the particle size of Pt dispersed on these catalysts.

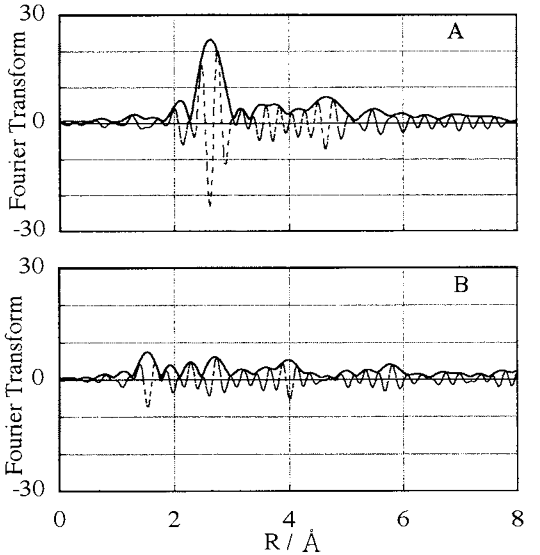

Figure 3. Fourier transforms of k^3-weighted Pt L_{III} EXAFS for Pt/SiO$_2$ prepared from PtMe(OSiPh$_3$)(cod) (A) and Pt(NO$_2$)$_2$(NH$_3$)$_2$ (B).[a] [a] Reasonable fitting parameters could not be obtained because curve-fitting did not converge in satisfactory R factor.

Based on the characterizations by TEM, EXAFS, CO adsorption and XPS, it is clearly shown that Pt atoms in Pt/SiO$_2$(S) forms larger clusters than those in Pt/SiO$_2$(N), and the dispersions are greatly influenced by the precursor of Pt. It should be noted that the maximum conversion of NOx was almost unchanged by the difference of the dispersions , however , the N$_2$/N$_2$O selectivity was dependent on them as shown in Figure 1. These results suggest that the reduction of NOx to N$_2$ and N$_2$O occurs on the clusters of appropriate number of Pt atoms. N$_2$O formation over Pt catalysts occurs via reaction between NO and adsorbed nitrogen.[12,13] In addition, the dissociation of NO into adsorbed nitrogen and oxygen is affected by surface structure of Pt particles.[14,15] It is plausible that the N$_2$/N$_2$O selectivity is structure-sensitive and the structure is influenced by Pt precursor, although another factors such as supports and reductants were reported.[16-19] Even if further investigations are needed to clarify the effect of structure on the activity and the selectivity, it is expected that the N$_2$/N$_2$O selectivity on supported Pt catalyst can be improved by using the effective precursor.

References and Notes

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