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Hydrogen Selective Catalytic Reduction of NO_x Assisted by In Situ Ammonia Formation over Pt Catalyst Supported on Fe-doped Tin Phosphate

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In situ formation of ammonia and NO_x reduction with high N_2 selectivity based on it were observed in the hydrogen selective catalytic reduction (H_2-SCR) of NO_x over a platinum catalyst supported on a Fe-doped SnP_2O_7 powder with strong solid acidity even under conditions of high oxygen contents of about 10 vol %.

Catalytic reduction of NO_x (NO and NO_2) under high concentration of oxygen (ca. 10 vol %) is an essential technique to make highly efficient diesel automobiles widely used. Many reduction methods using hydrocarbons,[1] carbon monoxide,[2] urea or ammonia,[3–5] and hydrogen[6–9] have been proposed to date. Among these, hydrogen selective catalytic reduction (H_2-SCR) is a promising candidate because NO_x can be reduced at lower temperature than with other reducing agents. Furthermore, the other reductants must be completely consumed during the deNO_x process since they are toxic themselves and cause additional air pollution. Meanwhile hydrogen is harmless, but the greenhouse effect gas N_2O is usually produced as a by-product in such H_2-SCR processes.[6]

Recently, Hibino et al. have reported that Pt/(Sn,In)P_2O_7 catalysts with proton conductivity highly promote the H_2-SCR for NO_x with low N_2O emission under 5 vol % oxygen atmosphere.[9,10] Also, the present authors have recently found that Pt catalysts supported on sulfated zirconia powders produce ammonium intermediate species even under much more oxygen-rich conditions than those of real exhaust gases and that they contribute to the increase of N_2 selectivity for reducing NO_x.[11] If one can produce such NH_3 in sufficient amount for NH_3-SCR, the formation of N_2O by-product should be retarded for the reaction. NO_x reduction using in situ produced ammonia or ammonium intermediate species have been also reported,[12] and the catalytic activity for NH_3-SCR of Pt supported on TiO_2 catalysts are improved by adding transition-metal ions such as Fe and Mn.[13] In this study, iron cation (Fe^{3+}) was doped to the Sn^{4+} sites of SnP_2O_7 in order to enhance the NH_3-SCR property that leads to high N_2 selectivity.

Tin pyrophosphate, substituted with trivalent ions (Sn,M)P_2O_7 (M = Fe or In), powders were prepared by a conventional solid-state reaction technique. Reagent grade $(NH_4)_2HPO_4$, SnO_2, and M_2O_3 were well mixed and calcined in alumina pots at 327 °C, and after grinding, they were heated again at 650 °C for 2.5 h in air. Then, 1 wt % platinum was loaded to each powder by an incipient impregnation method using a $Pt(NO_3)_2(NH_3)_2$ solution, followed by drying at 120 °C overnight and subsequently heating at 600 °C for 2 h in air. Platinum catalyst on undoped tin phosphate powder (Pt/SnP_2O_7) was also prepared by the same procedure as a comparison. Amount and size distribution of loaded Pt particles were analyzed by ICP-AES (SII, SPS4000) and TEM (JEOL, JEM-2010F) apparatuses to be 1.01 ± 0.01 (wt %) and 1–5 nm, respectively. The phase and solid acidity were characterized by XRD patterns and ammonia temperature-programmed desorption (NH_3-TPD) profiles.

Test reactions were performed on 0.1 g of $Pt/Sn_{0.9}M_{0.1}P_2O_7$ powder charged in a conventional fixed-bed quartz tube reactor (i.d.: ca. 7 mm) in a temperature range from 250 to 70 °C. The samples were kept at each temperature at least 1 h which was enough time to reach adsorption equilibrium. The reaction gas with a given composition (0.1 vol % NO, 0.4 vol % H_2, 10 vol % O_2, and balance of N_2) was fed with a flow rate of $50\,\mathrm{mL{\cdot}min^{-1}}$, and the outlet gas was passed through a gas cell equipped with KBr windows (optical length; 10 cm) to analyze the gas composition by an FTIR system (Perkin-Elmer SPECTRUM 2000 with an MCT detector). Concentrations of NO, N_2O, NO_2, and NH_3 were determined using the areas of their absorbance peaks at 1911, 2212, 1586, and $1120\,\mathrm{cm^{-1}}$, respectively. The N_2 yield based on NO_x reduction was calculated by subtracting NO, N_2O, NO_2, and NH_3 concentrations of outlet gas from the inlet NO concentration. The NO_x (NO and NO_2) conversion and $N_2 + NH_3$ selectivity were determined as follows: NO_x conversion, $([\mathrm{NO}]_{\mathrm{inlet}} - [\mathrm{NO}_x]_{\mathrm{oultlet}})/[\mathrm{NO}]_{\mathrm{inlet}} \times 100$ (%); $N_2 + NH_3$ selectivity, $(2 \times [\mathrm{N_2}]_{\mathrm{yield}} + [\mathrm{NH_3}]_{\mathrm{yield}})/(2 \times [\mathrm{N_2}]_{\mathrm{yield}} + 2 \times [\mathrm{N_2O}]_{\mathrm{yield}} + [\mathrm{NH_3}]_{\mathrm{yield}}) \times 100$ (%).

All the prepared $(Sn_{0.9}M_{0.1})P_2O_7$ samples crystallized with cubic symmetry of SnP_2O_7 (PDF #29-1352), and any impurity phase was not apparent in the XRD patterns. The respective cell parameters with 3σ standard deviation were 7.981 ± 0.010 Å (SnP_2O_7), 7.956 ± 0.005 Å ($Sn_{0.9}Fe_{0.1}P_2O_7$), and 8.047 ± 0.006 Å ($Sn_{0.9}In_{0.1}P_2O_7$), which have good correlation with ionic radii of dopant ions (Sn^{4+}; 0.69 Å, Fe^{3+}; 0.64 Å, In^{3+}; 0.80 Å),[14] suggesting that the dopant ions substituted the Sn^{4+} sites to form solid solutions.

The NO_x conversion and $N_2 + NH_3$ selectivity values for a series of catalysts are shown in Figure 1. The sole Pt/SnP_2O_7 catalyst exhibited high NO_x-reducing property at the temperature below 100 °C, but most of the product was N_2O. On the other hand, Fe^{3+} ion-doped catalyst ($Pt/Sn_{0.9}Fe_{0.1}P_2O_7$) showed high NO_x conversion at higher reaction temperature above 100 °C with high $N_2 + NH_3$ selectivity. In addition, much more gaseous ammonia production was also observed on the Fe-doped catalysts than the In-doped one. From these results, NO_x reduction may progress via two paths, e.g., H_2-SCR at the lower temperature and NH_3-SCR at temperature higher than 140 °C, the latter scheme is responsible for high $N_2 + NH_3$ selectivity.

Oxygen dependence on the ammonia production over the $Pt/(Sn_{0.9}M_{0.1})P_2O_7$ catalysts at 140 °C in gas flow containg

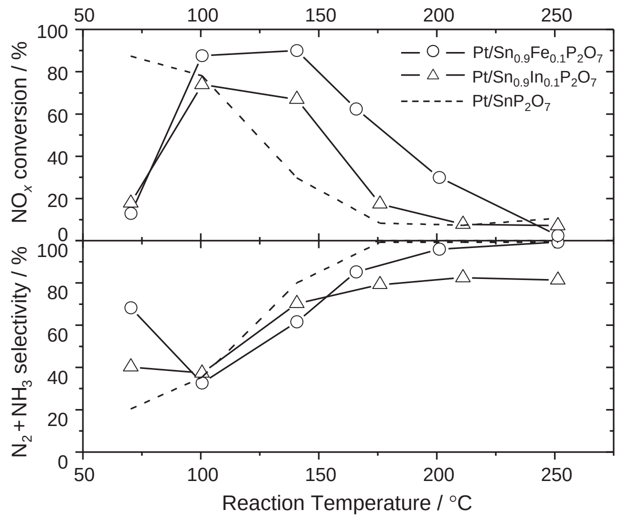

Figure 1. NO$_x$ conversion and $N_2 + NH_3$ selectivity profiles for a series of Pt/(Sn,M)P_2O_7 (M = Fe or In) catalysts. Weight of catalysts, 0.1 g; flow rate, 50 mL·min^{-1}. The reaction gas: 0.1 vol % NO, 0.4 vol % H_2, 10 vol % O_2, and balance of N_2.

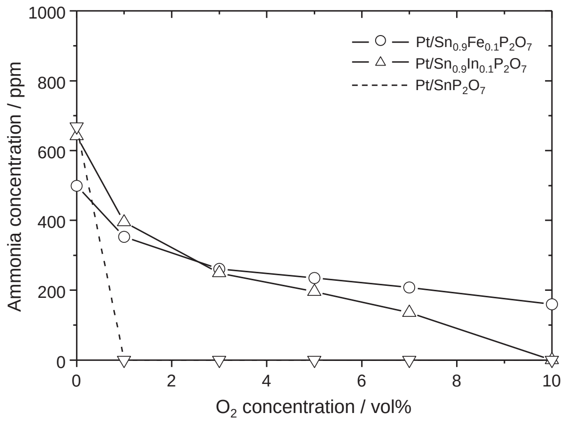

Figure 2. Oxygen concentration dependence on the ammonia concentration produced over a series of Pt/(Sn,M)P_2O_7 catalysts at 140 °C flowing reaction gases containing 0–10 vol % of O_2. Weight of catalysts and NO and H_2 concentration in reaction gas are the same as the above-mentioned conditions.

various amounts of oxygen is shown in Figure 2. By doping the trivalent cations, ammonia formation on them was considerably enhanced even at high oxygen concentration. The order of emitted amount of ammonia was Fe-doped > In-doped ≫ undoped sample. We have found that ammonia or ammonium intermediate species is produced favorably on the solid acid sites of catalyst supports.[11] In the present study, the order of solid acidity determined by higher desorption temperature of NH_3-TPD was Fe-doped (405 °C) > In-doped (350 °C) ≫ undoped (310 °C), and this tendency agreed with the above-mentioned ammonium formation ability. The higher catalytic performance of Fe-doped catalyst is ascribable to catalytic activity for the reaction between NO$_x$ and in situ produced ammonium species.

Although the In- and Fe-doped samples produce almost the same amount of ammonia at lower oxygen concentration conditions reported by Hibino et al.,[9] only the latter catalyst still forms gaseous ammonia in the 10 vol % of oxygen atmosphere. This implies that the reason that the good catalytic performance of Pt/(Sn,In)P_2O_7 is diminished at the high oxygen concentration.

Table 1. Space velocity dependence of NO conversion and product selectivity on Pt/($Sn_{0.9}Fe_{0.1}$)P_2O_7 catalyst at 140 °C[a]

	Space velocity/mL·min^{-1}		
	30	50	100
NO$_x$ conversion/%	94	90	78
N_2 selectivity/%	68	45	63
NH_3 selectivity/%	0	18	7
($N_2 + NH_3$ selectivity/%)	68	63	70
N_2O selectivity/%	32	37	30

[a]The reaction gas: 0.1 vol % NO, 0.4 vol % H_2, 10 vol % O_2, and balance of N_2.

The compositions of production gas on various space velocities at 140 °C are summarized in Table 1. While the N_2 selectivity decreased at space velocity higher than 50 mL·min^{-1}, more gaseous ammonia was evolved. Also, the N_2O selectivity remained at almost the same level under all space velocity conditions. This supports a deNO$_x$ process via two reaction schemes, H_2-SCR ($NO + H_2 \rightarrow N_2 + N_2O + H_2O$) and NH_3-SCR which consists of two steps, fast reduction to ammonia using hydrogen ($NO + H_2 \rightarrow NH_3 + H_2O$) and the subsequent slow NO$_x$ reduction using ammonia produced in situ ($NO + NH_3 \rightarrow N_2 + H_2O$). The N_2O by-product is mainly formed in the former H_2-SCR scheme, and thus one can attain high N_2 selectivity over the Pt/(Sn,M)P_2O_7 catalysts.

In conclusion, Fe-doped ($Sn_{0.9}Fe_{0.1}$)P_2O_7 forms strong acid sites on the surface, on which NO$_x$ is effectively reduced to ammonia or ammonium intermediates. Consequently, they contribute additional reduction for NO$_x$ as the desirable reductants in the N_2O-free pathway. The deNO$_x$ reaction over the Pt/($Sn_{0.9}Fe_{0.1}$)P_2O_7 catalysts must consist of two mechanisms, the H_2-SCR accompanying N_2O and the NH_3-SCR based on in situ ammonia formation.

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