Nitrous oxide free pathway for selective reduction of NO by hydrogen over supported Pt catalysts

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The presence of strong acid sites on a metal oxide support results in a reaction of adsorbed NH_4^+ species in a flow of $NO + O_2$, which is a N_2O free pathway in selective catalytic reduction of NO by H_2 over supported Pt catalysts.

Selective catalytic reduction of NO by hydrocarbons (HC-SCR) has received much attention because of its potential application to the removal of NOx from exhaust containing excess oxygen. Since the pioneering works by Iwamoto *et al.*[1] and Held *et al.*,[2] extensive research has been done on development of various types of de-NOx catalysts. Supported Pt catalyst is known to be the most active precious metal catalyst at low temperatures having high durability against sulfur and water vapour.[3,4] On the other hand, formation of N_2O as a by-product, which is a powerful greenhouse gas, is a serious problem of Pt-based catalysts for use in HC-SCR.[5–7] Recently, the selective reduction of NO by hydrogen (H_2-SCR) has been paid much attention because of high activity and less N_2O formation at low temperatures.[8–15] Yokota *et al.* reported that the addition of Na and Mo to Pt/SiO_2 broadens the temperature range of NOx conversion and suppresses N_2O formation.[8] Use of some types of supports, such as $La_{0.5}Ce_{0.5}MnO_3$ and $TiO_2–ZrO_2$, are also reported to be effective.[9,11,12] As for the reason for high nitrogen selectivity in H_2-SCR, contribution of reduced nitrogen intermediates, such as NH_x ($x = 0$–2) and NH_3, is suggested.[13–15] However, no clear idea is reported about the dependence of the selective pathway on catalytic functions of Pt itself, promoters, and metal oxide supports.

Through division of the influences of Pt and support on nitrogen selectivity and observation of surface species by *in situ* IR, this communication shows a contribution of surface NH_4^+ species and a role of strong acid sites of supports to the selective pathway for H_2-SCR under excess oxygen.

H–BEA, H–Y, $SiO_2–Al_2O_3$, SiO_2, and Al_2O_3 were supplied by the Committee of Reference Catalysts, Catalysis Society of Japan (JRC-HB25, JRC-Z-HY4.8, JRC-SAL-2, JRC-SIO-8, JRC-ALO-4). H–MFI ($SiO_2/Al_2O_3 = 39.4$) was supplied by Tosoh Corporation. Pt/zeolite catalysts were prepared by a conventional ion-exchange in an aqueous $Pt(NH_3)_4Cl_2$ solution at room temperature. After filtration, the sample was washed with distilled water and dried at 393 K. Pt/metal oxide catalysts were prepared by impregnating an aqueous $Pt(NH_3)_4Cl_2$ solution. These precursors were calcined at 773 K for 3 h in a flow of dried air. The Pt content was 1 wt% for all the catalysts. The catalytic activity was measured with a fixed-bed flow reactor at atmospheric pressure. The reaction gas containing a mixture of 1000 ppm NO, 5000 ppm H_2, 6.7% O_2 in He was fed to 0.05 g of catalyst at a total flow-rate of 100 cm^3 min^{-1}, corresponding to GHSV = 78,000 h^{-1}. After reaching a steady-state, the effluent gas was analysed by a gas chromatograph and a chemiluminescence NOx analyser. Selectivity was determined as (N_2 yield)/(N_2 yield + N_2O yield). *In situ* IR spectra were recorded on a JASCO FT/IR-620 equipped with a quartz IR cell connected to a flow system.[16] The sample was pressed into a 0.05 g self-supporting wafer and the spectra were measured at accumulating 100 scans at a resolution of 2 cm^{-1}. A reference spectrum of the catalyst wafer in He taken at the measurement temperature was subtracted from each spectrum.

For all the catalysts, the NO conversion increased with reaction temperature, reached a maximum at 373–423 K, and then decreased with further increase of temperature. Nitrogen selectivity increased as reaction temperature increased. For example, the nitrogen selectivity of Pt/MFI was 45% at 348 K and reached 82% at 398 K, where hydrogen conversion reached 100%. Above 398 K to 523 K, the nitrogen selectivity was 82–92%. The highest nitrogen yield over Pt/MFI was 81% at 396 K, which is almost comparable to that over 0.1 wt% Pt/ $La_{0.5}Ce_{0.5}MnO_3$ reported by Costa *et al.*[11]
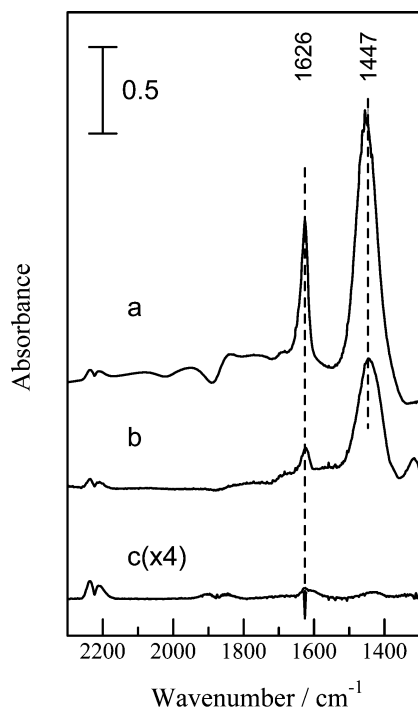
Table 1 shows conversions of NO and H_2 and nitrogen selectivity of various supported Pt catalysts at 348 K. At this reaction temperature, both conversions of NO and H_2 were less than 60%. It should be noted that there is not much effect of consecutive reaction on nitrogen selectivity, since nitrogen selectivity was confirmed to be constant when NO conversion was below 60% in a separate experiment varying W/F. The table clearly indicates that nitrogen selectivity is much affected by the type of support: Pt/zeolites showed high nitrogen selectivity, while Pt/Al_2O_3 and Pt/SiO_2 showed lower selectivity. $Pt/SiO_2–Al_2O_3$ showed medium selectivity in between Pt/zeolites and other Pt/metal oxides. A similar trend in nitrogen selectivity was also observed at higher temperatures.

Structures of supported Pt were characterized, and the results were compared with the above reaction data. The oxidation state of Pt was estimated by Pt L_{III}-edge XANES spectra[17] and dispersion of Pt was estimated by $CO–H_2$ titration.[18] There was no correlation between nitrogen selectivity and these structural parameters of Pt, suggesting there is not much contribution of the state of Pt to the selectivity. It can be expected that nitrogen selectivity depends on the nature of support materials.

Fig. 1 shows *in situ* IR spectra of adsorbed species on supported Pt catalysts under the H_2-SCR conditions. Two bands at 1447 cm^{-1} and 1626 cm^{-1} were observed for Pt/MFI and Pt/ $SiO_2–Al_2O_3$. The band at 1447 cm^{-1} is the typical absorption band of the NH_4^+ ion adsorbed on Brønsted acid sites.[19] Since the latter band was also observed in a flow of $H_2 + O_2$ at 348 K, the band at 1626 cm^{-1} can be assigned to adsorbed water. The assignment of the band at 1626 cm^{-1} to coordinately held NH_3 on Lewis acid sites can be neglected because of the presence of water vapour under the reaction conditions. It is obvious that the intensity of the band of adsorbed NH_4^+ is strongly affected by the type of supports: the band observed in Pt/MFI was very strong, while only a very weak band was observed in Pt/SiO_2. The intensity of the band agreed well with the nitrogen

**Table 1** Results of SCR reaction by H_2 over supported Pt (1 wt%) catalysts at 348 K

Catalyst	NO conversion (%)	H_2 conversion (%)	N_2 selectivity (%)
Pt/MFI	37	18	45
Pt/BEA	30	21	40
Pt/Y	20	11	31
$Pt/SiO_2–Al_2O_3$	58	7	19
Pt/SiO_2	44	8	8
Pt/Al_2O_3	26	16	11

Fig. 1 *In situ* IR spectra of adsorbed species on (a) Pt/MFI, (b) Pt/SiO$_2$–Al$_2$O$_3$, (c) Pt/SiO$_2$ in a flow of NO + H$_2$ + O$_2$ for 1 h at 348 K. The catalyst disk was pre-treated in a flow of 6.7% O$_2$ at 773 K for 1 h.

selectivity, *i.e.*, Pt/MFI having high nitrogen selectivity showed a strong band of NH$_4^+$, Pt/SiO$_2$–Al$_2$O$_3$ showed medium nitrogen selectivity and a medium intensity of the bands, and Pt/SiO$_2$ showed less nitrogen selectivity and a small band. This trend suggests that the formation of NH$_4^+$ is closely related to selective production of nitrogen. Burch *et al.* indicated gaseous NH$_3$ formation followed by storage and reduction of NO on Pt/ceria–zirconia.[13] Although their experiments were carried out in low O$_2$ concentration (0–5000 ppm), our data clearly indicate a contribution of NH$_4^+$ to the selective pathway even under excess O$_2$.

In Fig. 2, the dependence of N$_2$ production on the IR band at 1454 cm^{-1} was examined. As shown, very good correlation was observed between N$_2$ yield and the intensity of the band assignable to NH$_4^+$ species adsorbed on Brønsted acid sites. The sequence of N$_2$ yield agrees well with the acid strength of
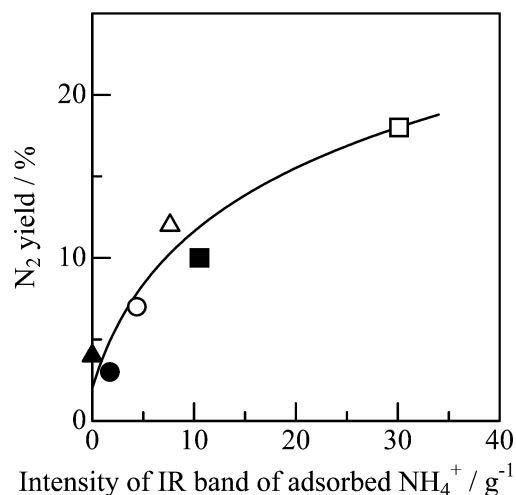
Fig. 2 N$_2$ yield as a function of intensity of IR band of adsorbed NH$_4^+$. Symbols represent (□) Pt/MFI, (△) Pt/BEA, (○) Pt/Y, (■) Pt/SiO$_2$–Al$_2$O$_3$, (▲) Pt/SiO$_2$ and (●) Pt/Al$_2$O$_3$, respectively.

support materials. Katada *et al.*[20] reported that the heat of adsorption of ammonia, which is a general measure of acid strength of zeolites, is 130, 120, and 110 kJ mol^{-1} for H–MFI, H–BEA, and H–Y, respectively. This sequence is in accordance with both N$_2$ yield and the IR band intensity. Due to the wide range of distribution of acid strength on non-zeolitic oxides, it is more difficult to compare the acid strength. However, the maximum acid strength of SiO$_2$–Al$_2$O$_3$ measured by a titration method is H$_0$ = -12 ~ -14,[21] which is higher than Al$_2$O$_3$ (H$_0$ = -7.2) and SiO$_2$ (chemically neutral).[22] Therefore, the higher N$_2$ yield of Pt/zeolites and Pt/SiO$_2$–Al$_2$O$_3$ should be due to the effect of the support. The role of the support should be in the stabilization of NH$_4^+$ species on Brønsted acid sites. As for the NH$_4^+$ formation, the possible pathway is NH$_3$ formation through hydrogenation of NO or N atoms on the Pt surface,[10] followed by adsorption of NH$_3$ on Brønsted acid sites of the supports.

The reaction of NH$_4^+$ species in a flow of NO + O$_2$ was confirmed. After a flow of 1000 ppm of NH$_3$ for 1 h at 348 K, the catalyst was exposed to a flow of NO + O$_2$ for 30 min. In the case of H–MFI, N$_2$ yield was 44% without the formation of N$_2$O, while in the case of Pt/MFI, N$_2$ yield was 27% and N$_2$O yield was 2%. This result demonstrates that a N$_2$O free pathway can proceed on Brønsted acid sites of the support using NH$_4^+$ as a reductant. The use of an acidic support may effectively trap NH$_3$ as NH$_4^+$ species, leading to highly selective reduction of NOx (probably NO$_2$) with NH$_3$ over acid sites. This "acid sites assisted pathway" would be an effective approach for the design of N$_2$O free SCR on supported Pt catalysts.

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