

Low-temperature Hydrogen-selective Catalytic Reduction of NO_x on Pt/Sulfated-ZrO₂ Catalysts under Excess Oxygen Conditions

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Platinum catalysts supported on sulfated zirconia powders highly promote the hydrogen-selective catalytic reduction (H₂-SCR) of NO_x at 100 °C with formation of ammonia intermediate species derived from protons of the sulfonate groups fixed as superacid sites on the surface, which are detected by in situ DRIFTS measurements.

Selective catalytic reduction of NO_x using hydrogen has attracted much attention^{1–6} as a potent candidate for removing NO_x from exhaust gas containing excess amounts of oxygen around 10 vol %, where the hydrogen is possibly supplied by on-site producing systems from the gas components, viz. water-gas-shift reaction, electrolysis of water, and so on. Although the H₂-SCR occurs at the lower temperature than HC-SCR⁷ or CO-SCR,⁸ much N₂O greenhouse gas usually accompanies as a by-product.¹ Some studies of such H₂-SCR characteristics on supported precious metal catalysts have noted that ammonia or ammonium species are generated from NO_x on Brønsted acid sites of the catalysts via an intermediate of NH₄NO₃ with little N₂O formation.^{3,4} The formation of ammonia or ammonium species and subsequent NO_x reduction with them desirably takes place on acidic support materials such as zeolites.⁵ Surface modifications of the support oxides with acidic functional groups have been made to create strong solid acid sites, and among them, especially sulfated zirconia is noteworthy as catalysts or support material with its strong acidity ($H_0 \leq -16.04$).⁹ In addition, it has good tolerance to the SO₂ impurity contained in real exhaust gases.⁷

In the present study, the H₂-SCR for NO_x on platinum catalyst supported on sulfated zirconia powders was characterized from the viewpoint of surface acidity. Furthermore, the reaction intermediates were detected by in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements to understand the reaction mechanism and evaluate the feasibility of this deNO_x system at a practical industrial level.

Sulfated zirconia powders were prepared from tetragonal ZrO₂ (ZRO-3; supplied by the Committee of Reference Catalysts, Catalysis Society of Japan) and reagent grade ammonium sulfate by calcination at 700 or 800 °C for 2 h in air. Then, 1 wt % of platinum was loaded to them by an incipient wetness impregnation method using a Pt(NO₃)₂(NH₃)₂ solution, followed by drying at 120 °C overnight and heating at 600 °C for 2 h in air. The conventional Pt/ZrO₂ catalyst was prepared using the same ZRO-3 powder and used as a reference. They were characterized by a series of measurements for FTIR spectra (KBr method; Jusco FT-IR/430), NH₃-TPD (temperature-programmed desorption) profiles, and BET surface area (about 80–90 m²/g) values.

Catalytic test reactions were performed on 0.1 g of platinum-loaded sulfated zirconia catalysts (denoted as Pt/s-ZrO₂(X), X represents the calcination temperature) individually charged in a conventional fixed-bed quartz tube reactor (i.d.: ca. 7 mm) at 70–250 °C. A stream of reaction gas (0.1 vol % NO, 0.4 vol % H₂, 10 vol % O₂, and balance of N₂) was fed with a flow rate of 30 mL·min⁻¹ and the outlet gas was introduced into a gas cell equipped with KBr windows (optical length; 10 cm) to analyze the gas composition by an FTIR apparatus (Perkin-Elmer SPECTRUM 2000 with an MCT detector). Concentrations of NO, N₂O, and NO₂ were determined using peak areas of their absorbance peaking at 1911, 2212, and 1586 cm⁻¹, respectively. The N₂ yield based on NO_x reduction was determined by subtracting the concentration value of NO, N₂O, and NO₂ in outlet gas from the inlet NO concentration. The NO_x (NO and NO₂) conversion and N₂ selectivity were determined as follows: NO_x conversion, $([\text{NO}]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}) / ([\text{NO}]_{\text{inlet}}) \times 100$ (%); N₂ selectivity, $[\text{N}_2]_{\text{yield}} / ([\text{N}_2]_{\text{yield}} + [\text{N}_2\text{O}]_{\text{yield}}) \times 100$ (%). In situ DRIFTS measurements were also carried out using a ZnSe window-equipped diffusion reflection cell (resolution; 4 cm⁻¹, 50 scans).

The NO_x conversion and N₂ selectivity of Pt/s-ZrO₂(700 or 800) and Pt/ZrO₂ are summarized in Table 1. The Pt/s-ZrO₂(700) exhibited the highest NO_x conversion (80%) with 66% N₂ selectivity at 100 °C. The above-mentioned catalytic activity maintained almost constant level at least for 8 h, and no gaseous ammonia was detected in the present study. The higher conversion and selectivity than values previously reported on Pt/ZrO₂ were attained at lower temperature (NO_x conversion, 72%; N₂ selectivity, 57% at 110 °C).² Although the NO_x conversion fell at above 140 °C, the N₂ selectivity was enhanced up to almost 100% with increasing reaction temperature. In the case of Pt/s-ZrO₂, the resultant NO_x consisted of mainly NO at lower temperature (<140 °C), while NO:NO₂ ratio in NO_x residue hardly changed on Pt/ZrO₂ catalyst over the whole temperature range. It implies that the NO_x reduction proceeds via the oxidative adsorption of NO molecules. The Pt/s-ZrO₂(800) showed

Table 1. NO_x conversion and N₂ selectivity profiles of Pt/ZrO₂ and Pt/s-ZrO₂(700 or 800) catalysts

Reaction temperature / °C	Pt/ZrO ₂		Pt/s-ZrO ₂ (700)		Pt/s-ZrO ₂ (800)	
	NO _x conversion / %	N ₂ selectivity / %	NO _x conversion / %	N ₂ selectivity / %	NO _x conversion / %	N ₂ selectivity / %
70	0	—	27	55	54	22
100	17	49	80	66	86	61
140	71	68	68	92	64	83
175	41	46	44	93	31	86
210	17	42	23	97	17	86
250	8	69	10	100	15	78

somewhat low N_2 selectivity compared with that of Pt/s-ZrO₂(700), and also nonfunctionalized Pt/ZrO₂ only showed poor NO_x reducing characteristics at 100 °C and N_2 selectivity hardly exceeding 60% even at much higher temperatures.

From the IR adsorption spectra (1388 cm⁻¹ ν (S–O–S), 1224, 1144, and 1056 cm⁻¹ ν (S–O)), the surface of zirconia was found to be covered with sulfate groups¹⁰ and peaks of law material (ammonium sulfate) were never observed. The ammonium species (3225, 3047, 2840, and 1430 cm⁻¹), *cis*-HNO₂ (1685 cm⁻¹) and NO₂⁻ (1260 cm⁻¹) group¹¹ were detected by in situ DRIFTS measurements on the Pt/s-ZrO₂ catalysts after feeding reaction gas (NO + O₂ + H₂) (Figure 1a). On the other hand, a peak around 1388 cm⁻¹ showed a negative absorbance peak that was due to the decline of ν (S–O–S) of the background s-ZrO₂. In the absence of hydrogen, no change of DRIFT spectrum was observed (Figure 1b and 1c). The ν (S–O–S) signal intensity was lowered in the presence of hydrogen (Figure 1d) and water vapor (Figure 1e). Continuous descent of ν (S–O–S) signal was observed by flowing reaction gas (Figure 1a) or water vapor (Figure 1e), while only the initial decline was recorded in the case of a hydrogen stream. This degradation is ascribable to the transformation of bridged S–O–S to S–OH groups by addition of H₂O (–S–O–S– + H₂O → 2(–SOH)) because the ν (S–O–S) mode is recovered by reoxidizing at 400 °C (Figure 1f). The generated S–OH groups act as Brønsted acid sites known as superacid sites. Nanba et al.¹² have proposed that hydrogen on surface hydroxy (Zr–OH) groups of Pt/ZrO₂ are responsible for the formation of ammonia intermediates which lead to NO_x reduction. The superacid (S–OH) species can donate protons to adsorbed NO_x species more strongly than Zr–OH group, result-

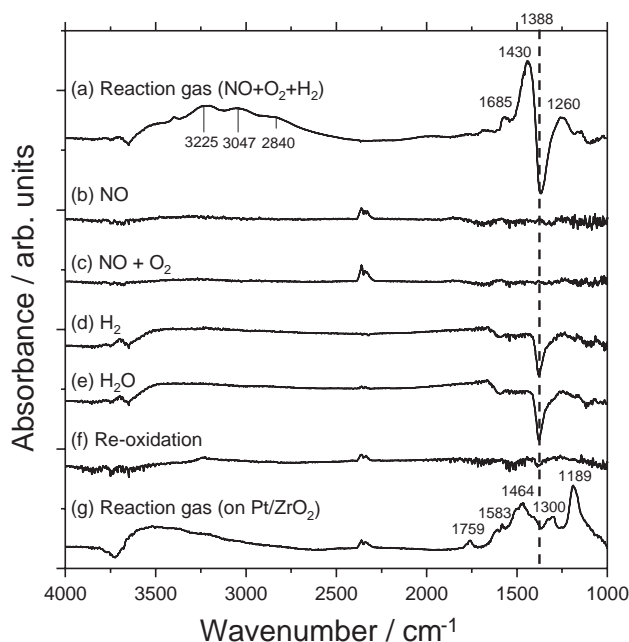


Figure 1. In situ DRIFT spectra of Pt/s-ZrO₂(700) at 100 °C in flow N_2 -based gases: (a) reaction gas (NO + O₂ + H₂), (b) 0.1 vol % NO, (c) 0.1 vol % NO and 10 vol % O₂, (d) 0.4 vol % H₂, (e) water vapor (about 3 kPa), (f) N_2 after reoxidization at 400 °C and (g) spectra of Pt-ZrO₂ under the same reaction gas as (a). Peaks at around 2400 cm⁻¹ are attributed to CO₂ impurity.

ing in the formation of ammonium species even at 100 °C. The following reduction involving ammonium species may proceed through the same pathway on the nonfunctionalized Pt/ZrO₂.⁴

On the other hand, the adsorbed intermediates on conventional Pt/ZrO₂ were nitrate groups (NO₃⁻) which are usually observed in H₂-SCR and no ammonium species was detected (Figure 1g). It is suggested that the acid sites of sulfate groups (S–OH) are responsible for the formation of ammonium intermediates.

The desorption peaks of NH₃-TPD for the catalysts were observed at 165 °C (Pt/ZrO₂), 190 and 500 °C (Pt/s-ZrO₂(700)), and 185 and 475 °C (Pt/s-ZrO₂(800)).¹⁴ The lower temperature peaks at 160–180 °C correspond to the desorption from zirconia surface, and those at 475–500 °C result from the elimination of sulfate groups.¹³ During calcination at high temperature sulfate groups were vaporized decreasing the strength and amount of superacid sites. As a result, the Pt/s-ZrO₂(800) catalysts showed less NO_x conversion and N_2 selectivity than the Pt/s-ZrO₂(700) powders. These results are in good agreement with the catalytic performance induced by the superacid sites of sulfated zirconia. Nonfunctionalized zirconia has no strong acid site, and thus Pt/ZrO₂ showed less catalytic activity for H₂-SCR of NO_x than Pt/s-ZrO₂s.

In conclusion, the Pt/s-ZrO₂ catalysts produce ammonia or ammonium ions as intermediate species even in the presence of excess oxygen (10 vol %), so they show good catalytic performance for the H₂-SCR of NO_x at a low temperature range around 100 °C. The –SOH superacid sites generated by hydrolysis of the bridged –S–O–S– groups on the surface are responsible for the formation of ammonium intermediates. The high N_2 selectivity is achieved through the reaction between ammonium species and adsorbed NO₃⁻ groups that release little N₂O.

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