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Catalytic performance of supported Ir catalysts for NO reduction with C_3H_6 and CO in slight lean conditions

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ABSTRACT

Supported Ir catalysts effectively catalyzed the NO reduction with CO and C_3H_6 under slight lean and high-temperature conditions, although supported Pt and Pd showed the activity for NO reduction in low temperature region with narrow window. The NO reduction activity of supported Ir catalysts was quite different depending on the support oxide. Among them, Ir/SiO_2 and Ir/CeO_2 were the highest and lowest active catalysts, respectively. Although no relationship between the reducibility estimated by H_2-TPR and the NO reduction activity was observed, TPO measurements revealed that the stability of Ir species in catalytically active reducing state is a key factor to determine the NO reduction activity. *In situ* FT-IR spectroscopy confirmed the formation of catalytically active reduced Ir species during the reaction. From the comparison of the wavenumber of IR band due to adsorbed CO species with the NO reduction activity, too strong Ir – support interaction causes the formation of stable Ir oxide species, resulting in the depression of NO reduction activity. The role of support oxide for Ir catalyst was concluded to stabilize the Ir species in catalytically active reducing state created during the reaction *via* the Ir – support interaction.

1. Introduction

Three-way catalysts (TWCs) can work simultaneously and efficiently to reduce NO and to oxidize CO and hydrocarbons at the theoretical air/fuel (A/F) ratio of around 14.6. However, the A/F ratio frequently fluctuates between fuel-lean and fuel-rich compositions under actual operating conditions. In particular, the deceleration with fuel-cut becomes analogous to the exhaust gas under the lean-burn high-temperature condition, resulting in NO_x emission even after passing the TWCs [1,2].

To achieve high fuel economy, lean-burn engines have been widely applied to gasoline and diesel vehicles. The NO_x abatement from lean-burn engines is still difficult problem because of the presence of excess O_2 in the exhaust. As a result of extensive research efforts to overcome this problem, the selective reduction of NO with urea and NO_x storage/reduction (NSR) techniques have already been developed [3–5], and applied to diesel and gasoline lean-burn engines. However, there is a problem that a sufficient NO_x removal efficiency can not be achieved in high-temperature range. In particular, a decrease in NO_x removal efficiency by using the NSR technique is pointed out as a prominent problem, which should be solved, because NO_x species absorbed in sorbent material are thermally unstable in high-temperature range [6]. The removal of NO_x in high-temperature and lean-burn conditions is highly required to meet the strict emission regulations.

The selective reduction of NO with fuel-derived reductants such as CO and hydrocarbons has been studied as one of the effective catalytic technologies for NO_x abatement in diesel and lean burn engine exhaust [7–10]. The active temperature regions of catalysts for NO reduction with hydrocarbons were reported to be strongly dependent on the type of active centers [11]. Metal oxide catalysts are active in high temperature region above 500 °C. The activity depression under actual operating conditions such as high space velocity (SV) is sever problem. On the other hand, supported platinum group metal (PGM) catalysts, such as Pt/Al_2O_3 and Pt/ZSM-5, show relatively high NO reduction activity even under the high SV conditions. However, in generally, the active temperature window is very narrow and located in low temperature region. In addition, high selectivity to N_2O as a product is another problem, which would be difficult to be overcome.

Among the supported precious metal catalysts, supported Ir catalysts show unique catalytic properties for NO reduction with fuel-derived reductants in the presence and absence of O_2 [10,12]. We have reported that Ir/SiO_2–based catalysts show excellent catalytic activity for the selective reduction of NO with fuel-derived reductants such as CO and H_2 in the presence of excess O_2 [13–15]. Ir catalysts supported

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on Al_2O_3, CeO_2, ZrO_2 and CeO_2-ZrO_2 also show excellent activity for NO reduction with C_3H_6 in a stoichiometric condition [16]. Therefore, it can be expected that Ir is a good candidate as highly active component, which improve the performance of TWCs for NO reduction in high-temperature and lean conditions.

In the present study, we have measured the catalytic activity of various PGM (Pt, Pd, Rh, Ir) catalysts supported on Al_2O_3 for NO reduction with CO and C_3H_6 in slight lean condition, and found that Ir/Al_2O_3 can effectively catalyze the NO reduction in high and wide temperature region. To understand the intrinsic performance of Ir catalysts, the effect of support oxides on the NO reduction activity and the surface state of Ir species during the reaction was investigated.

2. Experimental

Al_2O_3 supported PGM (Pt, Pd, Rh, Ir) catalysts were prepared by impregnation of Al_2O_3 (Mizusawa Chemicals, GB-45) with a solution of $Pt(NO_2)_2(NH_3)_2$ (Tanaka Kikinzoku Kogyo; Pt: 4.601 wt% in solution), $Pd(NO_2)_2(NH_3)_2$ (Tanaka Kikinzoku Kogyo; Pd: 4.553 wt% in solution), $Rh(NO_3)_3$ (Ishifuku Metal Industry; Rh: 4.46 wt% in solution) and Ir $(NO_3)_4$ (Ishifuku Metal Industry; Ir: 7.91 wt% in solution). After drying at 110 °C overnight, the samples were calcined at 600 °C for 5 h in air. Supported Ir catalysts were also prepared by the same manner as described above, where commercial CeO_2, CeO_2-ZrO_2 (ACZ-58) and ZrO_2 (RC-100) supplied from Daiichi Kigenso Kagaku Kogyo Co., Ltd. and sol-gel prepared SiO_2 [17] were employed as a support. The loading of PGM was fixed at 1 wt%.

The catalytic activity test was carried out using a flow reactor system by passing a slight lean gas mixture containing NO (0.05%), CO (0.1%), C_3H_6 (0.03%), O_2 (0.5%) and H_2O (5%) diluted in He at a rate of 50 $cm^3\ min^{-1}$ over 0.03 g of catalyst (SV = ca. 75,000 h^{-1}), which had been pretreated *in situ* in the flow of reaction gas at 600 °C for 1 h. The light-off activity was measured while raising the temperature from 100 to 600 °C at a rate of 3 °C min^{-1}. The effluent gas was analyzed with the use of on-line gas chromatograph equipped with TCD as a detector (Agilent Technologies, 490 Micro GC).

The amount of chemisorbed CO was measured with a pulse method (BP-1, HEMMI Slide Rule Co., Japan). The catalyst sample was first reduced with H_2 at 400 °C for 1 h and then cooled to room temperature in flowing He. Several pulses of CO were introduced into the sample until no more adsorption was observed. The dispersion of PGM, defined as the ratio of $PGM_{surface}$ over PGM_{total}, was calculated by assuming a CO to surface PGM atom ratio of 1:1 [18–20]. Temperature-programmed reduction by H_2 (H_2-TPR) was conducted to estimate the reducibility of Ir species. The H_2-TPR profiles were obtained from room temperature to 600 °C in a 30 $cm^3\ min^{-1}$ flow of 5% H_2/Ar at a heating rate of 10 °C min^{-1}. The consumption of H_2 was monitored using a TCD. Re-oxidation behavior of reduced Ir species was estimated by temperature-programmed oxidation (TPO). A catalyst sample was first reduced at 400 °C with 5% H_2/Ar for 1 h and cooled to room temperature in flowing Ar. Then the gas flow was switched to 5% O_2/Ar and the temperature was raised to 600 °C at a rate of 10 °C min^{-1}. The consumption of O_2 was monitored using a TCD.

Diffuse reflectance FT-IR spectra were recorded with a Nicolet NEXUS 670 FTIR spectrometer to observe the adsorbed chemical species on catalyst surface. Prior to each experiment, 30 mg of a catalyst placed in a diffuse reflectance high-temperature cell (Spectra-Tech) was pretreated with the reaction gas containing NO (0.05%), CO (0.1%), C_3H_6 (0.03%), O_2 (0.5%) and H_2O (2%) diluted in He at a rate of 50 $cm^3\ min^{-1}$ at 600 °C for 1 h, followed by cooling to desired temperatures in flowing He. Observation of surface species was carried out after introducing a reaction gas with the composition mentioned above. The background spectrum of the clean surface was measured in a He flow.

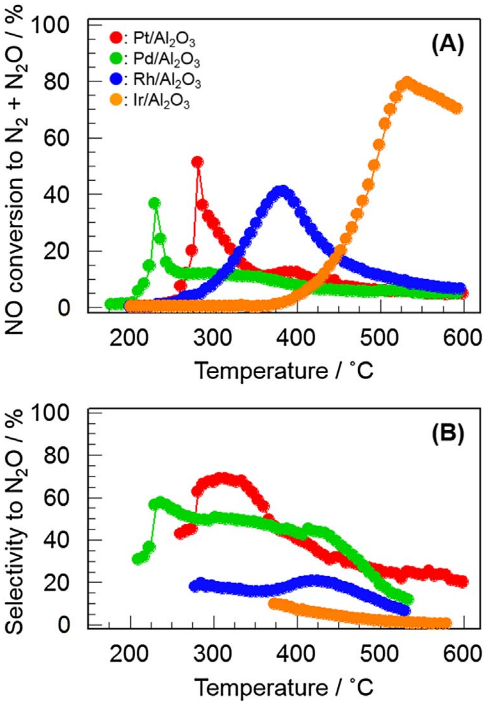

Fig. 1. Activity of Pt/Al_2O_3 (●), Pd/Al_2O_3 (●), Rh/Al_2O_3 (●) and Ir/Al_2O_3 (●) for NO reduction with CO and C_3H_6 in sligh lean conditions. (A) NO conversion to N_2 + N_2O, (B) N_2O selectivty. Reaction conditions: NO = 0.05%, CO = 0.1%, C_3H_6 = 0.03%, O_2 = 0.5%, H_2O = 5%, He balance, W/F = 0.036 $gscm^{-3}$, heating rate = 3 °C min^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

Fig. 1(A) shows the light-off curves for the conversion efficiency of NO to N_2 + N_2O over Pt/Al_2O_3, Pd/Al_2O_3, Rh/Al_2O_3 and Ir/Al_2O_3. It is well known that supported Pt and Pd catalysts can effectively catalyze the selective reduction of NO with hydrocarbons in low temperature region [21]. In accordance with literature, Pt/Al_2O_3 and Pd/Al_2O_3 showed the activity for NO reduction in the low and narrow temperature region around 200–300 °C. The selectivity of N_2O formation (N_2O/N_2 + N_2O) was, however, as high as *ca.* 60% (Fig. 1(B)). Rh/Al_2O_3 showed the NO reduction activity in relatively high and wide temperature region with *ca.* 20% of N_2O selectivity. It should be noted that Ir/Al_2O_3 shows different catalytic behavior compared with other supported PGM catalysts. Namely, the active temperature window is located in high and wide temperature region above 450 °C, and the maximum NO conversion is much higher than the other catalysts. It is also of interest that the N_2O selectivity is as low as *ca.* 10% (Fig. 1(B)). Among the catalysts tested here, supported Ir catalyst is a good candidate as a highly active deNO_x catalyst in high-temperature and slight lean conditions.

Fig. 2 shows the NO reduction activity of Ir catalysts supported on various oxides. Among the catalysts tested here, Ir/CeO_2 was the lowest active catalyst. On the other hand, the use of CeO_2-ZrO_2 as a support was effective for NO reduction to occur, although CeO_2 and CeO_2-ZrO_2 are the representative oxygen storage material [22,23]. This suggests that oxygen storage property is not a key role to determine the NO reduction performance of Ir catalyst. As can be seen in Fig. 2, Ir/SiO_2 was found to be the highest active catalyst, where NO reduction initiated at the lowest light-off temperature and the maximum NO conversion was achieved. Since support oxides did not effectively catalyse the NO reduction under the present reaction conditions, Ir must be the catalytically active component. In Table 1 are summarized the BET surface area of support oxide and Ir dispersion estimated by the amount of CO chemisorption. Relatively high Ir dispersion was obtained for Ir/