Surface Science 603 (2009) 2544–2550

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Effect of combination of noble metals and metal oxide supports on catalytic reduction of NO by H_2

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ARTICLE INFO

Article history:
Received 7 April 2009
Accepted for publication 28 May 2009
Available online 12 June 2009

Keywords:
NO reduction
NH_3 formation
N_2O formation
Noble metal
Platinum group metal
Metal oxide support
Time-of-flight mass spectrometry
Millisecond time resolution

ABSTRACT

We investigated the effects of combination of noble metals M (Rh, Pd, Ir, Pt) and metal oxide supports S (Al_2O_3, SiO_2, ZrO_2, CeO_2) on the NO + H_2 reaction using planar catalysts with M/S two layered thin films on Si substrate. In this study, NO reduction ability per metal atom were evaluated with a specially designed apparatus employing pulse valves for the injection of reactant molecules onto catalysts and a time-of-flight mass spectrometer to measure multiple transient products: NH_3, N_2 and N_2O simultaneously as well as with an atomic force microscopy to observe the surface area of metal particles. The catalytic performances of Rh and Ir catalysts were hardly affected by a choice of a metal oxide support, while Pd and Pt catalysts showed different catalytic activity and selectivity depending on the metal oxide supports. This assortment is consistent with ability to dissociate NO depending on metals without the effect of any support materials. There, the metals to the left of Rh and Ir on the periodic table favor dissociation of NO and those to the right of Pd and Pt tend to show molecular adsorption of NO. Therefore, the catalytic property of noble metals could be assorted into two groups, i.e. Rh and Ir group whose own property would mainly dominate the catalytic performance, and Pd and Pt group whose interaction with metal oxides supports would clearly contribute to the reaction of NO with H_2. NO reduction activity of Pd and Pt was found to be promoted above that of Rh and Ir, provided that Pd and Pt were supported by CeO_2 and ZrO_2.

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1. Introduction

The reduction of nitric oxide (NO) by hydrogen (H_2) is one of the fundamental processes occurring in the catalytic converter on vehicles [1]. NO must be reduced to nitrogen (N_2) efficiently with minimizing release of by-products: ammonia (NH_3) and nitrous oxide (N_2O). NH_3 is classified as a toxic air pollutant and contributes to the production of what is called as secondary particulate matter (PM) including ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(NH_4)_2SO_4$) [2,3]. N_2O is known to contribute to ozone layer depletion and to the greenhouse effect [4].

Many consecutive steps are known to take place during the NO + H_2 reaction, and many researchers involved in surface science have studied kinetics and selectivity of this reaction on Pt single crystal surface based on experiments with UHV systems [5–7] and numerical simulations [8–10]. As for other noble metals such as Rh, Pd and Ir, experimental works using UHV systems have been also reported [11,12]. Furthermore, NO chemisorption as well as reaction on various metal surfaces is studied extensively [13]. Commercial catalysts such as automobile catalysts have been studied in the form of metal-supported catalysts which consist of Pt, Pd and Rh on various metal oxide supports. As far as we know, however, systematic studies on the effects of the combination of noble metals and metal oxide supports such as Al_2O_3, SiO_2, ZrO_2 and CeO_2 have not yet seen in the reports on model system of the catalysts leading to the surface science study.

To clarify the mechanism of NH_3, N_2O and N_2 production and the controlling factor of the nitrogen oxides (NO_x) elimination in the vehicle exhaust, we utilized a specially designed apparatus for transient surface catalytic reaction analysis in millisecond time resolution [14,15]. This apparatus employs pulse valves and a time-of-flight mass spectrometer (TOF-MS) to measure more than one product simultaneously. When the gas pulses of NO and H_2 were injected onto the model planar Pt/Al_2O_3 catalyst surface in this system, the transient formation of NH_3, N_2O and N_2 was observed at the same time. This method is a technique to analyze catalytic reaction which occupies an intermediate place between those techniques of surface science under UHV and the conventional ones under atmospheric pressure such as fixed-bed flow reactors.

Thin films fabricated by sputter-deposition of two materials are expected to have distinctive catalytic activity at the nanometer

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doi:10.1016/j.susc.2009.05.031

scale interface of different materials. Using the technique mentioned above, we have been studying the catalytic activity of Pt and Al_2O_3 thin films using pulses of NO and H_2 [16,17]. In this paper the dynamic behavior of the NO + H_2 reaction on thin films composed of a noble metal: Rh, Pd, Ir, Pt and a metal oxide: Al_2O_3, SiO_2, ZrO_2, CeO_2 is investigated to obtain indispensable knowledge for automobile catalyst development. In this study, we discuss NO reduction abilities per metal atom and selectivity for N-containing products by knowing the transient formation of products per surface area of metal particles.

2. Experimental

We fabricated thin film samples by sputter-deposition under high vacuum using a noble metal (Rh, Pd, Ir, Pt) target and a metal oxide (Al_2O_3, SiO_2, ZrO_2, CeO_2) target. The deposition was performed at room temperature under a pressure of 3×10^{-1} Pa with a mixture of 10% O_2 and Ar. The metal oxide was deposited up to 40 nm on a Si substrate with (1 0 0) orientation. Then, the noble metal was deposited up to 5 nm on the metal oxide layer.

The experimental apparatus and procedures for the catalytic activity measurement are described in detail in Ref. [15]. We loaded a quartz tube reactor with the planar samples (surface area 3 mm × 3 mm and thickness 0.5 mm) together with solid SiC balls (3 mm in diameter) to separate them. The gas pulses of the reactants NO and H_2 in equimolar amounts were supplied into the reactor from pulse valves located at the inlet of the reactor. The amount of the NO and H_2 injection to the catalyst in the micro-tube reactor was approximately 1.2×10^{18} molecules. A skimmer located just in front of the outlet of the reactor sampled the reaction products: NH_3 ($m/z = 17$), N_2 ($m/z = 28$) and N_2O ($m/z = 44$) which departed from the catalyst surface and, these gases were then observed with a TOF-MS between the sample temperatures of 300 and 600 °C.

The surface structures of the films were observed by atomic force microscopy (AFM). We performed AFM measurement using Nanoscope AFM (Digital Instruments, Inc.) with a silicon nitride cantilever having a quadrangular pyramidal tip with a cone angle of 70° and a radius of 10 nm in air under the constant-force mode. As described in detail afterwards, surface area of the noble metal particles was estimated using numerical data of average radius of the metal particles and the number of the metal particles per unit area of the sample.

3. Results

3.1. NH_3, N_2 and N_2O formation behavior

Fig. 1 exemplifies the typical transient behaviors of formation of NH_3, N_2 and N_2O at 500 °C after the simultaneous injections of NO and H_2 pulses on the Pt catalysts individually supported on Al_2O_3, SiO_2, ZrO_2 and CeO_2. NH_3, N_2 and N_2O formation profiles at 500 °C on Pd, Rh, and Ir catalysts supported on Al_2O_3 are illustrated in Fig. 2. A sharp initial rise of NH_3 signal followed by a broad N_2 signal as well as N_2O signal is typically observed. Some N_2 profiles in Figs. 1 and 2 apparently consist of a sharp peak at around 150 ms and a broad one after 150 ms, in contrast with NH_3 and N_2O profiles. The experiment results obtained by the transient surface catalytic reaction analysis in millisecond time resolution suggest that there exist at least two reaction passes for N_2 production such as $N_{ads} + N_{ads} \rightarrow N_2$ and $NO_{ads} + NH_{ads} \rightarrow N_2 + OH_{ads}$ on Pt surface in the NO + H_2 reaction.

The temperature dependence of the conversion rate of NO into other products on Pt, Pd, Rh and Ir catalyst, individually supported on Al_2O_3, SiO_2, ZrO_2 and CeO_2 is illustrated in Fig. 3. The NO conversion rate was calculated using the previously reported quantitative analysis procedure [15] based on the integral of the profiles from 0 to 400 ms. The distinct feature was that the temperature dependence of the NO conversion rate of Pd catalysts and Pt catalysts showed wide differences depending on the support materials, while Rh catalysts and Ir catalysts showed almost the same NO conversion rate, respectively. Pd catalysts and Pt catalysts with CeO_2 support showed the highest NO conversion followed by those with ZrO_2, SiO_2 and Al_2O_3 supports.

Fig. 4 illustrates the temperature dependence of selectivity to NH_3, N_2 and N_2O of Pt, Pd, Rh and Ir catalysts. N_2 was major

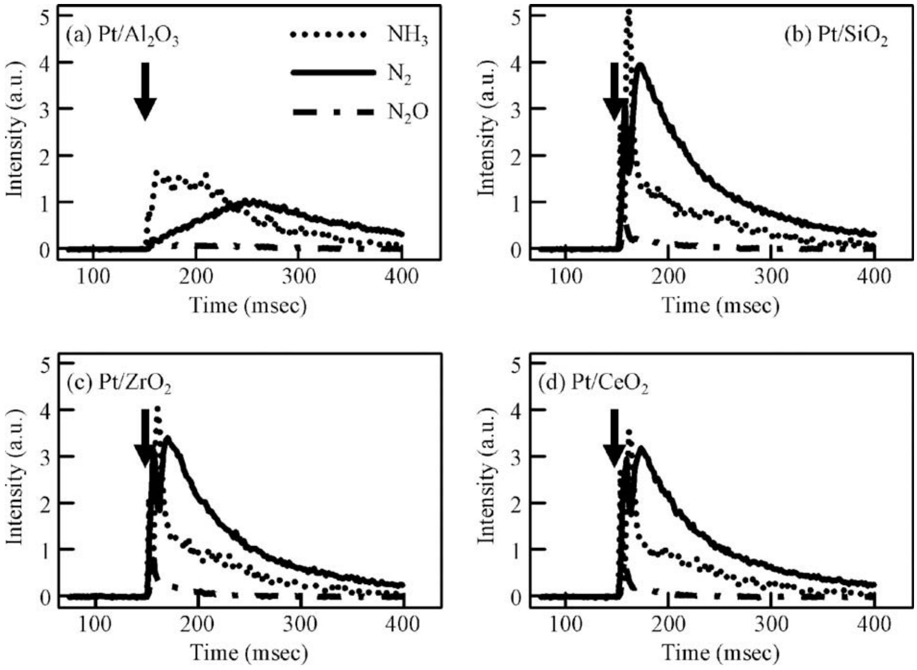

Fig. 1. Transient NH_3, N_2 and N_2O production from Pt catalysts supported on (a) Al_2O_3, (b) SiO_2, (c) ZrO_2 and (d) CeO_2 at 500 °C triggered by simultaneous injection of H_2 and NO pulses as indicated by thick arrow.

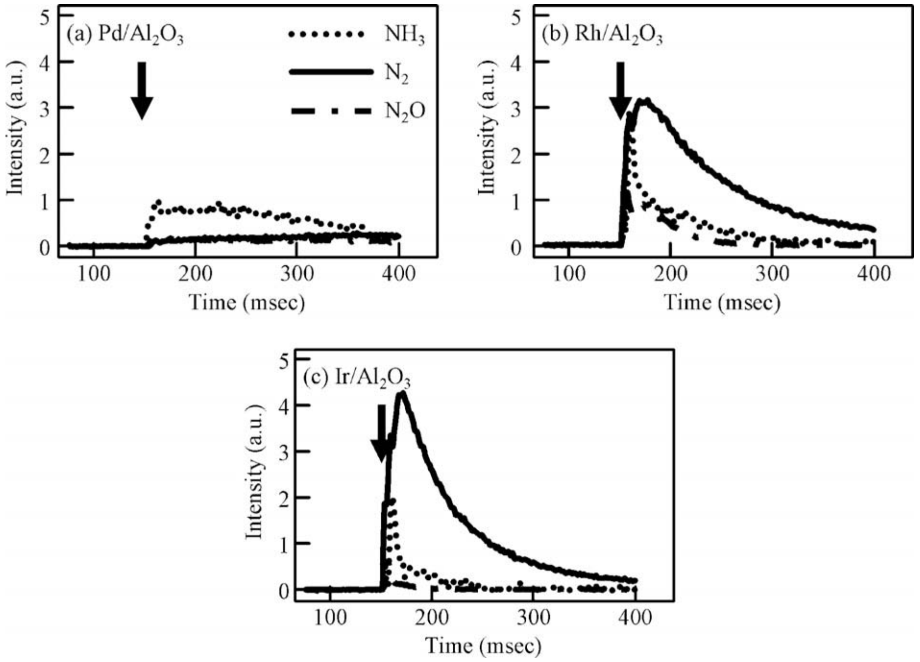

Fig. 2. Transient NH_3, N_2 and N_2O production from (a) Pd, (b) Rh and (c) Ir catalysts supported on Al_2O_3 at 500 °C triggered by simultaneous injection of H_2 and NO pulses as indicated by thick arrow.

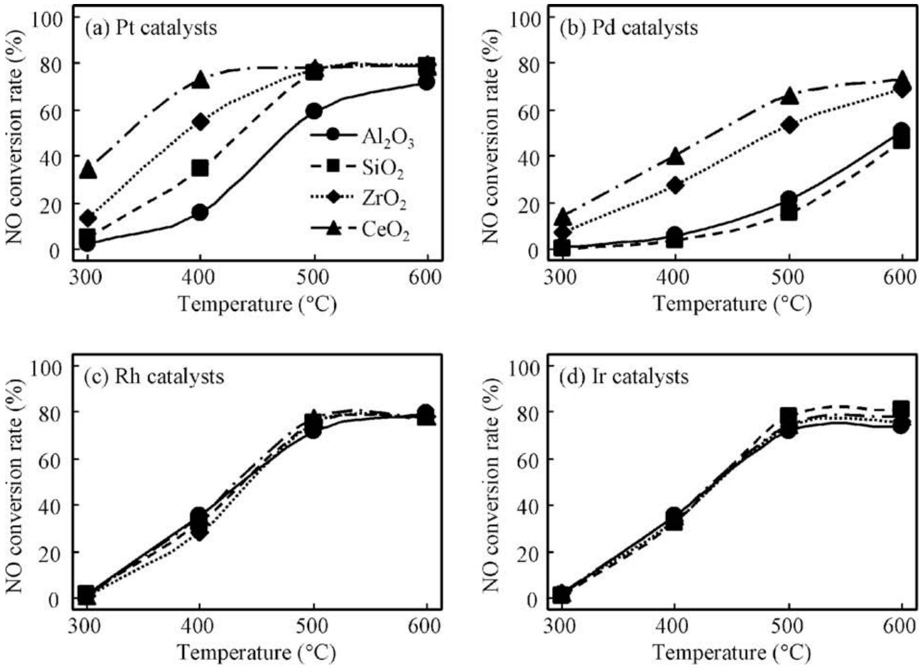

Fig. 3. Temperature dependence of the NO conversion rates over (a) Pt, (b) Pd, (c) Rh and (d) Ir catalysts.

product on Pt catalysts at all temperatures except for on Pt/Al_2O_3 at 400 °C. The selectivity for NH_3 was higher than that for N_2O in all temperature ranges. The tendency of the selectivity to N-containing products of Pd catalysts was quite different from the other noble metal catalysts. NH_3 formation is remarkable on Pd/CeO_2 at 400 °C and on Pd/Al_2O_3 and Pd/ZrO_2 below 500 °C as well as on Pd/SiO_2 at all temperatures. In the case of Rh catalysts and Ir catalysts, N_2 selectivity was dominant over the other products in all temperature ranges. The selectivity for N_2O was higher at 400 °C than above 500 °C in both Rh catalysts and Ir catalysts. At 400 °C, the selectivity for N_2O was more remarkable on Rh catalysts than Ir catalysts. Thus, metal oxide supports have a substantial effect on Pt catalysts and Pd catalysts in terms of the selectivity for the products.

3.2. Dispersion of noble metals

Fig. 5 exemplifies typical AFM images of Pt, Pd, Rh and Ir catalysts on Al_2O_3 after the catalytic activity measurement at the maximum temperature of 600 °C, where the scan size is

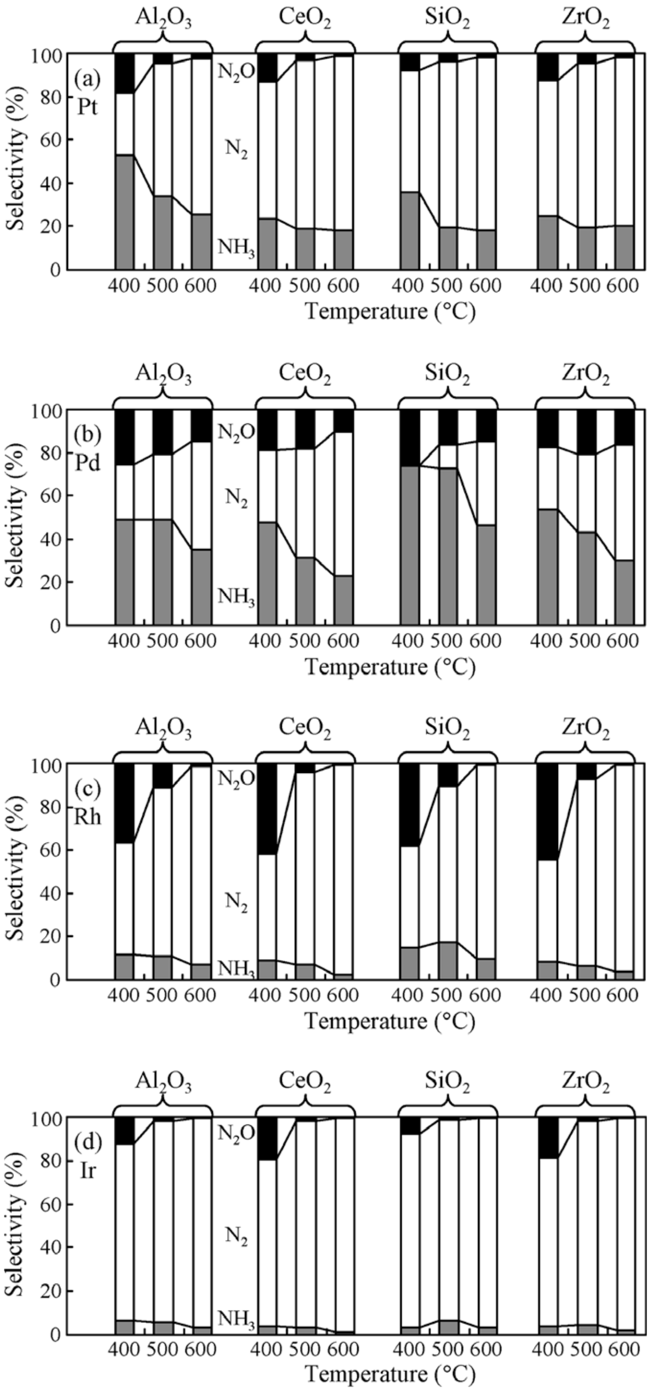

Fig. 4. Temperature dependence of the selectivity for NH_3, N_2 and N_2O over (a) Pt, (b) Pd, (c) Rh and (d) Ir catalysts.

1000 nm × 1000 nm. The sample showed noble metal islands dispersing on the metal oxide support surface, while the sample before the catalytic activity measurement showed a flat surface similar to that of the Si substrates. Scanning resolution is rather low; however it is enough to figure out the size of the individual particles and the number of the particles per unit surface area. The shape of the Pt crystallites is roughly hemispherical. Such Pt crystallites were also observed on α-Al_2O_3 and γ-Al_2O_3 substrates after thermal treatment by AFM observation [18,19]. For Pd and Rh catalysts, the surface morphology was almost similar to those of Pt catalyst. In the case of Ir catalysts, the morphology of the surface was somewhat different from the others. The growth of Ir particles was far more prohibited than those of Pt, Pd and Rh.

Table 1 gives the average size of metal particles and the number of metal particles per unit surface area of the substrate observed by AFM. The total volume of the metal particles per unit surface area of the substrate should equal to the volume of the deposited thin film, i.e. 1000 nm × 1000 nm × 5 nm, provided that the metal film is uniformly deposited on the metal oxide supports. Under the assumption that the particles have a shape which is partially cut out from hemisphere, the average height and the average curvature radius of the particles were calculated so that the total volume of the hemispherical particles corresponds to the volume of the deposited thin film. Then the surface area of the hemisphere in Table 1 was calculated. The amount of the noble metal used for the experiment was estimated by multiplying the area of the substrate (3 mm × 3 mm × 25 pieces), the thickness of the film (5 nm) and atomic density of the metal (6.022×10^{23} [atoms/mol] ÷ 195.08 [g/mol] × 21.37 [g/cm^3] = 6.60×10^{22} [atoms/cm^3] for Pt) together. From this estimation, the noble metal dispersion of the catalyst and the number of noble metal atoms which are exposed to the surface of the catalyst were calculated. As summarized in Table 2, the number of exposed noble metal atoms on the surface of noble metal particles ranged from 1.38 to 3.86×10^{15}. In the case of Ir catalysts, the values in Table 1 represent the surface coverage of Ir on the metal oxide supports, since the average size and the number of metal particles are difficult to be evaluated. Therefore, the values for Ir catalysts on upper row "dispersion" in Table 2 represent the ratio of surface to bulk atoms of the Ir particles.

3.3. NO reduction ability per noble metal atom

The amount of the NO and H_2 injection to the catalyst is approximately 1.2×10^{18} molecules. Since that is much larger than the number of noble metal atoms on the catalyst surface, the number of active site was assumed to correspond to the number of exposed noble metal atoms. On the basis of the number of noble metal atoms on the catalyst surface in Table 2 and the NO conversion rate at 400 °C in Fig. 3, where the values do not achieve a maximum of the conversion rate, turnover numbers of converted NO was calculated as shown in Fig. 6. These values are defined as the amount of NO molecules that reacted on a metal atom during a pulse of NO and H_2.

Fig. 6 shows that Rh catalysts and Ir catalysts whose turnover numbers of converted NO are respectively between 100 and 131 and between 128 and 160 possess nearly the same NO reduction ability regardless of the support material, which implies that the catalysis of Rh and Ir for NO reduction is not quite dependent on support materials. However, Pd catalysts whose turnover numbers of converted NO range from 26 to 190 and Pt catalysts whose turnover numbers range from 133 to 383 show different NO reduction ability depending on the support materials. Pd catalysts supported on ZrO_2 and on CeO_2 are comparably active to Rh catalysts and Ir catalysts at 400 °C, while those on Al_2O_3 and on SiO_2 supports are less active than other catalysts. In the case of Pt catalysts, those supported on ZrO_2 and on CeO_2 show higher NO reduction ability than those on Al_2O_3 and on SiO_2. CeO_2 followed by ZrO_2 supports seems to be effective for Pt catalysts as well as Pd catalysts on NO reduction by H_2.

4. Discussion

The product distribution of the NO + H_2 reaction depends on the reaction temperature and the NO/H_2 ratio. NH_3 was observed with Pt single crystal [5–7], Pt–Rh crystal [20] in thermal desorption spectroscopy (TDS) and Pt/SiO_2 catalyst [21] in temperature-programmed reduction (TPR) experiment. In general, NH_3 is

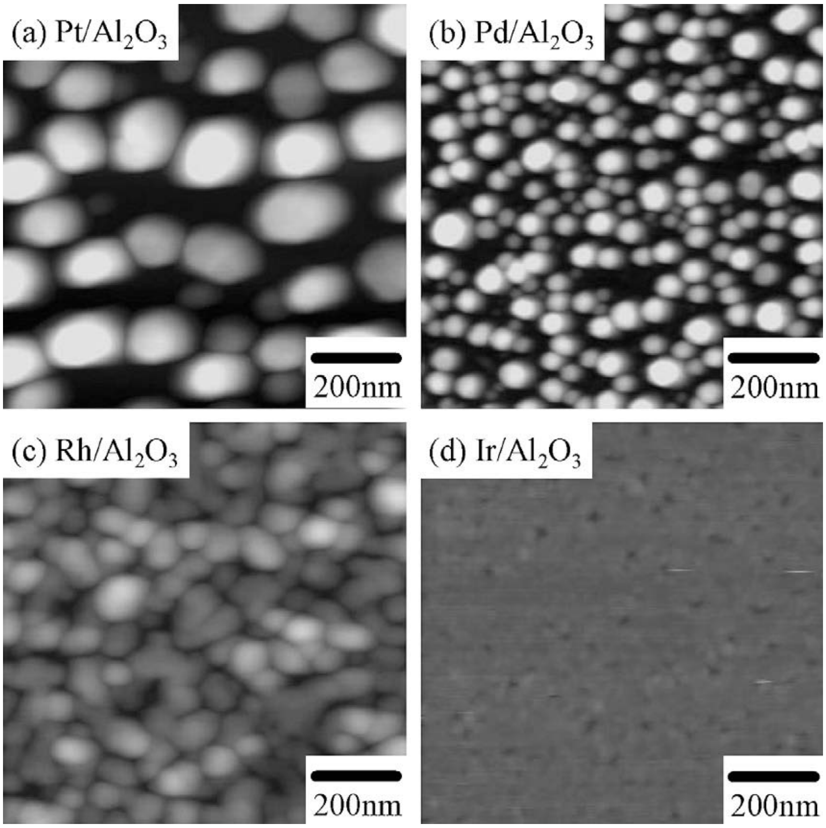

Fig. 5. AFM images of surface topography of (a) Pt, (b) Pd, (c) Rh and (d) Ir catalysts supported on Al_2O_3.

Table 1
Average size (nm) of metal particles on upper row and the number of metal particles per unit surface area (μm^{-2}) on lower row.

	Al_2O_3	SiO_2	ZrO_2	CeO_2
Pt	96.4	87.0	73.2	69.6
	34	122	114	123
Pd	54.4	81.4	88.2	88.4
	204	97	84	94
Rh	64.0	61.6	71.2	56.0
	180	187	161	222
Ir	(0.986)	(0.759)	(0.999)	(0.977)

The values for Ir catalysts represent the surface coverage of Ir on the metal oxide supports.

Table 2
The dispersion of metal particles on upper row and the surface atoms ($\times 10^{15}$) of metal particles on lower row.

	Al_2O_3	SiO_2	ZrO_2	CeO_2
Pt	0.0186	0.0392	0.0302	0.0304
	1.38	2.92	2.25	2.26
Pd	0.0337	0.0298	0.0294	0.0322
	2.59	2.29	2.26	2.47
Rh	0.0321	0.0323	0.0316	0.0338
	2.62	2.64	2.58	2.76
Ir	0.0475	0.0366	0.0482	0.0471
	3.81	2.93	3.86	3.77

prominent product in excessive H_2, but excessive NO decreased the NH_3 production [5,6]. N_2O is known to be produced under relatively low temperature conditions [20,21]. NO and H_2 is known to adsorb on the catalyst surface in the following processes, respectively.

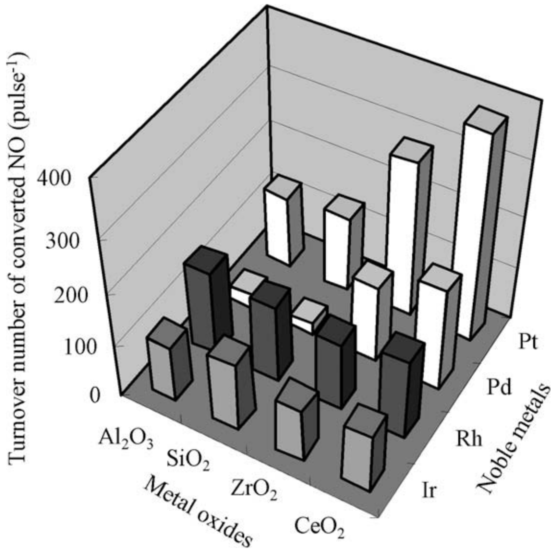

Fig. 6. Turnover number of converted NO per gas pulse on a metal atom of Pt, Pd, Rh and Ir catalysts, individually supported on Al_2O_3, SiO_2, ZrO_2 and CeO_2 at 400 °C.

$$NO \rightarrow NO_{ads} \tag{1}$$

$$NO_{ads} \rightarrow N_{ads} + O_{ads} \tag{2}$$

$$H_2 \rightarrow 2H_{ads} \tag{3}$$

NH_3 is thought to be produced from H_{ads} and N_{ads} in the following reaction processes on the same surface.

$$N_{ads} + H_{ads} \rightarrow NH_{ads} \tag{4}$$

$$NH_{ads} + H_{ads} \rightarrow NH_{2,ads} \tag{5}$$

$$NH_{2,ads} + H_{ads} \rightarrow NH_3 \tag{6}$$

At the same time, the following reactions for the production of N_2 and N_2O,

$$2N_{ads} \rightarrow N_2 \quad (7)$$

$$N_{ads} + NO_{ads} \rightarrow N_2O \quad (8)$$

are possible, as explained in temporal analysis of products (TAP) experiment with Pt/Al_2O_3 [22] and Pt/SiO_2 catalysts [23]. In addition to above reaction steps (7) and (8), NH_3 can react with NO to produce N_2 and N_2O according to the following reaction formula,

$$NH_3 \rightarrow NH_{x,ads} + H_{3-x,ads} \quad (9)$$

$$NO_{ads} + NH_{x,ads} \rightarrow N_2 + H_xO \quad (10)$$

$$NO_{ads} + NH_{x,ads} \rightarrow N_2O + H_{x,ads} \quad (11)$$

as observed on Pt and Pt–Rh metals in TAP [24,25], Pt single crystal under an ultra high vacuum (UHV) system with Q-MS [26] and Pt/Al_2O_3 with our experimental apparatus [16].

The transient experiments under moderate pressures with NO/H_2 ratio that is close to 1 revealed that the NO dissociation step (2) was the rate-determining step on Pt/Al_2O_3 [22]. The extensive studies on the catalytic NO chemisorption and reactions on single crystal metal surfaces [13] and NO decomposition on transition metals on $MgAl_2O_4$ support [27] summarizes that Pt surface mainly adsorbs NO as molecular chemisorption than dissociative chemisorption. The behavior on the Pd surface is in the same manner as that on the Pt surface. However, the metals such as Rh and Ir tend to dissociate NO than Pd and Pt.

Fig. 4 indicates that Pt catalysts and Pd catalysts especially on Al_2O_3 and SiO_2 produced large amount of NH_3. In the case of the conventional technique under atmospheric pressure such as fixed-bed flow reactors [1], it is usually difficult to observe such by-products NH_3 and N_2O because of consecutive reactions relating those products. As shown in Figs. 4 and 6, the catalytic performance of Rh and Ir were hardly affected by a choice of the metal oxide support. Moreover, the selectivity for N_2 formation of Rh catalysts and Ir catalysts were higher than that of Pd catalysts and Pt catalysts whose selectivity for NH_3 formation is relatively high in our experiments. Therefore, in the case of Rh and Ir catalysts, the strong NO dissociation ability of those noble metals seems to dominate NO reduction activity and selectivity without any contribution from metal oxide supports. It had been found that NO molecule chemisorbed on Rh horizontally leading to the NO dissociation while on Pd vertically on the basis of quantum chemistry simulation [28].

In opposite to Rh and Ir, Pd and Pt showed different catalytic activity and selectivity depending on metal oxide supports especially at low temperatures. It is clearly shown in Fig. 6 that CeO_2 and ZrO_2 enhanced activity for NO reduction on Pd and Pt at relatively low temperatures as compared with Al_2O_3 and SiO_2. Although the absence of support effects on NO decomposition was suggested regarding Pt/Al_2O_3 and Pt/SiO_2 catalysts [29], the long-term stable capacity to dissociate NO is known to be attributed to an oxygen spillover from the noble metal to the oxygen vacancies in the reduced CeO_2 [30,31]. As to ZrO_2, oxygen diffusion coefficient was higher than that of CeO_2 in the case of bulk diffusion, while surface diffusion coefficient on CeO_2 is much higher than ZrO_2 [32]. The same effect of the oxygen spillover is also expected. Therefore, the NO reduction activity for Pd as well as Pt metals on CeO_2 and ZrO_2 supports seems to be associated with ionized vacancies in the CeO_2 and ZrO_2 lattice located near the noble metals. The electron density of Pd and Pt is supposed to be increased, when oxygen spillover occurs from Pd and Pt toward ionized vacancies in the reduced CeO_2 and ZrO_2 supports. The electrons in Pd and Pt is likely to transfer to NO so that the dissociation of NO is favored. Thus, NO dissociation is considered to be enhanced by a change of the electronic structure of noble metal. As the temperature increases, NO dissociation seems to be initiated leading to high NO conversion rate and the selectivity for N_2 formation regardless of metal oxide supports.

5. Conclusions

The catalytic properties of thin films composed of noble metals and metal oxide supports were investigated with regard to NO reduction by H_2. The catalytic performances of Rh and Ir catalysts were hardly affected by a choice of a metal oxide support. N_2 was the dominant products on those catalysts. In contrast to this, the transient formation of NH_3 on Pd catalysts and Pt catalysts was higher than that on Ir catalysts and Rh catalysts. It was also noted that CeO_2 and ZrO_2 supports were more effective than Al_2O_3 and SiO_2 supports for Pt and Pd on NO conversion rate and N_2 formation selectivity at relatively low temperatures.

This assortment is consistent with ability to dissociate NO depending on metals without the effect of any support materials. There the border line between dissociative adsorption of NO and molecular adsorption passes between Rh and Pd on the periodic table. Our experimental results discriminated that the catalytic property of noble metals could be assorted into two groups, i.e. Rh and Ir group whose own property would mainly dominate the catalytic performance, and Pd and Pt group whose interaction with metal oxides supports would clearly contribute to the reaction of NO with H_2. The transient analysis clearly indicated the transient formation of NH_3 as well as N_2O in the middle of the NO reduction process especially on Pd catalysts and Pt catalysts. In addition, NO reduction activity of Pd and Pt was found to be promoted above that of Rh and Ir, provided that Pd and Pt were supported by CeO_2 and ZrO_2.

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