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Active Sites and Redox Properties of Supported Palladium Catalysts for Nitric Oxide Direct Decomposition

ATSUSHI OGATA,[1] AKIRA OBUCHI, KOICHI MIZUNO, AKIHIKO OHI,
AND HIDEO OHUCHI

Atmospheric Environmental Protection Department, National Institute for Resources and Environment,
16-3 Onogawa, Tsukuba Ibaraki 305, Japan

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Surface properties of supported palladium catalysts for NO decomposition were characterized using hydrogen adsorption, X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption and oxidation (TPD and TPO). Conversion of NO on Pd/MgO was proportional to the surface area of palladium. The interaction between palladium species and Mg^{2+} ions plays an important role in forming active sites for NO decomposition. Reduced palladium on MgO was not readily oxidized to PdO by oxygen even at high temperatures, in contrast to its behavior on SiO_2. Oxygen adsorbed on reduced Pd/MgO desorbed at temperatures lower than those for bulk PdO/MgO. It was concluded that NO decomposition on Pd/MgO catalysts proceeds mainly by a redox mechanism on partially reduced palladium species interacting with Mg^{2+} ions.

INTRODUCTION

Direct NO decomposition with catalysts has been studied since the beginning of this century (*1–4*). Recently, base metal catalysts such as Cu/ZSM-5, Ag-CoO_3O_4, perоveskites, etc., have been reported (*5–12*) to show significant activity. The most active noble metal catalysts are Pt/γ-Al_2O_3 and Pd/γ-Al_2O_3 (*13*), although a few examples of other active noble metal catalysts have been cited (*14*). Most applied research has been directed towards enhancing the activity of platinum catalysts. Little advancement has been made in the study of palladium catalysts for NO decomposition except fundamental research on single-crystal and polycrystal surfaces (*15–16*).

In a previous paper, we reported direct catalytic NO decomposition over palladium supported on various oxides (*17*). It was found that palladium catalysts supported on Mg-containing oxides such as MgO, $MgAl_2O_4$, and $Mg_2Si_3O_8$ exhibited higher catalytic activities than those supported on Al_2O_3 and SiO_2. In this paper, we have investigated the state of palladium species interacting with Mg^{2+} ions over the Pd/MgO catalyst by hydrogen adsorption, X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and temperature-programmed oxidation (TPO). Pd/SiO_2 was used as a reference sample.

EXPERIMENTAL

Catalyst preparation. Palladium catalysts were prepared by impregnation in a solution of $Pd(NO_3)_2$ (N.E. Chemcat Co., Reagent grade), followed by evaporation to dryness at 50°C using a rotary evaporator. All samples were calcined in air at 500°C overnight prior to use. The prepared catalysts contained 0.5 to 5 wt% of palladium. The oxides used as the supports were MgO (Nacalai-tesque), SiO_2 (Merck), and $MgAl_2O_4$ (Koujundo Chemical Laboratory Co., Ltd).

Catalytic reaction. Nitric oxide decomposition was carried out in a continuous flow

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[1] To whom correspondence should be addressed.

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reactor, comprised of a 16-mm-I.D. quartz tube containing 1 g of catalyst. A gas mixture of NO (1%) and He (Takachiho Chem., 99.9999%) was fed to the reactor at a rate of 80 cm^3/min. The concentrations of NO and N_2 before and after the reaction were analyzed by a chemiluminescence type NO analyzer equipped with NO_2–NO converter. At experimental conditions above 550°C, a gas chromatograph was used to confirm that the decomposition products were N_2 and O_2. Nitric oxide conversion was compatible with N_2 formed. Steady-state NO to N_2 conversion was achieved after 3 h. No deactivation in any of samples was observed during the course of the experiments, one of which was carried out for 12 h.

The NO decomposition obeyed a first-order reaction with respect to NO at 650°C on Pd/$MgAl_2O_4$, when NO concentration varied from 0.1 to 1%. The rate constants at 650°C were calculated assuming first-order kinetics and plug flow, i.e., $k = -\ln(1 - X_{NO}) \times (F/W)$, where k is rate constant (cm^3/g/min), X_{NO} NO conversion, F the flow rate (cm^3/min), and W the weight of the catalyst (g).

Sorption studies. Hydrogen adsorption was measured by a constant volume method using a conventional vacuum apparatus. The samples (0.5 to 1.0 g) were reduced at 200 Torr (1 Torr = 133.322 Pa) hydrogen at 400°C for 3 h, followed by evacuation at the same temperature. The hydrogen uptake was determined at a sample temperature of 150°C (*18–20*). The amount of chemisorbed hydrogen was determined by extrapolating isotherms obtained below 150 Torr to zero pressure. Under these conditions, no β-hydride phase was formed (*21*). Dispersion of palladium was calculated from the ratio of adsorbed hydrogen atoms to total palladium atoms in the catalysts (H/Pd). The particle size of the supported palladium was evaluated by assuming cubic particles of palladium having five exposed faces, i.e., the average particle size corresponds to the average cubic edge. Aben (*22*) and Alekseev *et al.* (*23*) reported that the average particle size over Pd/SiO_2 and Pd/γ-Al_2O_3 obtained by this method agreed with that obtained by transmittance electron microscopy.

X-ray photoelectron spectroscopy (XPS) studies. The XPS spectra were recorded on a Shimadzu ESCA 750 spectrometer using a Mg $K\alpha$ radiation source. The observed binding energy was corrected for the binding energy of C_{1s} (284.8 eV). Although samples were transferred from the reactor to the XPS chamber in open containers, the transfer was carried out as quickly as possible to minimize the exposure of the samples to air.

Temperature-programmed desorption and oxidation. In the TPD experiments, oxidized catalysts were heated in a helium stream and desorbed molecular oxygen was detected by a zirconia-type oxygen analyzer (Toray Model LC700H). In the TPO experiments, catalysts reduced by hydrogen at 400°C were slowly heated in a 1% O_2/He stream and oxygen uptake was determined by the same analyzer. Another TPD experiment designated TPD-r was performed. The sample was reduced in a hydrogen flow at 400°C for 2 h, then reoxidized in a 5% O_2/He at 200–500°C for 1 h. The samples were then heated in a He flow.

In these experiments, 1-g samples were placed in the same reactor used in the catalytic reaction studies. The samples were heated at a rate of 8°C/min from room temperature to 700°C in a gas flow of 80 cm^3/min.

RESULTS AND DISCUSSION

Dispersion of palladium and promotional effect of Mg^{2+} ions. In previous studies, Pd/$MgAl_2O_4$ exhibited the highest activity among palladium catalysts supported on Mg-containing oxides (*17*). In order to isolate the interaction between Mg^{2+} ions and the palladium catalyst from the influence of other elements, Pd/MgO was studied as a model catalyst. The relationship between the amount of palladium on the support and

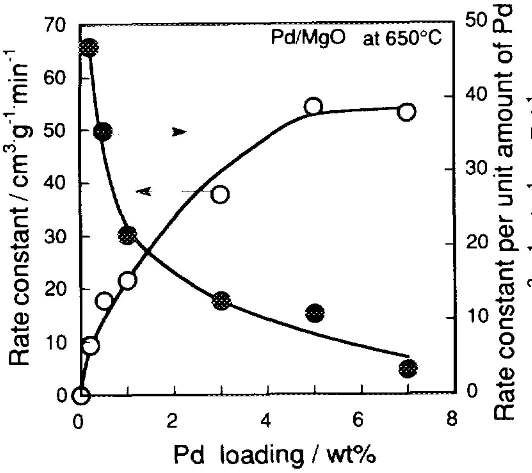

FIG. 1. Relation between the activity at 650°C and the palladium content on MgO.

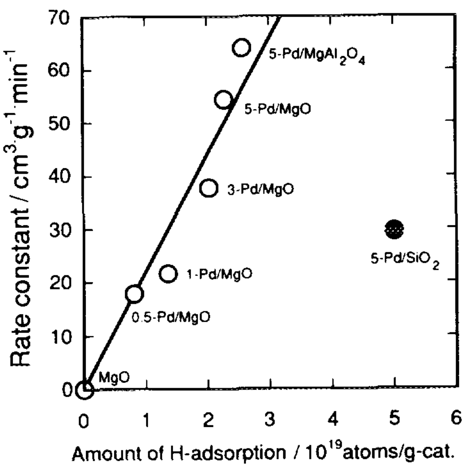

FIG. 2. Relation between the activity at 650°C and the amount of hydrogen adsorbed on the samples.

catalytic activity at 650°C is shown in Fig. 1. The catalytic activity expressed as rate constant increased with the amount of palladium on the samples, but specific activity expressed as rate constant per unit amount of palladium decreased with increased palladium loading.

We also investigated the dispersion of palladium over Pd/MgO by means of hydrogen adsorption. Table 1 summarizes the palladium dispersion and the average particle size evaluated. The catalyst which exhibited higher specific activity showed good dispersion.

Figure 2 shows the relationship between the catalytic activities at 650°C and amount of hydrogen adsorbed on the samples. The rate constant over Pd/MgO catlaysts depended on the amount of hydrogen adsorbed, i.e., on the amount of exposed palladium atoms. In addition, the rate constant over Pd/$MgAl_2O_4$ coincided with that over Pd/MgO. By contrast, the rate constant of 5 wt% Pd/SiO_2 deviated significantly from this relationship (see Fig. 2). This sample adsorbed a much larger amount of hydrogen than the Pd/MgO catalyst.

This evidence clearly shows that the inter-

TABLE 1

Dispersion and Particle Size of Palladium on Catalysts

Catalysts	Surface area (m^2/g-cat.)	Dispersion (H/Pd)	Particle size (Å)	Amount of H adsorption (atoms/g-cat.)
0.5 wt% Pd/MgO	—	0.28	32	0.81×10^{19}
1 wt% Pd/MgO	—	0.24	36	1.36×10^{19}
3 wt% Pd/MgO	6.0	0.12	73	2.03×10^{19}
5 wt% Pd/MgO	6.1	0.08	109	2.28×10^{19}
5 wt% Pd/$MgAl_2O_4$	23.2	0.09	97	2.57×10^{19}
5 wt% Pd/SiO_2	465[a]	0.18	50	5.00×10^{19}

[a] Surface area of the supports.

action between palladium species and Mg^{2+} ions plays an important role in forming an active site for NO decomposition.

The promotional effect of Mg^{2+} ions was not observed over catalysts using other elements of the platinum group (Pt, Rh, Ir, and Ru).

Valence state of palladium during reaction. NO decomposition on noble metal catalysts proceeds by NO adsorption on the reduced metal surface, accompanied by dissociation into N and O atoms and oxidation of the metal. In a catalytic reaction these dissociated atoms desorb as N_2 and O_2, reducing surface metal ions. By contrast, a stoichiometric reaction involves the reaction of oxygen with the metal and the evolution of N_2,

$$M^{n+} + NO \rightarrow M^{(n+2)+}O^{2-} + 1/2\ N_2,$$

where M is metal.

Our samples were oxidized prior to the reaction to eliminate the possibility of stoichiometric reaction. The valence state of palladium at steady-state reaction conditions is not known. The valence state of palladium was investigated by XPS spectra in the range of Pd $3d_{5/2}$ and $3d_{3/2}$ levels. Figures 3a and b show the XPS spectra obtained on fresh and used 5 wt% Pd/MgO, respectively. The peak of the Pd $3d_{5/2}$ binding energy for the fresh sample appeared at 336.5 eV (spectrum a), which has been assigned to Pd(2+) on the surface (*24*). After the reaction, both palladium peaks became broader and decreased in intensity (spectrum b). When the used sample was reoxidized at 600°C under air, a spectrum identical with that of the fresh sample was obtained (spectrum c).

The sample after the reaction was grayish, while the fresh and reoxidized samples were light-brown. The Pd/MgO catalysts reduced by hydrogen showed a grayish color and spectrum (d) having B.E. = 335.0 eV for $3d_{5/2}$. The differences between binding energies of oxidized and reduced sample was comparable to that between PdO and Pd (*24*). On the basis of these results, the change in the $3d_{5/2}$ peak after the reaction was attributed to a partial reduction in palladium.

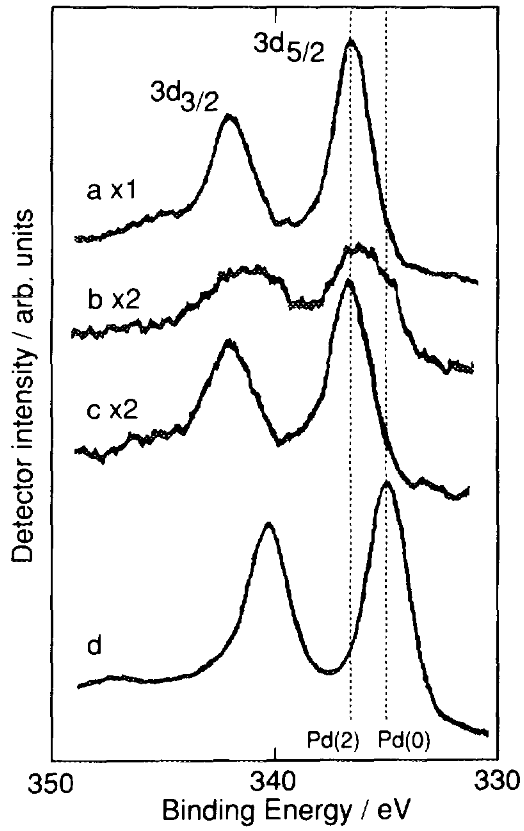

FIG. 3. XPS spectra of 5 wt% Pd/MgO (a) prior to use, (b) after the reaction, (c) reoxidized sample of (b), and (d) after the reduction by hydrogen.

Redox properties. XPS spectra indicated that the palladium species were partially reduced during the reaction, although the catalyst had been oxidized prior to the reaction. In order to determine the reduction temperature of oxidized catalyst, oxygen TPD experiments were performed on a fresh sample which had already been oxidized at 600°C. Palladium species in an oxidized state were reduced to palladium metal with evolution of lattice oxygen from PdO. Oxygen TPD spectra obtained over oxidized 5 wt% Pd/MgO and 5 wt% Pd/SiO_2 are shown in Figs.

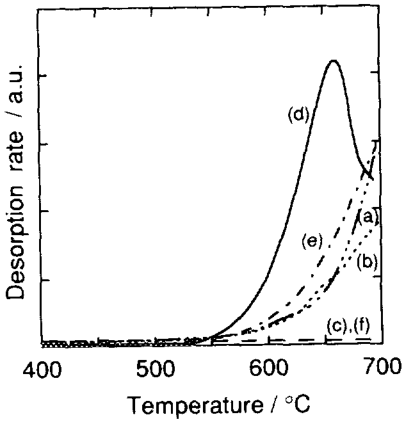

FIG. 4. TPD spectra of (a) oxidized 5 wt% Pd/MgO, (b) oxidized 5 wt% Pd/SiO_2 and (c) oxidized MgO, and TPD-r spectra of (d) reduced 5 wt% Pd/MgO, (e) reduced 5 wt% Pd/SiO_2, and (f) reduced MgO on which oxygen was preadsorbed at 400°C.

4a and b, respectively. Both TPD spectra exhibited the same desorption profiles and the palladium species began to be reduced above 550°C. Oxygen desorption from support was not observed as shown in Fig. 4c.

Figures 5a and b show the TPO spectra for reduced 5 wt% Pd/SiO_2 and 5 wt% Pd/MgO, respectively. The reduced palladium species on MgO gave a spectrum having two reoxidation peaks, while the palladium species on SiO_2 exhibited a single oxidation peak.

The reduced palladium species on MgO was not completely reoxidized to PdO but the reduced palladium species on SiO_2 were readily oxidized around 350°C. Furthermore, the "lower temperature peak/higher temperature peak" ratio on Pd/MgO catalysts increases as the palladium content on MgO decreases from 5 to 1%, as indicated in Fig. 5. Therefore, at least two kinds of palladium species having different affinities for oxygen exist on MgO after the reduction. The ratio of these species varies with the amount of palladium loading.

Oxygen desorption behavior of the palladium species, indicated by a lower temperature reoxidation peak, was investigated by oxygen TPD on the reduced sample which was preadsorbed oxygen at various temperature. This TPD experiment is abbreviated "TPD-r" to distinguish it from TPD experiments on the fully oxidized catalyst (Fig. 4a). Under oxygen flow at 400°C, only the palladium species represented by the lower temperature peak in TPO were oxidized. The palladium species represented by the higher temperature peak were not oxidized. As shown in Figs. 4d and e, a desorption peak around 650°C appeared on Pd/MgO, whereas essentially no peak was observed on Pd/SiO_2 below 700°C.

In the case of Pd/SiO_2, the TPD-r spectrum (Fig. 4e) is similar to the TPD spectrum of the fresh sample (Fig. 4b). This is reasonable because the reduced palladium species on SiO_2 was readily oxidized from Pd to PdO below 400°C as shown in the TPO experiment. Lam and Boudart (*25*) have reported that Pd(0) particles of an average size of 70 Å or smaller on Pd/SiO_2 were oxidized to PdO under an oxygen atmosphere around 265 to 307°C.

In contrast to Pd/SiO_2, the TPD-r peak for Pd/MgO varied as a function of the tem-

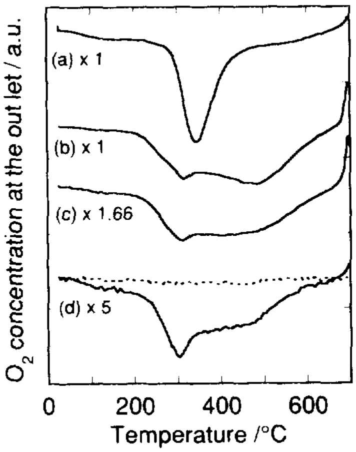

FIG. 5. TPO spectra of reduced Pd catalysts under 1% O_2/He atmosphere: (a) 5 wt% Pd/SiO_2 (relative sensitivity = 1), (b) 5 wt% Pd/MgO (relative sensitivity = 1), (c) 3 wt% Pd/MgO (relative sensitivity = 1.66), and (d) 1 wt% Pd/MgO (relative sensitivity = 5). A broken line indicates the TPO spectrum of MgO.

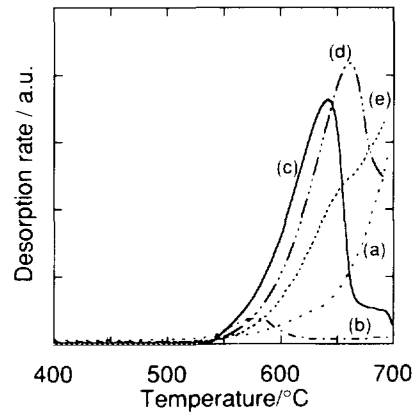

FIG. 6. TPD spectrum of (a) calcined 5 wt% Pd/MgO, and TPD-r spectra of reduced 5 wt% Pd/MgO on which oxygen was preadsorbed at (b) 200°C, (c) 300°C, (d) 400°C, and (e) 500°C.

perature at which oxygen was preadsorbed after reduction of the palladium on MgO. Figure 6 shows the TPD-r spectra of reduced 5 wt% Pd/MgO on which oxygen was preadsorbed at various temperatures. When the preadsorption temperature of oxygen was raised, from 200 to 400°C, the amount of desorbed oxygen increased, indicating difficulty in surface oxidation. However, when the preadsorption temperature was raised to 500°C, the amount of oxygen desorption decreased and the TPD-r experiment resembled the TPD experiment. The increased oxygen desorption disappeared when the sample was oxidized at higher temperatures.

The same TPO and TPD-r experiments were carried out on the 5 wt% Pd/$MgAl_2O_4$ catalyst. In the TPO experiment, the spectrum for Pd/$MgAl_2O_4$ resembled that for Pd/MgO, the lower temperature peak being considerably enhanced (*26*). In the TPD-r experiment on reduced Pd/$MgAl_2O_4$, the same TPD-r spectrum as seen in the Pd/MgO system was observed as shown in Fig. 7b. These results again suggest that palladium species interacting with Mg^{2+} ions exhibit the same redox properties.

The TPD-r experiment was also carried out on Pd/MgO that had been used for NO decomposition in order to elucidate the redox sites after the catalytic reaction. A desorption peak similar to that of the reduced Pd/MgO was observed on the used Pd/MgO catalyst around 650°C as shown in Fig. 7c. These results lead to the conclusion that NO decomposition proceeds by a redox mechanism on reduced palladium.

Redox model of palladium species on the support. On the basis of the above results, we now discuss the redox model of palladium species on the MgO surface. There exist two kinds of reduced palladium species that show different reoxidation temperatures in TPO. A new oxygen desorption peak below 650°C was observed in the TPD-r experiment, as shown in Fig. 6c. This peak is attributed to the desorption of the oxygen that adsorbed around 300°C in the TPO experiment. Furthermore, in the TPD-r experiments, when the adsorption temperature of oxygen was raised to over 500°C, not only was the amount of oxygen desorbed at 650°C decreased, but oxygen desorption at temperatures above 700°C was increased as shown in Fig. 6e. This evidence leads to the conclusion that oxygen adsorbed on reduced Pd/MgO must have diffused into the bulk palladium and transformed the metal

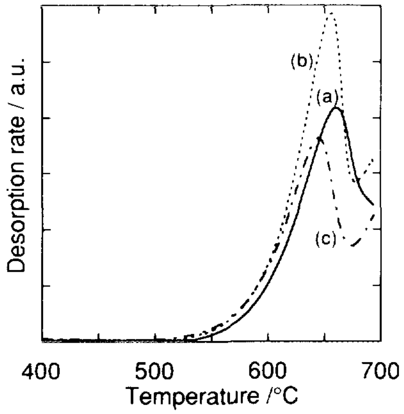

FIG. 7. TPD-r spectra of (a) reduced 5 wt% Pd/MgO, (b) reduced 5 wt% Pd/$MgAl_2O_4$, and (c) 5 wt% Pd/MgO after the NO decomposition on which oxygen preadsorbed at 400°C.

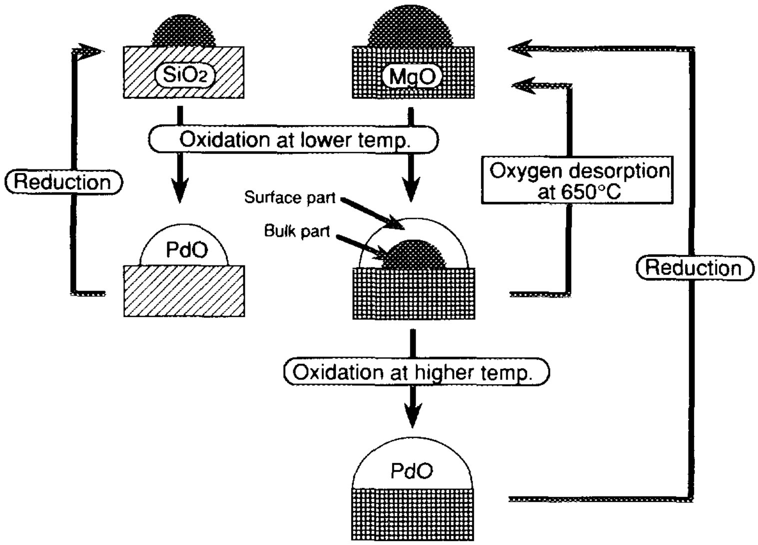

FIG. 8. Redox model of palladium species on MgO and SiO_2.

into a bulk oxide at higher temperatures. When the sample was reoxidized at higher temperatures, the properties of reduced palladium gradually disappeared. This clearly shows that the two kinds of palladium species shown in the TPO spectrum do not exist independently on MgO.

The results of hydrogen adsorption show that the catalytic activity was proportional to the surface area of palladium. Specific activity per unit amount of palladium increased with a decrease in the loading of palladium. This indicates that the sample with higher palladium loading had more palladium which was inaccessible to O_2 or NO. In the TPO experiment on Pd/MgO, the broad peak near 500°C became larger compared with the peak at 300°C with a decrease in the palladium dispersion. This shows that the ratio of the two kinds of palladium species on MgO depends on the particle size of palladium. Therefore, the lower and higher temperature peaks of TPO can reasonably be attributed to the oxidation of surface palladium and bulk palladium, respectively. From a rough calculation based on the amount of oxygen desorbed and the palladium dispersion of 5 wt% Pd/MgO, it was estimated that surface palladium comprises 3–4 layers at most. The redox models of palladium over MgO and SiO_2 are given in Fig. 8.

In summary, the desorption temperature of the TPD-r experiment shifted higher when oxygen was preadsorbed on samples at higher temperatures. This suggests a deep oxidation of the bulk palladium at higher temperatures. Oxygen was not easily desorbed when the bulk palladium was deeply oxidized. This observation supports the previous conclusion that the lower temperature peak in TPO may be attributed to surface oxidation. The difficulty in oxidizing the reduced Pd/MgO catalyst suggests that Mg^{2+} ions suppress the migration of oxygen atoms into the bulk palladium, unlike palladium on SiO_2.

CONCLUSION

The relationship between active sites and redox properties of a supported palladium catalyst for NO decomposition was revealed through an investigation of the state of palladium species in the Pd/MgO catalyst. It was found that palladium species interacting with Mg^{2+} had better redox properties than did Pd/SiO_2.

These results suggest that surface palladium species are partially reduced during NO decomposition and that this reaction proceeds mainly by a redox mechanism on the reduced palladium species.

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