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Marked particle size and support effect of Pd catalysts upon the direct decomposition of nitric oxide

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Abstract

The catalytic behavior of beryllia-supported Pd catalyst for the direct decomposition of NO was compared with that of silica supported one. The TOF of NO decomposition was one order of magnitude larger in the case of Pd/BeO. Over Pd/SiO_2, the TOF was increased with the increase of the Pd particle size. On the contrary, over Pd/BeO smaller Pd particles exhibited higher TOF for NO decomposition suggesting some strong electronic or structural interaction between Pd and beryllia. TPD spectra of NO(a) over reduced catalysts indicated that NO was adsorbed on Pd/SiO_2 more strongly than on Pd/BeO, and dissociation of NO(a) was easier on the former catalyst. FT-IR spectra of adsorbed NO at room temperature followed by the evacuation at elevated temperatures confirmed this. TPD spectra of O_2 desorbed from oxidized surface indicated that adsorption strength of O(a) is one of the most important factors to determine the catalytic activity of NO decomposition over supported Pd catalysts.

Keywords: Beryllia-supported Pd catalysts; Direct decomposition; Nitric oxide

1. Introduction

Although considerable progress has been made in the catalytic reduction of NO with various reducing agents such as H_2, CO, hydrocarbons and NH_3, the direct decomposition of this thermodynamically unstable molecule remains as a challenging problem in heterogeneous catalysis. Since the early work by Winter [1], who tested more than 40 metal oxides for NO decomposition in 1970s, it has been well recognized that many metal oxides have moderate activity for this reaction, including Ag-promoted cobalt oxide [2], oxygen-deficient Sr–Fe oxides [3], and certain perovskite-type compounds such as La–Sr–Co oxides, YBaCuO, and LaSrCuO [4–6]. Recently, Vannice and coworkers [7] have reported that Li/MgO and Sr/La_2O_3 are active for NO decomposition. They suggested oxygen defects on the surface as the active centers for NO decomposition, although the nature of these oxygen defect is not clear. Lunsford and coworkers [8] also have reported that Ba/MgO with barium loading $>$ 11 mol% is an unusual catalyst for NO decomposition in that the activity sharply decreases, in a reversible manner, when the reaction temperature exceeds a certain value. From Raman spectroscopic results, they concluded that a barium–nitro species is an intermediate in the catalytic cycle below the fall-off temperature.

The most promising catalyst for NO decomposition is presently Cu-ZSM-5 zeolite, first reported by Iwamoto and Hamada [9] to have stable activity even in the presence of oxygen. Extensive studies have been devoted to improve the activity of this and other zeolite-based catalysts as well as to understand

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the mechanism through which NO decomposition occurs [10–14]. The oxidation state of copper in the zeolite and their complexes with nitrogen oxide as well as its dispersion could be the key to explain its catalytic properties [15]. Recently, Chang and McCarty [16] have reported that a Co-ZSM-5 zeolite that contains Co^{2+} in the siliceous MFI framework has almost one order of magnitude higher activity for the decomposition of NO in the presence of O_2 than the most active catalyst, Cu-ZSM-5, previously reported.

Nevertheless, no catalyst was active and stable enough to be applied in practical use under exhaust conditions. Above-mentioned metal cations in zeolite-type catalysts and metal oxide catalysts have some disadvantages such as lack of hydrothermal stability at elevated temperatures and deactivation by SO_x present in the exhaust. On the other hand, noble metal catalyst has a potential to overcome these problems, although their catalytic activity for NO decomposition was rather low because of the self-poisoning of strongly adsorbed oxygen atoms produced by NO decomposition. It is surprising that few studies have been reported concerning the nitric oxide decomposition over supported noble metal catalysts other than Pt/Al_2O_3 [17] and Pd/Al_2O_3 [18]. Ogata et al. [19] have investigated the catalytic activity of supported Pd catalysts for NO decomposition and found that Mg^{2+} containing supported Pd catalysts such as $Pd/MgAl_2O_4$, Pd/MgO, $Pd/Mg_2Si_3O_8$ and $MgZrO_3$, exhibited higher activities than Pt/Al_2O_3, Pd/Al_2O_3 and Cu-ZSM-5 for NO decomposition at 550–750 °C. The interaction between Pd species and Mg^{2+} ions plays an important role in forming active sites for NO decomposition, having better redox properties than did Pd/SiO_2. It was concluded that the reaction proceeds mainly by a redox mechanism on partially reduced Pd species interaction with Mg^{2+} ions [20].

Recently, we have investigated support effect of NO decomposition over Pd catalysts by employing various alkaline earth oxides. We have found that beryllium oxide supported Pd catalyst has an excellent turnover frequency even larger than MgO supported catalysts. In this study, we have compared the catalytic behavior of beryllia-supported Pd catalyst with silica supported one, to elucidate the role of beryllium on this reaction.

2. Experimental

Silica (300 m^2/g) and beryllia (20 m^2/g) supported Pd/SiO_2 and Pd/BeO catalysts were prepared by a conventional impregnation method by employing $(CH_3COO)_2Pd$ as a precursor. The reaction was carried out in a quartz micro reactor connected to a continuous atmospheric flow system. The catalysts were oxidized by oxygen at 400 °C for 3 h, followed by H_2 reduction at 700 °C for 3 h. A flow of 1 vol.% NO/He (30 ml/min) at atmospheric pressure was used as a reaction gas, and the products were analyzed by TCD gas chromatography (molecular sieve 5 Å and Porapak Q). In the case of infrared spectroscopic experiments for NO adsorption and during NO decomposition reaction, a catalyst disk was kept inside an infrared cell, which was connected to the flow system. Infrared spectra were taken with JEOL Diamond 20 Fourier transform spectrometer.

The particle sizes and dispersion of Pd in the supported catalysts were determined by XRD line width measurements, TEM photograph as well as H_2 adsorption at room temperature. For the experiments of particle size dependence, loading amounts of Pd were changed from 0.2 to 20 wt.%. As will be mentioned in the next section, obtained Pd particle sizes were strongly dependent to the method of pretreatments, and above-described method was most suitable to prepare a uniform Pd particles.

3. Results and discussion

To investigate the particle size effect of Pd on NO decomposition, it is necessary to obtain catalysts with particle size distributions as uniform as possible. Accordingly, we investigated various pretreatment methods to obtain uniform distribution and checked the TEM images. As shown in Fig. 1, when the prepared catalyst precursor was reduced by hydrogen directly at 700 °C, the distribution was very broad from 20 to 180 Å and the average particle size was 80 Å. On the contrary, when the catalysts was first oxidized at 400 °C, and then reduce by hydrogen at 700 °C, the size distribution was very narrow and the average particle size was as small as 25 Å. Consequently, we applied this pretreatment method for the catalysts employed for the investigation of particle size effects.

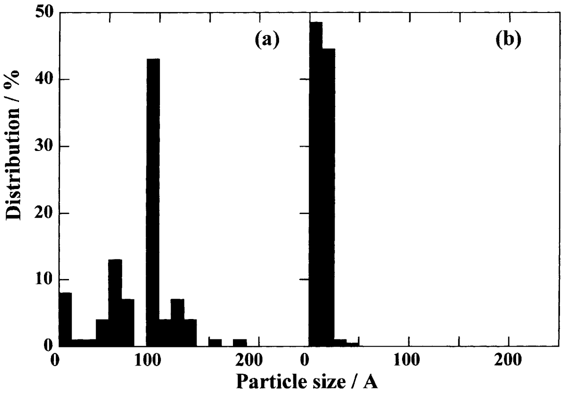

Fig. 1. Particle size distribution of Pd/SiO$_2$ determined by TEM photo: (a) pretreatment, reduction by H$_2$ at 700 °C; (b) pretreatment, oxidation by O$_2$ at 400 °C, followed by reduction by H$_2$ at 700° C.

The same pretreatment effects were obtained in the case of Pd/BeO catalysts. Table 1 summarizes the average particle sizes and H$_2$ dispersions of Pd employed in this study, determined by XRD line width, TEM photo as well as by H$_2$ adsorption at room temperature. We could obtain similar Pd particle sizes by these three methods, although XRD analysis and H$_2$ adsorption method gave a little bigger and a little smaller values than TEM analysis, respectively. In the case of silica supported catalysts, the particle sizes of Pd were increased from 20 to 90 Å accompanied with the increase of loading weight % from 1 to 20 wt.%, but did not change at all before and after the NO decomposition reaction at 700 °C. On the contrary, the particle sizes of Pd on beryllia catalysts were larger than those of silica supported one independent on the loading amount, but became two or three times larger after the NO decomposition reaction at 700 °C. The turnover frequencies of NO decomposition were determined using these particle sizes after the reaction was determined by TEM analysis.

Fig. 2 shows the time courses of NO decomposition over 5 wt.% Pd/SiO$_2$ catalyst at 600 °C, which was reduced by hydrogen at 700 °C. At the beginning of the reaction, NO conversion to N$_2$ was 100%, while no O$_2$ was observed, indicating the oxidation of the reduced Pd surface by formed oxygen. After 10 min of NO

Table 1
Average particle sizes and dispersions of Pd in various catalysts

Catalysts (wt.%)	Particle sizes (XRD) (Å)		Particle sizes (TEM) (Å)		H$_2$ dispersion
	Before reaction	After reaction	Before reaction	After reaction	After reaction (particle size: Å)
Pd/SiO$_2$					
1	–	40	20	20	0.55 (19)
5	20	50	25	25	0.44 (23)
20	20	70	90	90	0.12 (90)
Pd/BeO					
0.2	–	–	30	90	0.13 (85)
1	–	110	30	100	0.11 (100)
5	80	140	50	110	0.10 (105)
20	300	280	90	140	0.08 (130)

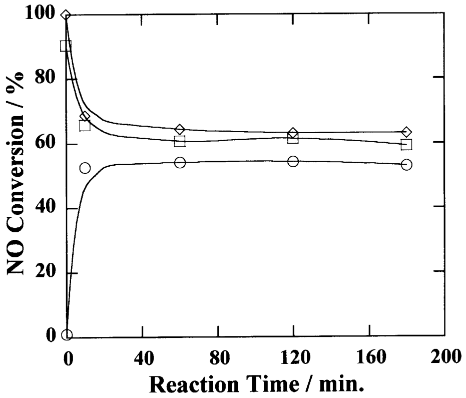

Fig. 2. Time courses of NO decomposition over 5 wt.% Pd/SiO_2 at 700 °C: (◇) NO, (☐) N_2, (○) O_2.

flowing, the conversion level of NO to N_2 was lowered to 65% accompanied with the increase of O_2 conversion up to 55%. Estimation of the amount of oxygen left on the Pd surface in this process revealed that a few oxygen layers were formed at the steady state of the reaction. When the NO decomposition started on the oxidized surface of Pd/SiO_2, considerable amounts of oxygen were desorbed from the catalyst at the beginning and similar steady-state surface was obtained in the case of reduced catalysts. As shown in Fig. 2, the amount of O_2 formed at the steady state was a few percent lower than that of N_2, although the formation of N_2O was negligible. Accordingly, NO_2 may be formed from the reaction of NO with O_2, which cannot be detected by gas chromatography.

Fig. 3 shows the temperature dependence of the NO conversion levels at the steady state of NO decomposition over Pd/SiO_2 and Pd/BeO_2 catalysts. In both the cases, the conversion was increased with the increase of the loading amount of Pd. More than 90% NO conversion was obtained over 20 wt.% Pd/SiO_2 and Pd/BeO catalysts at 700 °C, which is the highest value reported in the literature. The turnover frequencies of these catalysts were estimated using these data and the particle sizes of Pd in Table 1. Fig. 4 summarizes the dependence of the TOF (700 °C) of NO conversions as well as the particle sizes of Pd over both Pd/SiO_2 and Pd/BeO catalysts upon the amount of Pd loading. In the case of Pd/SiO_2, both TOF and particle sizes were increase with the increase of the Pd loading, indicating that larger Pd particle exhibited higher catalytic activity for NO decomposition. On the contrary, the dependency of Pd/BeO was completely opposite and smaller Pd particles possess higher TOF for NO decomposition, suggesting some electronic or structural interaction between Pd and beryllium oxide.

To clarify the role of beryllia in this reaction, temperature programmed desorption (TPD) of adsorbed NO at room temperature on the reduced catalysts was compared between these two catalysts. In the case of silica supported catalysts, the extent of NO desorbed

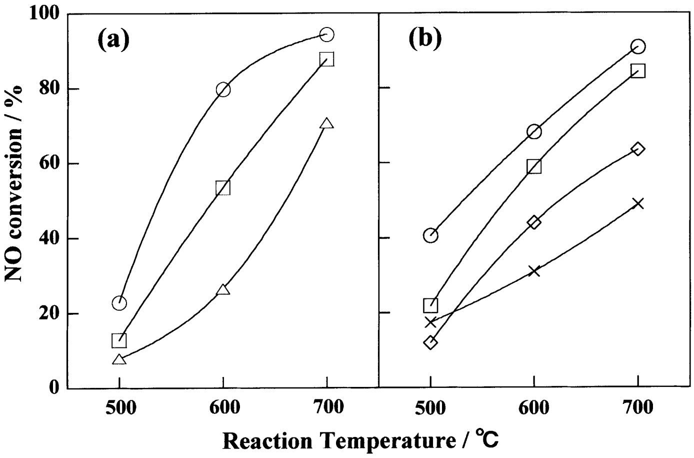

Fig. 3. Temperature dependence of NO conversion at the steady state of NO decomposition over (a) Pd/SiO_2 and (b) Pd/BeO: (○) 20 wt.%, (☐) 5 wt.%, (△) 1 wt.%, (×) 0.2 wt.%.

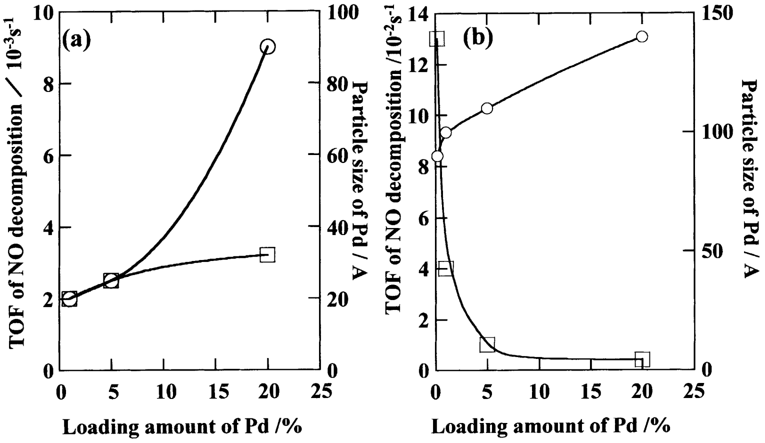

Fig. 4. Dependence of TOF (NO conversion) and Pd particle size upon the loading amount of Pd over (a) Pd/SiO_2 and (b) Pd/BeO: (○) particle size of Pd, (△) TOF of NO decomposition.

was very little and most of the adsorbed NO desorbed as N_2 leaving O(a) on the surface. Two maximum peaks of N_2 were observed at 180 and 550 °C, but no O_2 desorption was observed up to 800 °C, suggesting both Pd–N and Pd–O bonds are rather strong on Pd/SiO_2. On the contrary, over Pd/BeO catalysts the amount of desorbed NO is comparable to that of N_2 with only one TPD peak, indicating the weakening of NO adsorption strength due to the stronger electronic interaction between Pd and beryllia support as mentioned already. Moreover, desorption of O_2 was observed from 600 °C, suggesting Pd–N and Pd–O bonds became weaker by supporting on beryllia. To compare the adsorption strength of O_2 over Pd/SiO_2 and Pd/BeO, they were oxidized by O_2 at 300 °C for 2 h and then cooled down to the room temperature under He gas. In TPD experiment, only one maximum O_2 desorption peak was observed at 550 °C over Pd/BeO_2, while two desorption peaks were observed at 600 and 700 °C over Pd/SiO_2 (Fig. 5). This result also suggests the weakening of Pd–O bond by supporting on beryllia, which could be the reason why the

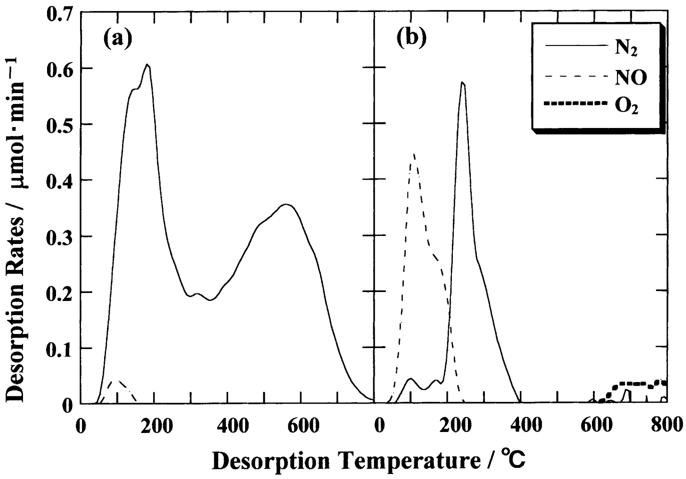

Fig. 5. TPD spectra of adsorbed NO over reduced (a) Pd/SiO_2 (5 wt.%) and (b) Pd/BeO (5 wt.%).

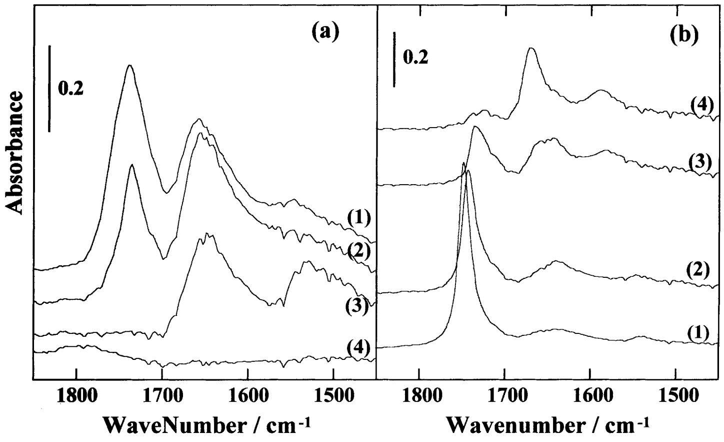

Fig. 6. FT-IR spectra of adsorbed NO over (a) Pd/SiO_2 (5 wt.%) and (b) Pd/BeO (5 wt.%): (1) adsorption at 300 K; (2) evacuation at 373 K; (3) evacuation at 473 K; (4) evacuation at 523 K.

TOF of Pd/BeO catalysts is one order of magnitude larger than those of Pd/SiO_2 catalysts.

To elucidate the particle size dependence in the case of Pd/BeO catalysts, the TPD spectra of adsorbed NO after the steady-state NO decomposition were compared over 0.2, 1 and 5 wt.% Pd/BeO catalysts. First of all, NO decomposition reaction was carried out at 700 °C for 3 h, and then the temperature was lowered to the room temperature under NO/He reaction gas. As mentioned already, Pd surface was mostly covered by O(a) during the reaction, and adsorbed NO on the steady-state surface was desorbed as NO molecules at around 250–300 °C without any dissociation into N(a) and O(a). It is interesting to note that the desorption temperature of O_2 became higher in the same order of the decrease of TOF, again suggesting the adsorption strength of O(a) is the important factor to determine the catalytic activity of NO decomposition.

Fig. 6 shows the FT-IR spectra of adsorbed NO at room temperature and its desorption at elevated temperatures over Pd/SiO_2 and Pd/BeO. Three main peaks were observed on both catalysts at around 1750, 1660, and 1550 cm^{-1}, which can be attributed to linear, two- and three-fold bridged NO(a) species, respectively [21]. But the relative intensities in these catalysts are considerably different, and only 1750 cm^{-1} peak was strong in the case of Pd/BeO catalyst, suggesting the weakening of the adsorption strength of NO. In the case of Pd/SiO_2, two- and three-fold bridged adsorbed NO had the tendency to be dissociated into N(a) and O(a) even at 250 °C as shown in TPD experiments. To study the electronic state of Pd, FT-IR spectra of adsorbed CO over the reduced surfaces were compared between Pd/SiO_2 and Pd/BeO. Both catalysts gave two typical IR bands on Pd metal, assignable to linear and bridged CO as follows: 2078 and 1960 cm^{-1} for Pd/SiO_2 and 2098 and 1970 cm^{-1} for Pd/BeO, which also indicates the existence of positively charged Pd species on beryllia with stronger electronic interaction.

4. Conclusion

The catalytic behavior of beryllia-supported Pd catalyst for the direct decomposition of NO was compared with that of silica supported one. The TOF of NO decomposition was increased with the increase of the Pd particle size over Pd/SiO_2. On the contrary, the dependency of Pd/BeO was completely opposite and smaller Pd particles possess higher TOF for NO decomposition, suggesting some strong interaction between Pd and beryllia. TPD spectra of NO(a) over reduced catalysts indicate that NO molecules are adsorbed on Pd/SiO_2 more strongly than on Pd/BeO, and dissociation of NO(a) is easier on the former catalyst, which were confirmed by FT-IR spectroscopy by observing adsorbed NO spectra at room temperature followed by the evacuation at elevated temperatures. TPD spectra of O_2 desorbed from oxidized steady-state surface indicated that adsorption strength of O(a) is one of the most important factors to determine the catalytic activity of NO decomposition over supported Pd catalysts.

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