HOKKAIDO UNIVERSITY

Title	Improvement of thermal stability of NO oxidation Pt/Al2O3 catalyst by addition of Pd
Author(s)	Kaneeda, M.; Iizuka, H.; Hiratsuka, T. et al.
Citation	Applied Catalysis B : Environmental, 90(3-4), 564-569 https://doi.org/10.1016/j.apcatb.2009.04.011
Issue Date	2009-08-17
Doc URL	https://hdl.handle.net/2115/38904
Type	journal article
File Information	90-3-4_p564-569.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Improvement of thermal stability of NO oxidation Pt/Al_2O_3 catalyst by addition of Pd

M. Kaneeda [a, c, *], H. Iizuka [a], T. Hiratsuka [b], N. Shinotsuka [b], M. Arai [c]

[a] Hitachi, Ltd. Energy and Environmental Systems Laboratory, 832-2 Horiguchi, Hitachinaka 312-8507, Japan
[b] Hitachi, Ltd. Automotive Systems, 2520 Oaza-takaba, Hitachinaka 312-8503, Japan
[c] Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

e-mail: masato.kaneeda.zc@hitachi.com
TEL +81-29-276-5633
FAX +81-29-276-5783

Abstract

The present work has been undertaken to tailor Pt/Al_2O_3 catalysts active for NO oxidation even after severe heat treatments in air. For this purpose, the addition of Pd has been attempted, which is less active for this reaction but can effectively suppress thermal sintering of the active metal Pt. Various Pd-modified Pt/Al_2O_3 catalysts were prepared, subjected to heat treatments in air at 800°C and 830°C, and then applied for NO oxidation at 300°C. The total NO oxidation activity was shown to be significantly enhanced by the addition of Pd, depending on the amount of Pd added. The Pd-modified catalysts are active even after the severe heat treatment at 830°C for a long time of 60 h. The optimized Pd-modified Pt/Al_2O_3 catalyst can show a maximum activity limited by chemical equilibrium under the conditions used. The bulk structures of supported noble metal particles were examined by XRD and their surface properties by CO chemisorption and EDX-TEM. From these characterization results as well as the reaction ones, the size of individual metal particles, the chemical composition of their surfaces, and the overall TOF value were determined for discussing possible reasons for the improvement of the thermal stability and the enhanced catalytic activity of Pt/Al_2O_3 catalysts by the Pd addition. The Pd-modified Pt/Al_2O_3 catalysts should be a promising one for NO oxidation of practical interest.

Keywords: *Platinum; Palladium; NO oxidation; Alumina; Bimetallic catalyst*

1. Introduction

It is important to remove nitrogen oxide (NOx) exhausted from various engines and combustors to protect the environment and so various NOx removal methods were proposed. Among these methods, catalytic NO oxidation to NO_2 has been attracting extensive attention; NO_2 will play an important role in future exhaust gas purification techniques. One example is the use of different catalytic components of noble metals and NO_2 adsorbents including alkali metals for lean burning engines [1, 2]. In a lean gas atmosphere, NO is mainly oxidized by the noble metals ($NO+1/2O_2 \rightarrow NO_2$) and the generated NO_2 is chemically adsorbed on the NO_2 adsorbent. Then, by changing the air-fuel ratio to a rich atmosphere, adsorbed NO_2 is reduced by reducing agents like CO and hydrocarbons in the exhaust gas. Another example is the selective catalytic reduction of NO by hydrocarbons (SCR-HC). Compared with NO, NO_2 reacts more easily with HC. Therefore, the SCR-HC is promoted by oxidizing NO to NO_2 in advance. It has been reported that the rate of SCR-HC is enhanced by mixing NO oxidation catalyst and SCR-HC catalyst mechanically [3]. Iwamoto et al. [4] proposed a method of intermediate addition of reductant (IAR). To prevent the undesired combustion of hydrocarbons by O_2, they used two reactors; after NO was oxidized to NO_2 in the first oxidation reactor, hydrocarbons were then added to the NO_2-containing gas for the SCR-HC in the second reactor. Moreover, NO_2 plays important roles not only for NOx removal but also for soot particle oxidation produced by diesel engines [5-8].

Those methods need the catalytic oxidation of NO to NO_2 and various catalysts have been reported for this reaction [1, 2, 9-15]. Among catalyst elements Pt is known to show high performance for this conversion and has already been commercially available. The metal is usually dispersed on a support, say Al_2O_3, for its good thermal stability [1, 2]. For practical use of Pt/Al_2O_3 catalysts in vehicle exhaust systems, however, higher thermal stability, even if used above 800°C, is required. In the present work, the authors have studied improvement of the thermal stability of those Pt catalysts. This paper will report the effectiveness of addition of Pd species, which is itself less active for the oxidation of NO to NO_2, and discuss possible reasons for this improvement of the thermal stability observed.

2. Experimental

2.1. Catalyst preparation

The catalyst samples of Pt and/or Pd on Al_2O_3 were prepared by the following method. Firstly, Al_2O_3 slurry was prepared by adding an Al_2O_3 with 200 m^2/g surface area to 5 wt% HNO_3 solution, followed by milling with vibration. This Al_2O_3 slurry was poured into

cordierite honeycombs (Nihongaishi, 400 cells/in^2) cells and coated on their surface. And these Al_2O_3-coated honeycombs were dried in air at 150°C for 2 h and calcined in air at 600°C for 1 h. Pt and Pd were supported on the alumina-coated cordierite honeycomb by impregnation method. The Al_2O_3-coated honeycomb was impregnated with an aqueous solution of $Pt(NH_3)_2(NO_3)_2$ and/or $Pd(NO_3)_3$ (Tanaka Kikinzoku), followed by drying and calcination in air under the same conditions as used for the Al_2O_3 coating. The nominal metal loading was changed for Pt up to 0.77 mol% and for Pd up to 0.68 mol% (Table1). The catalysts will be referred to by abbreviations given in Table 1 in the following sections.

2.2. NO oxidation test

An ordinary fixed-bed flow reactor was used to examine the NO oxidation activity of the catalysts prepared. The tubular reactor was vertically fixed to a vertical electric furnace, and the honeycomb catalyst (6 cm^3) was placed inside the reactor. The catalyst inlet temperature was set between 200°C and 500°C. Before the NO oxidation, the catalyst was pretreated in a stream of 0.6% CO and 0.3% H_2 diluted with N_2 at 500°C for 30 min. Then, a gaseous mixture containing 600 ppm NO and 5% O_2 diluted with N_2 was passed through the catalyst bed at a flow rate of 3000 cm^3 min^{-1}. The NOx concentration was measured with a NOx meter (chemiluminescence method; Horiba CLA-510). After the NO concentration at the reactor outlet was stable, the conversion of NO oxidation was calculated by:

NO conversion = 1- NO conc. at the outlet / NO conc. at the inlet.

For examining thermal stability of the catalysts, they were subjected to heat treatments in air at 800°C for 5 h or at 830°C for 60 h.

2.3. Catalyst characterization

The catalyst samples prepared were characterized by CO chemisorption, XRD and EDX-TEM. The CO chemisorption data were used to determine the amount of Pt and Pd atoms exposed on the catalyst surface. Prior to the CO chemisorption, the catalysts were pretreated in a stream of 10% CO diluted with He at 400°C for 30 min. The CO adsorption was made by pulse method; after the catalyst temperature was lowered to 100°C in the He gas carrier, a certain amount (0.5 cm^3) of 10% CO diluted with He gas was introduced into the reactor. The concentration of unadsorbed CO gas was measured with a thermal conductivity detector (Shimadzu, GC-8A). XRD (Rigaku, RU200) method was used to examine the average size of Pt and Pd crystallites, which was determined with the Debye-Scherrer equation from the XRD (311) line broadening. EDX-TEM (Hitachi, HF-2000) was used to examine the physical state and composition of noble metal particles dispersed on Al_2O_3.

3. Results and discussion

3.1. Catalytic activity for NO oxidation

First, the influence of heat treatment on NO oxidation activity was examined for a monometallic Pt(0.77) catalyst. Figure 1 shows the activities at 300°C for Pt(0.77) samples that were fresh and heat treated at 800°C for 5 h and 830°C for 60 h. The fresh catalyst indicates a conversion of 70%, but the conversion was smaller when the heat treatment conditions were more severe, dropping to 40% after the treatment at 830°C for 60 h. It is known that Pt easily sinters in an oxidation atmosphere at high temperature [16], and so this degradation may be caused by Pt sintering. The melting point is about 450°C for PtO_2 but a higher temperature of 870°C for PdO. Thus, the addition of Pd, which should be stable in air at high temperature, was expected to improve the thermal stability of the Pt/Al_2O_3 catalyst.

Then, the effectiveness of Pd addition was examined. Figure 2 shows the NO oxidation activities at 300°C for various catalysts of Pt and/or Pd on Al_2O_3 after heat treatment at 830°C for 60 h. For monometallic Pt catalysts, the NO conversion increased from 30% to 40% with an increase in the amount of Pt from 0.44 mol% to 0.77 mol%. But, it almost remained unchanged at 40% as the Pt content was further increased to 0.94 mol%. Although a small NO conversion was obtained with Pd alone, the addition of Pd in 0.30 mol% increased the activity of Pt/Al_2O_3 catalysts; a good conversion of 58% was obtained with the Pt(0.77)Pd(0.30) catalyst even after the severe heat treatment.

For the Pt(0.77)Pd(0.30) catalyst, the influence of heat treatments was further examined. Figure 3 shows the activities at 300°C for Pt(0.77)Pd(0.30) and monometallic Pt catalysts. The fresh monometallic catalysts, Pt(0.77) and Pt(0.94), indicated almost equal activities irrespective of the difference in the metal loading and they became deactivated in similar manners by the heat treatments at 800°C and 830°C. The addition of 0.30 mol% Pd did not change the activities of the fresh and 800°C-heated Pt(0.77) catalysts. It should be noted, however, that the catalyst remained unchanged in its activity after the treatment at 830°C for a longer time of 60 h. Pfeifer et al. studied NO oxidation activity of Pd-modified Pt catalysts, and reported that the catalysts were thermally stabilized by Pd addition [17]. But, heat treatment temperature in their study was 750°C and the effect of Pd addition to NO oxidation activity was small. Figure 3 shows the Pd addition to be less effective even if the heat treatment temperature was 800°C. The positive effect appeared remarkably when the catalysts were treated above 800°C for a longer time of 60 h.

Figure 4 shows the temperature dependence of NO oxidation activity of the catalysts including Pt, Pd, and both Pt and Pd after the severe heat treatment at 830°C for 60 h. Although the activity of Pd(0.30) catalyst was low at temperatures measured, the Pt(0.77)Pd(0.30) one was more active compared with the unmodified Pt(0.77) one at

temperatures above 300°C. At 350°C it showed its maximum activity limited by chemical equilibrium under the conditions used. Thus, the addition of Pd was effective to give a good thermal stability to the active Pt/Al_2O_3 catalyst for NO oxidation.

3.2 Catalyst characterization

Figure 5 shows the amounts of CO adsorbed on various noble metal catalysts heat-treated in air at 830°C for 60 h. The data for the catalysts with the same Pt loading are connected by dotted lines in Figure 5. For monometallic Pt catalysts, the amount of CO adsorbed was small and did not increase so much as the Pt amount was increased. Compared with these Pt catalysts, a monometallic Pd one Pd(0.30) adsorbed a much larger amount of CO. This indicated that Pd particles were highly dispersed on the Al_2O_3 support even after the severe heat treatment, in agreement with a fact that it was hard to sinter Pd catalyst on the SiO_2 support in air [16]. Although the amounts of CO adsorbed on Pd-modified Pt catalysts were smaller than that of the Pd(0.30) one, these were significantly larger compared with the monometallic Pt catalysts. From the present NO oxidation and CO adsorption results, one can say:

NO oxidation activity: Pt-Pd catalyst > Pt catalyst >> Pd catalyst

Metal dispersion: Pd catalyst > Pt-Pd catalyst > Pt catalyst

Pd itself was even less active, and so the Pd was assumed to prevent Pt sintering and to make the Pt retain its high NO oxidation activity.

To confirm that effect of Pd for preventing Pt sintering, the sizes of noble metal particles were measured by XRD for a few different catalysts before and after the heat treatment at 830°C for 60 h. For monometallic Pd(0.30) catalysts no XRD peaks were detected, which indicated a high Pd dispersion in accordance with the large CO adsorption (Figure 5). XRD peaks were detected for Pt(0.77) and Pt(0.77)Pd(0.30) catalysts. One diffraction peak corresponding to (311) plane was observed for Pt(0.77)Pd(0.30), indicating the formation of Pt and Pd bimetallic particles. The sizes of metal particles in these catalysts calculated from the XRD results are shown in Figure 6. The sizes for the fresh Pt(0.77) and Pt(0.77)Pd(0.30) samples were almost the same, about 25 nm, and so the addition of Pd was not influential in determining the metal dispersion before the heat treatment. A notable effect of Pd addition appeared for the heat treated catalysts: for Pt(0.77), the particle size increased to 61 nm; for Pt(0.77)Pd(0.30), it also increased but less significantly to 43 nm, resulting in the high NO oxidation activity achievable even after the heat treatment (Figure 3).

To study the effect of Pd addition in more detail, features of individual metal particles were directly examined by EDX-TEM for Pt(0.77), Pd(0.30) and Pt(0.77)Pd(0.30) catalysts that were heat treated at 830°C for 60 h. For Pd(0.30), the particles were observed to be small, just in a few nanometers. The TEM images for Pt(0.77) and Pt(0.77)Pd(0.30) are

shown in Figure 7. The size of noble metal particles in Pt(0.77)Pd(0.30) was smaller than that in Pt(0.77); the former was about 40 nm and the latter about 60 nm, which agreed with the results obtained from XRD. The chemical composition of the surface layer of individual particles was measured by EDX. A typical result is given in Figure 8. The EDX peaks of both Pt and Pd were observed for this particle examined. The coexistence of Pt and Pd were detected for all individual particles. It was reported that by adding Pd to Pt catalyst, bimetallic particles of Pt and Pd were formed [16, 18]. Fujikawa et al. [18] investigated metal particles in a $PtPd/SiO_2$-Al_2O_3 catalyst and reported that Pd was distributed on the Pt surface, leading to a Pd-rich surface. In our catalysts, bimetallic particles of Pt and Pd were likely to be formed, judging from the XRD and EDX data as above-mentioned. EDX analysis was used to estimate the chemical composition of surface layer of individual metal particles. Figure 9 shows the ratio of Pd/(Pt + Pd) measured by EDX for several metal particles different in the size. It was found that the relative Pd content decreased with an increase in the particle size. Thus, the present results demonstrated the effects of Pd addition on the size of metal particles (Figures 5 and 6) and the chemical composition on their surfaces (Figure 9), depending on the amount of Pd added.

3.3. Features of Pd-modified Pt/Al_2O_3 catalysts

The influence of Pd addition was considered on the basis of TOF, for which the number of exposed metal atoms (Pt and Pd) was determined by CO adsorption measurements.

For Pt catalysts in the absence of Pd, TOF was observed to decrease when the Pt loading was larger (Fig. 10). Ross et al. also researched NO oxidation with Pt/Al_2O_3 and they concluded that a clear dependence of TOF on the Pt loading was not observed [11]. We obtained the different structure sensitivity data with the Pt catalyst. This difference seemed to be originated from heat treatment; Ross et al. used fresh catalysts, but we heat-treated catalysts. The reason for this is not clear yet.

Figure 10 shows the TOF values of Pd-modified Pt(0.77) catalysts and Pd(0.30) catalyst heat-treated in air at 830°C for 60 h. The TOF decreased as the Pd content was increased, in particular on the addition of 30% Pd, for which the TOF decreased to about 1/2 of that of the Pt catalyst. For Pt-Pd and Pd-Rh catalysts, it was reported that these bimetallic particles with a PdO-rich surface were formed by heat treatment in air [16, 19, 20]. Such a PdO-rich surface should be formed in our catalysts during heat treatments in air and Pt particles were partially coated by PdO species. These species were able to prevent Pt oxidation and vaporization, and thereby the undesirable sintering. That is, the addition of Pd may contribute to improved thermal stability of dispersed Pt particles.

The total catalytic activity of a supported metal catalyst will be determined by its specific activity (TOF) and the degree of metal dispersion. Figure 11 illustrates the changes of these parameters with the Pd content for Pd-modified Pt/Al_2O_3 catalysts. The increasing Pd

content increases the metal dispersion but decreases the TOF since the relative content of even less active Pd on the surface of dispersed metal particles is increased. As a result, the total NO oxidation activity changes with the Pd content as depicted by dotted line in Figure 11, which explains the results of Figure 2. The maximum activity can be achievable at a certain content of Pd additive.

4. Conclusions

The present results demonstrate that the thermal stability of Pt/Al_2O_3 catalyst can be improved by the addition of Pd, which prevents the sintering of Pt species, and so the catalyst remains active for NO oxidation even after a severe heat treatment in air at 830°C for a longer time of 60 h. The addition of Pd decreases the size of bimetallic Pt/Pd particles and increases the relative content of Pd on their surfaces, resulting in the decrease of TOF value since Pd is less active. Then, a maximum activity is obtained on the addition of a certain amount of Pd. The present Pd-modified Pt/Al_2O_3 catalysts may be promising for the practical removal of NOx under severe conditions.

References

[1] M. Kaneeda, H. Iizuka, K. Higashiyama, T. Mukai, K. Ito, H. Hosoe, M. Sakanushi, K. Tokushima, T. Nishiyama, S. Konya, 16. Aachen Colloquium Automobile and Engine Technology (2007) 251
[2] M. Kaneeda, H. Iizuka, Y. Kitahara, T. Hiratsuka, H. Ohno, T. Takanohashi, N. Satoh, FISITA2004 Paper (2004) F2004V142
[3] C. Yokoyama, M. Misono, Catal. Lett., 29 (1994) 1
[4] M. Iwamoto, T. Zengyo, A. M. Hernandez, H. Arai, Appl. Catal. B 17 (1998) 259
[5] S. Kureti, W. Weisweiler, K. Hizbullah, Appl. Catal. B 43 (2003) 281
[6] L. Castoldi, R. Matarrese, L. Lietti, P. Forzatti, Appl. Catal. B 64 (2006) 25
[7] N. Nejar, M. Makkee, M.J. IIIan-Gomez, Appl. Catal. B 75 (2007) 11
[8] D. Reichert, H. Bockhorn, S. Kureti, Appl. Catal. B 80 (2008) 248
[9] J. Despres, M. Elsener, M. Koebel, O. Krocher, B. Schnyder, A. Wokaun, Appl. Catal. B 50 (2004) 73
[10] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, Catal. Today, 27 (1996) 63
[11] E. Xue, K. Seshan, J.R.H. Ross, Appl. Catal. B 11 (1996) 65
[12] P.J. Schmitz. R.J. Kudla, A.R. Drews, A.E. Chen, C.K. Lowe-Ma, R.W. McCabe, W.F.

Schneider, C.T. Goralski Jr., Appl. Catal. B 67 (2006) 246
[13] Joseph R. Theis, Erdogan Gulari, Appl. Catal. B 74 (2007) 40
[14] Q. Wang, S.Y. Park, L. Duan, J.S. Chung, Appl. Catal. B 85 (2008) 10
[15] M.F. Irfan, J.H. Goo, S.D. Kim, Appl. Catal. B 78 (2008) 267
[16] M. Chen, L.D. Schmidt, J. Catal., 56 (1979) 198
[17] M. Pfeifer, M. Kogel, P.C. Spurk and G. Jeske, SAE Paper 2007-01-0234 (2007)
[18] T. Fujikawa, K. Tsuji, H. Mizuguchi, H. Godo, K. Idei, K. Usui, Catal. Lett., 63 (1999) 27
[19] H. Muraki, H. Sobukawa, M. Kimura, A. Isogai, SAE Paper (1990) 900610
[20] B.M. Joshi, H.S. Gandhi, M. Shelef, Surf. Coat. Technol., 29 (1986) 131

Table 1 Various Pt and/or Pd catalysts on Al_2O_3 prepared and used for NO oxidation

Entry	Catalyst abbreviation	Pt		Pd	
		X (mol-%)	W (wt-%)	X (mol-%)	W (wt-%)
1	Pt(0.44)	0.44	0.84	—	—
2	Pt(0.77)	0.77	1.47	—	—
3	Pt(0.94)	0.94	1.79	—	—
4	Pd(0.30)	—	—	0.30	0.32
5	Pt(0.44)Pd(0.30)	0.44	0.84	0.30	0.32
6	Pt(0.60)Pd(0.30)	0.60	1.15	0.30	0.32
7	Pt(0.77)Pd(0.30)	0.77	1.47	0.30	0.32
8	Pt(0.44)Pd(0.68)	0.44	0.84	0.68	0.71
9	Pt(0.77)Pd(0.68)	0.77	1.47	0.68	0.71

X: Moles of metal per 1 mole of Al_2O_3. W: Weight of metal per unit weight of Al_2O_3.

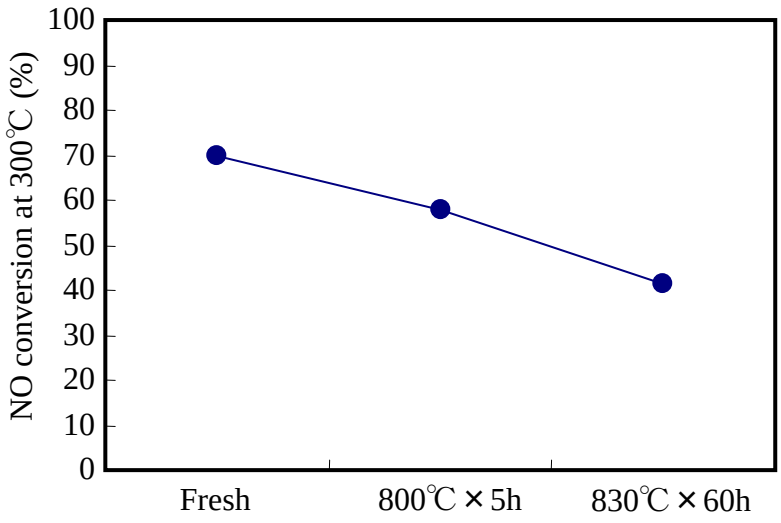

Fig. 1 Influence of heat treatments on the NO oxidation activity of a Pt/Al_2O_3 catalyst Pt(0.77)

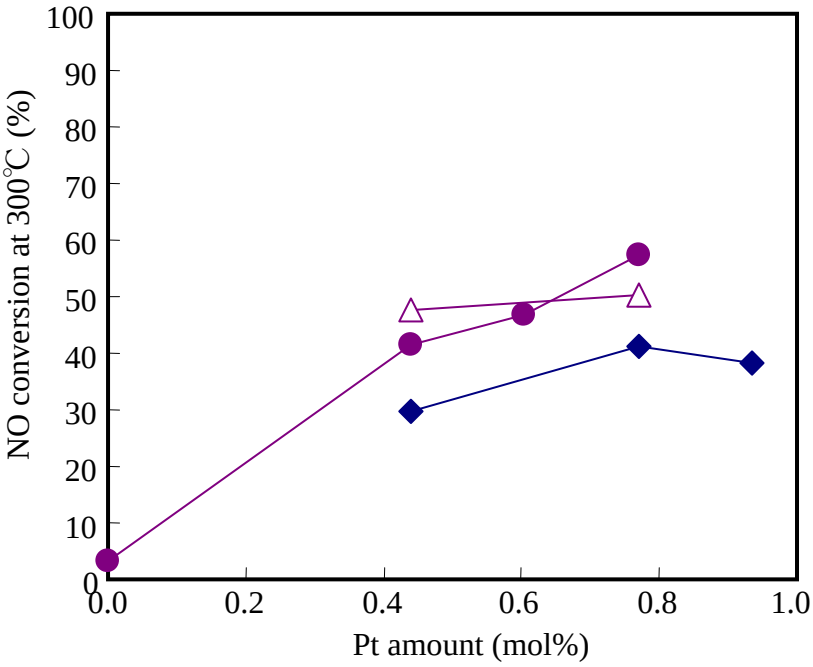

Fig. 2 The NO oxidation activity of various noble metal catalysts after heat treatment in air at 830℃ for 60 h. Pd content: ♦ none; ● 0.30 mol%; △ 0.68 mol%

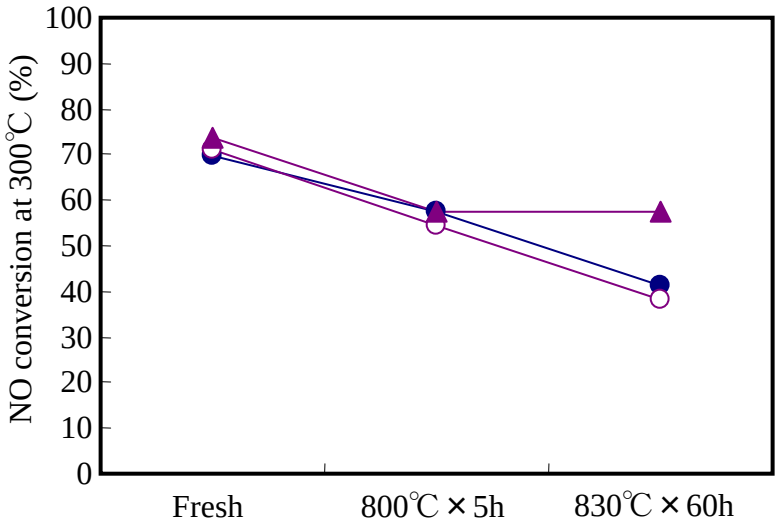

Fig. 3 The NO oxidation activity of different noble metal catalysts, Pt(0.77), Pt(0.94), and Pt(0.77)Pd(0.30), fresh and heat-treated at 800℃ and 830℃. Catalysts: (●) Pt(0.77), (○) Pt(0.94), (▲) Pt(0.77)Pd(0.30).

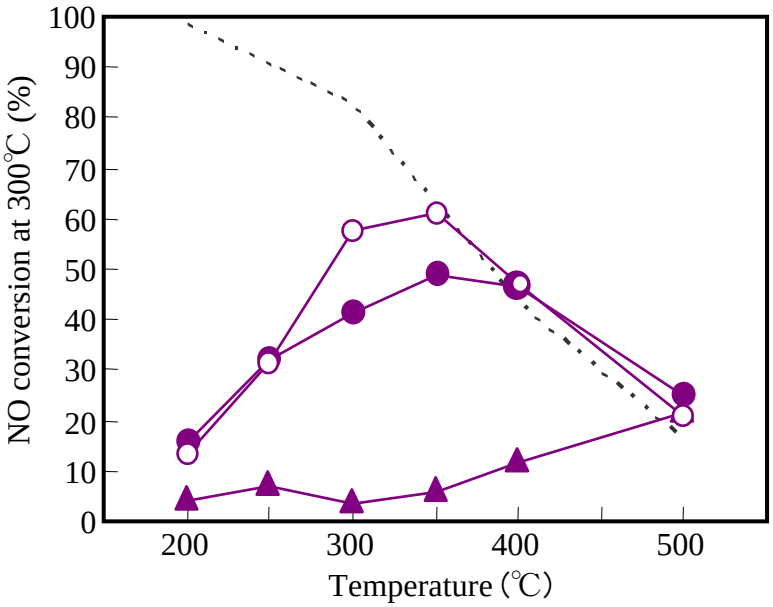

Fig. 4 NO oxidation activity at different temperatures for various noble metal catalysts after heat treatment at 830℃ for 60 h. Catalysts: (▲) Pd(0.30), (●) Pt(0.77), (○) Pt(0.77)Pd(0.30). Broken line is chemical equilibrium conversion attainable under the conditions used.

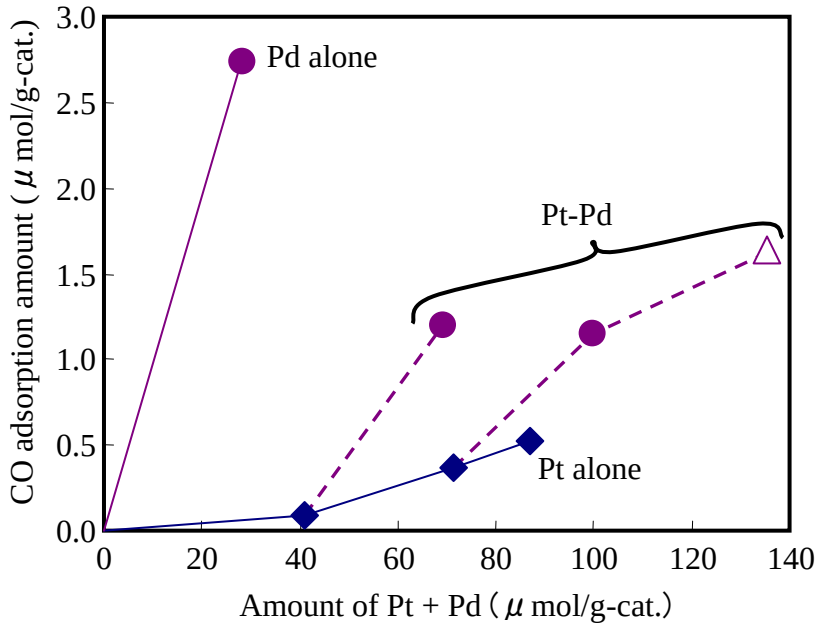

Fig. 5 The amount of CO adsorbed on various noble metal catalysts heat treated in air at 830℃ for 60 h. Pd contents: (♦) none, (●) 0.30 mol%, (△) 0.68 mol%.

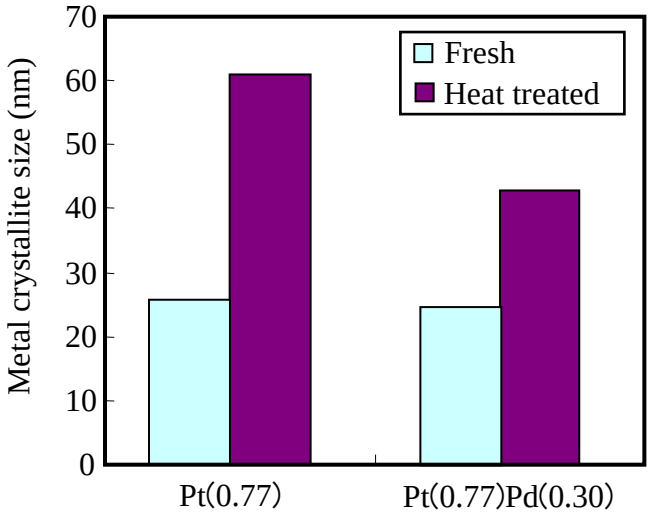

Fig. 6 Average metal crystallite size measured by XRD for fresh and heat treated Pt(0.77) and Pt(0.77)Pd(0.30) catalysts. Heat treatment: in air, 830℃, 60 h.

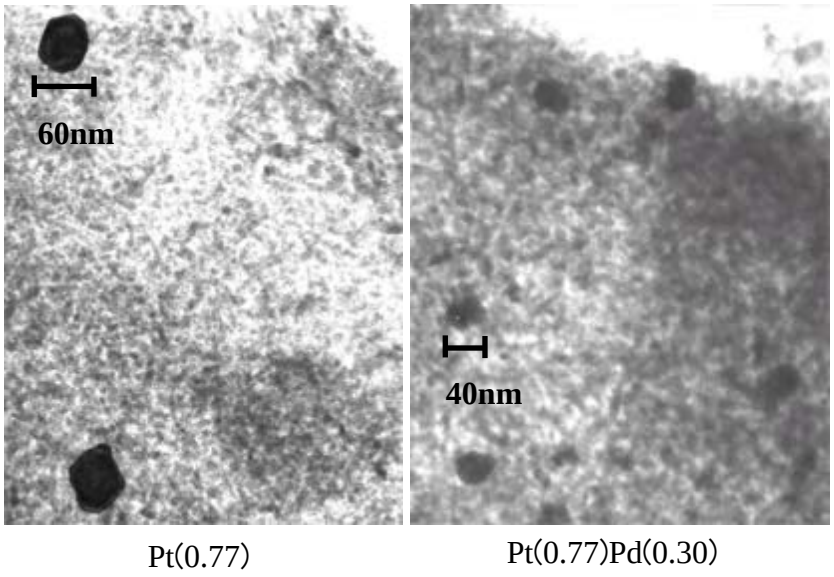

Fig. 7 TEM images for noble metal catalysts, Pt(0.77) and Pt(0.77)Pd(0.30), heat treated at 830℃ for 60 h（×125,000）

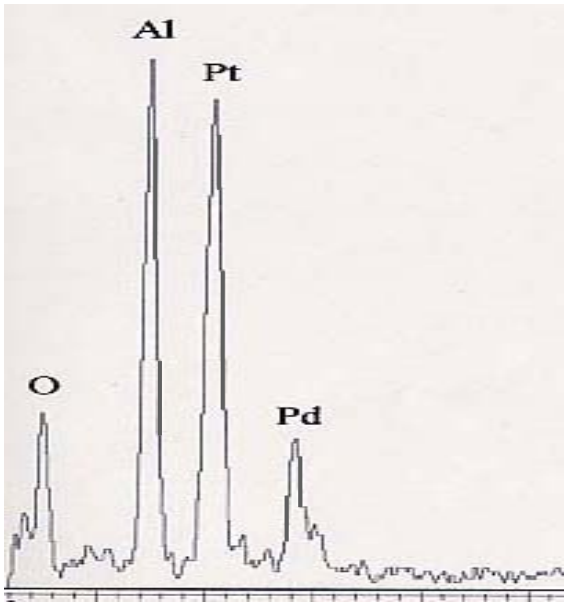

Fig. 8 A typical EDX analysis result for a catalyst of Pt(0.77)Pd(0.30) heat treated in air at 830℃ for 60 h

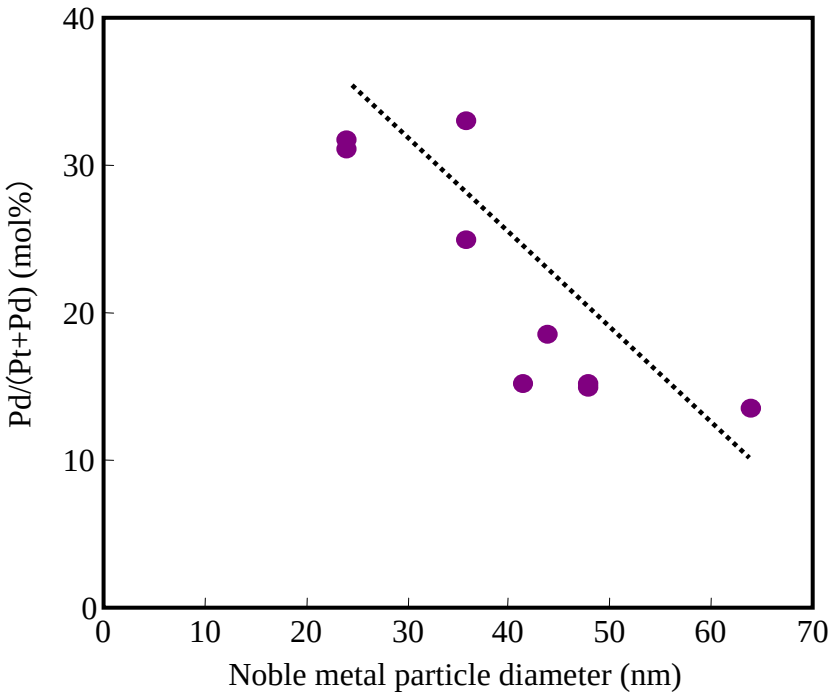

Fig. 9 Relationship between particle size and Pd content measured by TEM-EDX for individual noble metal particles in a Pt(0.77)Pd(0.30) catalyst sample heat treated in air at 830℃ for 60 h

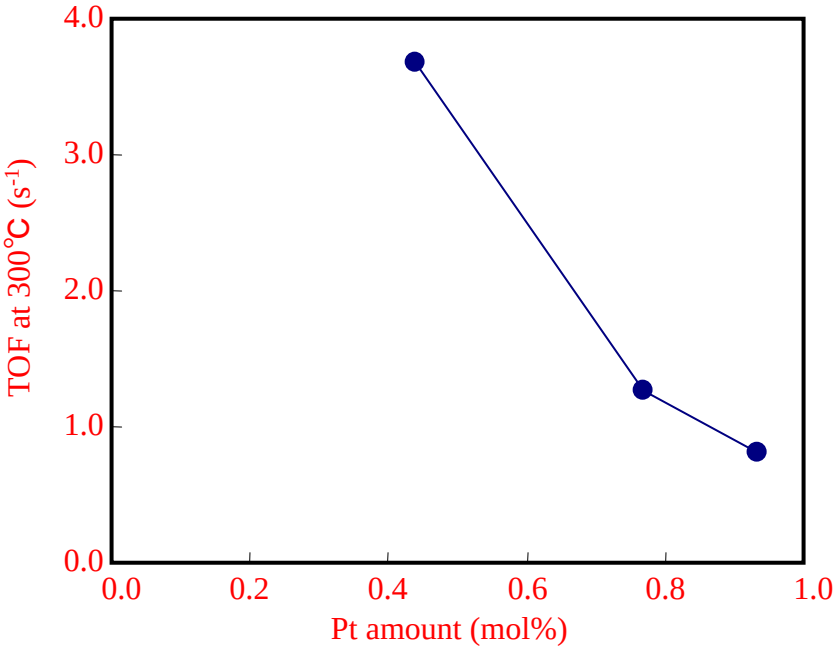

Fig. 10 Change of NO oxidation TOF with Pt amount for Pt catalysts heat treated in air at 830℃ for 60 h

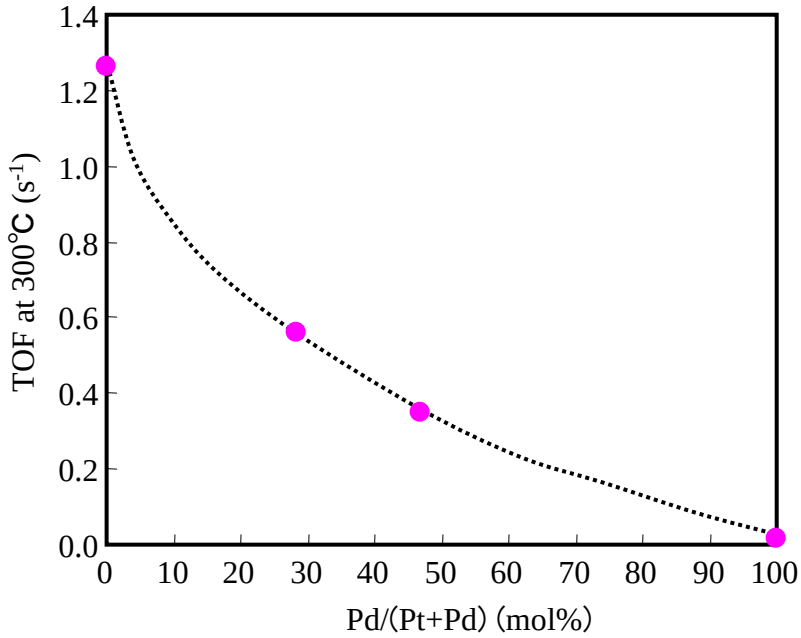

Fig. 11 Change of NO oxidation TOF with Pd content for Pd-modified Pt catalysts heat treated in air at 830℃ for 60 h

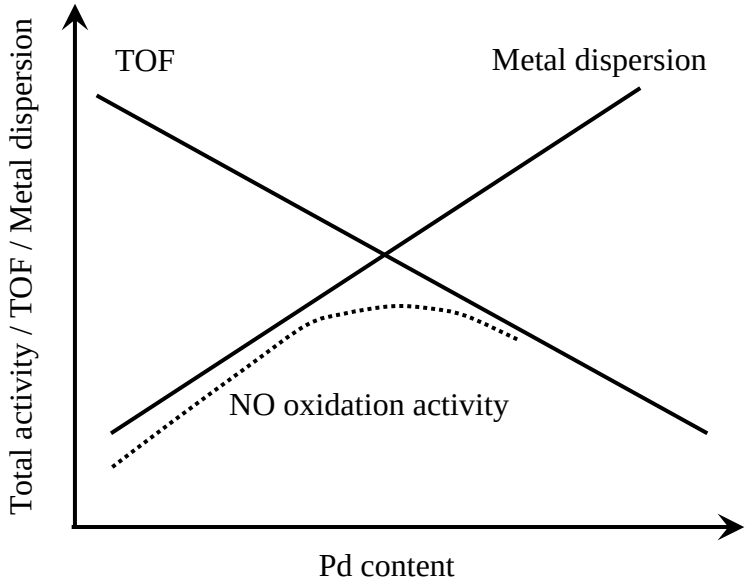

Fig. 12 Illustration of changes of metal dispersion, TOF, and total activity with Pd content for Pd-modified Pt/Al_2O_3 catalysts