

Effect of surface structure of supported palladium catalysts on the activity for direct decomposition of nitrogen monoxide

Masaaki Haneda,* Yoshiaki Kintaichi, Isao Nakamura, Tadahiro Fujitani, and Hideaki Hamada

Research Institute for Green Technology, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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Abstract

The active sites for direct decomposition of NO on supported palladium catalysts were investigated by a comparative study with single-crystal palladium surfaces. In the study of powder catalysts, the activity of Pd/Al₂O₃ was found to be significantly affected by the type of palladium precursor. Pd/Al₂O₃ catalysts prepared from palladium nitrate showed the highest activity, expressed in terms of turnover frequency (TOF), for NO decomposition to N₂. In studies using single-crystal model catalysts reported previously [I. Nakamura, T. Fujitani, and H. Hamada, *Surf. Sci.* 514 (2002) 409], the adsorption, dissociation, and desorption behavior of NO was closely related to the surface structures, the stepped surface palladium being active for dissociation of NO. NO adsorption by FT-IR spectroscopy confirmed the presence of the stepped palladium sites on Pd/Al₂O₃ catalysts, and the specific activity (TOF_{step}) for NO decomposition to N₂, calculated on the basis of number of step sites estimated from the amount of chemisorbed NO, was not changed for all the Pd/Al₂O₃ catalysts. These results suggest that direct decomposition of NO mainly proceeds on the step sites of palladium. This is in agreement with the results obtained for single-crystal model catalysts. The present study shows that the activity of powder catalyst can be well interpreted by its surface structure, indicating the usefulness of surface science techniques.

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1. Introduction

Air pollution caused by nitrogen oxides (NO_x) emitted from combustors and engines is one of the most serious environmental problems. The removal of NO_x from exhaust gases is therefore an important issue for environmental protection. Although catalytic NO reduction processes have already been put to practical use such as three-way catalyst for gasoline-fueled vehicles and ammonia SCR process for large-scale boilers, the development of effective catalysts for direct decomposition of NO still remains a challenging subject of study for the solution of NO_x problems [1–3]. Direct decomposition of NO, which is a thermodynamically favorable reaction, is considered to be the most desirable reaction for NO_x removal from combustion gases because no reduc-

ing agents are necessary, making the process very simple and less costly.

Until now, many studies have been done on this reaction, resulting in the discovery of a large number of catalysts. In particular, Cu-ZSM-5 catalyst found by Iwamoto et al. [4] has attracted much attention due to its excellent activity for NO decomposition, although the activity is still insufficient for practical use. In addition to Cu-ZSM-5, noble metal catalysts have also been extensively studied because of their high thermal stability and high tolerance toward H₂O and SO₂ present in exhaust gases. Although most of the previous works have been concerned with platinum catalysts [5–8], the performance of palladium catalysts, which show comparable activity to platinum, was also reported [9–12]. Ogata et al. [9] investigated the effect of metal oxide support for palladium catalysts and reported that the activity of Pd/MgO above 923 K is higher than that of Pt/γ-Al₂O₃ and Cu-ZSM-5. The effect of MgO support was accounted for by the formation of partially reduced palladium species inter-

* Corresponding author.

E-mail address: m.haneda@aist.go.jp (M. Haneda).

acting with Mg^{2+} ions, on which NO decomposition mainly proceeds by a redox mechanism [10]. However, no details of active sites including surface structures have yet been clarified.

Surface science using single-crystal surfaces is widely known to be a very useful tool in the investigation of reaction mechanisms and active sites for catalytic reactions at the atomic level [13]. Because catalytic reactions take place on catalyst surfaces, the essentials should be the same between single-crystal model catalysts and powder catalysts. Recently, we investigated the effect of surface structure on adsorption and decomposition of NO over palladium single crystal surfaces and revealed that NO decomposition is a structure-sensitive reaction [14]. Dissociation of NO to $\text{N}_{(a)}$ and $\text{O}_{(a)}$, resulting in the formation of N_2 , proceeds only on the stepped palladium surfaces. However, no one has tried to understand the nature of active sites for NO direct decomposition over powder catalysts. In the present study, we performed a comparative study for NO decomposition over palladium single-crystal surfaces and supported palladium catalysts to clarify the surface structure of the active sites. We would also like to demonstrate the validity of surface science techniques for understanding catalytic reactions under practical conditions.

2. Experimental

Pd/Al₂O₃ catalysts were prepared by impregnating alumina powder (Mizusawa Chemical, GB-45, 190 m² g⁻¹) with a solution of a palladium salt [Pd(NH₃)₄](NO₃)₂, Pd(NO₃)₂, Pd(CH₃COO)₂, or (NH₄)₂[PdCl₄], followed by drying at 383 K and calcination at 773 K for 5 h in flowing air. The samples are abbreviated as *x* wt% Pd(precursor salt)/Al₂O₃. The palladium loading was fixed at 5 wt%. The details of the catalysts used in the present study are given in Table 1.

The BET surface area of the samples was determined using a conventional flow apparatus (Micromeritics Flow-sorb II 2300) by nitrogen adsorption at 77 K. The amount of chemisorbed CO and NO was measured with a pulse method. The sample (0.02 to 0.1 g) was first reduced at

673 K in flowing H₂ for 1 h, followed by cooling to either room temperature for CO chemisorption or 373 K for NO chemisorption in flowing He. Several pulses of CO or NO were introduced onto the sample until no more adsorption was observed. FT-IR measurement of adsorbed specific probe molecules was conducted to get information on the surface properties of Pd/Al₂O₃. A self-supporting sample disk of about 10 mg cm⁻² placed in an IR cell with CaF₂ windows was reduced at 673 K in flowing H₂ for 2 h and then evacuated at the same temperature. The reduced sample disk was exposed to 1.3 kPa of probe molecules (CO or NO) at room temperature and then evacuated at the elevated temperatures. All the IR spectra were recorded at room temperature using a Shimadzu FT-IR 8600PC with an MCT detector at a resolution of 4 cm⁻¹.

The direct decomposition of NO was carried out in a fixed-bed continuous flow reactor. Typically, 0.1 g catalyst was used to obtain a NO conversion level below 30%. Prior to the reaction, a catalyst placed in the reactor bed was reduced in situ at 673 K with an H₂ flow for 1 h. After this treatment, the reduction of the palladium oxide to palladium metal was confirmed by X-ray diffraction (XRD) measurement. After heating to 773 K in flowing He, a reaction gas mixture composed of 970 ppm NO and He as the balance gas was fed through the catalyst bed at a rate of 30 cm³ min⁻¹. The reaction temperature was changed from 773 to 1073 K with steps of 100 K. All the activity values were measured under steady-state conditions. The effluent gas was analyzed by gas chromatography (Shimadzu GC8A TCD) using a Molecular Sieve 5A column (for the analysis of O₂, N₂, and NO) and a Porapak Q column (for that of N₂O). In the present study, the formation of N₂O was negligible.

3. Results

Table 1 summarizes the amount of CO adsorption measured by the pulse method. The amount of CO adsorption, corresponding to the number of palladium atoms exposed on the surface, was strongly dependent upon palladium precursor. For the fresh catalysts, the largest amount of CO adsorption was obtained when (NH₄)₂[PdCl₄] was used as a pre-

Table 1
Physicochemical properties of the catalysts

| Catalyst | Precursor of palladium | BET surface area (m ² g cat ⁻¹) | Amount of CO adsorption (molecules g cat ⁻¹) |
|---|---|---|---|
| Before reaction | | | |
| 5 wt% Pd(A)/Al ₂ O ₃ | [Pd(NH ₃) ₄](NO ₃) ₂ | 160 | 3.10 × 10 ¹⁹ |
| 5 wt% Pd(N)/Al ₂ O ₃ | Pd(NO ₃) ₂ | 166 | 1.80 × 10 ¹⁹ |
| 5 wt% Pd(AC)/Al ₂ O ₃ | Pd(CH ₃ COO) ₂ | 159 | 4.51 × 10 ¹⁹ |
| 5 wt% Pd(CL)/Al ₂ O ₃ | (NH ₄) ₂ [PdCl ₄] | 165 | 10.6 × 10 ¹⁹ |
| After reaction at 973 K | | | |
| 5 wt% Pd(A)/Al ₂ O ₃ | [Pd(NH ₃) ₄](NO ₃) ₂ | 148 | 1.43 × 10 ¹⁹ |
| 5 wt% Pd(N)/Al ₂ O ₃ | Pd(NO ₃) ₂ | 152 | 0.80 × 10 ¹⁹ |
| 5 wt% Pd(AC)/Al ₂ O ₃ | Pd(CH ₃ COO) ₂ | 150 | 1.68 × 10 ¹⁹ |
| 5 wt% Pd(CL)/Al ₂ O ₃ | (NH ₄) ₂ [PdCl ₄] | 140 | 1.50 × 10 ¹⁹ |

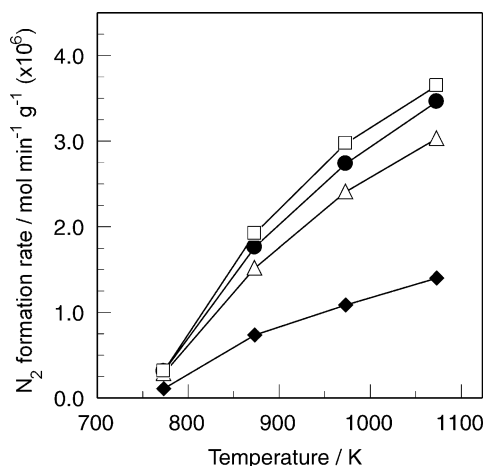


Fig. 1. Temperature dependencies of N₂ formation rate for NO decomposition over (●) 5 wt% Pd(A)/Al₂O₃, (△) 5 wt% Pd(N)/Al₂O₃, (□) 5 wt% Pd(AC)/Al₂O₃, and (◆) 5 wt% Pd(CL)/Al₂O₃.

cursor. This is in agreement with previous reports [15–17] in which the use of chloride-containing precursors (e.g., PdCl₂) improves palladium dispersion due to the formation of palladium oxychloride species strongly anchoring on the Al₂O₃ surface. The amount of CO adsorption on all the catalysts decreased considerably after NO decomposition reaction at 973 K, suggesting a coagulation of palladium particles during the reaction.

The catalytic activity of 5 wt% Pd/Al₂O₃ prepared from different palladium precursors for direct decomposition of NO was measured. At temperatures where steady-state activity was attained, O₂ was always detected with an N₂/O₂ ratio of ca. unity, suggesting that direct decomposition of NO proceeds catalytically on Pd/Al₂O₃. As shown in Fig. 1, no significant difference in the rate of N₂ formation was observed for all the Pd/Al₂O₃ catalysts except Pd(CL)/Al₂O₃, which was prepared from (NH₄)₂[PdCl₄], over the entire temperature range. It is interesting that Pd(CL)/Al₂O₃ showed very low activity despite its highest palladium dispersion. This is probably because Cl⁻ ions remaining on the surface even after calcination inhibit direct decomposition of NO, as in the case of Co₃O₄ [18] and Pd/MgO [9].

Fig. 2 shows the turnover frequencies (TOF) for NO decomposition to N₂ on 5 wt% Pd/Al₂O₃ catalysts at 773 and 973 K, where the TOF at 773 and 973 K was calculated on the basis of the number of surface palladium atoms estimated by CO chemisorption for the catalysts before and after the reaction at 973 K, respectively (Table 1). It is evident that the TOF strongly depends upon the palladium precursor employed here. Namely, the TOF decreased in the order of Pd(N)/Al₂O₃ > Pd(A)/Al₂O₃ > Pd(AC)/Al₂O₃ ≫ Pd(CL)/Al₂O₃. This result suggests that the surface structure of palladium and/or the nature of catalytically active sites are different depending on palladium precursors.

Fig. 3 shows the FT-IR spectra of CO adsorbed on 5 wt% Pd/Al₂O₃ catalysts after evacuation of the gas phase at room temperature. Three IR absorption bands were detected at

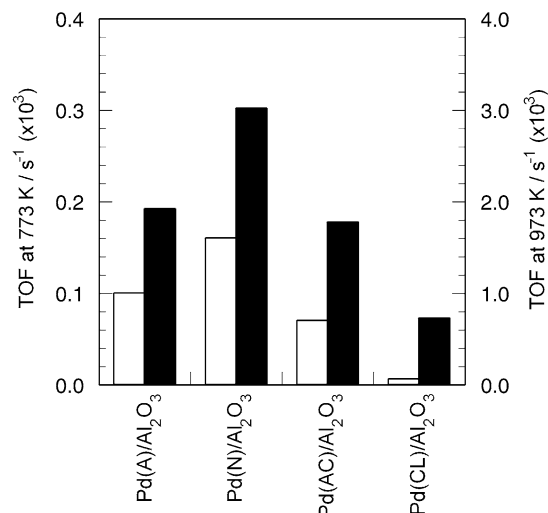


Fig. 2. Turnover frequencies for NO decomposition to N₂ over 5 wt% Pd/Al₂O₃ prepared from different palladium precursor at 773 K (□) and 973 K (■).

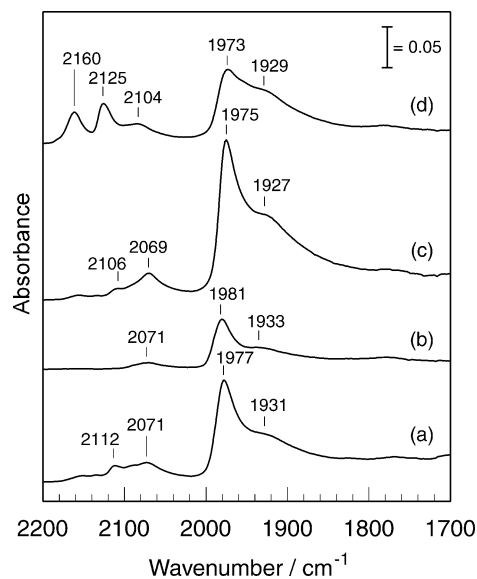


Fig. 3. FT-IR spectra of CO adsorbed on 5 wt% Pd/Al₂O₃ reduced at 673 K, followed by evacuation at room temperature. (a) Pd(A)/Al₂O₃, (b) Pd(N)/Al₂O₃, (c) Pd(AC)/Al₂O₃, and (d) Pd(CL)/Al₂O₃.

around 2070, 1980, and 1930 cm⁻¹. According to the reference by Eischens et al. [19], the IR band at 2070 cm⁻¹ is assigned to linearly bonded CO, and the 1980 and 1930 cm⁻¹ bands to bridge-bonded CO. In the IR spectrum for Pd(CL)/Al₂O₃, additional IR bands assignable to monocarbonyl Pd²⁺-CO and Pd⁺-CO species [20–22] were also observed at 2160 and 2125 cm⁻¹, respectively. The surface property of palladium on Pd(CL)/Al₂O₃ prepared from (NH₄)₂[PdCl₄] seems to be different from that on the other Pd/Al₂O₃ catalysts.

Fig. 4 shows the FT-IR spectra of NO adsorbed on 5 wt% Pd/Al₂O₃ catalysts. Well-resolved IR bands were detected at around 1730, 1670, and 1585 cm⁻¹ on the four Pd/Al₂O₃ catalysts after evacuation at room temperature (Fig. 4A). The

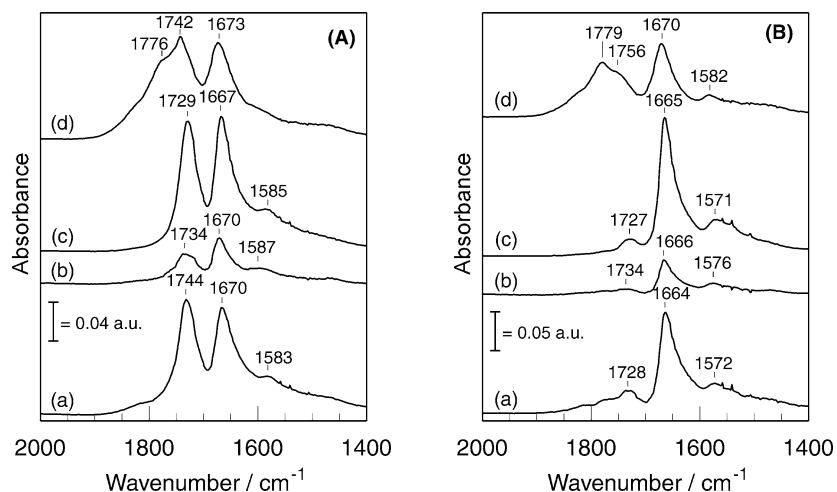


Fig. 4. FT-IR spectra of NO adsorbed on 5 wt% Pd/Al₂O₃ reduced at 673 K, followed by evacuation at room temperature (A) and 373 K (B). (a) Pd(A)/Al₂O₃, (b) Pd(N)/Al₂O₃, (c) Pd(AC)/Al₂O₃, and (d) Pd(CL)/Al₂O₃.

significant difference in the overall band intensities is due to the difference in the number of surface palladium atoms exposed, as shown in Table 1, except for Pd(CL)/Al₂O₃. The exceptional behavior of Pd(CL)/Al₂O₃ is probably due to an altered surface property of palladium particles by interaction with residual Cl⁻ ions, as suggested above in the FT-IR results for CO adsorption. The feature of IR spectra observed here is similar to that for Pd/SiO₂ reported by Moriki et al. [23] and El Hamdaoui et al. [24]. The 1730 cm⁻¹ band can be assigned to NO linearly adsorbed on one surface palladium atom, and the 1670 cm⁻¹ band to NO bonded to one palladium atom in the bent form. The IR band at 1585 cm⁻¹ would also be due to NO bridge-bonded between two palladium atoms. In addition to these IR bands, an additional shoulder band was detected at 1776 cm⁻¹ for Pd(CL)/Al₂O₃. Generally, IR bands for NO adsorbed on cationic metal sites tend to shift to high wavenumbers [25]. Taking into account the results of FT-IR for CO adsorption (Fig. 3), the 1776 cm⁻¹ band is probably due to NO species adsorbed on Pdⁿ⁺ sites. Among these bands, the IR bands located above 1700 cm⁻¹ almost disappeared by evacuation at 373 K (Fig. 4B), although in the case of Pd(CL)/Al₂O₃ the 1779 and 1756 cm⁻¹ bands were still observed after evacuation. The surface properties of Pd(CL)/Al₂O₃ seems to be different from those of the other Pd/Al₂O₃ catalysts.

4. Discussion

A comparison of the catalytic activity of Pd/Al₂O₃ prepared from different palladium precursors for direct decomposition of NO shows that there is no significant difference in the N₂ formation rate on all the Pd/Al₂O₃ catalysts except Pd(CL)/Al₂O₃ (Fig. 1). When normalized on a TOF basis (Fig. 2), however, Pd(N)/Al₂O₃ prepared from Pd(NO₃)₂ was the most active catalyst. This result suggests that using different palladium precursors may produce palladium

species with different surface structures directly related to the active sites.

Since catalysis is a surface process, results obtained by surface science approach should be in conformity with conventional powder catalysts. In fact, the importance of surface crystalline anisotropy has been demonstrated so far in several catalytic reactions [13,26]. NO decomposition over a palladium surface is also expected to be sensitive to crystal faces exposed. Recently, we investigated the effect of surface structure on adsorption and decomposition of NO over palladium single-crystal surfaces and revealed that dissociation of NO to N_(a) and O_(a), resulting in the formation of N₂, proceeds only on the stepped palladium surfaces [14]. It was also found that adsorption of NO on palladium surfaces gives rise to IR absorption bands with different frequency depending upon crystal faces exposed. Namely, the IR bands at 1583, 1666, and 1674 cm⁻¹ were observed by exposing NO onto Pd(111), (100), and (311) single-crystal surfaces, respectively. Taking into account the site geometry of Pd(311) [(Pd(S)[2(111) × (100)])], it is likely that NO is adsorbed on the twofold bridge sites of the (100) step as a bent form (see a model in Fig. 5B). We gave a reaction model in which NO decomposition proceeds only on the stepped palladium sites (Fig. 5B).

In the case of Pd/Al₂O₃ catalysts, the presence of different crystal faces exposed on the palladium surface can be deduced from the FT-IR spectra of adsorbed NO (Fig. 4). Three distinct IR bands were detected at around 1730, 1670, and 1585 cm⁻¹ after adsorption of NO on Pd/Al₂O₃, followed by evacuation at room temperature (Fig. 4A). The high-wavenumber band (ca. 1730 cm⁻¹) has been ascribed to NO linearly bonded atop sites of a Pd(111) surface [27]. On the other hand, the 1670 cm⁻¹ band would be due to NO adsorbed on the (100) sites, because its band feature is consistent with that observed for NO species on the Pd(100) and Pd(311) single-crystal surfaces [14]. It should be noted that the 1730 cm⁻¹ band decreased by brief evacuation at 373 K

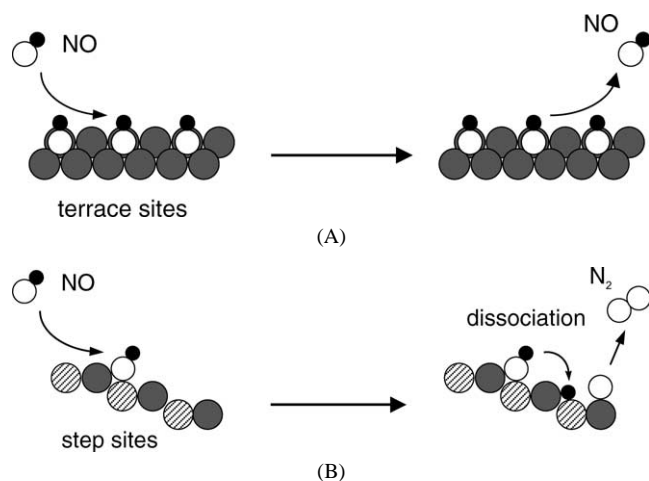


Fig. 5. A model of NO adsorption and decomposition over (A) terrace and (B) stepped palladium surfaces.

while the 1670 cm^{-1} band slightly increased (Fig. 4B). From steric reasons, the linear species are favored at high coverages and the bent form at low coverages [23,28]. Therefore, the 1670 cm^{-1} band can be assigned to NO in the bent form. Taking into account the site geometry and configuration for NO [29], the formation of the bent NO species would be favored on the step sites and/or defect sites rather than on the terrace sites.

Considering the results obtained for single-crystal model catalyst, the participation of the step sites in NO decomposition can be deduced for Pd/Al₂O₃ catalysts. The fraction of step sites exposed on the surface was then estimated from the IR spectra obtained after evacuation at 373 K. It can be expected that there is no significant difference in the extinction coefficients for several NO species because no formation of dimer species ((NO)₂) on Pd/Al₂O₃ was recognized (Fig. 4). Therefore, the fraction of step sites was calculated by dividing the peak area of the 1670 cm^{-1} band ($1700\text{--}1600\text{ cm}^{-1}$) by the total band area for NO species adsorbed on palladium ($1800\text{--}1500\text{ cm}^{-1}$). As given in Table 2, the fraction of step sites exposed was found to be higher on Pd(N)/Al₂O₃ than on Pd(A)/Al₂O₃ and Pd(AC)/Al₂O₃. Despite high palladium dispersion, the fraction of step sites

on Pd(CL)/Al₂O₃ was the lowest. This is probably because the surface property is changed by Cl⁻ ions originating from the palladium precursor, as suggested by the FT-IR results of CO adsorption (Fig. 3), where the presence of cationic palladium (Pd⁺, Pd²⁺) created by the strong interaction with residual Cl⁻ ions was recognized. As can be seen in Table 2, a good correlation was recognized between the fraction of the step sites on the palladium surface and the TOF for NO decomposition to N₂, suggesting that the reaction proceeds mainly on the stepped sites of palladium.

In order to consider whether the step sites truly act as active sites for direct decomposition of NO over Pd/Al₂O₃ catalysts, the TOF_{step} was calculated on the basis of number of step sites estimated by multiplying the amount of chemisorbed NO at 373 K by the fraction of step sites. If NO decomposition proceeds mainly on the step sites, the TOF_{step} must be the same for all the Pd/Al₂O₃ catalysts. As summarized in Table 3, no significant difference in the TOF_{step} on Pd/Al₂O₃ catalysts was observed irrespective of palladium precursor. This finding clearly indicates that the reaction proceeds mainly on the stepped sites of palladium. Consequently, the conclusion obtained for single-crystal model catalysts using surface science technique is in conformity with the results obtained for powder catalysts.

5. Conclusions

The activity of Pd/Al₂O₃ for the direct decomposition of NO was significantly affected by the type of palladium precursor. When normalized on a TOF basis, Pd(N)/Al₂O₃ prepared from Pd(NO₃)₂ was the most active catalyst, and the TOF for N₂ formation decreased in the order of Pd(N)/Al₂O₃ > Pd(A)/Al₂O₃ > Pd(AC)/Al₂O₃ ≫ Pd(CL)/Al₂O₃. From the comparison with the IRA results for NO adsorption on palladium single-crystal surfaces reported previously [14], the presence of the stepped palladium sites on Pd/Al₂O₃ catalysts was confirmed. No significant differences in the TOF_{step}, calculated on the basis of number of step sites estimated from the amount of chemisorbed NO, were observed for Pd/Al₂O₃ catalysts irrespective of palladium precursor. In agreement with the

Table 2

TOF for NO decomposition to N₂ at 773 K and fraction of step sites on the surface estimated from IR peak area due to NO species adsorbed on 5 wt% Pd/Al₂O₃

| Catalysts | TOF at 773 K ^a (s ⁻¹ × 10 ⁻³) | Peak area of IR bands ^b (a.u. cm ⁻¹) | | Fraction of step sites on the surface ^c |
|---------------------------------------|--|---|---|---|
| | | Total NO species (1800–1500 cm ⁻¹) | NO on step sites (1700–1600 cm ⁻¹) | |
| Pd(A)/Al ₂ O ₃ | 0.10 | 6.76 | 3.86 | 0.57 |
| Pd(N)/Al ₂ O ₃ | 0.16 | 2.06 | 1.58 | 0.77 |
| Pd(AC)/Al ₂ O ₃ | 0.07 | 9.25 | 5.22 | 0.56 |
| Pd(CL)/Al ₂ O ₃ | 0.01 | 12.6 | 2.46 | 0.20 |

^a TOF was calculated on the basis of surface palladium atoms estimated by CO chemisorption.

^b Peak area of IR bands were calculated for IR spectra observed after evacuation at 373 K given in Fig. 4B.

^c Fraction of step sites was calculated by dividing the peak area of the IR band due to NO species adsorbed on step sites ($1700\text{--}1600\text{ cm}^{-1}$) by that due to total NO species adsorbed on palladium ($1800\text{--}1500\text{ cm}^{-1}$).

Table 3

Results of NO chemisorption measurements, and TOF_{step} for N₂ formation at 773 K normalized by the number of step sites on 5 wt% Pd/Al₂O₃

| Catalysts | Amount of chemisorbed NO ^a ($\mu\text{mol g cat}^{-1}$) | Fraction of step sites | Number of step sites ^b (atoms g cat ⁻¹) | N ₂ formation rate at 773 K ($\mu\text{mol min}^{-1} \text{g}^{-1}$) | TOF _{step} ^c at 773 K ($\text{s}^{-1} \times 10^{-3}$) |
|---------------------------------------|---|------------------------|---|--|---|
| Pd(A)/Al ₂ O ₃ | 51.65 | 0.57 | 1.77×10^{19} | 0.31 | 0.18 |
| Pd(N)/Al ₂ O ₃ | 25.13 | 0.77 | 1.16×10^{19} | 0.29 | 0.25 |
| Pd(AC)/Al ₂ O ₃ | 51.67 | 0.56 | 1.74×10^{19} | 0.31 | 0.18 |
| Pd(CL)/Al ₂ O ₃ | 49.99 | 0.20 | 0.60×10^{19} | 0.11 | 0.18 |

^a Amount of chemisorbed NO was measured by a pulse method at 373 K.^b Number of step sites was calculated by multiplying the amount of chemisorbed NO by the fraction of step sites.^c TOF_{step} was calculated on the basis of number of step sites.

conclusion obtained for palladium single-crystal model catalysts [14], direct decomposition of NO was considered to mainly proceed on the stepped palladium sites of Pd/Al₂O₃. It should be emphasized that the essentials in the catalytic reaction are quite the same both on single-crystal surfaces and powder catalysts. Comprehensive studies using single-crystal catalysts and powder catalysts would give us a new approach for catalyst design.

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