

Comprehensive study combining surface science and real catalyst for NO direct decomposition

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The catalytic activity of Pd/Al₂O₃ prepared from various palladium precursors for direct NO decomposition is closely related to the fraction of surface step sites capable of dissociating NO, on the basis of a surface science study using single-crystal model catalyst.

Catalysis plays a very important role in solving air pollution problems caused by nitrogen oxides (NO_x). Among various catalytic methods to remove NO_x from exhaust gases, the direct decomposition of NO, 2NO → N₂ + O₂, still remains a challenging subject of study because this is definitely the most ideal method for the solution of NO_x problems.^{1,2} Although extensive studies to find active catalysts have been made since the beginning of the 20th century,^{3–5} no catalysts with sufficient activity for practical use have been reported for this thermodynamically acceptable reaction. On the other hand, kinetic studies of direct NO decomposition on clean single-crystal surfaces have been widely investigated using surface science techniques.² Because the catalytic reaction occurs predominantly on the catalyst surface, the essentials of the catalytic reaction on a single-crystal surface thus obtained should be the same as those on a powder catalyst. In fact, a variety of investigations on industrial reactions, for instance, ammonia synthesis on Fe,⁶ were performed to bridge the gap between single crystal surfaces and real supported catalysts. However, no one has tried to understand the nature of active sites for NO direct decomposition. We report here the first comparative study of direct NO decomposition over supported palladium catalysts and palladium single-crystal surfaces in which an excellent agreement between the catalysis on a single-crystal model and a powder catalyst has been found.

Adsorption, dissociation and desorption of NO on Pd(111), (100) and (311) single-crystal surfaces were carried out in an ultra-high vacuum apparatus composed of four chambers used for TPD and infrared reflection absorption (IRA) measurements.⁷ NO adsorption was made by exposing the single-crystal disk to 30 L (1 L = 1.0 × 10⁻⁶ Torr s, 1 Torr = 133.3 Pa) of NO (99.9%) at 320 K. The IRA spectra of adsorbed NO were measured by using an infrared spectrometer (Mattson model RS/2) with an MCT detector at a resolution of 4 cm⁻¹. The TPD experiments with NO were performed at a 1.0 K s⁻¹ heating rate, and the desorbed species were monitored by a quadrupole mass spectrometer.

Four kinds of 5 wt% Pd/Al₂O₃ catalysts were prepared by impregnating alumina powder (Mizusawa Chemical, GB-45, 190 m² g⁻¹) with a solution of [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 were abbreviated as Pd(A)/Al₂O₃, Pd(N)/Al₂O₃, Pd(AC)/Al₂O₃ and Pd(CL)/Al₂O₃, respectively. The dispersion of supported palladium was determined from the amount of chemisorbed CO measured by a pulse method, and then calculated by assuming a stoichiometry of 1.06 CO/Pd.⁸ The adsorbed state of NO was studied by infrared spectroscopy, following exposure of NO at 1.3 kPa to a self-supporting sample disk (10 mg cm⁻²) prereduced at 673 K. 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. A reaction gas mixture composed of 1000 ppm NO and He as the balance gas was fed through the catalyst (0.5 g), prereduced *in situ* at 673 K with a hydrogen flow for 1 h, at a rate of 30 cm³min⁻¹. The effluent gas was analyzed on-line by two gas chromatographs equipped with a Molecular Sieve 5A column (for the analysis of O₂, N₂ and NO) and a Porapak Q column (for that of N₂O).

The exposure of NO onto Pd(111), (100) and (311) (Pd(S)[2(111) × (100)]) surfaces gave IR absorption bands at 1583, 1666 and 1674 cm⁻¹, respectively. From the literature data,⁹ the peak at 1583 cm⁻¹ for Pd(111) and the peak at 1666 cm⁻¹ for Pd(100) can be assigned to NO adsorbed on the three-fold hollow site and two-fold bridge site, respectively. On the other hand, the band at 1674 cm⁻¹ on Pd(311) can be identified as the NO adsorbed on the two-fold bridge site of the (100) step, since LEED analysis confirmed that no reconstruction of Pd(311) occurred during NO exposure. Taking into account the site geometry on Pd(311), it is likely that NO is adsorbed on the (100) step sites as a bent form.

The thermal reactivity of NO adsorbed on the Pd surface was significantly affected by the surface structure of palladium. As shown by the TPD spectra in Fig. 1, only the desorption peak due to NO was detected at 550 and 540 K on Pd(111) and Pd(100), respectively, whereas the desorption of N₂ was observed at around 500–600 K on Pd(311). The present result indicates that NO dissociation can be promoted on the stepped sites of Pd(311) but not on the (111) and (100) terrace sites. As mentioned above, NO adsorbed on the Pd(311) is present in a bent form. The bent form of NO would easily fit in a position in which the oxygen atom is close to the Pd atom of the (111) terrace site, resulting in the dissociation of NO.⁹ This is the reason why NO dissociation and the subsequent formation of N₂ were observed only on the steps sites of Pd(311) surface.

Fig. 2 shows the catalytic activity of 5 wt% Pd/Al₂O₃ prepared using different palladium precursors for the direct NO decomposition. No significant difference in the activity was observed for all the Pd/Al₂O₃ catalysts, except Pd(CL)/Al₂O₃, over the entire temperature range. The catalytic activity decreased in the order Pd(AC)/Al₂O₃ > Pd(A)/Al₂O₃ > Pd(N)/

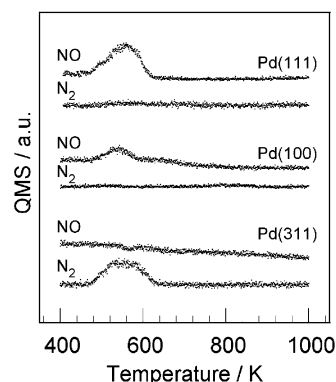


Fig. 1 TPD spectra following adsorption of NO on Pd(111), Pd(100) and Pd(311) surfaces with an exposure of 30 L at 320 K.

Table 1 Palladium dispersion, catalytic activity of 5 wt% Pd/Al₂O₃ for direct NO decomposition at 773 K and fraction of step sites on the surface estimated from IR peak area due to adsorbed NO species

Catalysts	Pd dispersion (1.06CO/Pd)	Rate of N ₂ formation at 773 K (μmol min ⁻¹ g ⁻¹)	TOF at 773 K (s ⁻¹ × 10 ⁻³)	Peak area of IR bands ^a (au cm ⁻¹)		
				Total NO species (1800–1500 cm ⁻¹)	NO on step sites (1700–1600 cm ⁻¹)	Fraction of step sites on the surface ^b
Pd(A)/Al ₂ O ₃	0.10	0.31	0.11	6.76	3.86	0.57
Pd(N)/Al ₂ O ₃	0.04	0.29	0.25	2.06	1.58	0.77
Pd(AC)/Al ₂ O ₃	0.15	0.31	0.07	9.25	5.22	0.56
Pd(CL)/Al ₂ O ₃	0.35	0.10	0.01	12.6	2.46	0.20

^a Peak area of IR bands were calculated for IR spectra observed after evacuation at 373 K given in Fig. 3(B). ^b Fraction of step sites was calculated by dividing the peak area of the IR band due to NO species adsorbed on step sites (1700–1600 cm⁻¹) by that due to total NO species adsorbed on palladium (1800–1500 cm⁻¹).

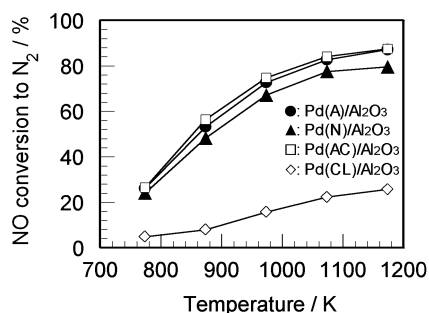


Fig. 2 Catalytic activity of 5 wt% Pd/Al₂O₃ for direct decomposition of NO. Conditions: NO = 1000 ppm, gas flow rate = 30 cm³min⁻¹, W/F = 1.0 gscm⁻³.

Al₂O₃ ≫ Pd(CL)/Al₂O₃. The reduced activity of Pd(CL)/Al₂O₃ would be due to the presence of Cl⁻ ions originating from the Pd precursor; in fact Cl⁻ ions are known to inhibit the activity of Pd/MgO for the direct NO decomposition.¹⁰ Table 1 summarizes the turnover frequencies (TOFs), calculated on the basis of the number of surface palladium atoms determined from CO adsorption, for the direct NO decomposition to N₂ at 773 K over 5 wt% Pd/Al₂O₃. The TOF was found to strongly depend on the palladium precursor, and the highest TOF was obtained on Pd(N)/Al₂O₃. Taking into account the results obtained by the surface science approach mentioned above, the surface structure, particularly the crystal plane of palladium exposed on the surface, seems to be different.

To identify the surface structure of the supported palladium catalysts, the adsorbed state of NO was studied by infrared spectroscopy. As shown in Fig. 3(A), well-resolved IR bands were detected at 1730, 1670 and 1585 cm⁻¹ on the four Pd/

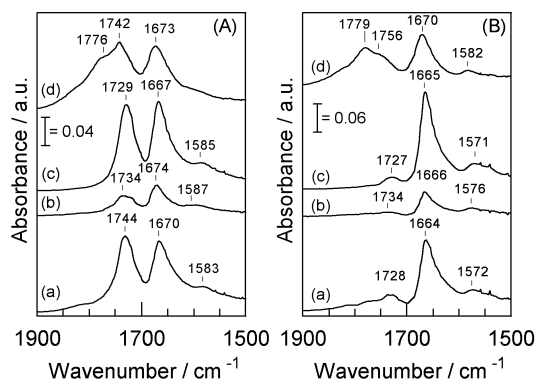


Fig. 3 FT-IR spectra of NO adsorbed on 5 wt% Pd/Al₂O₃ reduced at 673 K, followed by evacuation at room temperature (A) and 373 K (B). (a) Pd(A)/Al₂O₃, (b) Pd(N)/Al₂O₃, (c) Pd(AC)/Al₂O₃ and (d) Pd(CL)/Al₂O₃.

Al₂O₃ catalysts after evacuation at room temperature. The significant difference in the overall band intensities was due to the difference in the palladium dispersion, as given by CO chemisorption in Table 1. From the comparison with the IR spectra observed for the palladium single crystal, the IR band at 1670 cm⁻¹ would be due to NO adsorbed on the (100) sites. The 1730 and 1585 cm⁻¹ bands can be assigned to NO linearly bonded atop sites of Pd(111)⁹ and to NO adsorbed on the three-fold hollow site of Pd(111), respectively. Among these bands, the 1730 cm⁻¹ band decreased by evacuation at 373 K, while the 1670 cm⁻¹ band slightly increased (Fig. 3(B)). From steric reasons, it can be expected that linear species are favored at high coverages and the bent form at low coverages. 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, 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 the single-crystal model catalyst, the participation of the step sites in NO decomposition can be deduced on 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, where its value was calculated by dividing the peak area of the 1670 cm⁻¹ band (1700–1600 cm⁻¹) by the total band area for NO species adsorbed on palladium (1800–1500 cm⁻¹). As given in Table 1, the fraction of step sites exposed was found to be higher on Pd(N)/Al₂O₃ than on Pd(A)/Al₂O₃ and Pd(AC)/Al₂O₃. Interestingly, a good correlation was recognized between the fraction of the step sites on the palladium surface and the TOF for NO decomposition, suggesting that the reaction proceeds mainly on the stepped sites of palladium. This conclusion is in good agreement with that obtained for the single-crystal model catalysts using surface science techniques.

It should be emphasized that the essentials of the catalytic reaction are quite the same both on the single-crystal surface and the powder catalyst. Comprehensive studies using single-crystal and powder catalysts would give us a new approach for catalyst design.

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