

TiO₂-supported Noble Metal Catalysts for the NO-CO and NO-CO-H₂O-H₂-O₂ Reactions

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TiO₂-supported noble metal catalysts, such as Pt-, Pd-, and Rh-TiO₂, are much more active for the NO-CO reaction in the presence or absence of H₂O, H₂, and O₂ than the corresponding Al₂O₃- or other supported catalysts. They are effective even in an oxidative gas composition range for the NO-CO-(H₂O)-H₂-O₂ reaction, producing no NH₃ in the NO-CO-H₂O reaction. Comparison of the catalytic activity and properties of Pt-TiO₂ with those of other supported catalysts suggests that the higher activity of the TiO₂-supported catalysts could be attributed to their ability to activate NO molecules by the dissociative adsorption at lower temperatures.

The reduction of NO in automotive exhaust over supported Pt group catalysts has been extensively investigated by many workers, Al₂O₃ being commonly employed as the catalyst support.¹⁻³⁾ However, few studies have been made on supports other than Al₂O₃ or Al₂O₃-based materials. As a result, no supports more effective for NO-CO reaction than Al₂O₃ are known. In the present investigation, a few types of TiO₂ were employed as a support for noble metals such as Pt, Rh, Pd, and Ru and their catalytic activities for the NO-CO reaction in the presence or absence of H₂O, H₂, and O₂ were determined and compared with those of the corresponding Al₂O₃-supported catalysts. Various supported Pt catalysts such as Pt-TiO₂, Pt-Al₂O₃, Pt-SiO₂, and Pt-SiO₂-Al₂O₃ were also employed, the catalytic activities and properties of the catalysts and supports being measured and compared with each other, and the role of the TiO₂ support in the catalytic activity was discussed.

Experimental

Catalyst Support. TiO₂(a) : TiO₂(anatase) was prepared by neutralization of HCl-acidic solution of TiCl₄ (Oosaka Titanium Co., Ltd., pH=0.1—0.2, 3.8 mol dm⁻³ TiCl₄) with ammonia water (1 mol dm⁻³) up to a pH ca. 6, followed by washing of the precipitate obtained with water several times, drying at 393 K for 18 h, and calcination in air at 823 K for 4 h. TiO₂(a-s) : TiO₂(anatase) containing a very small amount of SO₄²⁻ was prepared from the TiCl₄ solution according to a procedure similar to that of Funaki and Saeiki.⁵⁾ The resulting TiO₂ was calcined in the air at 823 K for 4 h. TiO₂(r-HSA) : TiO₂(rutile) with higher BET surface area as compared with the conventional rutile type TiO₂ was prepared from the TiCl₄-solution by evaporation followed by drying and air calcination. TiO₂(r-LSA) : TiO₂(rutile) with low BET surface area was prepared from TiO₂(a) by air calcination at 1273 K for 5 h. The BET surface area of TiO₂(a), TiO₂(a-s), TiO₂(r-HSA), and TiO₂(r-LSA) were 78, 73, 16, and 1 m² g⁻¹, respectively. Al₂O₃(γ), SiO₂·Al₂O₃, SiO₂, MgO: These supports were prepared by the same procedure as reported⁶⁾. Calcination was carried out in the air at 873 K for 4 h. The BET surface area of Al₂O₃, SiO₂, SiO₂·Al₂O₃, and MgO were 240, 150, 265, and 50 m² g⁻¹, respectively.

Catalyst. Supported noble metal catalysts (Tables 1—3) were prepared by impregnation of the support materials such as TiO₂(a), Al₂O₃(γ) with a solution of H₂PtCl₆·6H₂O, RhCl₃·3H₂O, RuCl₃·3H₂O, or PdCl₂, and subsequent evaporation and drying at 393 K for 18 h. Before the activity

test, the catalysts were activated *in situ* by reduction with H₂ at 773 K for 1 h, followed by the purge of hydrogen in the reactor with oxygen-free dry helium at the same temperature for 1 h.

Reaction and Analysis. The reaction was carried out by use of the conventional flow system with a fixed bed of catalyst under gas compositions, NO(3*), CO(3*), H₂O(0*—6%), H₂(0*—6%), O₂(0*—6%), and He(bal-ance*), where * denotes a standard gas composition. The flow rate of the reactant/helium gas mixture was kept at 100 cm³ min⁻¹. The reaction temperature ranged from 423 to 673 K, being mostly fixed at 573 K. The composition of the product gas was determined by gas chromatography and mass spectrometry.

Measurement of Catalytic Properties. The structure of support materials was determined by an X-ray powder diffraction method. The BET surface areas of the supports or catalysts were measured by a high speed surface area analyzer (Shimadzu Micromeritics). The number of surface Pt atoms of the supported Pt catalysts was estimated by conventional H₂-O₂ pulse titration. Adsorption experiments for NO and CO were carried out in a gas adsorption heat analyzer (Tokyo Riko GAC-2) connected to a vacuum system equipped with mercury and oil manometers and a calibrated pirani vacuum gauge. Heat of adsorption and gas uptakes can be measured calorimetrically and volumetrically. Temperature programmed desorption (TPD) experiments were carried out in a vacuum system equipped with a pirani gauge and a mass spectrometer under the following conditions. One gram of the sample was put in a quartz tube. After reduction of the sample with H₂ at 773 K for 1 h and subsequent outgassing at the same temperature for several hours (Activation Method I), NO was adsorbed to the sample at room temperature and 1.33 × 10³ Pa, followed by evacuation at room temperature for 20 min. The temperature then rose *in vacuo* with a constant rate of 10 K min⁻¹. The total pressure response of the gas desorbed from the sample was measured with a pirani gauge, the composition of the gas being monitored periodically with a mass spectrometer. The following activation method (Activation Method II) was also employed. Before the NO-adsorption, the sample which had been activated by Activation method I was oxidized with O₂ at 773 K for 10 min, evacuated at the same temperature for 10 min, reduced with H₂ at 493 K for 15 min, followed by evacuation at 493 K for 5 min and then at 623 K for 20 min.

Results and Discussion

The catalytic activities of various supported Pt catalysts for the NO-CO reaction were measured and

TABLE 1. CATALYTIC ACTIVITIES AND PROPERTIES OF SUPPORTED Pt CATALYSTS

Catalyst ^{a)}	NO ^{b)} conversion %	Turn over frequency ^{b,e)} s ⁻¹	Selectivity to N ₂ ^{b)} %	BET area m ² g ⁻¹	Surface Pt atoms ^{e)} 10 ¹⁸ g ⁻¹	Gas adsorption ^{f)}			
						Uptakes ^{g)}		Heats	
						10 ⁻⁵ mol g ⁻¹		kcal mol ⁻¹	
						NO	CO	NO	CO
Pt-TiO ₂	100 (100) ^{d)}	>2.75 (>2.75)	85 (85)	65	1.7	3.3 (2.5)	6.4 (1.2)	33 (29)	89 (70)
Pt-TiO ₂ (r-LSA)	1	≈0.47	—	1	0.1	Small		—	
Pt-Al ₂ O ₃ (γ)	100 ^{h)} (85) ^{d,h)}	>0.55 (≈0.45) ^{d)}	57 (57)	240	8.9	6.6 (0)	4.2 (0)	46 (—)	27 (—)
Pt-SiO ₂ ·Al ₂ O ₃	16	0.17	46	270	4.4	3.8 (0.5)	1.5 (0)	10 (6)	29 (—)
Pt-SiO ₂	9	0.21	39	150	2	3.1 (0.7)	0.5 (0)	9 (—)	55 (—)
Pt-MgO	10	≈1.1	68	50	0.2	1.1 (1.2)	0.1 (0)	21 (31)	— (—)

a) Pt 1 wt%. b) At 573 K, NO, CO: 3%, He: 94%, 100 cm³ min⁻¹, catalyst: 0.3 g. c) The values were roughly estimated by the relation: Turn over frequency (s⁻¹) = apparent rate of NO consumption (mol s⁻¹)/surface Pt (mol), after 10 min. d) After 60 min. e) From an H₂-O₂ pulse titration method. f) At 298 K. g) The values in () correspond to those for the supports themselves. h) The decrease in the catalytic activity is due to the formation of surface NCO species.

TABLE 2. COMPARISON OF ACTIVITIES OF TiO-SUPPORTED METAL CATALYSTS WITH THOSE OF Al₂O₃-SUPPORTED ONES^{a)}

Support	Promoter	NO conversion/%		
		523 K	573 K	623 K
TiO ₂	Rh	9	76	100
	Pd	25	30	45
	Pt	≈2	9	21
	Ru	≈0	≈1	10
Al ₂ O ₃ (γ)	Rh	≈1	50	100
	Pd	≈3	17	40
	Pt	0	6	10
	Ru	0	≈1	6

a) NO, CO, 3%, He 94% flow rate 100 cm³ min⁻¹, catalyst: 0.01 g (1 wt%).

compared with each other. Conversion of NO distinctly depends on the support materials and decreases in the following order in the reaction temperature range 423—623 K: Pt-TiO₂(a-s)[100*, 98**] > Pt-TiO₂(a)[100*, 96**] > Pt-TiO₂(r-HSA)[100*, 87**] > Pt-Al₂O₃(γ)[100*, 25**] > Pt-SiO₂·Al₂O₃[16*] > Pt-MgO[10*] > Pt-SiO₂[9*] > Pt-TiO₂(r-LSA)[≈1*] > Pt-Al₂O₃(α)[0*]. The numeral in [] represents the % conversion of NO, after 10 min from the start of reaction, at 523 K and at $W/F=3 \times 10^{-3}$ g min cm⁻³ (*) or at $W/F=4 \times 10^{-4}$ g min cm⁻³ (**). The selectivity to N₂ also depends on the support materials (Table 1). TiO₂, even a rutile type, unless its surface area is extremely small, gives better results. Similar carrier-effects were obtained when Rh, Pd, and Ru were employed instead of Pt. The catalytic activities of the TiO₂-supported noble metal catalysts are compared with those of the Al₂O₃-supported ones in Table 2.

TABLE 3. ACTIVITIES OF Pt-Al₂O₃(γ), Pt-TiO₂(a), AND Pd-TiO₂(a) CATALYSTS FOR NO-CO-H₂O OR NO-CO-H₂-O₂ REACTION

Catalyst	Reaction	% Conversion of NO or (NO+NO ₂)	% Yield of	
			(N ₂ +N ₂ O)	NH ₃
Pt-Al ₂ O ₃ (γ)	A	72	52	20
Pt-TiO ₂ (a)	A	100	100	0
Pt-Al ₂ O ₃ (γ)	B	100 ^{a)} (35) ^{b,c)}	35	0
Pt-TiO ₂ (a)	B	100 ^{a)} (49) ^{b)}	49	0
Pd-TiO ₂ (a)	B	100 ^{a)} (67) ^{b)}	67	0
Pd-TiO ₂ (a)	C	99 ^{a)} (75) ^{b)}	75	0

Reaction conditions, temperature: 573 K, flow rate: 100 cm³ min⁻¹; A: NO, CO 3%, H₂O 1.7%, He 92.3%, $W/F=3 \times 10^{-3}$ g min cm⁻³, after 150 min; B: NO, CO, O₂ 3%, H₂ 5%, He 86%, $W/F=1 \times 10^{-4}$ g min cm⁻³, after 5 min; C: NO, CO 2%, H₂ 3%, O₂ 5%, He 88%, $W/F=2 \times 10^{-4}$ g min cm⁻³. a) Conversion of NO including a non-catalytic reaction: NO + (1/2)O₂ → NO₂. b) Conversion of (NO+NO₂). c) The catalytic activity gradually decreased with increase in the time on stream.

TiO₂-supported noble metal catalysts show higher catalytic activity and selectivity to N₂. In addition they have the advantage of (a) producing very minor NH₃ in both NO-CO-H₂O and NO-CO-H₂O-H₂-O₂ reactions and (b) working effectively even in a rather oxidative gas composition range for the NO-CO-(H₂O)-H₂-O₂. Examples are given in Table 3. We see that Pt-TiO₂(a) gives no NH₃ when the NO-CO reaction is carried out in the presence of H₂O vapor. Pd-TiO₂, which has a significant catalytic activity for the NO-CO reaction even around 473 K, is a very active for the NO-CO-(H₂O)-H₂-O₂ reaction when the ratio of O₂ to H₂ is near 2, while Pt-Al₂O₃(γ), which is a conventional catalyst gives rise to high

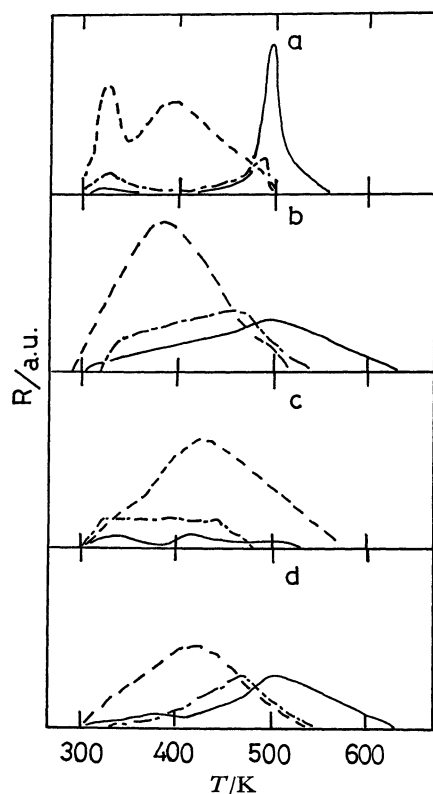


Fig. 1. TPD profiles for NO-preadsorbed catalysts and support.

a: Pt-Al₂O₃(γ),* b: Pt-TiO₂(a),* c: TiO₂(a),* d: Pt-TiO₂(a),** T: Temperature, R: Response of desorbed gas.

NO was adsorbed at 293 K after Activation Method I(*) or after Activation Method II(**).

----: NO, —: N₂, — · —: N₂O.

concentration of NH₃ in the NO-CO-H₂O reaction under the same conditions, not working effectively in such an O₂-rich region.

Some catalytic properties of the supported Pt catalysts are summarized in Table 1. The surface area of Pt depends on the support. Pt on TiO₂(a) is less dispersed than that Al₂O₃(γ) or SiO₂·Al₂O₃. Baker *et al.*, who studied the particle size of Pt on the thin film of titanium oxide, aluminium oxide, *etc.* by means of electron microscopy have shown that the mean particle size of Pt in the Pt-titanium oxide (Ti₄O₇) sample reduced with H₂ below 825 K is almost the same as that of Pt in the Pt-aluminium oxide sample⁴. The disagreement of the relative dispersion of Pt may fall in the difference in the method of preparation.

Comparison of the catalytic activities with the BET surface area of the catalyst and with the number of Pt surface atoms (corresponding to the surface area of Pt metal particles dispersed over the supports) or roughly estimated turn over frequencies for the consumption of NO (Table 1) led us to the conclusion that the surface area of Pt as well as that of the catalyst is not always a dominant factor in the catalytic activity. In other words, the catalyst with larger BET area or Pt surface area does not necessarily exhibit higher activity although the low catalytic activity of Pt-TiO₂(r-LSA) might be attributed to the low surface

area of Pt. Table 1 indicates that the highly active catalysts, Pt-Al₂O₃(γ) and Pt-TiO₂(a), are characterized by their higher heat of adsorption for NO and also by both high NO and CO uptakes, while the other less active catalysts lack either one or both of the terms. For example, the lower activity of Pt-SiO₂ and Pt-SiO₂·Al₂O₃ might be due to their poor ability to activate NO molecules compared with Pt-Al₂O₃(γ) and Pt-TiO₂(a), since they have lower heat of adsorption for NO.

In order to clarify why Pt-TiO₂(a) is more active than Pt-Al₂O₃(γ), in particular at lower temperatures, temperature programmed desorption (TPD) experiments with respect to the NO-preadsorbed Pt-Al₂O₃(γ) and Pt-TiO₂(a) were carried out. The results are shown in Figs. 1a and 1b, respectively. For Pt-Al₂O₃(γ), there is a relatively sharp desorption peak of N₂ around 503 K, which was formed from the NO molecules adsorbed on the catalyst. The result closely agrees with that reported by Unland who concluded that the dissociation of NO on Pt-Al₂O₃(γ) occurs above 503 K.⁶⁻⁸ On the contrary, the TPD spectrum for Pt-TiO₂(a), in our case, was found to differ from that for Pt-Al₂O₃(γ), the spectrum being characterized by the following two points: (a) N₂-desorption occurs at lower temperatures around 373 K, indicating that NO molecules dissociate on Pt-TiO₂(a) at much lower temperature on Pt-Al₂O₃(γ), and (b) the spectrum of N₂-desorption spreads over a wide temperature range. This might be due to the heterogeneity of the active site on the Pt-TiO₂(a) catalyst.

It should be noted that N₂ and N₂O are formed not only by the reaction between the adsorbed NO molecules and Pt but also by the reaction between those and the TiO₂(a) support, since the support is probably reduced to some extent during the course of activation with H₂ at 773 K and adsorbs NO molecules. In fact an EPR experiment showed the presence of Ti³⁺ in the TiO₂(a) support activated by Activation Method I. NO-preadsorbed TiO₂(a) gave a TPD spectrum consisting of N₂, N₂O, and NO (Fig. 1c). A comparison of Figs. 1b and 1c, however, suggests that both N₂ and N₂O are formed mostly by the reaction between the adsorbed NO molecules and Pt, especially above 423 K. A TPD experiment for a Pt-TiO₂(a) catalyst which had been previously activated by Activation Method II was carried out (Fig. 1d). An EPR experiment revealed that the concentration of Ti³⁺ in Pt-TiO₂(a) activated by Activation Method II is negligible-less than one tenth of that in the Pt-TiO₂(a) sample activated by Activation Method I. This indicates that Activation Method II gives an almost fully oxidized TiO₂(a) support. In fact a TPD experiment showed that neither N₂ nor N₂O is liberated from NO-preadsorbed TiO₂(a) previously activated by Activation Method II. On the contrary, the Pt surface area of the Pt-TiO₂(a) catalyst activated by Activation Method II was close to that of Pt-TiO₂(a) activated by Activation Method I. These results indicate that the Pt-TiO₂(a) catalyst activated by Activation Method II consists of almost completely reduced Pt and almost fully oxidized TiO₂(a). No reaction between NO and the fully oxidized TiO₂(a)

support can be expected, the formation of N₂ and N₂O shown in Fig. 1d being ascribed to the reaction between NO and Pt on the TiO₂(a) support.

IR studies on the surface NCO species formed on the catalysts during the course of NO-CO reaction showed that the NCO species is formed on TiO₂-supported catalysts at lower temperatures than on the corresponding Al₂O₃-supported catalyst. The NCO species, for example, was observed not on Pt-Al₂O₃(γ) at 473 K but on Pt-TiO₂(a) at the same temperature. The result suggests that the dissociation of NO occurs on the TiO₂-supported ones, since the NCO seems to be produced by the reaction between a CO molecule and an adsorbed N atom formed by the dissociation of an adsorbed NO molecule.

The big difference in catalytic activity between Pt-TiO₂(a) and the other supported Pt catalysts is not attributed to the difference of the surface area of Pt but to that of the NO-dissociation ability of the catalysts. The reason why the TiO₂-supported catalysts easily dissociated NO at lower temperature than the others is still unknown. However, an explanation is that the NO-dissociation ability might be due to the high concentrations of free electrons of the TiO₂ support or Ti³⁺ ions having thermally emissive electrons; probably, the back donation of one of these electrons into a π^* (antibonding) orbital of the adsorbed NO molecule through the dispersed Pt metal on TiO₂ weakens the N-O bond.

In conclusion, TiO₂, either anatase or rutile unless

its surface area is extremely low, was found to be a most effective support for different noble metal catalysts in the NO-CO reaction even in the presence of H₂O, H₂, and O₂. The high catalytic activity of the TiO₂-supported catalyst could be attributed, at least, to its ability to activate NO molecules by dissociative adsorption at lower temperatures.

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