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TiO_2-supported Noble Metal Catalysts for the NO-CO and NO-CO-H_2O-H_2-O_2 Reactions

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TiO_2-supported noble metal catalysts, such as Pt–, Pd–, and Rh–TiO_2, are much more active for the NO–CO reaction in the presence or absence of H_2O, H_2, and O_2 than the corresponding Al_2O_3– or other supported catalysts. They are effective even in an oxidative gas composition range for the NO–CO–(H_2O)–H_2–O_2 reaction, producing no NH_3 in the NO–CO–H_2O reaction. Comparison of the catalytic activity and properties of Pt–TiO_2 with those of other supported catalysts suggests that the higher activity of the TiO_2-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, Al_2O_3 being commonly employed as the catalyst support.[1–3)] However, few studies have been made on supports other than Al_2O_3 or Al_2O_3-based materials. As a result, no supports more effective for NO–CO reaction than Al_2O_3 are known. In the present investigation, a few types of TiO_2 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 H_2O, H_2, and O_2 were determined and compared with those of the corresponding Al_2O_3-supported catalysts. Various supported Pt catalysts such as Pt–TiO_2, Pt–Al_2O_3, Pt–SiO_2, and Pt–SiO_2–Al_2O_3 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 TiO_2 support in the catalytic activity was discussed.

Experimental

Catalyst Support. TiO_2(a) : TiO_2(anatase) was prepared by neutralization of HCl-acidic solution of $TiCl_4$ (Oosaka Titanium Co., Ltd., pH=0.1—0.2, 3.8 mol dm^{-3} $TiCl_4$) 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. TiO_2(a-s) : TiO_2(anatase) containing a very small amount of SO_4^{2-} was prepared from the $TiCl_4$ solution according to a procedure similar to that of Funaki and Saeki.[5)] The resulting TiO_2 was calcined in the air at 823 K for 4 h. TiO_2(r-HSA) : TiO_2(rutile) with higher BET surface area as compared with the conventional rutile type TiO_2 was prepared from the $TiCl_4$-solution by evaporation followed by drying and air calcination. TiO_2(r-LSA) : TiO_2(rutile) with low BET surface area was prepared from TiO_2(a) by air calcination at 1273 K for 5 h. The BET surface area of TiO_2(a), TiO_2(a-s), TiO_2 (r-HSA), and TiO_2(r-LSA) were 78, 73, 16, and 1 $m^2\,g^{-1}$, respectively. $Al_2O_3(\gamma)$, $SiO_2 \cdot Al_2O_3$, SiO_2, MgO: These supports were prepared by the same procedure as reported[6)]. Calcination was carried out in the air at 873 K for 4 h. The BET surface area of Al_2O_3, SiO_2, $SiO_2 \cdot Al_2O_3$, and MgO were 240, 150, 265, and 50 $m^2\,g^{-1}$, respectively.

Catalyst. Supported noble metal catalysts (Tables 1—3) were prepared by impregnation of the support materials such as TiO_2(a), $Al_2O_3(\gamma)$ with a solution of $H_2PtCl_6 \cdot 6H_2O$, $RhCl_3 \cdot 3H_2O$, $RuCl_3 \cdot 3H_2O$, or $PdCl_2$, and subsequent evaporation and drying at 393 K for 18 h. Before the activity test, the catalysts were activated *in situ* by reduction with H_2 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*%), H_2O(0*—6%), H_2(0*—6%), O_2(0*—6%), and He(balance*), where * denotes a standard gas composition. The flow rate of the reactant/helium gas mixture was kept at 100 $cm^3\,min^{-1}$. 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 H_2–O_2 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 programed 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 H_2 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 1.33×10^3 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 O_2 at 773 K for 10 min, evacuated at the same temperature for 10 min, reduced with H_2 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,c]	Selctivity to N_2[b]	BET area	Surface Pt atoms[e]	Gas adsorption[f]			
						Uptakes[g]		Heats	
						10^{-5} mol g^{-1}		kcal mol^{-1}	
	%	s^{-1}	%	m^2 g^{-1}	10^{18} g^{-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_2O_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_2O_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 cm^3 min^{-1}, catalyst: 0.3 g. c) The values were roughly estimated by the relation: Turn over frequency (s^{-1}) = apprant rate of NO consumption (mol s^{-1})/surface Pt (mol), after 10 min. d) After 60 min. e) From an H_2-O_2 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 Al_2O_3-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_2O_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 cm^3 min^{-1}, catalyst: 0.01 g(1 wt%).

Table 3. Activities of Pt-Al_2O_3(γ), Pt-TiO_2(a), and Pd-TiO_2(a) catalysts for NO-CO-H_2O or NO-CO-H_2-O_2 reaction

Catalyst	Reaction	% Conversion of NO or (NO+NO_2)	% Yield of	
			(N_2+N_2O)	NH_3
Pt-Al_2O_3(γ)	A	72	52	20
Pt-TiO_2(a)	A	100	100	0
Pt-Al_2O_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 cm^3 min^{-1}; A: NO, CO 3%, H_2O 1.7%, He 92.3%, $W/F=3\times10^{-3}$ g min cm^{-3}, after 150 min; B: NO, CO, O_2 3%, H_2 5%, He 86%, $W/F=1\times10^{-4}$ g min cm^{-3}, after 5 min; C: NO, CO 2%, H_2 3%, O_2 5%, He 88%, $W/F=2\times10^{-4}$ g min cm^{-3}. a) Conversion of NO including a non-catalytic reaction: NO+(1/2)O_2→NO_2. b) Conversion of (NO+NO_2). c) The catalytic activity gradually decreased with increase in the time on stream.

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-TiO_2(a-s)[100*, 98**]>Pt-TiO_2(a)[100*, 96**]>Pt-TiO_2(r-HSA)[100*, 87**]> Pt-Al_2O_3(γ)[100*, 25**] > Pt-SiO_2·Al_2O_3[16*] > Pt-MgO[10*] > Pt-SiO_2[9*] > Pt-TiO_2(r-LSA)[≈1*] > Pt-Al_2O_3(α)[0*]. The numeral in [ ] represents the % conversion of NO, after 10 min from the start of reaction, at 523 K and at $W/F=3\times10^{-3}$ g min cm^{-3} (*) or at $W/F=4\times10^{-4}$ g min cm^{-3}(**). The selectivity to N_2 also depends on the support meterials (Table 1). TiO_2, 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 TiO_2-supported noble metal catalysts are compared with those of the Al_2O_3-supported ones in Table 2.

TiO_2-supported noble metal catalysts show higher catalytic activity and selectivity to N_2. In addition they have the advantage of (a) producing very minor NH_3 in both NO-CO-H_2O and NO-CO-H_2O-H_2-O_2 reactions and (b) working effectively even in a rather oxidative gas composition range for the NO-CO-(H_2O)-H_2-O_2. Examples are given in Table 3. We see that Pt-TiO_2(a) gives no NH_3 when the NO-CO reaction is carried out in the presence of H_2O vapor. Pd-TiO_2, which has a significant catalytic activity for the NO-CO reaction even around 473 K, is a very active for the NO-CO-(H_2O)-H_2-O_2 reaction when the ratio of O_2 to H_2 is near 2, while Pt-Al_2O_3(γ), which is a conventional catalyst gives rise to high

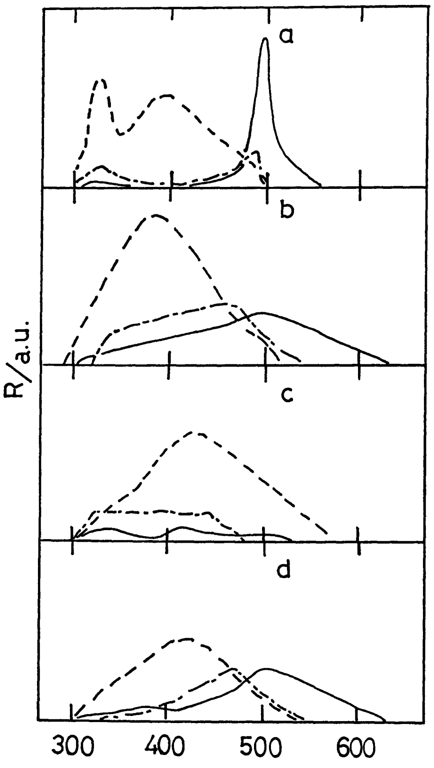

Fig. 1. TPD profiles for NO-preadsorbed catalysts and support.
a: Pt–$Al_2O_3(\gamma)$,* b: Pt–TiO_2(a),* c: TiO_2(a),* d: Pt–TiO_2(a),** T: Temperature, R: Response of desorbed gas.
NO was adsorbed at 293 K after Activation Method I(*) or after Activation Method II(**).
----: NO, ——: N_2, —·—·—: N_2O.

concentration of NH_3 in the NO–CO–H_2O reaction under the same conditions, not working effectively in such an O_2-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 TiO_2(a) is less dispersed than that $Al_2O_3(\gamma)$ or $SiO_2 \cdot Al_2O_3$. 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 (Ti_4O_7) sample reduced with H_2 below 825 K is almost the same as that of Pt in the Pt–aluminium oxide sample[4]. 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–TiO_2(r-LSA) might be attributed to the low surface area of Pt. Table 1 indicates that the highly active catalysts, Pt–$Al_2O_3(\gamma)$ and Pt–TiO_2(a), are characterized by their higher heat of a 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–SiO_2 and Pt–$SiO_2 \cdot Al_2O_3$ might be due to their poor ability to activate NO molecules compared with Pt–$Al_2O_3(\gamma)$ and Pt–TiO_2(a), since they have lower heat of adsorption for NO.

In order to clarify why Pt–TiO_2(a) is more active than Pt–$Al_2O_3(\gamma)$, in particular at lower temperatures, temperature programmed desorption (TPD) experiments with respect to the NO-preadsorbed Pt–$Al_2O_3(\gamma)$ and Pt–TiO_2(a) were carried out. The results are shown in Figs. 1a and 1b, respectively. For Pt–$Al_2O_3(\gamma)$, there is a relatively sharp desorption peak of N_2 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–$Al_2O_3(\gamma)$ occurs above 503 K.[6–8] On the contrary, the TPD spectrum for Pt–TiO_2(a), in our case, was found to differ from that for Pt–$Al_2O_3(\gamma)$, the spectrum being characterized by the following two points: (a) N_2-desorption occurs at lower temperatures around 373 K, indicating that NO molecules dessociate on Pt–TiO_2(a) at much lower temperature on Pt–$Al_2O_3(\gamma)$, and (b) the spectrum of N_2-desorption spreads over a wide temperature range. This might be due to the heterogeneity of the active site on the Pt–TiO_2(a) catalyst.

It should be noted that N_2 and N_2O are formed not only by the reaction between the adsorbed NO molecules and Pt but also by the reaction between those and the TiO_2(a) support, since the support is probably reduced to some extent during the course of activation with H_2 at 773 K and adsorbs NO molecules. In fact an EPR experiment showed the presence of Ti^{3+} in the TiO_2(a) support activated by Activation Method I. NO-preadsorbed TiO_2(a) gave a TPD spectrum consisting of N_2, N_2O, and NO (Fig. 1c). A comparison of Figs. 1b and 1c, however, suggests that both N_2 and N_2O are formed mostly by the reaction between the adsorbed NO molecules and Pt, especially above 423 K. A TPD experiment for a Pt–TiO_2(a) catalyst which had been previously activated by Activation Method II was carried out (Fig. 1d). An EPR experiment revealed that the concentration of Ti^{3+} in Pt–TiO_2(a) activated by Activation Method II is negligible-less than one tenth of that in the Pt–TiO_2(a) sample activated by Activation Method I. This indicates that Activation Method II gives an almost fully oxidized TiO_2(a) support. In fact a TPD experiment showed that nither N_2 nor N_2O is liberated from NO-preadsorbed TiO_2(a) previously activated by Activation Method II. On the contrary, the Pt surface area of the Pt–TiO_2(a) catalyst activated by Activation Method II was close to that of Pt–TiO_2(a) activated by Activation Method I. These results indicate that the Pt–TiO_2(a) catalyst activated by Activation Method II consists of almost completely reduced Pt and almost fully oxidized TiO_2(a). No reaction between NO and the fully oxidized TiO_2(a) support can be expected, the formation of N_2 and N_2O shown in Fig. 1d being ascribed to the reaction between NO and Pt on the TiO_2(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 TiO_2-supported catalysts at lower temperatures than on the corresponding Al_2O_3-supported catalyst. The NCO species, for example, was observed not on Pt–$Al_2O_3(\gamma)$ at 473 K but on Pt–TiO_2(a) at the same temperature. The result suggests that the dissociation of NO occurs on the TiO_2-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–TiO_2(a) and the other suppored 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 TiO_2-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 TiO_2 support or Ti^{3+} 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 TiO_2 weakens the N–O bond.

In conclusion, TiO_2, 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 H_2O, H_2, and O_2. The high catalytic activity of the TiO_2-supported catalyst could be attributed, at least, to its ability to activate NO molecules by dissociative adsorption at lower temperatures.

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