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STRUCTURES AND PROPERTIES OF TiO_2 DISPERSED OVER SiO_2 GEL AND THE CATALYTIC ACTIVITY OF $Pt/TiO_2/SiO_2$ IN NO-CO REACTION

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TiO_2/SiO_2(70-90 wt%TiO_2) prepared by deposition of TiO_2 on to SiO_2 gel are significantly effective catalyst supports for Pt in NO-CO reaction. The presence of SiO_2 distinctly changes the structures and properties of TiO_2 and definitely increases the thermal stability of the dispersed anatase TiO_2, on which Pt is selectively deposited and gives the high catalytic activity.

Recently, studies on the catalytic properties of TiO_2 are getting more important, since TiO_2 often behaves as an excellent catalyst or catalyst support in certain reactions.[1-5] It has been found, for example, that Pt/TiO_2 is much more effective for the NO-CO reaction in the presence or absence of H_2O, H_2, and O_2 than Pt/Al_2O_3 which is known to be one of typical NO removal catalysts.[1] However, if TiO_2 is used as a catalyst or catalyst support, especially as a support for NO removal catalysts in auto exhaust, one should find that it has several definite disadvatages as follows; (1) TiO_2 supports tend to sinter when they are used at high temperatures. (2) The mechanical strength of high surface area-TiO_2 supports should not be enough to be used in the practical NO removal processes. (3) They are more costly in practice than the typical conventional support materials such as SiO_2, Al_2O_3, etc.. The idea employed in the present work is as follows: if TiO_2 is deposited or coated over other stable, strong, and cheap high area materials, the disadvatages may be removed without the sucrifice of the advatages of TiO_2 itself and TiO_2 will be much more extensively employed in practical catalytic processes, especially in auto exhaust in which the use of TiO_2-coated monolithic supports may be expected.[6] In general, it may become important to study the catalytic properties of the supports prepared by depositing a certain catalytically effective "real" support material over other catalytically inert but essential materials. In the present work, two different TiO_2/SiO_2 systems prepared in unusual fashions by the deposition of TiO_2 on to SiO_2 gel were employed as support materials for Pt. The structures and some physicochemical properties of TiO_2 in the TiO_2/SiO_2 or $Pt/TiO_2/SiO_2$ systems were investigated by X-ray, EPR, and other experimental techniques and compared with the catalytic activity of $Pt/TiO_2/SiO_2$ in the NO-CO reaction.

TiO_2(I) was prepared from an HCl-acidic $TiCl_4$-solution(pH=0.0-0.2, 4.0 mol dm^{-3} $TiCl_4$, from Oosaka Titanium Co., Ltd.) by evaporating as such, drying at 120°C for

18 h followed by air calcication at 550°C for 3 h. TiO_2(II) was prepared by neutralization of the $TiCl_4$-solution with ammonia water(1 mol dm^{-3}) up to a pH of 6.0±0.1. The resulting precipitate was washed by water several times, dried at 120°C for 18 h and calcined in air at 550°C for 3 h. SiO_2(32-60mesh) was prepared by evaporating a solution of silica(Snowtex 0, from Nissan Chemicals & Industry), drying at 120°C for 18 h, followed by air calcination at 600°C for 4 h. TiO_2/SiO_2(I) were prepared by impregnating the SiO_2 with the $TiCl_4$-solution, evaporating and drying at 120°C for 18 h, followed by air calcination at 550°C for 3 h. TiO_2/SiO_2(II) were prepared by the following method. The $TiCl_4$-Solution was neutralized by the ammonia water up to a pH of 6.0±0.1 in the presence of the SiO_2, in which TiO_2 was deposited over the SiO_2. The resulting solid was washed with water several times and dried at 120 °C for 18 h, followed by air calcination at 550°C for 3 h. Pt/TiO_2(I), Pt/TiO_2(II), $Pt/TiO_2/SiO_2$(I), and $Pt/TiO_2/SiO_2$(II) were prepared by impregnating the respective support with a solution of $H_2PtCl_6 \cdot 6H_2O$, evaporating and drying at 120°C for 18 h. Before the reaction, the catalysts were activated *in situ* by heating in H_2 at 500°C for 1 h, followed by dry helium at 500°C for 3 h. The reaction was conducted in a conventional flow reactor. The detail reaction conditions are shown in the legend of Fig.1. The reactants(NO,CO) and products (N_2,N_2O,CO_2) were analyzed by gas chromatograph. The structures of support materials were determined by a conventional X-ray powder diffraction method. The relative amounts of Ti^{3+} in the catalysts or supports were measured at 77 K by an EPR spectrometer. The IR spectra of the catalysts were measured at room temperature by a conventional vacuum cell method[7].

The catalytic activity of $Pt/TiO_2/SiO_2$(I) in the NO-CO reaction markedly depends on the composition of the support as shown in Fig.1a. The profile of the activity is unique and chracterized by several points as follows: (1) TiO_2/SiO_2(I)(≳60 wt% TiO_2) are distinctly more effective than TiO_2/SiO_2(<60 % TiO_2). The deposition of fairly large amounts of TiO_2 over SiO_2 is necessary to obtain a high catalytic activity. (2) $Pt/TiO_2/SiO_2$(I)(70-90 %) are significantly more active than Pt/TiO_2(I) and the maximun activity appears around 80 % of TiO_2. (3) The deactivation of the catalysts, which is known to be caused by the formation of surface NCO species during the reaction[7], is much slower for $Pt/TiO_2/SiO_2$(I) than for Pt/TiO_2(I). The BET surface area(S_B) and the number of surface Pt atoms(N_s) of the catalysts are slown in Fig.1c. S_B of the catalyst, which is actually the same as that of the support, monotonously decreases with increase in the concentrations of TiO_2. N_S varies gradually and smoothly with the contents of TiO_2. Therefore, the unique activity patterns in Fig.1a may not be attributable to the variation of N_s as well as S_B[8].

The interactions of Pt with TiO_2/SiO_2(I) were studied by measuring the IR spectra of the NCO species formed on Pt/TiO_2(I), Pt/SiO_2, and $Pt/TiO_2/SiO_2$(I) during the NO-CO reaction. Comparisons among the spectra shown in Fig.2 indicate that Pt selectively interacts with "TiO_2" in TiO_2/SiO_2 even in the case that the mol ratio of TiO_2 to SiO_2 is almost unity. Since the catalytic activity of $Pt/TiO_2/SiO_2$(I)(50 wt% TiO_2) is distinctly low, the abrupt change in the activity around 60 wt% TiO_2 is not ascribed to the change in catalyst components from Pt/"SiO_2" to Pt/"TiO_2" in $Pt/TiO_2/SiO_2$(I).

X-ray studies revealed that TiO_2(I) is almost pure rutile TiO_2, which can be

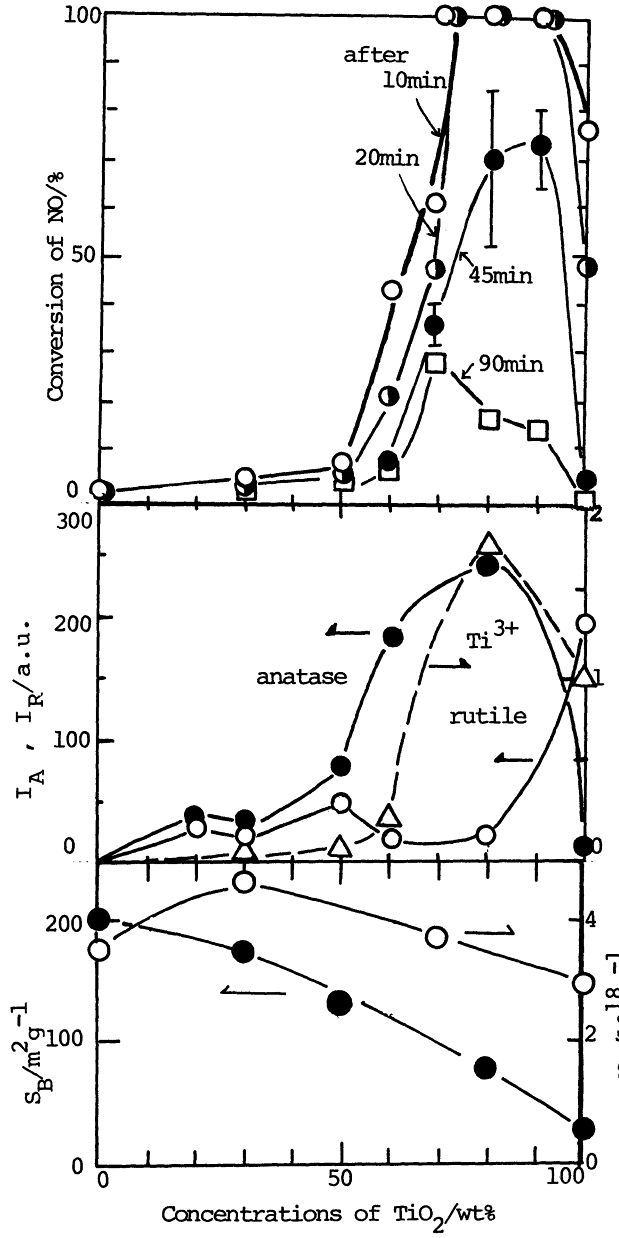

Fig. 1 Effects of the composition of TiO_2/SiO_2 (I) supports on the catalytic activities of Pt/TiO_2/SiO_2(I)(Pt 1wt%) for the NO-CO reaction,a, and the catalytic properties, b and c; a: Catalyst 0.01g, NO 3%, CO 3%, He balance, Flow rate $100cm^3min^{-1}$, Reaction temperature 350°C ,(The supports themselves were actually inactive for the reaction under the same conditions.), The catalytic activities decrease with the time on stream because of the formation of the surface NCO species on the catalysts. However, the presence of H_2, O_2, and/or H_2O in the reactants decomposes the NCO and keeps the catalytic activities constant and high., b: I_A , I_R see Table 1, I Relative intensities of Ti^{3+} in the catalysts., c: S_B , N_s see text, N_s were estimated by a conventional H_2-O_2 titration method.

Table 1 Thermal Stabilities of TiO_2 and TiO_2/SiO_2 Systems

Calcination Conditions		550°C 3h	700°C 1h	800°C 1h
TiO_2(I)	I_A	15-20	0	0
	I_R	380-400	~400	~400
	S_B	15-20	3-6	1-3
TiO_2(II)	I_A	440-460	-----	~10
	I_R	0-10	-----	~400
	S_B	55-70	-----	3-6
TiO_2/SiO_2 (I) (80wt%)	I_A	450-470	250-300	~0
	I_R	60-90	150-250	350-360
	S_B	65-85	55-65	30-40
TiO_2/SiO_2 (II) (80wt%)	I_A	470-490	-----	470-490
	I_R	20-30	-----	20-30
	S_B	130-160	-----	110-130
SiO_2	S_B	190-210	-----	160-180

I_A, I_R: Integrated Intensities of X-ray Diffraction Peaks/a.u., I_A Anatase(2θ=25.3°), I_R Rutile(2θ=27.4°), S_B: BET Surface Areas of the Supports/m^2g^{-1}

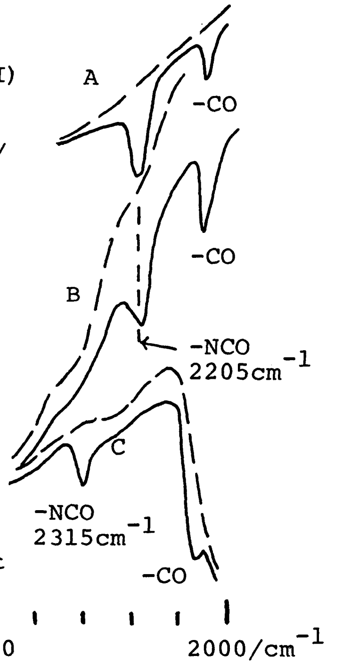

Fig. 2 IR spectra of the NCO formed on Pt/TiO_2(I) ,A, Pt/TiO_2/SiO_2(I) (50wt%TiO_2) ,B, and Pt/SiO_2,C, in the NO-CO reaction at 350°C.

expected by the results reported by Funaki[9], while TiO_2/SiO_2(I) has both abatase and rutile. The ratio of anatase to rutile distinctly varies with the composition of the support as shown in Fig.1b. The anatase is predominant in the composition range from 60 to 90 wt% TiO_2. A comparison between Fig.1a.and Fig.1b suggests that the crystalline TiO_2 may take an important role in the high catalytic activity. The difference in the activity between Pt/TiO_2(I) and Pt/TiO_2/SiO_2(I)(70-90 %) may be *partially* attributable to the difference in the structures of TiO_2 since one experiment showed that Pt/TiO_2(II)-anatase(see Table 1) is about 1.3 times more active than Pt/TiO_2(I)-rutile in the initial stage of the NO-CO reaction at 350°C.

The EPR studies showed that the concentrations of Ti^{3+} in the fresh catalysts markedly vary with the composition of the support as shown in Fig.1b, and Pt/TiO_2/SiO_2(I)(80 % TiO_2) has larger amounts of the Ti^{3+} which can be oxidized by NO or O_2 and reproduced by CO or H_2 around 350°C than either Pt/TiO_2(I) or Pt/TiO_2/SiO_2(I)(50 % TiO_2). The reasons why the catalytic activity varies with the amounts of Ti^{3+} is still obscure. However, the following explanation may be conceivable; the variations in the oxidation-reduction properties of the Ti^{3+}/Ti^{4+} system in the catalysts change the electronic properties of Pt on "TiO_2" and the rate of the oxidation of Pt by the dissociative adsorption of NO and /or that of the reduction of the oxidized Pt by CO are increased.

The X-ray studies also showed that the thermal stabilities of TiO_2 are markedly increased by the incorporation of SiO_2 and vary with the preparation methods as shown in Table 1. The table shows that the air calcination of either pure TiO_2 above 700°C definitely decreases its surface area and changes the structure of TiO_2(II) from anatase to rutile, while the anatase over SiO_2 hardly changes to rutile, especially for TiO_2/SiO_2(II). The presence of SiO_2 gel particles stabilizes the dispersed anatase TiO_2 and keeps S_B significantly high. Either Pt/TiO_2/SiO_2(80 wt% TiO_2) which had been calcined at 800°C still had the high catalytic activity, while the catalytic activity of either Pt/TiO_2 calcined at 800°C was negligible.

References and Notes

1) R.Nakamura, S.Nakai, K.Sugiyama, and E.Echigoya, Bull.Chem.Soc.Japan, to be published; R.Nakamura, S.Nakai, and E.Echigoya, Preprints of 33th Congress, Chem.Soc.Japan,1976,Hokkaido; E.Echigoya,"Jidosha no Haiki-joka ni Kansuru Kiso-Kenkyu" edited by O.Hirao, 1978, 261.
2) M.Akimoto, M. Usami, and E.Echigoya, Bull.Chem.Soc.Japan, 51, 2195 (1978).
3) K.Tanabe, M.Itoh, K.Morishige, and H.Hattori,"Preparation of Catalysts", edited by B.Delmon, Elsevier Publ., Co., Amsterdam. 1975, 65.
4) T.Kawai and T.Satake, Chem.Phys.Lett.,72, 87 (1980).
5) S.Okazaki,"Kinzoku-Sankabutsu to Fukugo-Sankabutsu", edited by K.Tanabe, T. Seiyama, and K.Fueki, Kodansha, 1978, 101.
6) J.H.Burton and R.L.Garton, "Advanced Materials in Catalysis", Acad.,Press.,1977,239.
7) H.Niiyama, M.Tanaka, H.Iida, and E.Echigoya, Bull.Chem.Soc.Japan, 49, 2027,(1976).
8) Strictly, N_S may be corrected by considering "SMSI". See "K.Kunimori, T.Okouchi, and T.Uchijima, Chem.Lett. , 1980, 1513".
9) K.Funaki and Y.Saeki, Kogyo Kagaku Zasshi, 59, 1291, 1295 (1956).

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