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Fixation of Heteropoly Anion on TiO_2 Modified with a Silane Coupling Agent

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12-tungstophosphate anion (PW_{12}) was effectively fixed on TiO_2 chemically modified with γ-anilinopropyl-trimethoxysilane (AnPS). The fixation was confirmed by FT-IR spectroscopy to be caused by the interactions between the functional group of AnPS and the surface OH group on TiO_2 and the bridge oxygen ion in the PW_{12}-Keggin unit.

Heteropoly acids and its related compounds have been applied to several industrial processes as an effective catalyst. The basic reactions, in many cases, take place in the crystalline states and in concentrated aqueous solutions.[1] In order to homogeneously disperse and tightly fix such heteropoly anions, we have attempted a modification of the carrier surfaces with silane coupling agents which have anion-exchangeable groups. In this paper, we preliminarily report on a prominent effect by modification of TiO_2 with γ-anilinopropyl-trimethoxysilane (AnPS) on the fixation of 12-tungstophosphate anion (PW_{12} anion). A state of fixation is also discussed based on FT-IR diffuse reflectance spectroscopy.

TiO_2-surfaces were modified with AnPS as follows. 5.0 g of TiO_2(Rutile), which were offered from the Catalyst Society of Japan, JRC-TiO-3 and -5 (S=40 and 2.6 m^2/g respectively),[2] were heated at 110 °C for 30 min under a vacuum at about 0.1 Pa. After the samples were cooled to 25 °C, 50 ml of AnPS-acetic acid solutions (0.2 - 2.0 w/w%) were added and reacted with stirring for 10 min. The TiO_2 powder was then separated from the solution by filtration, cured at 110 °C for 30 min, and fully washed with methanol to remove any unreacted and physisorbed AnPS. The samples thus obtained were designated as AnPS-TiO_2. 2.0 g of TiO_2 thus modified with various concentration of AnPS and unmodified TiO_2 were heated at 110 °C for 30 min under a vacuum at about 0.1 Pa. 100 ml of PW_{12} aqueous solutions (0.04 mol dm^{-3}) were added to these TiO_2's after cooling to 25 °C and allowed to stand for 20 h in order to allow full adsorption of the PW_{12} anion. The TiO_2 samples were separated from the solution by filtration and dried at 110 °C for 30 min. The samples thus obtained were designated PW_{12}/TiO_2 and PW_{12}/AnPS-TiO_2. The surface concentrations of AnPS and PW_{12} anions on those samples were determined by gravimetrical, spectrophotometrical, and electrochemical analyses.

A Perkin-Elmer 1760X infrared spectrometer with a diffuse reflectance accessory supplied by Spectra-Teck Inc. was used to record infrared spectra of the samples, which were usually diluted with KBr powder. The spectra were aquired with 128 scans at 4 cm^{-1} resolution, to which a "Kubelka-Munk correction" was applied.

FT-IR spectra of AnPS on TiO_2 and the PW_{12} anion on AnPS-TiO_2 are illustrated in Fig.1. The characteristic bands for AnPS appear in the 1605 - 1435 cm^{-1} region. The band intensities increased with the AnPS concentration upon treatment, as described quantitatively below. The characteristic bands for the PW_{12} (Keggin) anion are seen in the 1080 - 800 cm^{-1} region. The characteristic bands of AnPS weaken considerably as seen in the comparison of Fig.1-(d) with Fig.1-(b), which might be caused by an interaction of AnPS with the PW_{12} anion.

The subtraction of Fig.1-(a) from -(b) was successfully done as shown in Fig.2-(a), in which the band region for AnPS is significantly expanded. The subtraction spectrum between Fig.1-(c) and -(d) is also given in Fig.2-(b). By comparing Fig.2-(a) with Fig.2-(b), it is clarified that the characteristic bands deform and significatly weaken accompanied with fixation of the PW_{12} anion. Furthermore, the 1505 cm^{-1} and 1435 cm^{-1} bands, which have been assigned to the deformation modes of the NH and CH_2 groups, respectively,[3] tend to shift toward the lower wave numbers. The subtraction spectra were also recorded successfully in the region characteristic of the PW_{12} anion, as shown in Fig.3. Figure.3-(a) indicates the spectrum of $H_3PW_{12}O_{40}\cdot nH_2O$ itself in a crystelline state and Figs.3 -(b) and -(c) are the subtraction spectra between PW_{12}/TiO_2 and TiO_2 and between PW_{12}/AnPS-TiO_2 and AnPS-TiO_2, respectively. The W-O_b-W stretching bands corresponding to the "bridge oxgen",[4] are affected by a shift to some extent toward the higher wave numbers. Thus, strong interactions between the functional group of AnPS and

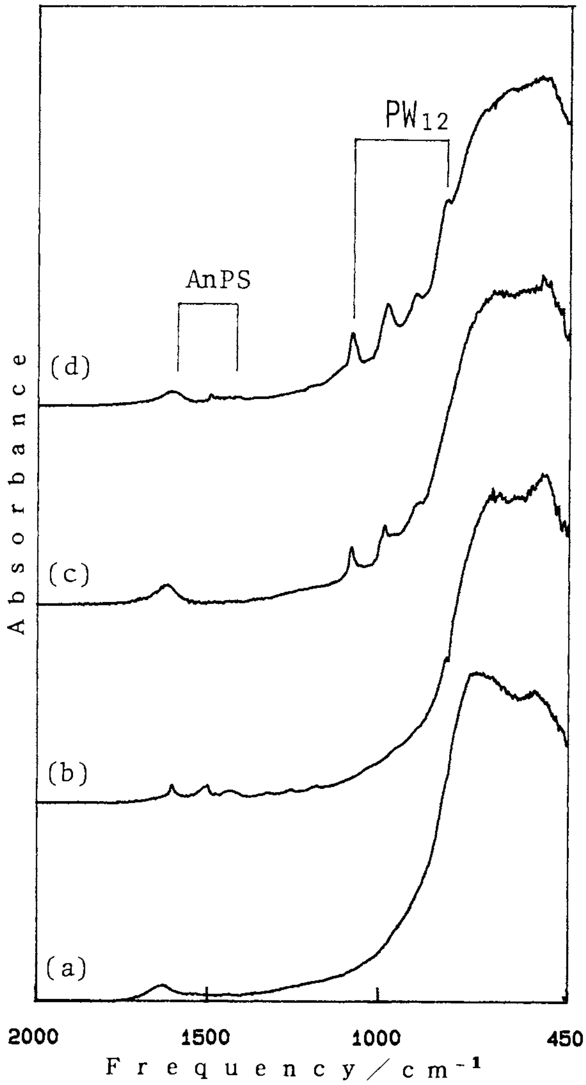

Fig.1. FT-IR diffuse reflectance spectra of variously treated TiO_2 samples as described in text. (a) TiO-3, (b) TiO-3 modified with 2.0 w/w% of AnPS (AnPS-TiO-3), (c) PW_{12} anion deposited directly on TiO-3 (PW_{12}/TiO-3, 0.04 mol dm^{-3} PW_{12}), (d) PW_{12} anion deposited on AnPS-TiO-3 (PW_{12}/AnPS-TiO-3, 2.0 w/w% AnPS and 0.04 mol dm^{-3} PW_{12}).

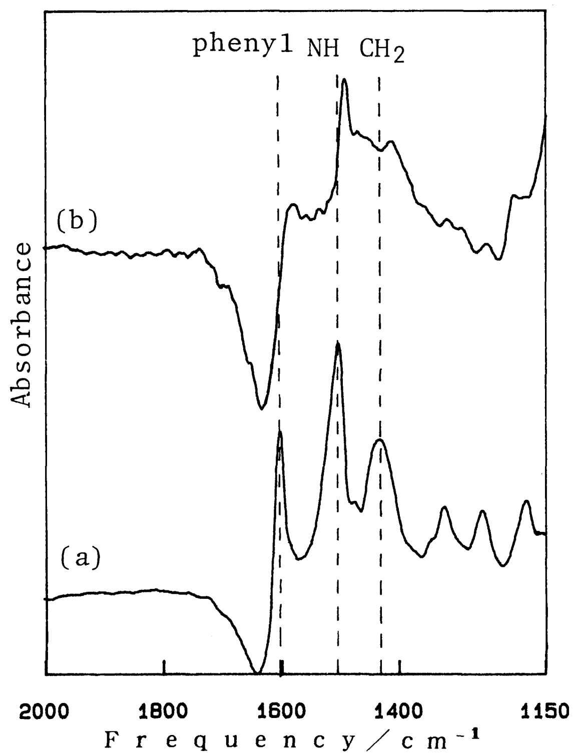

Fig.2. Subtraction spectra in the band region for AnPS. (a) the subtraction of Fig.1-(a) from Fig.1-(b) (AnPS-TiO-3), (b) the subtraction of Fig.1-(c) from Fig.1 -(d) (AnPS-TiO-3 fixing PW_{12}), in which the 1605 cm^{-1} band(phenyl) is not seen due to the large negative absorbance in the OH group region.

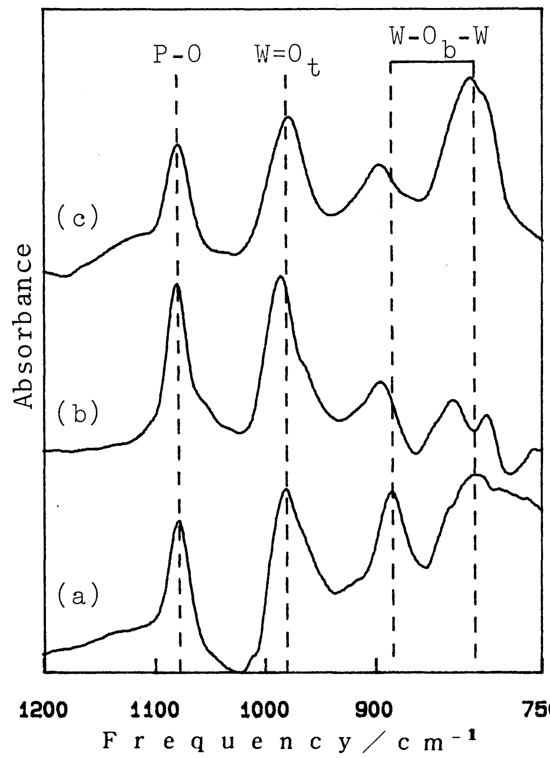

Fig.3. Subtraction spectra in the band region for PW_{12} anion. (a) $H_3PW_{12}O_{40}\cdot nH_2O$ as crystalline powder, (b) the subtraction of Fig.1-(a) from Fig.1-(c) (PW_{12} fixed on TiO_2), (c) that of Fig.1-(b) from Fig.1-(d) (PW_{12} fixed on AnPS-TiO-3).

the surface OH group on TiO_2 and the bridge oxygen in the PW_{12} anion are suggested. In fact, the bridge oxgen has been regarded to be an active center in the oxdation-reduction processes.[4] The band shifts in Fig.3 would be caused from the differences in the strength of the interactions, $O_b\cdots H_3{}^+O$ (Fig.3-a) and $O_b\cdots HO\text{-}(TiO_2)$ (b), and $O_b\cdots (C_6H_5)NH_2{}^+\text{-}$ (c). Similar changes in the characteristic bands for AnPS and the PW_{12} anion were also observed in the other TiO-3 samples treated with the lower concentration of AnPS and in the TiO-5 samples.

The characteristic bands for AnPS increase with AnPS concentration upon treatment as previously described above. The band intensity for the phenyl group at 1605 cm^{-1} was evaluated based on the subtraction spectrum and plotted versus the AnPS concentration used for the treatment, as shown in Fig.4-(A). We can see that the surface concentration increases with the AnPS concentration both in TiO-3 and TiO-5, although the slopes differ greatly from one another for the difference in the surface areas. In fact, the surface coverages (θ) of AnPS have been estimated to be in about 0 - 0.2 and 0 - 1.5 for the AnPS-TiO-3 and -5 samples, respectively.

We also evaluated the band intensities for the PW_{12} anion on the carriers treated with various concentration of AnPS. The intensities of the P-O stretching band relative to the main band for the TiO_2 carrier were plotted versus the band intensities of AnPS on TiO_2, as shown in Fig.4-(B). The amounts of PW_{12} anion fixed on the carriers were clarified to be linearly proportional to the surface AnPS concentration in both TiO-3 and -5. The coverage of the PW_{12} anion on the unmodified TiO-3 was estimated as ca. 1.0, while for TiO-5 it could not be measured. Therefore, it is noticed that the PW_{12} anion has been concentrated up to θ=1.7 on the TiO-3 carrier by only 20 percent of the surface modification with AnPS, although the reason is unknown at present.

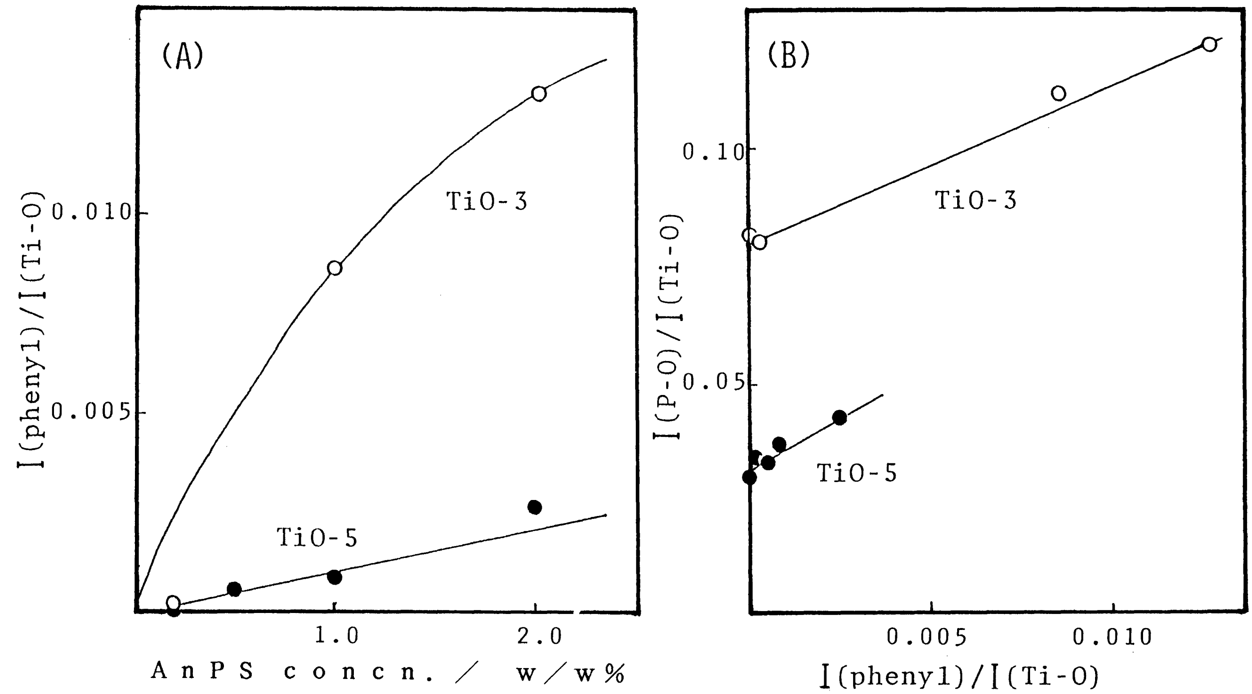

Fig.4. (A) Plots of the relative band intensities for ν (phenyl) in AnPS on TiO_2 versus the AnPS concentration upon treatment, (B) the plots of the relative band intensities for ν (P-O) in PW_{12} on AnPS-TiO_2 versus the relative intensities of ν (phenyl) in AnPS on modified TiO_2 .

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