Dispersion and Fixation of 12-Tungstophosphate Anion on a Silica Surface Modified with Silane Agents Having an Amine Group and Their Catalytic Properties

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Silica gel (SiO_2) was modified by a dip-cure method with silane coupling agents having an amine-group: (3-anilinopropyl), (3-aminopropyl), and *N*-[3-(2-aminoethyl)aminopropyl] trimethoxysilanes. 12-tungstophosphate (PW_{12}) was deposited on the carriers as a test catalyst material. The amounts and the dispersed states of the silane agents and PW_{12} on the modified SiO_2 were successfully analysed by gravimetry as well as UV and FT-IR spectrometries. The amount of PW_{12} deposited increased in proportion to the amount of the silane agents on SiO_2 in the case of deposition under a constant concentration of PW_{12}-solution, although only a little PW_{12} was deposited directly on SiO_2. The acidic site of PW_{12} was confirmed to interact directly with the amine-group on the modified SiO_2, and the strength of the interaction was correlated with the basicity of the amine-group. The activity per gram of catalyst for the dehydration of 2-propanol as a test reaction is generally higher than that on a directly deposited one, although the activity per PW_{12} unit certainly decreases with the SiO_2-modification. The activity was confirmed to increase by a pretreatment at high temperatures, such that the amine-group was completely decomposed. It was clearly shown that the present modification method could be effectively applied for preparing a highly dispersed heteropoly acid catalyst on carriers.

The surfaces of metals, glasses, metal oxides, and active carbons have been modified with organosilanes (R_nSiX_{4-n}[1)]) in order to design and produce new composite and functional materials. The carriers of chromatography,[2)] functional electrodes,[3)] reinforced composite materials,[4)] and heterogeneous catalysts[5)] have developed using such a technique. Some of the interesting applications so far reported include the concentration of metal ions on modified carriers by using a functional action of the silane agents[6)] and modified carriers with silane agents having an amine-group as a phase-transfer catalyst.[7)] The surfaces of materials modified with silane agents have been characterized by FT-IR[8)] and XPS.[9)]

The chemistry of heteropoly acids and its related compounds has been developed over a wide scope.[10)] Applications of polyacids to partial oxidation and acid-base reactions as catalysts have been attempted; excellent activity and an interesting property as catalysts have been reported.[11)] They work well, in general, in the state of a concentrated solution,[12)] in its crystalline states,[13)] and in deposited states on carriers.[14)] We have been interested in applying the modification technique mentioned above to prepare a well dispersed support catalyst, taking notice of the anion-exchangeability of the amine-group of the silane agents. Thus, an effective dispersion of 12-tungstophosphate anion (PW_{12}) over a TiO_2-surface premodified with (3-anilinopropyl)-trimethoxysilane (AnPS) was investigated by FT-IR measurements.[15)]

In the present study we attempted to fix the PW_{12} anion as a test material on a SiO_2-carrier modified with silane coupling agents, which have different amine-groups, and examined in detail the effect of the amine-function group to the fixation. As a result, PW_{12} was fixed more strongly in relation to the basicity of the amine-group and was concentrated much more with the extent of the modification of SiO_2, as previously communicated.[16)] The applicability of the present modification method to the preparation of a heteropoly acid catalyst dispersed on carriers is emphasized.

Experimental

1) Materials and Procedures. 12-Tungstophosphate (PW_{12}) was prepared according to Wu and Pope,[17)] as follows: After 50 g of $Na_2WO_4\cdot 2H_2O$ was dissolved in 50 ml of boiling water, 5 ml of 15 mol dm^{-3} H_3PO_4 and 40 ml of 12 M HCl (1 M=1 mol dm^{-3}) were added to the solution with stirring. The solution was left standing for 20 h, and a white precipitate was filterd out. The Na-12-tungstophosphate, thus obtained, was dissolved again in 60 ml of pure water, then mixed with 70 ml of diethylether and 30 ml of 12 M HCl in a separating funnel. Finally, we obtained the free acid of 12-tungstophosphate, $H_3PW_{12}O_{40}\cdot nH_2O$ ($n=29$), from the solution.[18)] All of the reagents used were of extra-pure grade purchased from Kanto Chemical Co., Ltd.

The chemical modification of SiO_2 with silane agents was carried out by a dip-cure method as follows.[19)] Silica gel from Aldlich, (No. 643, mean pore radius 150 Å and surface area 300 m^2 g^{-1}) was used. As the silane agent, (3-anilinopropyl)trimethoxysilane [$C_6H_5NH-(CH_2)_3-Si(OCH_3)_3$; AnPS], (3-aminopropyl)trimethoxysilane [$NH_2-(CH_2)_3-Si(OCH_3)_3$; APS], and *N*-[3-(2-aminoethyl)aminopropyl]trimethoxysilane [$NH_2-(CH_2)_2-NH-(CH_2)_3-Si(OCH_3)_3$; DAPS], which were purchased from Kanto Chemical Co., Ltd., were used without further treatment. Given amount of silane agents were dissolved in 50 ml of 0.2 mol dm^{-3} acetic acid solution to prepare 0.5, 1.0, 2.0, and 5.0w/w% concentrations. 5.0 g of the SiO_2-powder was added into the solutions and stirred vigorously for 10 min. After that, the SiO_2-powder was filtered out with a suction funnel and was cured at 80 °C for 30 min to make the agents react with the hydroxyl group of the SiO_2-surface. In order to remove any unreacted part of the agents from the surface, the SiO_2-powder was washed once with methanol and was then cured again at 80 °C for 30 min.

A 0.0119 mol dm^{-3} aqueous solution of PW_{12} was prepared. 3.0 g of the SiO_2-powders (variously modified) was added into 50 ml of the PW_{12}-solution and stirred for 2 h to make PW_{12} absorb. The SiO_2-samples were filtered out with a suction and then completly dried at 110 °C to prepare the PW_{12}-catalysts deposited on the SiO_2-powders modified with the silane agents. The thus-obtained samples were subjected to characterization and a test of catalytic activity (below).

2) Measurements and Analyses. **2.1) Estimation of the Amounts of Silane Agents Present on the Modified SiO_2-Surfaces:** 0.5, 1.0, and 2.0 g of the SiO_2-powders were taken into a glass filter and accurately weighted. The 0.2 mol dm^{-3} acetic acid solution was poured into the filter and left standing for 10 min in order to make the solution adhere to the SiO_2-surface. After the acetic acid solution was filtered out by suction, the filter containing the SiO_2-powders was again accurately weighted in order to evaluate the adhensive amount of the solution on the SiO_2. From the difference in the two weights, we could easily determine the remaining amounts of the silane agent on the SiO_2-surface.

2.2) Estimation of the Amounts of PW_{12} Deposited on the Modified SiO_2: PW_{12}-crystals were dissolved in pure water to prepare a 0.0119 mol dm^{-3} PW_{12} solution. The UV-spectrum of the solution was measured over the range 210—350 nm using a Shimadzu UV-spectrometer (model UV-120-020). The absorbance at 268 nm was previously reported to vary linearly with the PW_{12}-concentration, which could be used as a calibration curve. The amounts of absorbed PW_{12} was estimated from the difference between the absorbances before and after adsorption.

2.3) FT-IR Analyses: FT-IR spectrum for PW_{12} deposited on modified SiO_2 was measured by a FT-IR apparatus of Perkin–Elmer (Model 1760X) equipped with a diffuse reflectance attachment (Spectra-Teck Inc.). The sample was mixed with a finely divided KBr-powder at a concentration of ca. 5—10w/w%. The spectrum was recorded over the range 450—4000 cm^{-1} with 36 scans, and then corrected using the Kubelka–Munk equation.

2.4) Measurement of Catalytic Activity: The catalytic activity for the dehydration of 2-propanol as a test reaction was measured by the use of a closed circulation reactor (ca. 0.5 dm^3). 20 mg of the catalyst was charged in a reaction tube; after preheating at 300 °C in air for 30 min, the temperatures were controlled at 200—300 °C within 0.5 °C. Alcohol vapor was then introduced in order to start the reaction. The pressure change during the initial stage of 10—70 min was recorded with a pressure guage, in which the pressure of 2-propanol was kept constant at ca. 8.4 Torr (the vapor pressure at 0 °C, 1 Torr=133.32 Pa) during the reaction. For a convenient activity test, the usual-type micro-pulse apparatus was used.

Results and Discussion

1) Quantitative Analysis and Characterization of SiO_2-Surfaces Chemically Modified with Silane Agents. The FT-IR spectra of SiO_2 modified with AnPS are illustrated in Fig. 1. The characteristic band for the anilino-group of AnPS appears in the 1430—1610 cm^{-1} range. The intensity increases along with the AnPS concentration.[19] The intensity of the 1603 cm^{-1} band, which has been assigned to the anilino-group, was normarized by the Si–O–Si stretching band at ca. 1100 cm^{-1} in the modified SiO_2. The relative intensity, [$I(1603)/I(1100)$], was plotted against the AnPS-concentration (Fig. 2). Curve-a shows the relative intensity and curve-b shows the absolute amount of AnPS loaded on the SiO_2-surface, which was evaluated based on a gravimetrical measurement. The relative intensity deviates considerably from linearity at 4.0w/w%. This may have been caused by the removal of the unreacted part of the silane agents from the surface upon washing with methanol. The SiO_2-surface should be modified with the silane agents through a dehydration condensation reaction between the surface hydroxyl-group (Si–OH) and the silanol of the agent (R–Si–$(OH)_3$), to which R–Si–$(OCH_3)_3$ was converted in the acidic solution, with the curing procedure.[19] The surface area per gram AnPS was 307 m^2 g^{-1} and the BET surface area of SiO_2 used was 300 m^2 g^{-1}. Therefore, the surface coverage (θ) of AnPS on SiO_2, which was treated with 1.0, 2.0, and 5.0w/w% of the solutions, was estimated to be 1.1, 2.2, and 5.4%, respectively. The extent of the surface modification was very low, 1—5%. Similar results were obtained for APS and DAPS.

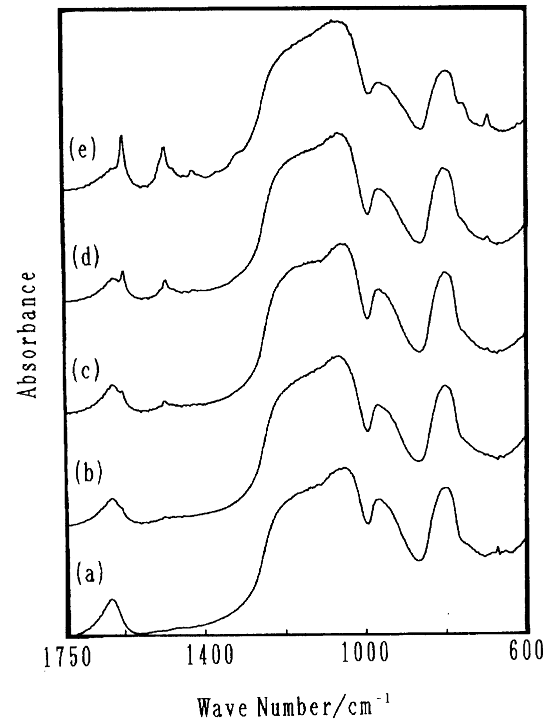

Fig. 1. FT-IR diffuse reflectance spectra of AnPS–SiO_2 modified with various concentration of AnPS solution. (a) SiO_2 as a reference, (b) AnPS (0.5w/w%)–SiO_2, (c) 1.0w/w%, (d) 2.0w/w%, (e) 5.0w/w%.

2) Quantitative Analysis and Characterization

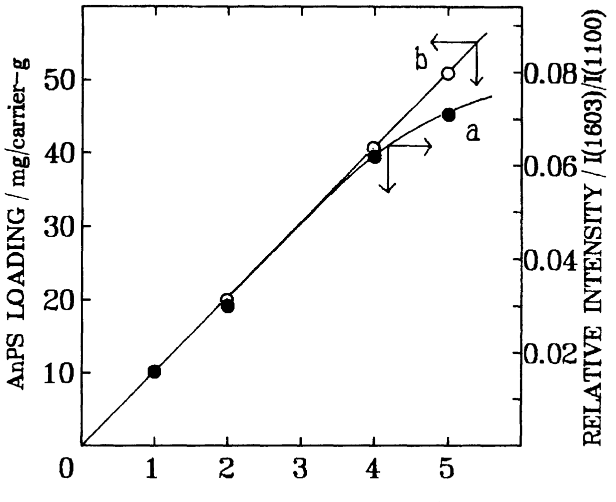

Fig. 2. Plots of AnPS loaded versus AnPS concentration in the modification (curve-b) and IR relative band intensity $I\delta$(N–H)/$I\nu$(Si–O) versus AnPS concentration (curve-a).

of PW_{12} Dispersed on Modified SiO_2. The adsorption of PW_{12} on premodified SiO_2 was performed in a solution having a constant PW_{12}-concentration (0.0119 mol dm^{-3}). The amounts of adsorbed PW_{12} were determined by the UV spectra of the PW_{12}-solution. The data are summarized in Table 1 (the coverage was evaluated approximately assuming the cross section of PW_{12} to be 1.8 nm^2·molecule^{-1} [18)]). The amounts of adsorbed PW_{12} and the coverages are plotted against the silane agent concentration in Fig. 3. The amounts of adsorbed PW_{12} increased in proportion to the concentration of the silane agents; furthermore, the inclination of the linear curves is in the order DAPS>APS>AnPS. It is therefore suggested that the degree of an interaction between PW_{12} and the modified surfaces greatly depends upon the basicity of the amine-group.

Table 1. Amounts of PW_{12} Loaded on the Carriers Variously Modified with Silane Agents and the Surface Coverage Estimated

Samples		PW_{12} loading	Coverage
		$\times 10^{-5}$ mol·carrier-g^{-1}	%
PW_{12}/SiO_2		0.73	2.6
PW_{12}/AnPS–SiO_2	(1.0w/w%)[a)]	1.11	4.1
	(2.0w/w%)	2.45	8.8
	(5.0w/w%)	6.70	24.1
PW_{12}/APS–SiO_2	(1.0w/w%)	1.56	5.6
	(2.0w/w%)	1.93	7.0
	(5.0w/w%)	7.38	26.6
PW_{12}/DAPS–SiO_2	(1.0w/w%)	1.67	6.0
	(2.0w/w%)	3.92	14.1
	(5.0w/w%)	8.06	29.0

a) Concentration of silane agents in the modification.

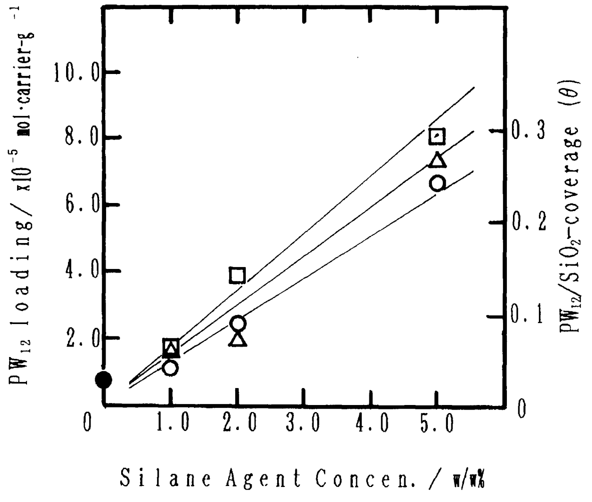

Fig. 3. Plots of PW_{12} loaded on SiO_2 and coverage of PW_{12} (θ) versus silane agents concentration. PW_{12}/AnPS–SiO_2 (○), PW_{12}/APS–SiO_2 (△), PW_{12}/DAPS–SiO_2 (□), and (●) PW_{12}/SiO_2.

The FT-IR spectra for PW_{12} deposited on SiO_2 modified by AnPS (PW_{12}/AnPS–SiO_2) are illustrated in Fig. 4. The N–H deformation band at 1500 cm^{-1} deforms considerably with the PW_{12} deposition, indicating a strong interaction of the anilino-group with PW_{12}. The characteristic band of PW_{12}, which usually appears

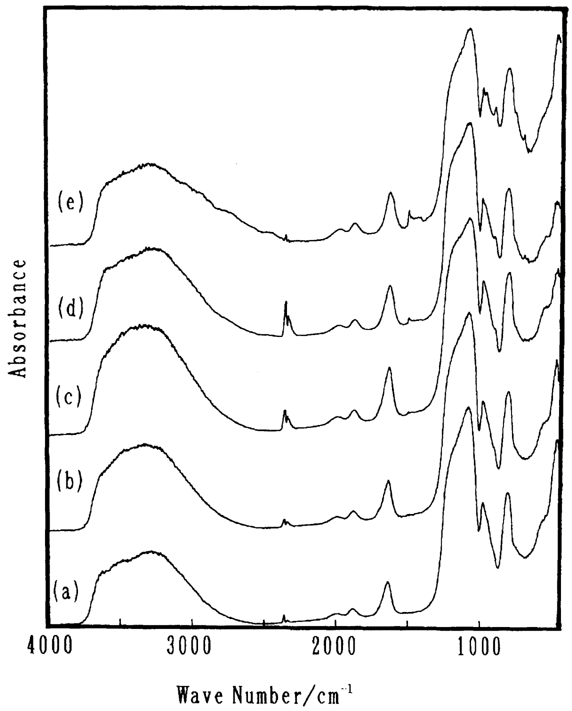

Fig. 4. FT-IR diffuse reflectance spectra of PW_{12} on SiO_2 modified with various AnPS concentration. (a) PW_{12}/SiO_2 as a reference, (b) PW_{12}/AnPS-(0.5w/w%)–SiO_2, (c) 1.0w/w%, (d) 2.0w/w%, (e) 5.0w/w%.

in the 800—1100 cm^{-1} region,[20] was hidden in the huge band of SiO_2 (Si–O–Si). With PW_{12} deposited on SiO_2, which was treated with 5.0w/w% of AnPS solution, a large deformation appears in the 800—1100 cm^{-1} region. We attempted to obtain the subtraction spectrum of AnPS–SiO_2 from PW_{12}/AnPS–SiO_2. The subtraction spectra are given in Fig. 5, in which the spectrum for $H_3PW_{12}O_{40}\cdot nH_2O$ in a crystalline state was added as a reference (spectrum-a).

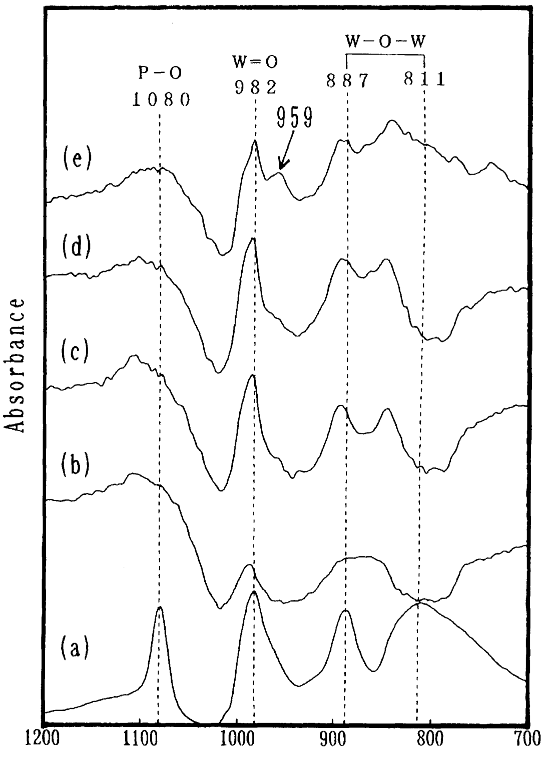

Fig. 5. The subtraction spectra between PW_{12}/AnPS–SiO_2 and the corresponding AnPS–SiO_2 carriers. (a) PW_{12} in crystalline state as a reference, (b) PW_{12}/SiO_2, (c) PW_{12}/AnPS(1.0w/w%)–SiO_2, (d) 2.0w/w%, (e) 5.0w/w%.

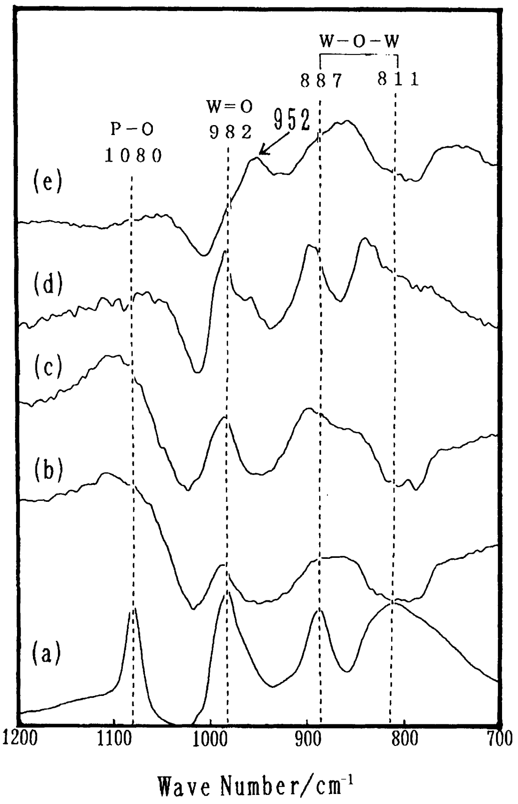

Fig. 6. The subtraction spectra between PW_{12}/APS–SiO_2 and the corresponding APS–SiO_2 carriers. (a) PW_{12} in crystalline state as a reference, (b) PW_{12}/SiO_2, (c) PW_{12}/APS(1.0w/w%)–SiO_2, (d) 2.0w/w%, (e) 5.0w/w%.

The P–O stretching band at 1080 cm^{-1} and the W–O–W stretching band at 811 cm^{-1} could not be clearly found in the subtraction spectrum, due to an overlapping with the peak-top of the SiO_2 bands. Since the W=O and W–O–W stretching bands clearly appear at 982 and 887 cm^{-1}, respectively, PW_{12} is proved to be present while keeping the Keggin structure[21] on all of the catalyst: PW_{12}/SiO_2 (b) and PW_{12}/AnPS–SiO_2 (c)—(e). We can see that a new band appears at 959 cm^{-1}; its intensity tends to grow with increasing the AnPS-concentration, while at the same time the original W=O band at 982 cm^{-1} decreases. In the case of the PW_{12}/AnPS–TiO_2, in which the TiO_2-surface had been fully premodified by the silane agent by a reflux method, a set of the characteristic bands for the PW_{11}-anion $[PW_{11}O_{39}]^{7-}$ (1079, 1047, 953, and 895 cm^{-1}) was observed in addition that for PW_{12}.[20] PW_{12} is reversibly converted to the lacunaly PW_{11}-anion:[10,22]

$$[PW_{12}O_{40}]^{3-} + (5-x)OH^{-} \rightleftarrows [H_xPW_{11}O_{39}]^{(7-x)-} + HWO_4^{-} + (2-x)H_2O. \quad (1)$$

Thus, it is suggested from the change in both bands (at 982 and 959 cm^{-1}) that the relative concentration of PW_{11} to PW_{12} depends upon the extent of the premodification with the silane agent.

A similar tendency was found in PW_{12}/APS– and DAPS–SiO_2, as shown in Figs. 6 and 7, respectively. From a comparison among Figs. 5 and 7, the intensities of the new W=O band relative to the original band are in the order DAPS>APS>AnPS. The peak position of the new W=O bands for PW_{12}/DAPS, APS, and AnPS–SiO_2 sifts from 982 cm^{-1} (the original) to 946, 952, and 959 cm^{-1}, respectively. The results show that the degree of the shift is in the order, DAPS>APS>AnPS; thus, the extent of the interaction between PW_{12} and the amine-group in the silane agents tends to increase in this order. The intensities of the new W=O bands at 959—946 cm^{-1} (I) relative to the original band at 982 cm^{-1} (I_0), $I/(I_0+I)$, were estimated based on the spectra given in Figs. 5, 6, and 7. The results are plotted against the concentration of the silane agents, as

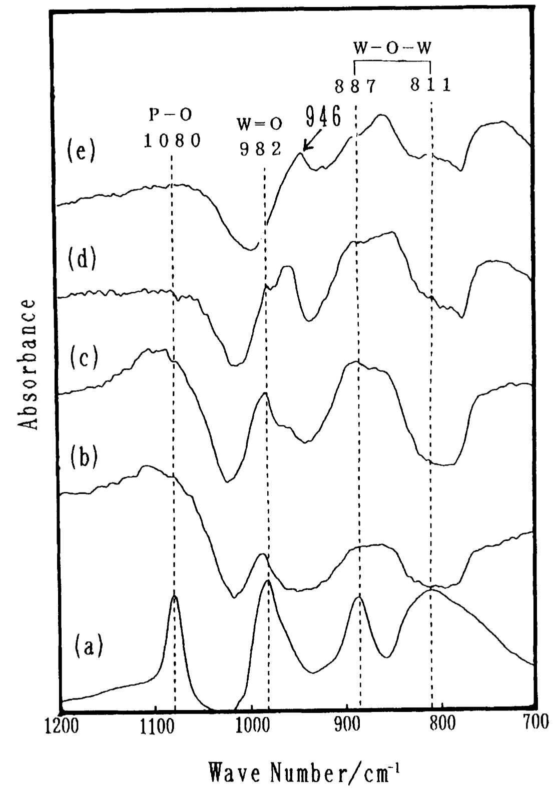

Fig. 7. The subtraction spectra between PW_{12}/DAPS–SiO_2 and the corresponding DAPS–SiO_2 carriers. (a) PW_{12} in crystalline state as a reference, (b) PW_{12}/SiO_2. (c) PW_{12}/DAPS(1.0w/w%)–SiO_2, (d) 2.0w/w%, (e) 5.0w/w%.

shown in Fig. 8. We can see that the extent of the increase in the relative intensity of the new W=O band with the concentration of the silane agent varies depending upon the type of amine-group of the agents. The inclination of the curves, even though the points at 5.0w/w% deviate greatly from linear relations, could be related to the strength of the interaction with the amine-group and, thus, their pK_a-values. For instance, the pK_a-value for propylamine-group (APS) has been reported to be 10.5 and that for methylaniline-group (AnPS) to be 4.85,[23] although corresponding data for DAPS are lacking. However, since the inclination for PW_{12}/DAPS–SiO_2 is quite large, a high pK_a-value for DAPS should be expected; futher, PW_{12} should be more strongly fixed as PW_{11} on the DAPS–SiO_2 carrier. It is therefore clearly understood that the higher is the concentration of the silane agents upon a modification and the stronger is the basicity of the amine-group, the heteropoly anion is much more fixed and, further, the higher is the PW_{11}-to-PW_{12} ratio on the modified surfaces.

3) Catalytic Activity of PW_{12} Deposited on SiO_2 Modified Variously with the Silane Agents.

In order to examine the catalytic activites of PW_{12} deposited on SiO_2 modified with silane agents, the dehydration of 2-propanol was performed as a test reaction.

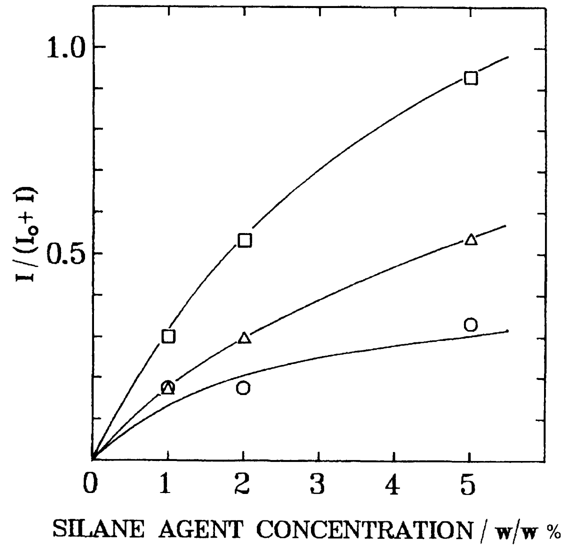

Fig. 8. Plots of the IR relative band intensity, $I/(I_0+I)$, versus silane agents concentration in the modification. PW_{12}/AnPS–SiO_2 (○), PW_{12}/APS–SiO_2 (△), PW_{12}/DAPS–SiO_2 (□).

The initial mean rates per PW_{12} unit on a modified catalyst were evaluated from a plot against the inverse temperature (Fig. 9). With the modified catalyst, the activity per PW_{12} unit decreases; further, the activation energy tends to increase, as compared with an unmodified catalyst. However, the total acitivity (per gram of catalyst) of the modified catalyst is generally higher than that of the unmodified catalyst, because PW_{12} is concentrated on the modified SiO_2, and is also dispersed

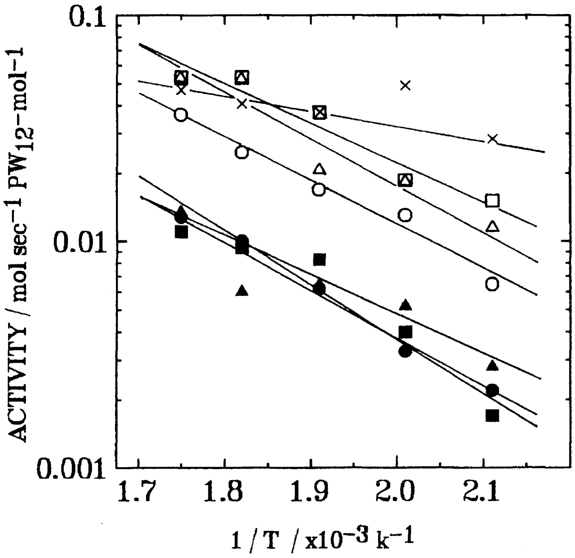

Fig. 9. Arrhenius plots for over all rate of dehydration of 2-propanol on PW_{12}/AnPS–SiO_2 (○), PW_{12}/APS–SiO_2 (△), PW_{12}/DAPS–SiO_2 (□), and (×) PW_{12}/SiO_2. The open and closed signs indicate the activities for PW_{12} dispersed on the carriers modified with 1.0 and 5.0w/w% of the silane agents, respectively.

through the interaction, as mentioned above (cf. Fig. 3). This tendency can be explained by assuming that the acidic site which has been characterized on the oxygen ion in W–O–W of PW_{12}[24] should disappear for an interaction with the amine-groups. However, we cannot clearly explain the reason why the catalytic activity per unit PW_{12} of the 5.0w/w%-modified catalyst becomes lower than that of the 1.0w/w%-modified catalyst.

The activity was recovered by a pretreatment at 450 °C or higher; in fact, the amine-group of the modified catalyst was found to decompose above the temperatures.[15] For instance, the activites or dehydration of 2-propanol on PW_{12}/AnPS(5.0w/w%)–SiO_2 and PW_{12}/SiO_2, as measured at 100 °C by a pulse apparatus, are as follows: The conversion (on 20 mg catalyst and for 0.5 μl alcohol pulse) was 23% on PW_{12}/AnPS-(5.0w/w%)–SiO_2 pretreated at 300 °C; it changed to 50% upon a pretreatment at 500 °C. On the other hand, it was 11% on PW_{12}/SiO_2 pretreated at 300 °C; it changed to 5% upon a pretreatment at 500 °C. An increase in the activity in the former case means that the anilino-group is decomposed by a pretreatment at 500 °C[25] and, thus, the acidic sites on PW_{12} are released without any changes in the concentration of PW_{12}. The decrease in the acitivity in the latter case is reasonably explained as follows. In the case of a direct deposition (PW_{12}/SiO_2), PW_{12} might be considerably condensed into pores of the SiO_2-carrier. If so, the catalyst would behave as a bulky material (i.e., as a quasi-liquid phase as has been proposed by Misono[13a)]), even though they are supported on the carrier. That is, after a pretreatment at 300 °C a considerable amount of water remains in the catalyst, so that alcohol molecules can penetrate into the inner part of the bulky PW_{12} and then react with the PW_{12} ion. Upon a pretreatment at 500 °C, since the water is considerably removed, alcohol molecules would be limited to react only on the bulk surfaces.

It is therefore demonstrated that the present premodification method is very effective for preparing a supported heteropoly acid catalyst. In fact, 12-tungstophosphate (PW_{12}) as a test material was homogeneously concentrated through an interaction with the amine-group on the modified surface. Furthermore, the efficiency of holding PW_{12} and PW_{11} depended upon the basicity of the amine-group. The premodification method of carriers with silane agents should be applicable to the preparation of supported heteropoly acid catalysts by appropriate selections of the silane agents and the concentration upon the treatment.

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