Dispersion of phosphovanadates on silica gel chemically modified with silane coupling agents having an amino group and their catalytic activities for methanol oxidation

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Phosphotetradecavanadate (PV14) was dispersed on a silica gel chemically modified with a silane coupling agent (AnPS-SiO_2) by an equilibrium adsorption method. The PV14 contents approximately correlated with the V(IV) spin contents by ESR. PV14 dispersed on AnPS-SiO_2 resulted in a quite high selectivity for formaldehyde such as 97% in methanol oxidation.

Keywords: silane coupling agents; chemical modification of silica gel; phosphotetradecavanadate; methanol oxidation

1. Introduction

Heteropolyacids (HPA) with a Keggin structure have been widely used in acid–base and redox reaction processes as highly active catalysts [1]. They have also been applied to basic studies of catalysts as a model material, because the acidic and redox properties can be systematically regulated by varying the combination of the hetero and poly atoms [2,3]. In particular, many investigators have intended to utilize the catalytic abilities of HPA in deposited and/or dispersed states on carriers [4,5]. The structures of HPA are usually subject to changes by direct interaction with carriers, and thus the deposited states vary greatly depending upon the preparation conditions. Many problems now remain in the preparation of supported HPA catalysts. We have attempted to disperse HPA homogeneously over carrier surfaces which have been previously modified with silane coupling agents containing an amino group, taking note of the anion exchangeability of the group [6].

In the present study, phosphotetradecavanadate anion (PV14) was dispersed on silica gel (SiO_2) which was chemically modified with silane agents to examine the catalytic activity for methanol oxidation as a test reaction. Phosphododecatungstate (PW12) and phosphododecamolybdate (PMo12) catalysts were similarly prepared for comparison. By comparing the catalytic features among the modified and unmodified SiO_2-supported catalysts, it will be especially elucidated that the PV14 units are dispersed on the carrier surface through interaction with the amino group and, at the same time, the acidic sites are effectively restricted but redox sites are retained so that a quite high selectivity for formaldehyde is realized. The dispersed states of PV14 are briefly discussed on the basis of electron spin resonance (ESR) spectroscopic data.

2. Experimental

2.1. Materials and procedures

10 g of silica gel (SiO_2; Aldrich No. 643, mean pore radius, 15 nm and surface area, 300 $m^2\ g^{-1}$) was previously heated at 110°C in a N_2 stream for 1 h, and then it was placed in a flask containing 100 ml of a toluene solution of 3-anilinopropyltrimethoxysilane (AnPS) (1.175 mol dm^{-3}). The modification was carried out under a reflux of toluene for 2 h, according to the literature [7]. After that, the SiO_2 carrier was washed repeatedly with diethyl ether and methanol and was dried at 110°C for 0.5 h in a dry box. For comparison, the SiO_2 carrier was similarly modified with other silane agents such as 3-aminopropyltrimethoxysilane (APS) and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DAPS). The samples thus obtained are abbreviated below as AnPS-, APS-, and DAPS-SiO_2, respectively.

Phosphotetradecavanadate anion ($H_nPV_{14}O_{42}^{(9-n)-}$; PV14) was prepared according to the literature [8] as follows: 85% H_3PO_4 and a given NH_4VO_3 solution were mixed at an atomic ratio (V)/(P) of 4.0. After the pH of the solution was adjusted exactly to 2.0 with 1 N HNO_3 solution, a guanidine hydrochloride solution was added dropwise to the solution with stirring to obtain a reddish-brown precipitate of the guanidium phosphotetradecavanadate (guanid-PV14). ICP analysis of the precipitate showed that the atomic ratio (V)/(P) was equal to ca. 14. Upon preparation of the PV14 catalyst deposited on the AnPS-modified SiO_2, the usual equilibrium adsorption method was adopted; AnPS-SiO_2 was

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immersed into the H_3PO_4–NH_4VO_3 solution, (V)/(P) = 4.0, the pH of which had been adjusted exactly to 2.0. The initial concentration was evaluated to be 8.0×10^{-3} mol dm^{-3} as PV14. After the adsorption at 25°C for 2 h, the samples were filtered and dried at 110°C for 1 h. For comparison, the adsorption procedures were also carried out in other pH regions such as 4.0 and 7.0. The samples thus obtained were abbreviated as PV(2), PV(4), and PV(7)/AnPS-SiO_2, respectively. Isovanadates, the initial concentration of which was 12.57×10^{-2} mol dm^{-3} as NH_4VO_3, were also adsorbed similarly at pH = 2.0 on the modified SiO_2; the sample is abbreviated as V(2)/AnPS-SiO_2. The SiO_2-supported PW12 and PMo12 catalysts were similarly prepared as follows: $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ which were synthesized according to the literature [9] were also dispersed on the carrier from a solution having a regulated concentration (0.69×10^{-3} mol dm^{-3}) by the equilibrium adsorption method.

Measurement of the adsorption isotherms of PV14 on the unmodified and modified SiO_2 was attempted at pH = 2.0 in the concentration range of (0.016–1.70) $\times 10^{-2}$ mol dm^{-3}. The concentration and the adsorbed amounts of PV14 were determined by UV spectrophotometry, as described in the next section.

2.2. Analysis

The UV spectrum of the PV14 solution was measured over the range of 210–350 nm on a Shimadzu UV spectrometer model UV-120-02. The absorbance at 260 nm was previously calibrated as a function of the concentration. The adsorbed amounts of PV14 on the carrier were estimated from the difference between the absorbances before and after the adsorption procedures using the calibration curve. The atomic ratios (V)/(P) in the solutions of the phosphovanadate variously prepared were determined by ICP analyses. The apparatus used was a Shimadzu model ICPS-1000III. The FT-IR spectra of AnPS-SiO_2 and PV/AnPS-SiO_2 were measured on an FT-IR apparatus, Parkin-Elmer model 1760X, equipped with a diffuse reflectance attachment (Spectra-Teck Inc.). The sample was diluted with a finely divided KBr powder at a concentration of ca. 10 wt%. The spectrum was recorded over the range of 450–4000 cm^{-1} with 30 scans and then corrected using the Kubelka–Munk equation. ESR measurements were carried out at 25°C on a JEOL model JES-TE200 spectrometer (X-band, 9.4 GHz and 0.1 mT modulation). The samples were packed into quartz tubes (inner diameter, 3 mm) for the measurements. The tubes were sealed after evacuation below 10^{-3} Torr at 25°C. The V(IV) spin concentrations on the PV/AnPS-SiO_2 samples were determined by comparison with the ESR intensity of a given amount of V(IV)OSO_4 deposited on SiO_2. A diluted Mn(II) sample was also used as an internal standard.

2.3. Reaction

The oxidation of methanol was used as a test reaction in a continuous-flow fixed-bed microreactor at 200–300°C. 40 mg of the catalyst which was previously calcined at 300°C was held in a reactor (a Pyrex tube, with an inner diameter of 6 mm; the sample is placed between two layers of quartz wool). The reactant feed was usually a mixture of methanol, oxygen, and nitrogen in the ratio (%) 11/18/71. This mixture was obtained by passing a N_2/O_2 flow through a methanol saturator maintained at 11°C. When the effects of the CH_3OH and O_2 pressures on the catalytic activity were measured, the mixing ratios (partial pressures) were varied in the ranges of P_{CH_3OH}: 4–15% and P_{O_2}: 5–40%. The gas flow rate was usually kept at 30 ml min^{-1}. Gas chromatographic analysis was used to determine the composition of the feed before or after the reactor. The steady state was attained usually at about 1.5 h after the reagent mixture was admitted to the catalyst, and then catalytic measurements were performed.

3. Results and discussion

3.1. Deposited states of phosphovanadates on the AnPS-modified SiO_2

The FT-IR characteristic bands for the anilino group of the modified-SiO_2 surface were recognized at 1510 and 1605 cm^{-1}. The degree of the modification was estimated as ca. 8% of the monolayer according to the intensities of the 1605 cm^{-1} band divided by the siloxane bands at 1090 cm^{-1}, $I(1605)/I(1090)$, as described in the previous paper [6c]. Phosphovanadate was precipitated as a guanidine salt and adsorbed on the AnPS-modified SiO_2 at various pHs. The atomic ratios (V)/(P) of those samples were determined by ICP analysis, as summarized in table 1. This result certainly indicates that the phosphovanadate can be adsorbed on the modified SiO_2 in the state of PV14 similar to the case of the guanidine salt, when the pH was exactly controlled at 2.0 [8]. The phosphovanadate might be adsorbed on the surface in some degraded states such as PV8 and PV4 at the other pHs 4 and 7, respectively.

Adsorption isotherms of PV14 on the unmodified and modified SiO_2 were measured as described in the

Table 1
The atomic ratios (V)/(P) of guanid-PV14 and phosphovanadates adsorbed on AnPS-SiO_2 at various pHs (2.0, 4.0, and 7.0)

Sample	(V)/(P)
guanid-PV14	14.8
PV(2)/AnPS(3)-SiO_2	14.8
PV(4)/AnPS(3)-SiO_2	8.0
PV(7)/AnPS(3)-SiO_2	4.0

experimental section. The results are summarized in table 2. The final point of the adsorption corresponds to a coverage of ca. 0.44 on AnPS-SiO_2. On the other hand, the adsorbed amounts could not be determined on the unmodified SiO_2 because of the slight change in the concentration with adsorption; that is, very little adsorption occurred on the unmodified SiO_2. Upon the evaluation of the surface coverage, (a) PV14 was assumed to be formed quantitatively from the H_3PO_4–NH_4VO_3 solution at pH = 2.0, (b) 1.8 nm^2 was adopted as the molecular cross-sectional area of the PV14 unit, although 1.44 nm^2 had been assumed as the cross-sectional area of the PW12 Keggin unit by Haber et al. [4], and (c) 248 m^2 g^{-1} was adopted as the BET surface area of AnPS-SiO_2 as was previously determined.

The ESR spectra for the PV(2)/AnPS-SiO_2 sample, the coverage of which was 0.33, showed a clear and intense signal which has been assigned to a quite isolated V(IV) ion [10], while no signal was detected in the PV(2)/SiO_2 sample, as compared in figs. 1a and 1b. The shape of the signal of the sample does not vary much by the heat treatment at 300°C in air and in the mixed gas of CH_3OH, O_2, and N_2 (a ratio of 11 / 18 / 71 (%)) as shown in figs. 1c and 1d, except for the central parts. The results suggest that the states of the PV14 catalyst are not subject to great change even after the heat treatment and the reaction at 300°C.

The V(IV) spin concentration of PV(2)/AnPS-SiO_2 (a1–a4) was estimated as summarized in the last column of table 2. It is noted that the V(IV) spin concentration approximately correlates with the PV14 loading, when PV14 was deposited by the equilibrium adsorption method on the AnPS-modified SiO_2. The V(IV) ion is expected to be caused by the direct interaction of PV14 with the functional group of AnPS. It was quite difficult to investigate the deposited states of PV14 on the modified surface by FT-IR because the characteristic band for PV14 was greatly interrupted by overlapping of the large Si–O–Si bands of the SiO_2 carrier (900–1200 cm^{-1}). The characteristic bands of AnPS were greatly deformed upon deposition of PV14, suggesting interaction with PV14.

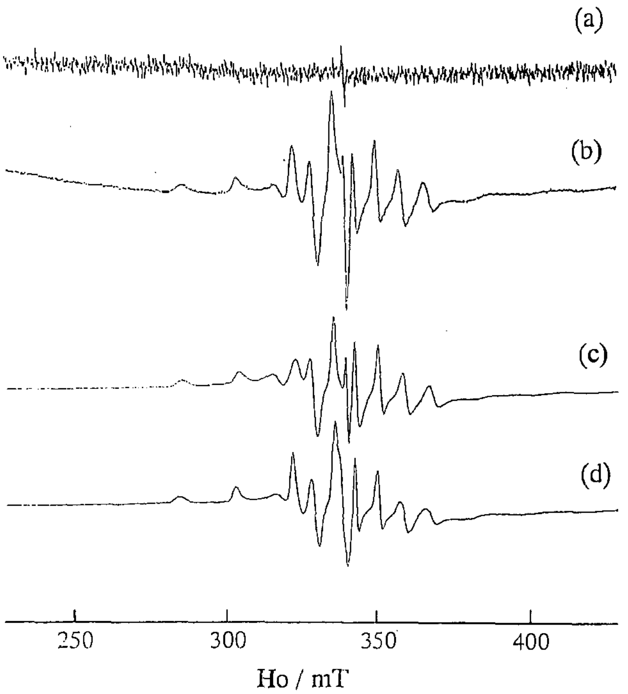

Fig. 1. ESR spectra of phosphovanadate (at pH = 2.0) adsorbed on SiO_2 and the AnPS-SiO_2 at 25°C and its changes with heat treatments: (a) PV(2)/SiO_2, (b) PV(2)/AnPS-SiO_2, (c) after heat treatment (b) in air at 300°C for 0.5 h, (d) after heat treatment (c) under a reacting gas mixture ($CH_3OH/O_2/N_2$ = 11/18/71) at 300°C for 1 h.

3.2. Catalytic activities of phosphovanadates dispersed on SiO_2 and AnPS-SiO_2 for methanol oxidation

Activities of the PV(2), (4), and (7)/AnPS-SiO_2 catalysts for methanol oxidation were preliminarily investigated. The results are summarized in table 3. The reaction on PV(2)/AnPS-SiO_2 results in a selectivity for HCHO as high as 97% in a high conversion (30%). In the PV(4) and PV(7)/AnPS-SiO_2 samples, both the conversion and selectivity became rather low. This might be related to the decrease in the atomic ratio (V)/(P) (table 1) without any explanation at present. On the other hand, in V(2)/AnPS-SiO_2 a quite high conversion such as 75% is obtained at 300°C, although the activity is in fact considerably suppressed at 260°C without a change in the HCHO selectivity, as shown in the parentheses (run 4). A selectivity for CH_3OCH_3 such as 24% suggests that acidic sites remain to a certain extent on the vanadium oxide catalyst fixed on the AnPS-modified SiO_2. A coagulated species such as $HV_{10}O_{28}^{n-}$ [11], for instance, would be suggested to activate methanol molecules on the modified surface. With V(2)/SiO_2, the conversion

Table 2
Adsorption isotherm data for phosphovanadate on AnPS-SiO_2 at pH = 2.0 at 25°C for 2 h, the PV14 loading, and the V(IV) spin concentration

Sample	Initial concn. (10^{-2} mol dm^{-3})	Final concn. (10^{-2} mol dm^{-3})	PV14 loading (10^{-5} mol g-carrier^{-1})	Coverage θ	V(IV) spin concentration (10^{-5} mol g-carrier^{-1})
PV(2)/AnPS-SiO_2(a1)	0.016	0.001	0.14	0.01	–
PV(2)/AnPS-SiO_2(a2)	0.167	0.015	1.5	0.07	3.4
PV(2)/AnPS-SiO_2(a3)	0.838	0.046	7.9	0.35	19.3
PV(2)/AnPS-SiO_2(a4)	1.714	0.715	10.0	0.44	22.0

Table 3
Comparisons of the catalytic properties for methanol oxidation at 300°C among isovanadate and phosphovanadates deposited variously on SiO_2 and AnPS-SiO_2

Run No.	Catalysts	CH_3OH conversion (%)	Selectivity (%)				
			HCHO	CH_3OCH_3	$HCOOCH_3$	CO_2	CO
1	PV(2)/AnPS-SiO_2	30	97	3	–	–	–
2	PV(4)/AnPS-SiO_2	13	73	–	14	–	13
3	PV(7)/AnPS-SiO_2	23	67	–	3	–	30
4	V(2)/AnPS-SiO_2	75 (24) [a]	74 (73)	9 (24)	– (3)	–	17 (0)
5	V(2)/SiO_2	7	11	–	62	27	–

[a] The values in parentheses denote those at 260°C.

and the HCHO selectivity are greatly diminished (run 5). This might be caused by some degradation of the vanadium oxide by direct interaction with the SiO_2 surface in addition to poor deposition. We now briefly point out without further discussion [12–14] that a highly active vanadium oxide catalyst can be effectively prepared when isovanadate ion is adsorbed on the AnPS-modified SiO_2 at a pH regulated exactly at 2.0.

For comparison, the effects of the AnPS modification on the catalytic feature of the SiO_2-supported PW12 and PMo12 catalysts were also examined, as shown in table 4. The CH_3OCH_3 product is produced on the PW12 powders, suggesting that it proceeds on acidic site [15]. In the case of PW12/AnPS-SiO_2, the acidic process is greatly suppressed, but after calcination at 500°C it nearly recovers (runs 2 and 3). On the PMo12 powders the HCHO and CH_3OCH_3 products are yielded at 55 and 45%, respectively, suggesting that the reaction proceeds evenly on the redox and acidic sites [16]. On PMo12/AnPS-SiO_2, a rather high conversion is recognized in contrast with the PW12 catalyst (runs 4 and 5). The situation seems to be complicated in the PMo12 catalyst system [16] so that we will not discuss further the effects of the modification.

SiO_2 itself shows a slight activity for methanol oxidation at 300°C while the AnPS-SiO_2 carrier does not (runs 6 and 7). The PV(2)/SiO_2 catalyst gives only a low yield of HCHO but rather high yields of further reaction products such as $HCOOCH_3$, CO, and CO_2, while guanid-PV14 gives only HCHO (runs 8 and 9). This suggests that the catalytic feature of SiO_2 itself appears preferentially because of a very low concentration of the phosphovanadates and/or a degraded structure of PV14. On PV(2)/AnPS-SiO_2, in contrast with this, the activity is greatly increased but the intrinsic property of PV14 [17] is completely retained (run 1 in table 3). This result suggests that the PV14 species is dispersed on the modified surface with retaining the structure through interaction with the functional group of AnPS, and at the same time, the acidic site on PV14 is adequately controlled similar to the case of guanid-PV14. Similar results are obtained on the PV(2)/APS-SiO_2 and DAPS-SiO_2 catalysts, although they are less selective for HCHO (runs 10 and 11).

Table 4
Comparisons of the catalytic properties for methanol oxidation among the AnPS-modified SiO_2-supported PW12, PMo12, and PV14 and the effects of the modification on the catalytic features [a]

Run No.	Catalysts	CH_3OH conversion (%)	Selectivity (%)				
			HCHO	CH_3OCH_3	$HCOOCH_3$	CO_2	CO
1	$H_3PW_{12}O_{40}$ (PW12) powders (40 mg)	45	–	100	–	–	–
2	PW12/AnPS-SiO_2	4	–	100	–	–	–
3	PW12/AnPS-SiO_2 calc. at 500°C	36	2	98	–	–	–
4	$H_3PMo_{12}O_{40}(PMo_{12})$ powder (20 mg)	4	55	45	–	–	–
5	PMo12/AnPS-SiO_2	36	37	18	27	3	15
6	SiO_2	5	32	–	51	17	–
7	AnPS-SiO_2	0	–	–	–	–	–
8	guanid-PV14 powders (2.1 mg)	4	100	–	–	–	–
9	PV(2)/SiO_2	14	33	–	43	8	16
10	PV(2)/APS-SiO_2	37	89	11	–	–	–
11	PV(2)/DAPS-SiO_2	35	89	11	–	–	–

[a] The reaction was carried out in runs 1–5 at 260°C and runs 6–11 at 300°C.

The kinetic parameters for methanol oxidation on PV(2)/AnPS-SiO_2 were examined based on the conversion under a high selectivity for HCHO of more than 90% as follows. The reaction order (m) for O_2 was determined at 300°C to be $m = 1.0$ in the range of 5–18% and $m = 0$ for 18–40%. The reaction order (n) for CH_3OH was $n = 0$ in the range of 4–15%. The apparent activation energy (E_a) was obtained as $E_a = 92\ \mathrm{kJ\ mol^{-1}}$ in the temperature range of 240–300°C under $P_{O_2} = 18\%$ and $P_{CH_3OH} = 11\%$. Thus, in this study, the reaction is known to proceed as usual under conditions such that the reacting sites on the PV14 catalysts are fully saturated with both reactants.

The present results are summarized as follows: (a) the surface concentration of the PV14 species approximately correlated with the V(IV) spin concentration and (b) the intrinsic redox property of guanid-PV14 was retained on the carrier surfaces previously modified with the silane agents. Therefore, it is concluded that only the redox property is quite favorably exhibited but the acidic property is adequately restricted through interaction with the amino group on the PV14/AnPS-SiO_2 catalyst. Thus an excellent catalyst is reasonably prepared by application of the pre-modification of carriers with silane agents.

However, a detailed model of the interaction between PV14 and the modified surface remains in the future. Various reaction mechanisms for methanol oxidation on PW12 [15], PMo12 [16], and vanadium oxides [12] have been proposed. On PV(2)/AnPS-SiO_2, a mechanism in which a terminal V=O group plays an important role [12] seems to be applied rather favorably, but its details also remain to be investigated in the future.

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