Bull. Chem. Soc. Jpn., *63*, *2076—2082 (1990)* [Vol. 63, No. 7

Studies of the Acidity and Ionic Conductivity of Silica-Supported Heteropoly Compounds. III. Paramagnetic Species Involved in the Dehydration Reaction on Supported 12-Molybdophosphoric Acid and Its Salts

Reiji Ohtsuka and Jun-ichi Kobayashi*
Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Johoku, Hamamatsu 432

(Received December 18, 1989)

ESR studies on the dehydration reaction of *t*-butyl alcohol have been carried out while trying to characterize 12-molybdophosphoroc acid ($H_3PMo_{12}O_{40}$) and its salts supported on silica. In $H_3PMo_{12}O_{40}$ supported on silica ESR spectra showed three signals due to molybdenum(V) with three different surroundings: at the interface near the silica support, at the outer surface of the $H_3PMo_{12}O_{40}$ layer and in the bulk of $H_3PMo_{12}O_{40}$. For $K_3PMo_{12}O_{40}$ supported on silica, crystalline $K_3PMo_{12}O_{40}$ is formed on silica, even at low loadings. The ESR spectra of partially potassium-substituted catalysts is also examined.

We have clarified the dehydration mechanisms of liquid and gaseous *t*-butyl alcohol (TBA) in the presence of heteropoly compounds (HPC) such as $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, and their sodium, potassium, cesium, ammonium, and bismuth oxide salts supported on silica;[1,2] the dehydration of liquid and gaseous TBA proceed through pseudo-liquid and outer-surface mechanisms, respectively.[1] Also, a linear relationship has been established between the catalytic activity and acidity function.[2] At higher loadings of HPC, it is found that the way of stacking HPC molecules on silica is a prominent factor regarding catalytic activity.[1,2]

In the present study, therefore, we have applied electron spin resonance (ESR) spectroscopy to the characterization of $H_3PMo_{12}O_{40}$ and their potassium salts supported on silica in order to elucidate the structural difference among them. Also, the change in the ESR spectra of the catalysts used for the dehydration of TBA is discussed in connection with the reaction mechanisms of TBA.

Experimental

Supported HPC catalysts on AEROSIL-200 (abbreviated SiO_2-200) containing polyanion $PMo_{12}O_{40}^{3-}$, such as H_3PMo/SiO_2-200 and $K_nH_{3-n}PMo/SiO_2$-200, were prepared by the same procedure as described previously,[1] in which H_3PMo and $K_nH_{3-n}PMo$ stand for $H_3PM_{12}O_{40}$ and $K_nH_{3-n}PMo_{12}O_{40}$, respectively, and *n* denotes the number of substituted hydrogen-ions.

Dehydration of *t*-Butyl Alcohol. The dehydration of liquid and gaseous TBA was carried out in a batch system at 355.3 K and in a flow-system at 413—513 K, respectively. Details of the procedure were given in a previous paper.[1]

ESR Measurement. The samples for ESR measurements were prepared as follows: As-prepared catalysts were calcined at 573 K for 3 h in air. Partially reduced catalysts were prepared, followed by reduction under a hydrogen stream of 30 $cm^3\,min^{-1}$ at 373 K. After the dehydration reaction of liquid TBA, the catalysts were dried at 383 K for 24 h in air before measurements.

The ESR spectra were recorded on a JEOL JES-FE-1XG spectrometer either at 77 or 293 K, operating in the X-band (9. 130±0.003 GHz). Mn^{2+} doped in MgO and ECHO EFM-2000 NMR field meter were used for calibrating the magnetic field.

The observed spectra were doubly integrated using a Graphtec DT-1000 digitizer in order to estimate the relative spin concentration of molybdenum(V) Σ (g^{-1} or g-supt^{-1}).[3,4] Some of the observed spectra were simulated with the aid of a NEC PC-98XL personal computer using a TURBO PASCAL program in order to deconvoluve the signals.[5-7]

X-Ray Diffractometry. Powder X-ray diffraction data (XRD) were obtained with a Rigaku-Denki Model D-3F diffractometer using nickel-filtered Cu*K*α radiation.

Results and Discussion

ESR Spectra for Support-Free $H_3PMo_{12}O_{40}$. The ESR spectrum of as-received $H_3PMo_{12}O_{40}\cdot 29H_2O$ recorded at 77 K shows only a sharp symmetrical signal (abbreviated as signal Mo-1) at 333 mT (spectrum B in Fig. 1). According to Fricke and Öhlmann,[8] the narrow signal is one characteristic of strongly delocalized electrons; thus, electron hopping occurs amoung the twelve molybdenum atoms of the Keggin anion.

After heat treating at 573 K a signal with axial symmetry (abbreviated signal Mo-2) appears at 332 mT in the ESR spectrum at 77 and 293 K (spectrum C in Fig. 1). The axial symmetry of the signal indicates that an electron is localized on a molybdenum atom.[8] Since support-free $H_3PMo_{12}O_{40}$ is almost completely dehydrated to form an anhydrous type at 573 K, the mobility of electrons in solid $H_3PMo_{12}O_{40}$ is drastically reduced above the temperature. It is, therefore, reasonable that anhydrous $H_3PMo_{12}O_{40}$ gives a signal with axial symmetry.

ESR Spectra for As-Prepared H_3PMo/SiO_2-200. In the ESR spectrum of as-prepared H_3PMo/SiO_2-200 at 77 K the signals assigned to two different kinds of molybdenum(V) appear at 335.5 and 330 mT, respectively (spectra A and B in Fig. 2), and their relative intensity varies slightly with the amount of $H_3PMo_{12}O_{40}$ supported. Both signals at 335.5 and

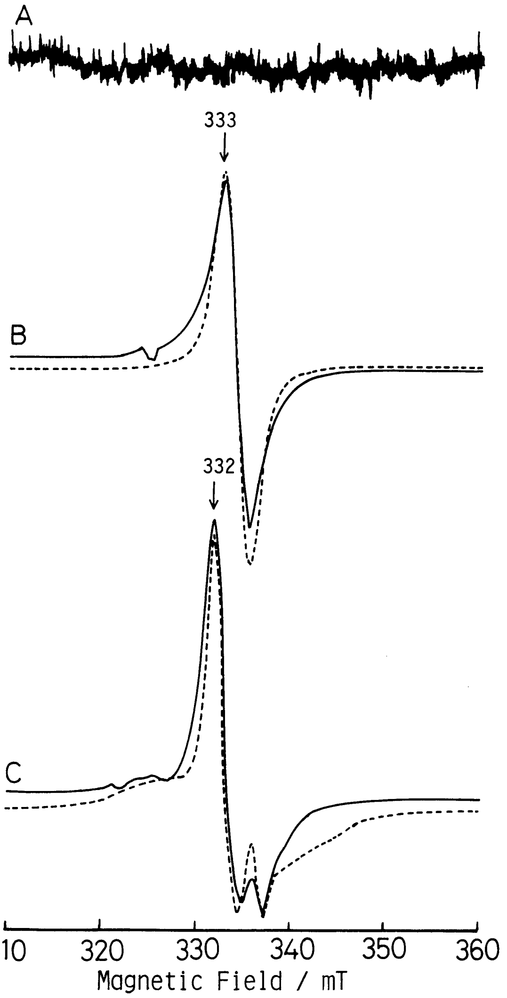

Fig. 1. ESR spectra of the as-received $H_3PMo_{12}O_{40}\cdot 29H_2O$ recorded at various temperature; A: 293 K, B: 77 K, and C: that of the support-free anhydrous $H_3PMo_{12}O_{40}$ calcined at 573 K recorded at 77 K. (Broken lines show the calculated curves).

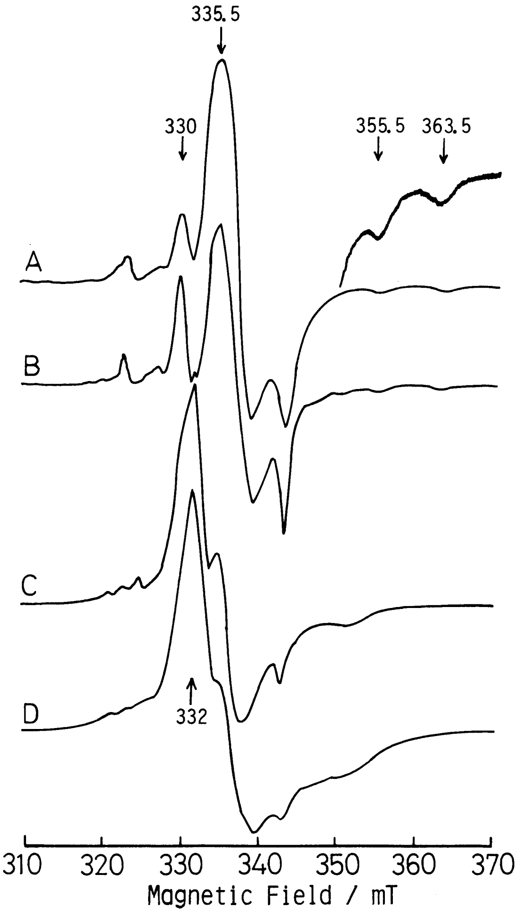

Fig. 2. ESR spectra of the as-prepared H_3PMo/SiO_2-200 with various loadings of $H_3PMo_{12}O_{40}$; A: $m=0.05$, B: $m=1.00$ mmol g-supt^{-1} H_3PMo/SiO_2-200, and that of 1.00 mmol g-supt^{-1} H_3PMo/SiO_2-200 reduced under hydrogen stream at various temperature; C: 373 K, D: 423 K.

330 mT (abbreviated Mo-3 and Mo-4, respectively) show axial symmetry. At $m=0.05$—1.00 (m is the amount of $H_3PMo_{12}O_{40}$ supported on SiO_2-200 (mmol g-supt^{-1})) the relative intensity ratio of signal Mo-4 to signal Mo-3 is in the range 0.18—0.38.

In Fig. 2 it can be noticed that signals Mo-3 and Mo-4 overlap around 345 mT (Fig. 9 and 10). Moreover, additional lines at 355.5 and 363.5 mT are observed. Since the intensities of the lines are proportional to that at 330 mT (Fig. 3), they are assigned to a hfs of $m_I=3/2$ and $5/2$ of molybdenum(V) and belong to a signal Mo-4. Assuming axial symmetry for all signals which appeared, a computer simulation was carried out to estimate the ESR parameters for the respective molybdenum(V) atoms. The obtained results are summarized in Table 1.

Although twelve molybdenum atoms in a Keggin structural unit are equivalent to each other, the spectra in Fig. 2 indicates that there are two different surroundings for molybdenum(V) in $H_3PMo_{12}O_{40}$ supported on silica. With respect to the assignment of signals Mo-3 and Mo-4, it is noteworthy that the surface area of the supported catalysts is larger than that of the support-free ones by a factor of 100.[10] For this reason, signal Mo-3 has been assigned to molybdenum(V) of $H_3PMo_{12}O_{40}$ on the surface.

Reduction of H_3PMo/SiO_2-200. Again, in Fig. 2 it is found that the reduction of 1.00 mmol g-supt^{-1} H_3PMo/SiO_2-200 at 373 and 423 K gives signals Mo-2 and Mo-5, respectively, in addition to signals Mo-3 and Mo-4. For the new signal, Mo-5, with a broad line, similar signals were observed in the spectra of strongly reduced $H_3PMo_{12}O_{40}$.[11] It is, therefore, implied that the broad signal is attributed to a spin-spin interaction among molybdenum(V) ions,[9] since it has been proposed that the Keggin structural framework is collapsed owing to a loss of bridging oxygen at 423 K. This leads to spin–spin interaction of

Table 1. Critical ESR Parameters and the Assignments for the Respective Signals of Heteropoly Compounds

Signal	Resonance field[a)] mT	$g_{/\!/}$	$g_\perp$	Δg	$A_{/\!/}$ mT	$A_\perp$ mT	ΔH[b)] mT	Assignment and reference
Mo-1	333	1.955[e)]		0.000	—	—	1.6	The support-free $H_3PMo_{12}O_{40}\cdot 29H_2O$ and K_3PMo/SiO_2-200
Mo-2	332	1.950	1.955	0.005	4.0	1.2	3.0[f)]	The support-free anhydrous $H_3PMo_{12}O_{40}$ $H_3PMo_{12}O_{40}$ in bulk layer of H_3PMo/SiO_2-200
Mo-3	335.5	1.915	1.935	0.020	5.0	0.8	4.0[f)]	$H_3PMo_{12}O_{40}$ at the outer surface of H_3PMo/SiO_2-200
Mo-4	330, 355.5,[d)] 363.5[d)]	1.904	1.970	0.066	8.5	0.3	2.3[f)]	$H_3PMo_{12}O_{40}$ at the interface near silica support
Mo-5[c)]	—	—	—	—	—	—	—	$H_3PMo_{12}O_{40}$ destructed by H_2 reduction (broad signal)

a) The most characteristic resonance peak in the signal is listed as a resonance field referred in the text and figures. b) ΔH is the full half width of Lorentz function. c) ESR parameters could not be determined. d) These weak resonance correspond to ^{95,97}Mo hfs of $m_I=3/2$ and $5/2$ respectively. e) Isotropic g-value. f) These values are the mean for the value of ΔH at each nuclear spin quantum number m_I.

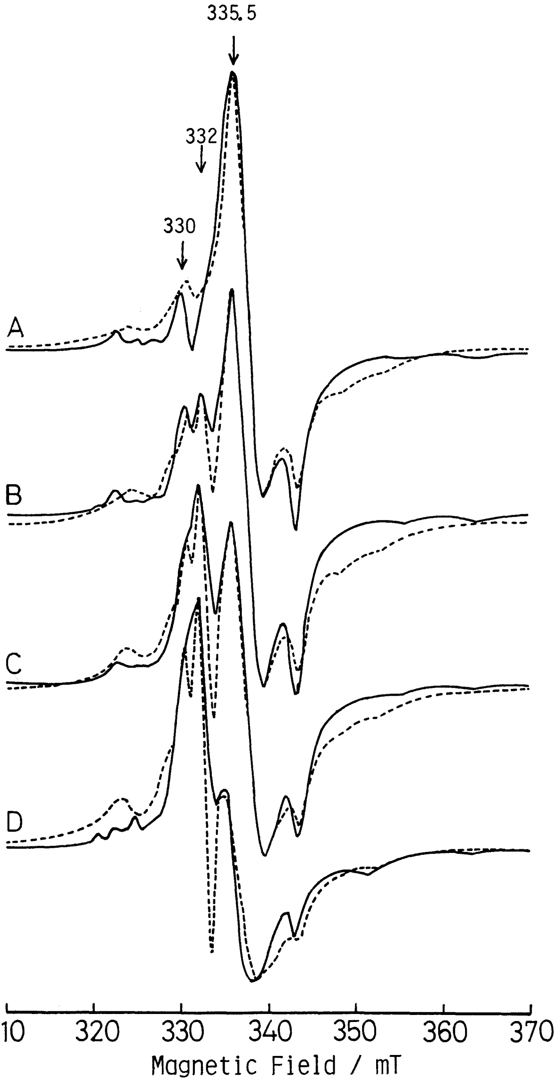

Fig. 3. Effect of the amount of $H_3PMo_{12}O_{40}$ supported on the ESR spectra of the reduced H_3PMo/SiO_2-200; A: m=0.15, B: m=0.40, C: m=0.70, D: m=1.00 mmol g-supt^{-1} H_3PMo/SiO_2-200. (Broken lines show the calculated curves).

molybdenum(V) atoms,[11,12)] supported by the fact that the intensity ratio of signal Mo-3 to Mo-4 decreases with increasing reduction temperature.

Effect of the Amount of $H_3PMo_{12}O_{40}$ Supported. Figure 3 shows the ESR spectral change of H_3PMo/SiO_2-200 reduced at 373 K with the amount of $H_3PMo_{12}O_{40}$ supported. The relative spin concentration, Σ, for reduced H_3PMo/SiO_2-200 is larger than that for the as-prepared one by a factor of more than 20. As can be seen from Fig. 3, a marked change in the ESR spectral pattern was observed upon increasing the amount of $H_3PMo_{12}O_{40}$ supported: At a low loading of $H_3PMo_{12}O_{40}$ their spectra were the same as those of the as-prepared H_3PMo/SiO_2-200, while at higher loadings signal Mo-2 appears in addition to two other signals, Mo-3 and Mo-4. Particularly, it is remarkable that signal Mo-2 is observed only at loadings higher than the monolayer thickness of $H_3PMo_{12}O_{40}$ on silica. It is supposed that there are three different $H_3PMo_{12}O_{40}$ groups in H_3PMo/SiO_2-200; one is at the interface near the silica support, one at the outer surface of the $H_3PMo_{12}O_{40}$ layer supported and others in bulk $H_3PMo_{12}O_{40}$ layers. The bulk layer is only formed under higher loadings. It is, therefore, presumed that signals Mo-2 and Mo-4 can be assigned to the $H_3PMo_{12}O_{40}$ in the bulk layer and at the interface, respectively.

Also, a spectral simulation gives the ESR parameters and the relative spin concentration, Σ. In Fig. 4 the overall value of Σ for reduced H_3PMo/SiO_2-200 is plotted against the $H_3PMo_{12}O_{40}$ content in the catalyst, together with those calculated for the respective values of Σ. As can be seen from Fig. 4a, a linear relationship between the overall value of Σ for the observed spectra and the content of $H_3PMo_{12}O_{40}$ (wt%) are quantitatively established.

For plots of the values of Σ_2, Σ_3, and Σ_4 for signals Mo-2, Mo-3, and Mo-4 in the ESR spectra of reduced H_3PMo/SiO_2-200, respectively, against the amount of

$H_3PMo_{12}O_{40}$, the value of Σ_3 increases linearly upon increasing the amount of $H_3PMo_{12}O_{40}$ supported at low loading less than $m=0.30$ and then approaches a plateau. On the other hand, the values of Σ_4 and Σ_2 increase with the amount of $H_3PMo_{12}O_{40}$ supported at higher loading than $m=0.3$ and 0.6, respectively.

For the formation of the first or second monolayer of $H_3PMo_{12}O_{40}$ on the surface of the silica support, critical values of $m=0.30$ or $m=0.60$ can be worked out, respectively, using the effective cross section per $H_3PMo_{12}O_{40}$ molecule.[1] These values agree with the experimental ones shown in Fig. 4 b, supporting that the assignments of signals Mo-2 and Mo-4 as being reasonable. This also corresponds to the dependence of the catalytic activity on the amount of $H_3PMo_{12}O_{40}$ supported.[1] Taking into consideration the fact that $H_3PMo_{12}O_{40}$ groups stack upon themselves, it is supported that signal Mo-3 can be assigned to $H_3PMo_{12}O_{40}$ at the outer surface.

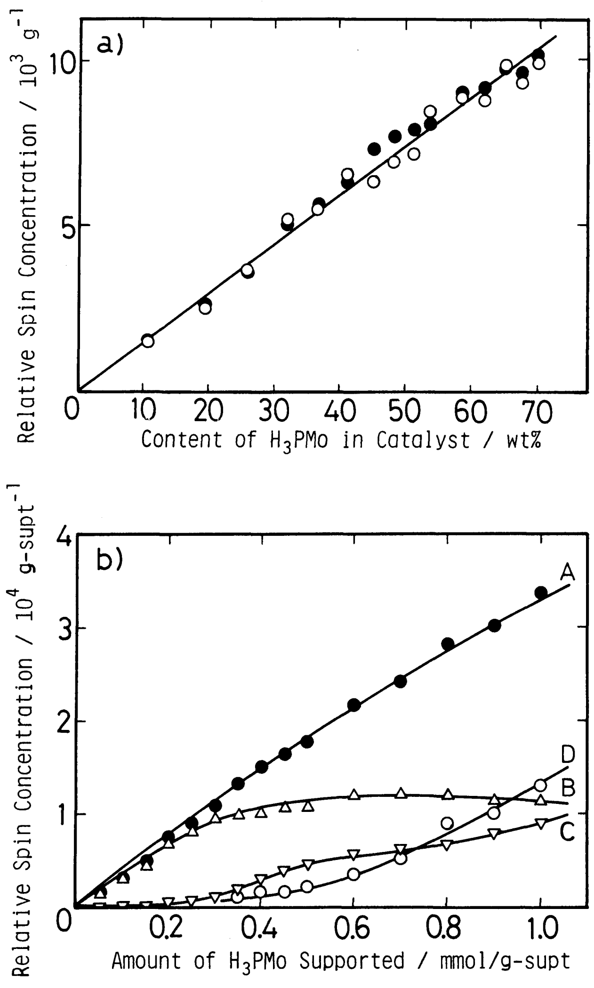

Fig. 4. The plots of the relative spin concentration against a) the content of $H_3PMo_{12}O_{40}$ in catalyst and b) the amount of $H_3PMo_{12}O_{40}$ supported; a) overall values of Σ for the observed spectra (○) and the calculated lines (●); b) A: overall value of Σ, B: Σ_3, C: Σ_4, D: Σ_2.

Interestingly, signals Mo-2 and Mo-4 are observed even under low loading of $H_3PMo_{12}O_{40}$. It is, therefore, presumed that $H_3PMo_{12}O_{40}$ molecules aggregate during on earlier stage of loading owing to the network formation of $H_3PMo_{12}O_{40}$ and/or the stacking of $H_3PMo_{12}O_{40}$ on themselves, as discussed later in terms of the XRD results. Figure 5 shows schematic illustrations of the stacking method.

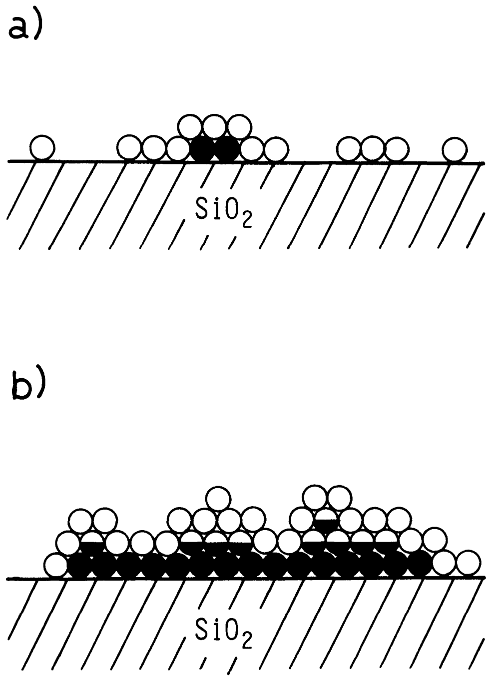

Fig. 5. The schematic illustration for the way of stacking of $H_3PMo_{12}O_{40}$; a) at low loading of $H_3PMo_{12}O_{40}$ and b) at higher loadings; ○, ●, and ◓ indicate the $H_3PMo_{12}O_{40}$ molecules giving signals Mo-3, Mo-4, and Mo-2 respectively.

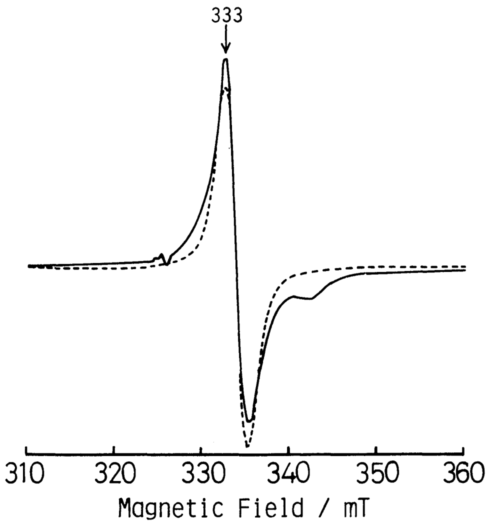

Fig. 6. ESR spectrum of the reduced K_3PMo/SiO_2-200 of 0.05 mmol g-supt^{-1}. (Broken line shows the calculated line).

Potassium-Substituted HPC Supported on Silica. In Fig. 6, a representative ESR spectrum for K_3PMo/SiO_2-200 is shown. In the ESR spectrum of as-prepared K_3PMo/SiO_2-200 only a sharp symmerical signal with a full half width of 1.6 mT was observed at 333 mT. A computer simulation for this signal gave a g-value of 1.955, the same as signal Mo-1 in support-free $H_3PMo_{12}O_{40}\cdot 29H_2O$. The spectral pattern is independent of the amount of $K_3PMo_{12}O_{40}$ supported, and does not change after a reduction of the catalysts. It is also presumed that the aggregation of HPC molecules takes place significantly during the early stage of $K_3PMo_{12}O_{40}$ deposition on silica.

This presumption was proved by X-ray diffractometry (XRD): The diffraction lines due to the cubic lattice of $K_3PMo_{12}O_{40}$ appear even at low loading of $K_3PMo_{12}O_{40}$ (less than m=0.30, the critical amount for the formation of a monolayer). $H_3PMo_{12}O_{40}$, however, does not give any diffraction line under the same loading (Fig. 7). It is, thus, concluded that crystalline $K_3PMo_{12}O_{40}$ is formed on silica, even under the low loadings.

Figure 8 shows the ESR spectra of potassium-substituted catalysts reduced at 373 K. For a KH_2PMo/SiO_2-200 catalyst, the obtained resonance comprises signals Mo-1, Mo-3, and Mo-4; their relative intensity is independent of the amount of HPC loaded. For a K_2HPMo/SiO_2 catalyst, on the other hand, a marked change in the relative intensity was observed with the amount of HPC supported: At low HPC loading,

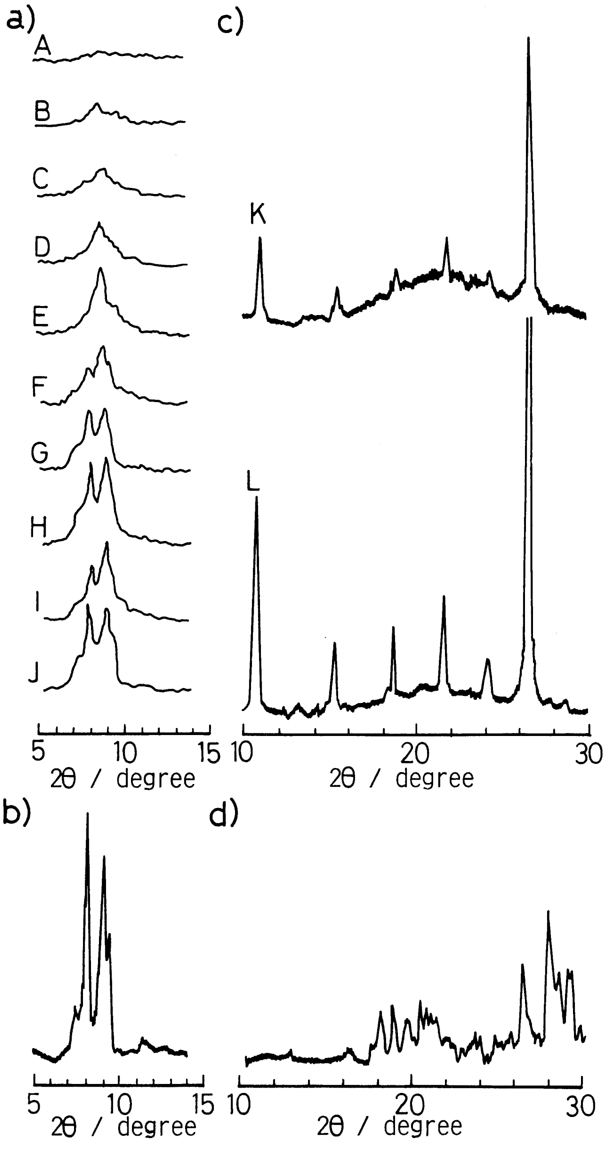

Fig. 7. Powder X-ray diffraction pattern of a) H_3PMo/SiO_2-200 with various loadings of $H_3PMo_{12}O_{40}$; A: m=0.10, B: m=0.20, C: m=0.30, D: m=0.40, E: m=0.50, F: m=0.60, G: m=0.70, H: m=0.80, I: m=0.90, J: m=1.00 mmol g-supt^{-1} H_3PMo/SiO_2-200, b) the support-free anhydrous $H_3PMo_{12}O_{40}$, c) K_3PMo/SiO_2-200 with various loadings of $K_3PMo_{12}O_{40}$; K: m=0.10, L: m=0.30 mmol g-supt^{-1} K_3PMo/SiO_2-200 and d) the as-received $H_3PMo_{12}O_{40}\cdot 29H_2O$.

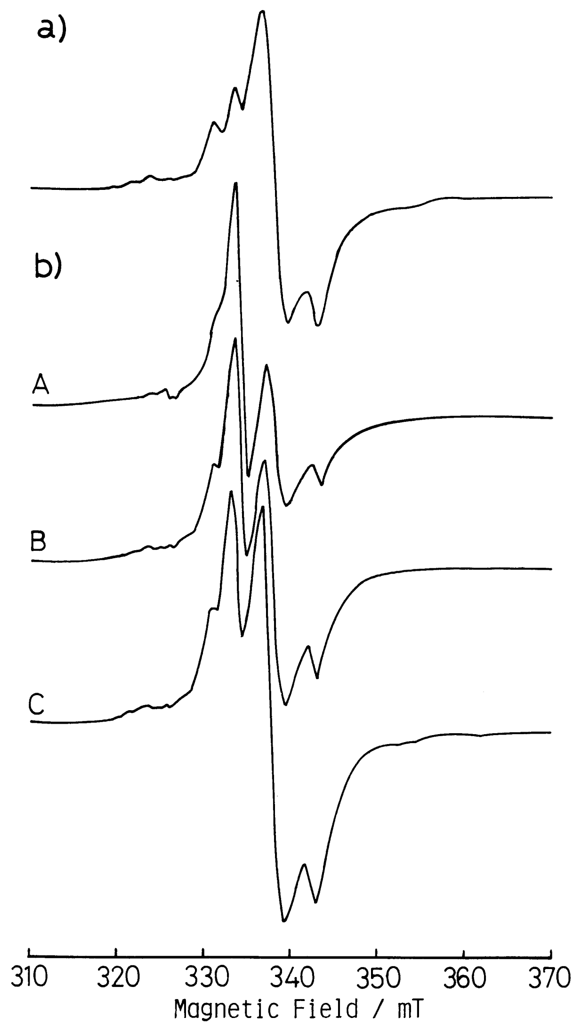

Fig. 8. ESR spectra of a) the reduced KH_2PMo/SiO_2-200; m=0.30 mmol g-supt^{-1} and b) the reduced K_2HPMo/SiO_2-200 with various loadings of $K_2HPMo_{12}O_{40}$; A: m=0.15, B: m=0.40, C: m=0.70 mmol g-supt^{-1}.

signals Mo-1 and Mo-3 appear, while at higher loading signal Mo-4 appears in addition. It is particularly interesting that signal Mo-4 is observed only under loading more than a monolayer thickness of $K_2HPMo_{12}O_{40}$ on silica.

It is presumed that signal Mo-1 and signals Mo-3 and Mo-4 can be assigned to crystalline $K_3PMo_{12}O_{40}$ and supported $H_3PMo_{12}O_{40}$, respectively. For KH_2PMo/SiO_2-200 and K_2HPMo/SiO_2-200, it is, therefore, obvious that mixtures of $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ are formed on silica.

Correlation between ESR Spectra for H_3PMo/SiO_2-200 and the Catalytic Reaction. It is interesting that the color of an $H_3PMo_{12}O_{40}$ catalyst turned from yellow to blue during the dehydration of liquid and gaseous TBA under all conditions examined, indicating that hexavalent molybdenum is partially reduced to the pentavalent form. In Fig. 9, the ESR spectra of the catalysts after dehydration of TBA are shown. A sharp signal with g=2.0054 appears at 325 mT in all of the obtained spectra. It is natural that this signal is assigned to free radicals in a carbonaceous residue.

For the catalysts, after dehydration of liquid TBA, the relative intensity ratios of signals Mo-2 and Mo-4 to signal Mo-3 increase with increasing the amount of $H_3PMo_{12}O_{40}$ supported (spectra A—C in Fig. 9). This phenomenon is similar to that for the reduced $H_3PMo_{12}O_{40}$ (Fig. 3). This proves that both the surface and inner molybdenum atoms are reduced to the +5 state during dehydration of liquid TBA. In conclusion, it is deduced that the dehydration of liquid TBA proceeds through a pseudo-liquid mechanism.[1]

For the dehydration of gaseous TBA, on the contrary, we did not find any significant change in the ESR spectral pattern, except for the intensity (spectra A and B in Fig. 2 and spectrum D in Fig. 9). This means that TBA molecules are adsorbed and react on the outer surface of the catalysts, supporting the idea that the dehydration of gaseous TBA proceeds through an outer surface mechanism.[1]

ESR Spectra for Potassium-Substituted Catalyst after Catalytic Reaction. For the potassium-substituted catalyst K_3PMo/SiO_2-200, no change in the ESR spectra was found after the reaction, except for the intensity. Figure 10 shows the ESR spectra of K_2HPMo/SiO_2-200 after dehydration of gaseous TBA. For partially potassium-substituted catalysts $KH_2PMo/$

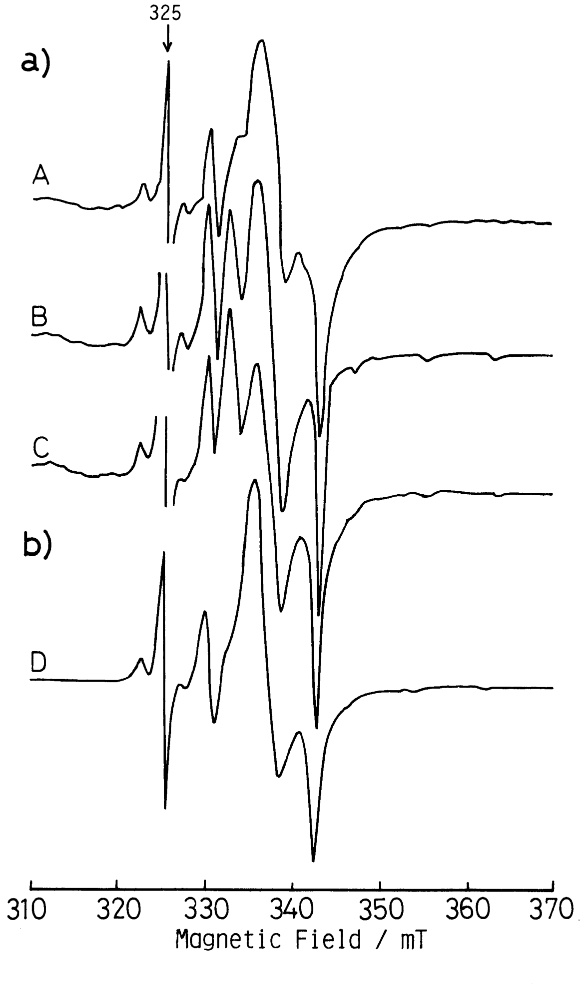

Fig. 9. ESR spectra of H_3PMo/SiO_2-200 catalysts after the dehydrations of a) liquid TBA; A: m=0.10, B: m=0.45, C: m=0.70 mmol g-supt^{-1} H_3PMo/SiO_2-200, and b) gaseous TBA.

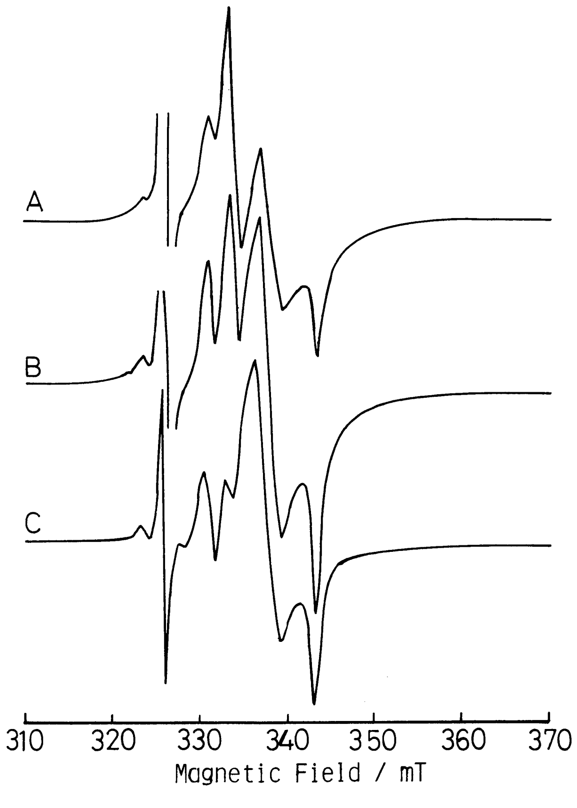

Fig. 10. ESR spectra of K_2HPMo/SiO_2-200 catalysts after the dehydrations of gaseous TBA; A: m=0.15, B: m=0.30, C: m=0.50 mmol g-supt^{-1} K_2HPMo/SiO_2-200.

SiO_2-200 and K_2HPMo/SiO_2-200, on the contrary, three signals assigned to signals Mo-1, Mo-3, and Mo-4 were observed after the dehydration of gaseous TBA. The relative intensity ratio of signal Mo-3 to signal Mo-1 increased markedly upon increasing the amount of HPC loaded. Assuming that the mixture of species $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ with different mole ratios are formed, the spectral change implies that species $H_3PMo_{12}O_{40}$ and $K_3PMo_{12}O_{40}$ distribute heterogeneously on the surface of the catalysts. It is also presumed that the outer surface of the catalyst is predominantly covered with $H_3PMo_{12}O_{40}$. The results obtained in this study coincide with our previous conclusion based on the fact that the catalytic activity depends on m.1)

For the dehydration of liquid TBA, on the other hand, the ESR spectra consists of signals Mo-1, Mo-3, and Mo-4. The relative intensity of signal Mo-1 increases with the amount of HPC loaded, suggesting that TBA molecules react even at the inner site of the HPC layer. This bears out the idea that the dehydration of liquid TBA in the presence of potassium-substituted catalysts proceeds through a pseudo-liquid mechanism.1)

References

1) R. Ohtsuka, Y. Morioka, and J. Kobayashi, *Bull. Chem. Soc. Jpn.*, **62**, 3195 (1989).

2) R. Ohtsuka, Y. Morioka, and J. Kobayashi, to be published in *Bull. Chem. Soc. Jpn.*

3) R. S. Alger,"Electron Paramagnetic Resonance," John Wiley and Sons, New York (1986), p. 201.

4) H. Hasegawa, "Jitsuyou ESR Nyumon," ed by K. Ishizu, Kodansya, Tokyo (1981), Chap. 2-2.

5) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions," Clarendon Press, Oxford (1970).

6) G. R. Hanson, G. L. Wilson, T. D. Bailey, J. R. Pilbrow, and A. G. Wedd, *J. Am. Chem. Soc.*, **109**, 2609 (1987).

7) G. Louis and M. Che, *J. Phys. Chem.*, **91**, 2785 (1987).

8) R. Fricke and G. Öhlmann, *J. Chem. Soc., Faraday Trans. 1*, **82**, 263 (1986).

9) R. Fricke, H.-G. Jerschkewitz, and G. Öhlmann, *J. Chem. Soc., Faraday Trans. 1*, **82**, 3479 (1986).

10) J. B. Black, N. J. Clayden, P. L. Gai, J. B. Scott, E. M. Serwicka, and J. B. Goodenough, *J. Catal.*, **106**, 1 (1987).

11) R. Fricke and G. Öhlmann, *J. Chem. Soc., Faraday Trans. 1*, **82**, 273 (1986).

12) K. Eguchi, Y. Toyozawa, N. Yamazoe, and T. Seiyama, *J. Catal.*, **83**, 32 (1983).