Mobility and Exchange of Protons and Methanol Molecules in $H_3PW_{12}O_{40}$ Pseudoliquid Phase Detected by Solid State NMR

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The dynamic behavior of CH_3OH molecules absorbed in the "pseudoliquid phase" of a heteropolyacid, $H_3PW_{12}O_{40}$, was analyzed by high resolution solid-state ^{13}C, ^1H and ^{31}P NMR. When CH_3OH absorbed was less than 3 molecules/ heteropolyanion, CH_3OH molecules were all protonated and the rest of the protons remained presumably directly bonded to the bridging oxygen atoms of heteropolyanion. The hydroxyl protons of CH_3OH and the protons of heteropolyacid exchanged rapidly in a wide range of absorption level, and CH_3OH molecules became very mobile when the absorption amount exceeded 6 molecules / anion.

Heteropolyacids are good cluster models of mixed oxide catalysts, and the catalytic process can be described at the molecular level.[1] An interesting property of the heteropolyacids when they are used as solid catalysts is "pseudoliquid phase".[2] Polar molecules such as alcohols and ethers are readily transferred in or out of the three-dimensional bulk phase, sometimes expanding or shrinking the distance between the anions.[2,3] This behavior is due to the flexible nature of the secondary structure of the solid heteropolyacid. This pseudoliquid phase behavior often brings about high catalytic activities[4] and unique selectivities.[5]

Previously,[6] we observed by solid state NMR a protonated ethanol monomer as well as a dimer in the pseudoliquid, which are possible reaction intermediates of the dehydration of ethanol to ethylene and diethylether, respectively. The unique selectivity of this reaction was explained as a function of concentrations of these species.[6]

In this study, the dynamic behavior of CH_3OH molecules absorbed in the pseudoliquid phase of $H_3PW_{12}O_{40}$ was analyzed by means of solid-state NMR and we found that rapid proton exchange occurred in the wide range of absorbed amounts of methanol. We also observed a stepwise increase in the mobility of CH_3OH. E. g., the motion of CH_3OH was greatly accelerated above 6 molecules / anion.

The samples were prepared using a glass made high vacuum system (200 cm^3). After $H_3PW_{12}O_{40}$ was dehydrated at 403 K for 1 h, the calculated amount of $^{13}CH_3OH$ (99% ^{13}C) was introduced at 273 K. The molar ratio of $^{13}CH_3OH$ and $H_3PW_{12}O_{40}$, which is designated by n, was varied from 0 to 9. Then the sample was moved into a small glass cell (ca. 0.1 cm^3) and the gas was all collected into the cell by cooling with liquid N_2, followed by sealing the glass tube with fire. This cell was set into a zirconia rotor (6 mm in diameter). NMR spectra were recorded with JNM-EX270 equipped with CP-MAS probe (JEOL). Single pulse excitation with proton decoupling was used to obtain ^{13}C and ^{31}P NMR spectra. The spectra were reproducible in repeated experiments.

^{13}C NMR (not shown) gave a sharp peak at 55.0 ppm for the sample with $n = 1$. The low-field shift from liquid CH_3OH (at 49 ppm) indicates that $^{13}CH_3OH$ molecule was protonated in the pseudoliquid phase, as in the case of ethanol absorbed in $H_3PW_{12}O_{40}$, where the shift of CH_2 by protonation was 8 ppm.[6] The peak slightly shifted to upper field as n increased. For $n = 9$, the peak was observed at 52 ppm.

Figure 1 shows ^{31}P NMR spectra of the samples with $n = 1, 3, 6$, and 7. For $n=0$, a sharp peak was observed at -10.0 ppm. When n was less than 3, broad peaks were observed in the range of -11 ~ -14 ppm, while a sharp peak at -15.2 ppm appeared for $n \geqq 3$. In the case of $Cs_xH_{3-x}PW_{12}O_{40}$,[7] ^{31}P NMR gave four peaks at -10.9, -12.1, -13.5 and -14.9 ppm, which were reasonably assigned to polyanions having different numbers of protons directly bonded to their bridging oxygen atoms, that is, 3, 2, 1 and 0 proton(s), respectively. For $n = 3$ (the ratio of CH_3OH / H of heteropolyacid = 1) or above (Figure 1b - d), ^{31}P NMR gave a narrow peak at -15.0 ~ -15.2 ppm. The peak position is close to that of $H_3PW_{12}O_{40} \cdot 6H_2O$ (at -15.1 ppm), of which the protons are bonded to water molecules, and also to that of $Cs_3PW_{12}O_{40}$ (at -14.9 ppm), which has no proton.[6,7] Hence, the sole peaks at around -15 ppm for $n \geqq 3$ show that all protons were transferred from polyanions to CH_3OH molecules forming $CH_3OH_2^+$ or $(CH_3OH)_2H^+$. Uniform as well as mobile nature of this species probably gave a narrow peak. For $n < 3$ (Figure 1a), the chemical shifts of the ^{31}P NMR peaks which appeared at around -11 ~ -14 ppm indicate that a part of protons still remained directly bonded to the heteropolyanion framework and the rest was transfered to methanol. This is consistent with the stoichiometry: $3\ H^+ + n\ CH_3OH \rightarrow (3 - n)\ H^+ + n\ CH_3OH_2^+$. Unlike $Cs_xH_{3-x}PW_{12}O_{40}$ the peaks are not resolved. This is probably because the protons on heteropolyanions are moving between neighboring anions, causing coalescence of the four peaks.

Thus, ^{13}C and ^{31}P NMR demonstrate that all of CH_3OH molecules are protonated to form $CH_3OH_2^+$ in pseudoliquid phase

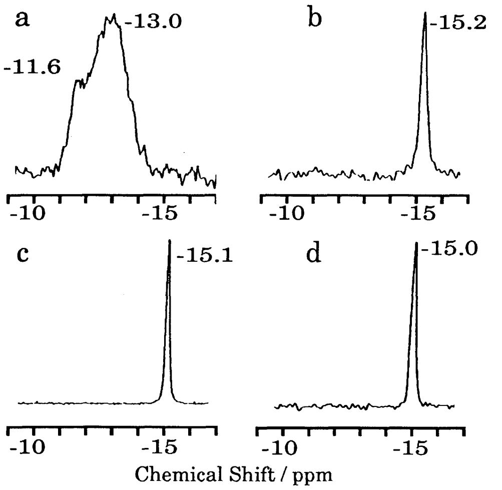

Figure 1. ^{31}P MAS NMR of $^{13}CH_3OH$ absorbed in $H_3PW_{12}O_{40}$. The molar ratio of $^{13}CH_3OH$ to $H_3PW_{12}O_{40}$, n, (a) 1, (b) 3, (c) 6, and (d) 7.

for $n = 3$ or below.

Figure 2 shows ^{1}H NMR spectra of the samples with n =1, 6, 7 and 9. For n=0, a broad peak was observed at 10.0 ppm. The peak at around 5 ppm is attributed to the methyl group of $^{13}CH_3OH$. Besides this methyl proton, one peak was observed at around 10 ppm for all samples. This peak is assigned to the combined peak of hydroxyl protons of $^{13}CH_3OH$ molecules and acidic protons of $H_3PW_{12}O_{40}$, considering the chmeical shift. Even when n>3, no hydroxyl signal due to non-protonated methanol at around 6 ppm was observed. This indicates that these protons are mobile and exchanging the positions rapidly with each other. In order to confirm this, the ^{1}H NMR spectra were quantitatively analyzed. Figure 3 illustrates the comparison of the observed intensity ratio of the methyl peak to the coalesced peak with the ratio calculated assuming the rapid exchange. For example, the ratio calculated for n (= $CH_3OH/H_3PW_{12}O_{40}$) = 6 is (3·6)/(6·1+3) = 2. The broad background of ^{1}H spectra observed for -10 to 0 ppm was subtracted from the observed peak intensities. The uncertainty of the ratios due to the subtraction of broad background was indicated by error bars in Figure 3. A linear correlation in Figure 3 demonstrates the rapid exchange of protons. Although the data for n<3 cannot be firm evidence for this due to the smaller differences in the chemical shift, this is consistent with the unresolved ^{31}P NMR for n=1 (Figure 1a).

The mobility of protons produced on the surface of Ag salts of heteropolyacid have been discussed based on ^{1}H NMR line width.[8] As for the line width of ^{1}H NMR peaks (Figure 2), drastic narrowing was noted for both methyl and hydroxyl peaks when n exceeded 6. The splitting of the signal of methyl proton is due to spin-spin coupling with ^{13}C nuclei (enriched $^{13}CH_3OH$ was used). When $n \leq 6$, the peaks were broadened because of strong homonuclear dipole-dipole interaction between hydroxyl and methyl protons. This narrowing indicates that $^{13}CH_3OH$ molecule was highly mobile in the pseudoliquid phase at $n = 7$. The broad peaks for $n = 6$ (the ratio of CH_3OH / H of heteropolyacid is 2) or below suggests that $^{13}CH_3OH$ molecules form protonated monomers, $CH_3OH_2^+$, and dimers, $(CH_3OH)_2H^+$, which were relatively stable and less mobile in the pseudoliquid matrix. This is possibly related to the fact that $H_3PW_{12}O_{40}\cdot 6H_2O$ forms a stable structure.[9] The flexible and loose secondary structure would make it possible. The remarkable change in the linewidth of ^{1}H NMR around n = 6 suggests that slightly excess amount of $^{13}CH_3OH$ enhanced the mobility of the whole $^{13}CH_3OH$ molecules.

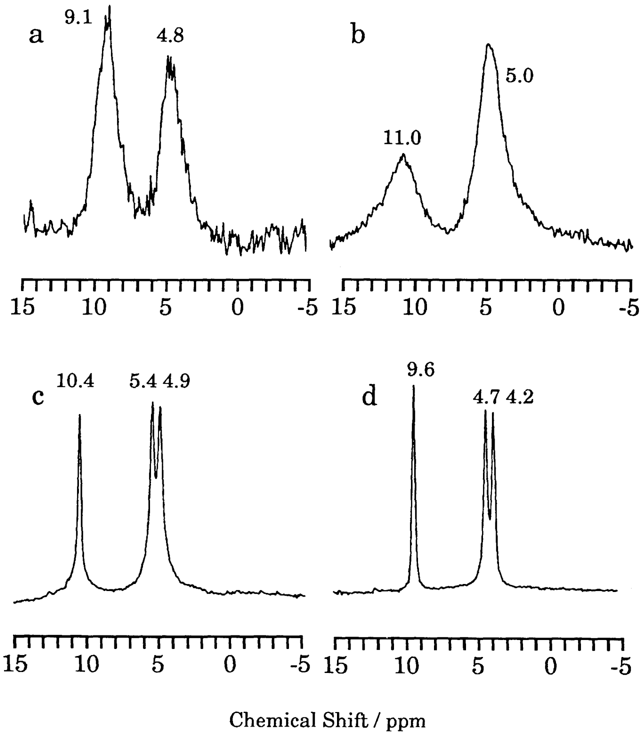

Figure 2. ^{1}H MAS NMR of $^{13}CH_3OH$ absorbed in $H_3PW_{12}O_{40}$. The molar ratio of $^{13}CH_3OH$ to $H_3PW_{12}O_{40}$, n, is (a) 1, (b) 6, (c) 7, and (d) 9.

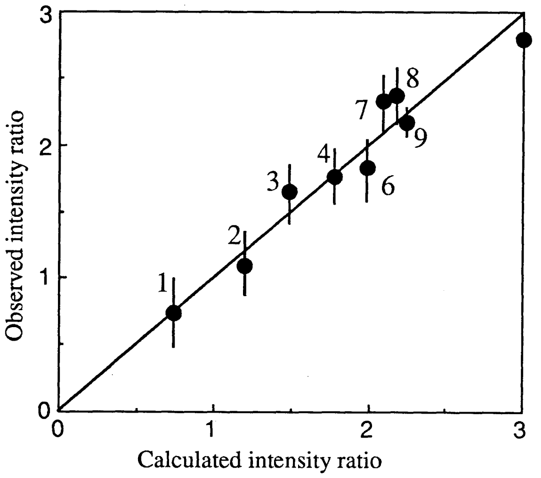

Figure 3. Comparison of the calculated with the observed intensity ratio of two peaks in ^{1}H MAS NMR for various values of n. The ratios of methyl / hydroxyl were calculated by $3n / (n+3)$. See text. n are indicated in the figure.

References and Notes

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