^{1}H NMR studies on the dynamic property of protons in Pd^0–$H_3PW_{12}O_{40}$ systems in the presence of dihydrogen

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Abstract

The dynamic property of protons in the catalysts consisting of Pd^0 metal and $H_3PW_{12}O_{40}$ in the presence of dihydrogen was investigated with ^{1}H MAS and broad-line NMR techniques. The protons in $H_3PW_{12}O_{40}$ were observed at 9.1 ppm in ^{1}H MAS NMR. When a composite catalyst consisting of Pd(II) and $H_3PW_{12}O_{40}$ was reduced with dihydrogen, the intensity of the 9.1 ppm signal increased. In addition, hydrogen atoms adsorbed on metallic palladium were observed at 19.8 ppm. The temperature dependence of ^{1}H MAS NMR reveals the dynamic nature of protons in the catalyst consisting of Pd^0 metal and $H_3PW_{12}O_{40}$. When the composite catalyst was heated to 333 K in the presence of dihydrogen, the line widths of the two peaks were broadened and the peak of hydrogen atoms shifted toward that of acidic protons, indicating that the interconversion occurs between the hydrogen atoms on Pd^0 metal and protons in $H_3PW_{12}O_{40}$ and that hydrogen atoms formed on Pd^0 metal spill-over to the surrounding heteropolyanions. The line width of the peak at 9.1 ppm of the composite catalyst in the presence of dihydrogen depended on the spinning rate in ^{1}H MAS NMR at 373 K, indicating that the protons in the catalyst are mobile. On the other hand, the line width was independent of spinning rate in the case of $H_3PW_{12}O_{40}$ at this temperature. This clearly shows that the presence of dihydrogen and Pd^0 metal modify the dynamic nature of protons in $H_3PW_{12}O_{40}$.

Keywords: ^{1}H NMR; Acidic protons; Heteropoly acid; Palladium metal; Dihydrogen

1. Introduction

Heteropolyacids such as dodecatungstophosphate ($H_3PW_{12}O_{40}$, HTP) are highly acidic and can serve as solid acid catalysts [1–5]. Ono et al. reported that the catalytic activity for methanol conversion to hydrocarbons considerably enhanced when HTP coexists with palladium or platinum catalysts [6,7]. The activity enhancement was observed only when dihydro-

gen exists in the system; the activity depends on the dihydrogen pressure and the effect of dihydrogen was partially reversible. Both HTP and Pd^0 metal supported on carbon also shows a very high activity for the isomerization of hexane in the presence of dihydrogen [8]. Recently, Hattori and coworkers reported that the catalytic activity of sulfated zirconia for hexane isomerization was enhanced in the presence of dihydrogen when transition metals were incorporated to the catalyst [9,10].

The active sites for methanol conversion were

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acidic protons [11]. Therefore, the increase in the catalytic activity may be ascribed to the formation of very active protons and/or increase in the activity of the individual protons.

We have proposed the following mechanism for the generation of acidic protons in HTP in the presence of palladium metal and dihydrogen [6].

$$H_2 \overset{Pd^0}{\rightleftarrows} 2H \tag{1}$$

$$H + PW_{12}O_{40}^{3-} \rightleftarrows H^+ + PW_{12}O_{40}^{4-} \tag{2}$$
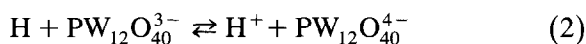
Dihydrogen molecules from the gas phase may dissociate into hydrogen atoms over the metal. The hydrogen atoms thus formed spillover and interact with surrounding heteropoly anions, $PW_{12}O_{40}^{3-}$ to be converted into protons.

According to the above mechanism, we can speculate that metallic palladium serves as a catalyst for the interconversion between hydrogen atoms and acidic protons. This hypothesis prompted us to investigate the mechanism of the proton generation and the properties of highly active protons.

Recently, we have reported that the variable temperature measurements of ^1H MAS NMR offer valuable information on the dynamic nature of the protons in partially reduced $Ag_3PW_{12}O_{40}$ with dihydrogen [12]. Thus, we have suggested that the difference of mobility is the major factor for much higher activity of the silver salt than that of HTP.

In this work, we will report the ^1H NMR evidence of the interconversion between hydrogen atoms and acidic protons and the mobility of protons in the catalysts consisting of metallic Pd and HTP.

2. Experimental

2.1. Preparation of the catalysts consisting of metallic Pd and $H_3PW_{12}O_{40}$

HTP obtained from Wako Pure Chemicals was recrystallized from water at room tempera-

ture. The composite catalysts consisting of metallic Pd and HTP were prepared as follows: an aqueous solution of $Pd(NO_3)_2$ (0.1 mol dm^{-3}) was added to that of HTP (0.2 mol dm^{-3}) at room temperature. The solution was stirred at 353 K for 30 min and then evaporated to dryness at the same temperature. The solid material thus obtained is hereafter denoted as $Pd(II)(x)$/HTP. Here, x is hereafter denoted as the molar ratio of $Pd(NO_3)_2$ and HTP used for the catalyst preparation.

The composite catalysts were prepared in a glass tube as follows: $Pd(II)(x)$/HTP was heated at 393 K for 1 h and then at 523 K for 2 h under vacuum. The sample was then cooled to 423 K and reduced with 13.3 kPa of dihydrogen for 30 min at the same temperature. Dihydrogen consumption was manometrically monitored during the reduction. The water formed during reduction was trapped by a trap kept at 77 K. The reduced material will be denoted as $Pd^0(x)$/HTP.

2.2. ^1H MAS NMR measurements

^1H NMR spectra were measured on samples sealed in a glass capsule, which was completely fitted to a zirconium rotor (i.d. 5.5 mm) of a double-bearing MAS probe head.

The sample was prepared as follows: a 1.5 g of $Pd(II)(x)$/HTP was reduced as described above. The $Pd^0(x)$/HTP obtained was cooled to 298 K and the dihydrogen pressure was then adjusted to 13.3 kPa. Since the glass capsule was attached to the side arms of the glass tube, the $Pd^0(x)$/HTP was transferred from the glass tube into the glass capsule. The neck of the capsule was sealed with a flame torch, after the capsule was cooled with liquid nitrogen. The weight of the sample was ca. 200 mg.

^1H MAS NMR spectra were recorded between 298 and 373 K with Bruker MSL 300 or 400 with 3 and 1 μs, respectively, without using the window function for Fourier transformation of the free induction decay. The spectrum width was 10 kHz. The number of scans

was 32 times. The acquisition time and the repetition time were 0.2 and 20 s, respectively. The intensities of NMR lines were compared with the peak areas incorporating the spinning side bands when the relative amount of protons was compared.

Broad-line ^1H NMR spectra were recorded at 298 K by using a high-power and wide-band (2 MHz) ^1H FTNMR spectrometer (JEOL, GX 270) with 1 μs of 90° pulse. The sample was prepared as in the case of ^1H MAS NMR measurements. The chemical shift was expressed relative to tetramethylsilane (TMS) with usual conventions.

2.3. Methanol conversion into hydrocarbons over Pd^0 / HTP composite catalyst

Pd(II)(x)/HTP was packed in a reactor of silica tubing (10 mm i.d.) placed in a vertical furnace. The Pd(II)(x)/HTP was heated under dinitrogen at 523 K for 1.5 h and then reduced under a stream of dihydrogen (30 kPa) and dinitrogen (71 kPa) at 503 K for 30 min.

The conversion of methanol into hydrocarbons was carried out with a continuous-flow reactor operating at atmospheric pressure. Methanol was derived by means of a motor-driven syringe and vaporized in the pre-heating zone of the reactor containing 10 cm^3 of quartz. The gas of hydrocarbons were analyzed with a gas chromatograph equipped with a Prapak Q column. The gases CO, CO_2 and CH_4 were analyzed with an active carbon column. The yields of the products were calculated on a carbon-number basis.

3. Results and discussion

3.1. Time course of reduction of Pd(II) / HTP with hydrogen

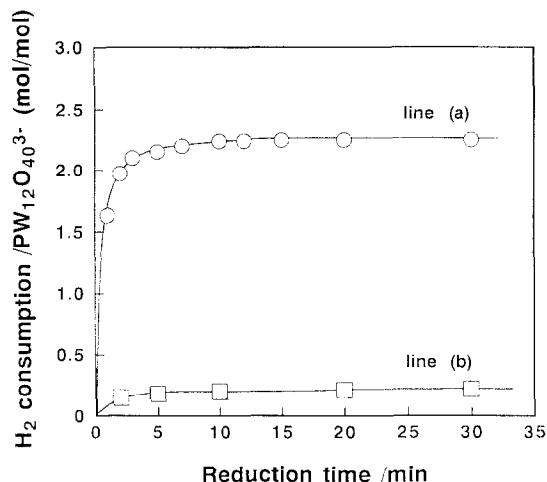Pd(II)(1.5)/HTP was reduced with dihydrogen of 13.3 kPa at 423 K in a conventional

Fig. 1. The time course of the amount of dihydrogen consumption. Line (a): Pd(II)(1.5)/HTP was contacted to 13.3 kPa of dihydrogen at 423 K. Line (b): Pd^0(1.5)/HTP evacuated at 423 K for 1 h was re-exposed to 13.3 kPa of dihydrogen at 423 K.

gas-circulation system. The amount of dihydrogen consumed was shown in Fig. 1 as a function of the reduction time. Dihydrogen was rapidly consumed at the beginning and reached a limiting value of 2.2 mol per mol of heteropolyanion in 10 min. This amount is more than that required for Pd(II) reduction to Pd^0 (1.5 mol). The difference (0.7 mol) corresponds to the reduction of the heteropolyanion and/or adsorption of dihydrogen. In fact, 0.8 mol of water was trapped during the reduction. This means that 1.4 mol of dihydrogen was retained in the solid, Pd^0(1.5)/HTP. The water was formed by the reduction of HTP with hydrogen atoms and/or dihydrogen (Eq. 3).

$$H_3PW_{12}O_{40} + 2H\,(or\,H_2)$$
$$\rightarrow H_2O + H_3PW_{12}O_{39} \qquad (3)$$
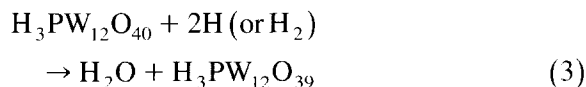
The Pd^0(1.5)/HTP sample was evacuated at 423 K for 1 h, and then reexposed to 13.3 kPa of dihydrogen at 423 K. As shown in Fig. 1, a rapid consumption of dihydrogen was observed and the amount of dihydrogen consumed corresponded to 0.16 mol per mol heteropolyanion. This amount of dihydrogen corresponds to that of reversibly sorbed hydrogen.

3.2. ^1H MAS NMR of protons in $Pd^0(1.5)/HTP$

^1H MAS NMR spectra of HTP and Pd(II)(1.5)/HTP were recorded at 298 K with the resonance frequency of 400 MHz. The protons in HTP were observed at (9.1 ± 0.1) ppm.
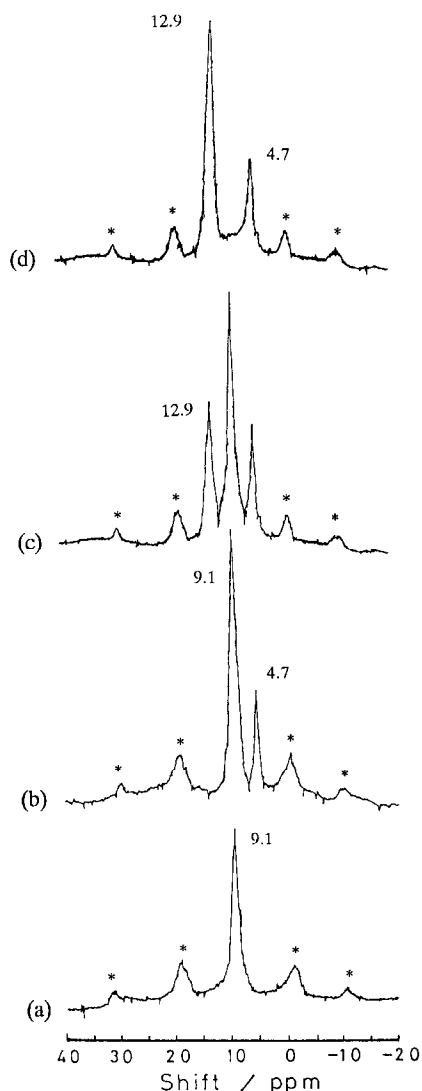

Fig. 2. Generation of acidic protons upon reduction of Pd(II)(1.5)/HTP. ^1H MAS NMR spectra were measured at 298 K. The resonance frequency was 400 MHz. (a) Pd(1.5)(II)/HTP, (b) $Pd^0(1.5)/HTP$ in the presence 13.3 kPa of dihydrogen, (c) $Pd^0(1.5)/HTP$ exposed to deuterated pyridine (1.3 kPa) at 303 K for 0.5 h and then evacuated at 303 K for 0.5 h, (d) $Pd^0(1.5)/HTP$ exposed to deuterated pyridine (1.3 kPa) at 373 K for 1 h and then evacuated at 373 K for 0.5 h. (*) shows the spinning side bands.

In the case of Pd(II)(1.5)/HTP, the peak was also observed at the same chemical shift value (Fig. 2(a)). As expected, the peak intensity was almost the same as that of HTP.

^1H MAS NMR spectrum of $Pd^0(1.5)/HTP$ in the presence of dihydrogen (13.3 kPa) was measured at 298 K. The peak was observed at (4.7 ± 0.1) ppm together with the peak at 9.1 ppm, whose peak area was about 1.5 times larger than that of Pd(II)(1.5)/HTP. These results show that the protons at 4.7 ppm and a part of protons at 9.1 ppm have been generated upon dihydrogen treatment. The peak at 4.7 ppm is attributed to H_2O molecules formed during the dihydrogen treatment, since a peak at 4.6 ppm was observed by adsorbing H_2O molecules on $Na_3PW_{12}O_{40}$ (the molar ratio of H_2O to $Na_3PW_{12}O_{40} = 1$). At this stage, however, it is not exactly excluded that the peak at 4.7 ppm is attributed to an another form of adsorbed hydrogen atoms. There is another peak at 19.8 ppm, which is not seen in Fig. 2, because of the overlap with the side bands, as will be described later.

To confirm whether the protons at 9.1 ppm are acidic or not, deuterated pyridine (C_5D_5N, D-Py) was adsorbed on $Pd^0(1.5)/HTP$ in the presence of dihydrogen: $Pd^0(1.5)/HTP$ was exposed to 1.3 kPa of D-Py at 303 K for 0.5 h and then evacuated at the same temperature for 0.5 h. As shown in Fig. 2(c), the intensity of the peak at 9.1 ppm decreased to about 2/3 of that for the original $Pd^0(1.5)/HTP$ and a new peak due to the deuterated pyridinium ion ($C_5D_5NH^+$) was observed at 12.9 ppm [13,14]. The peak at 9.1 ppm completely disappeared upon absorption of D-Py on $Pd^0(1.5)/HTP$ at 373 K for 1 h, while the peak at 4.7 ppm remained almost unchanged as expected (Fig. 2(d)). The disappearance of protons at 9.1 ppm shows that these protons are acidic.

These results show that the protons generated by the reduction of Pd(II) with dihydrogen can not be distinguished from those in the original HTP by the NMR chemical shift and all the protons at 9.1 ppm are acidic.

3.3. NMR spectra of hydrogen atoms on Pd^0 metal

When the ^1H MAS NMR spectrum of $Pd^0(1.5)$/HTP under dihydrogen atmosphere was acquired at the resonance frequency of 300 MHz, a small peak was observed at 19.8 ppm besides the peaks at 9.1 ppm and 4.7 ppm (Fig. 3). We assign this peak to hydrogen atoms adsorbed on metallic palladium. Sheng and Gay reported ^1H MAS NMR spectra of hydrogen atoms on Pd^0 metal supported on silica [15]. The signal was observed at wide range from ca. 10 to 80 ppm, depending on the amount of adsorbed dihydrogen. They also reported that the chemical shifts of hydrogen atoms on Pt^0, Ir^0 and Rh^0 metal were observed at wide range [15]. For example, the signal due to hydrogen atoms on Pt metal was observed at range from ca. 20 to 50 ppm. While the chemical shifts of hydrogen atoms on Ru^0 and Os^0 metal were independent of the amount of adsorbed dihydrogen, being about 50 and 15 ppm, respectively.

To further investigate the protons at 19.8 ppm, ^1H FT NMR (broad-line ^1H NMR) spectra of $Pd^0(x)$/HTP ($x = 0.1$, 0.75 and 1.5) under dihydrogen atmosphere were measured at 298

Fig. 4. The broad-line ^1H NMR spectra of $Pd^0(x)$/HTP in the presence of dihydrogen (13.3 kPa). (a) $x = 0.1$, (b) $x = 0.75$, (c) $x = 1.5$. All spectra were measured at 298 K.

K. The protons around 20 ppm can be separated from other protons. The spectra are shown in Fig. 4(a)–(c). In the case of $Pd^0(1.5)$/HTP, two peaks were clearly observed around 9 and 20 ppm (Fig. 4(a)). The latter peak disappeared by simply evacuating $Pd^0(1.5)$/HTP at 303 K for 10 min.

The intensity of the peak at 20 ppm increased by increasing the amount of Pd^0 metal as shown in Fig. 4(a)–(c), supporting the assignment of this peak to hydrogen atoms adsorbed on palladium.
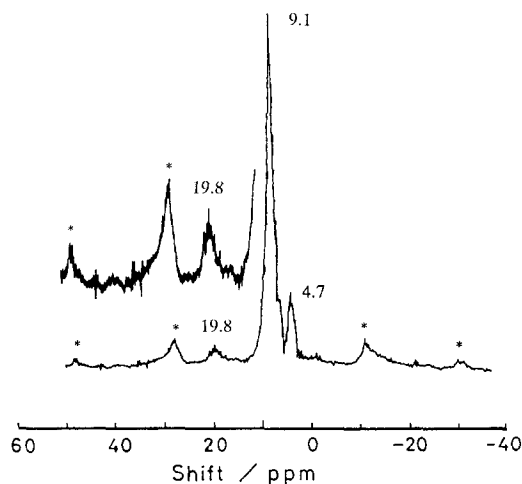

Fig. 3. ^1H MAS NMR spectrum of $Pd^0(1.5)$/HTP in the presence of dihydrogen. The dihydrogen pressure was 13.3 kPa. The spectrum was measured at 298 K. The resonance frequency was 300 MHz. The spinning rate of the sample: 5.8 kHz. (*) shows the spinning side bands.
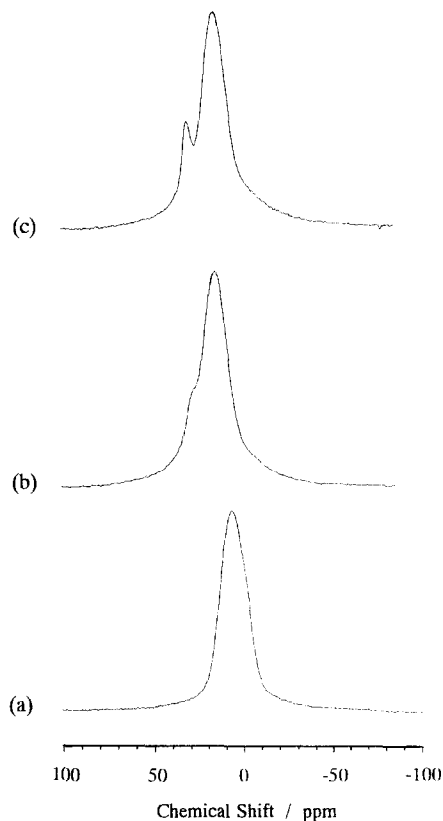
3.4. Partially reversible generation of protons in $Pd^0(1.5)$ / HTP

As described above, the adsorption of dihydrogen on $Pd^0(1.5)$/HTP was partially re-

versible. To know how the three types of protons behave with the adsorption–desorption cycle of dihydrogen, ^1H MAS NMR spectra of $Pd^0(1.5)$/HTP were recorded at 298 K in the presence and absence of dihydrogen. The spectrum of $Pd(II)(1.5)$/HTP and that of $Pd^0(1.5)$/HTP in the presence of 13.3 kPa dihydrogen are shown in Fig. 5(a) and Fig. 5(b), respectively. When $Pd(II)(1.5)$/HTP was reduced with dihydrogen, the three types of protons were clearly seen, namely, hydrogen atoms on metallic palladium (19.8 ppm), acidic protons (9.1 ppm) and water molecules (4.7 ppm) (Fig. 5(b)). Upon evacuation the sample at 423 K for 1 h, the peak due to protons on palladium metal disappeared and the intensity of the peak due to water molecules decreased considerably, while the peak intensity of the acidic protons decreased to about 2/3 of that before evacuation (Fig. 5(c)).

The sample was then reexposed to dihydrogen (13.3 kPa) at 423 K for 30 min. The three peaks reappeared (Fig. 5(d)). The intensity did not completely recovered to that before dihydrogen evacuation, but it was about 1.2 times larger than that before reexposure to dihydrogen. This shows the presence of protons, which are reversibly formed and disappeared by the adsorption–desorption cycle of dihydrogen. Upon reexposure to dihydrogen, the intensity of the peak at 19.8 ppm was recovered, indicating that adsorption of dihydrogen on metallic palladium is reversible. The reappearance of the peak at 4.2 ppm shows that the reduction of the heteropolyanion further proceeds by the second exposure to dihydrogen.

3.5. Influence of temperature on the ^1H MAS NMR spectra of $Pd^0(1.5)$ / HTP in the presence of dihydrogen

The spectra of $Pd^0(1.5)$/HTP under dihydrogen atmosphere were recorded by raising the sample temperature (Fig. 6). The signal at 9.1 and 18.9 ppm were broadened by raising the temperature to 333 K, and further broadened at 373 K. The peak at 19.8 ppm shifted to higher field at 333 K, and merged into the peak at 9.1 ppm at 373 K. These spectral change suggests that the exchange of the two types of protons occurs at higher temperatures. The intensities of the spinning side bands decreased at 333 K and disappeared at 373 K.

3.6. Spinning rate dependence of ^1H MAS NMR of $Pd^0(x)$ / HTP

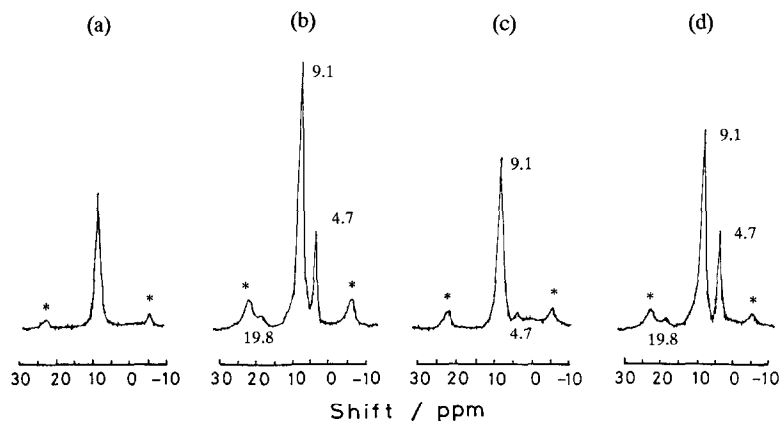When the thermal motion is a major contribution to the line width in MAS NMR, the line

Fig. 5. The reversible generation of protons. (a) $Pd(II)(1.5)$/HTP.(b) $Pd^0(1.5)$/HTP in the presence of dihydrogen (13.3 kPa). (c) $Pd^0(1.5)$/HTP evacuated at 423 K for 1 h. (d) The sample (c) reexposed to dihydrogen (13.3 kPa) at 423 K for 30 min. The spectrum was measured at 298 K. The resonance frequency was 300 MHz. (*) shows the spinning side bands.

width (Δv^{MAS}) is theoretically expressed by following equation [16].

$$\Delta v^{MAS} = (M_{IS}/3\pi)\left\{2\tau_C/\left[1 + (\omega_R\tau_C)^2\right]\right.$$
$$\left. + \tau_C/\left[1 + (2\omega_R\tau_C)^2\right]\right\} \qquad (4)$$

where ω_R is the spinning rate, M_{IS} is the second moment for the central line and τ_C is the correlation time.

To know whether the thermal motion of the protons contributes to the line width of ^{1}H MAS NMR spectrum of Pd^0(0.1)/HTP, the effect of the spinning rate on the line width of the signal in the presence of dihydrogen was examined at 298 and 373 K.
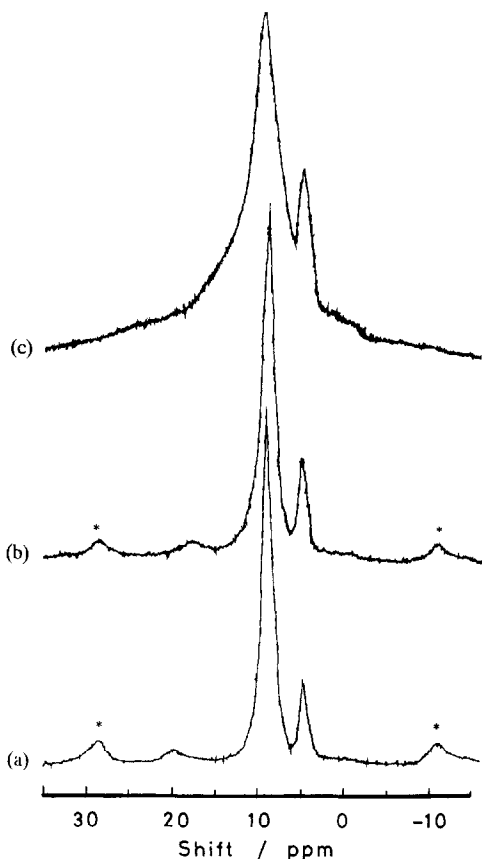
As shown in Fig. 6, the line width of the

Fig. 7. Influence of the spinning rate on the line width of the peak due to acidic protons in Pd^0(0.1)/HTP under dihydrogen (13.3 kPa). (□) 298 K, (○) 373 K.

Fig. 6. The temperature dependence of ^{1}H MAS NMR spectrum of Pd^0(1.5)/HTP in the presence of dihydrogen. (a) 298 K, (b) 333 K and (c) 373 K. The spinning rate of the sample was 5.8 kHz. The resonance frequency was 300 MHz. (*) shows the spinning side bands.
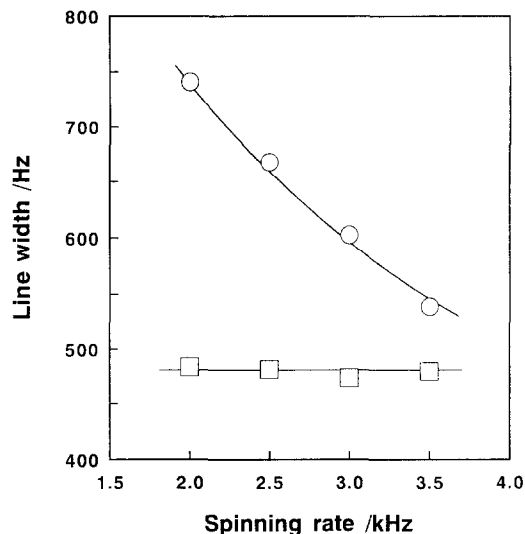
signal of Pd^0(0.1)/HTP significantly changed with the spinning rate at 373 K, decreasing from $(7.4 \pm 0.3) \times 10^2$ Hz to $(5.4 \pm 0.3) \times 10^2$ Hz by increasing the spinning rate from 2.0 to 3.5 kHz. When the values of the line widths and the spinning rates shown in Fig. 7, are considered as variables of the simultaneous equations in Eq. (4), τ_C and M_{IS} are obtained as (31 ± 3) μs and $(1.1 \pm 0.2) \times 10^8$ s^{-2} at 373 K, respectively. This implies that the thermal motion greatly contributes to the line width of the peak at 9.1 ppm. On the other hand, the line width was not influenced by spinning rate at 298 K, indicating that the thermal motion is not responsible for the line width at this temperature [17].

The line width of HTP was independent of the spinning rate at both 298 K and 373 K, being $(4.8 \pm 0.2) \times 10^2$ Hz and $(5.0 \pm 0.2) \times 10^2$ Hz, respectively.

The results described above indicate that the protons in Pd$^0(x)$/HTP under hydrogen are more mobile than those in HTP. The difference of the mobility between the protons in Pd$^0(x)$/HTP and those of HTP may explain the difference in the catalytic activities of the two catalysts for methanol conversion and hexane isomerization.
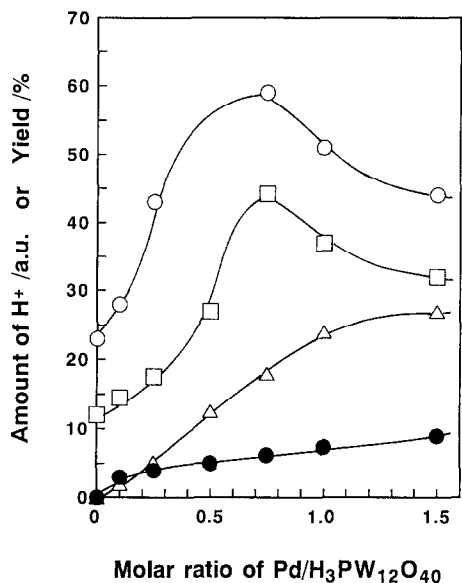
Fig. 8. The influence of the amount of palladium (x) on the amounts of acidic protons and the catalytic activity for the methanol conversion over $Pd^0(x)/HTP$. ($\bigcirc$) The amount of protons. $Pd(II)(x)/HTP$ was reduced with 13.3 kPa of hydrogen at 423 K for 0.5 h. ^1H MAS NMR spectra in the presence of dihydrogen (13.3 kPa) were measured at 298 K. ($\square$) Yield of hydrocarbons except CH_4, ($\triangle$) yield of CH_4 and ($\bullet$) yield of $(CO+CO_2)$. Reaction temperature: 503 K. Methanol: 30 kPa, H_2: 30 kPa, N_2: 71 kPa. $W/F = 150$ g h mol^{-1}. W and F are denoted as catalyst weight and the total rate of methanol plus dinitrogen and dihydrogen. The catalyst was reduced with mixture of dihydrogen (30 kPa) and dinitrogen (71 kPa) at 503 K for 30 min.

3.7. Influence of the amount of Pd^0 in $Pd^0(x)$ / HTP on the generation of protons and the catalytic activity for the methanol conversion

Fig. 8 shows the relations between the amount of palladium, x and that of proton in $Pd^0(x)/HTP$. The amount of acidic protons at 9.1 ppm (a peak area of ^1H MAS NMR) increased by increasing the amount of palladium, and reached maximum around x equal to 0.75, where the amount of protons at 9.1 ppm is about 2 times as large as that of HTP.

The change the yield of hydrocarbons for the methanol conversion and that of $(CO + CO_2)$ were also examined in the presence of dihydrogen (Fig. 8). Main hydrocarbons were alkanes whose carbon number is lower than 5 and did

not contain alkenes. The yield of hydrocarbons except CH_4 changed the nearly the same manner as the change of the amount of protons observed at 9.1 ppm, as shown in Fig. 8. The yield of hydrocarbons over $Pd^0(0.75)/HTP$, which retained the largest amount of protons, was the highest. The yield is about 3.5 times higher than that over HTP itself. Theses results indicate that the protons generated in $Pd^0(x)/HTP$ show higher catalytic activity than the protons in HTP in the presence of dihydrogen.

The yield of CH_4 and that of $(CO + CO_2)$ increased with increasing the amount of palladium. Since the variation of the amounts of these products was different from that of the amount of acidic protons, they are formed over Pd^0 metal, not over Brønsted acid sites.

4. Conclusions

(1) Reduction of $Pd(II)$ with dihydrogen in $Pd(II)/HTP$ results in the formation of acidic protons, whose nature cannot be distinguishable from the protons originally present in HTP.

(2) Reduction also results in the formation of hydrogen atoms adsorbed on metallic palladium.

(3) The interconversion between acidic protons in HTP and hydrogen atoms adsorbed on metallic palladium occurs at and above 333 K.

(4) The mobility of acidic protons in the presence of palladium and dihydrogen is higher than that of protons in the parent heteropoly acids. This may explain much higher catalytic activity of transition metal–HTP composite catalysts than HTP itself in the presence of dihydrogen.

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