Selective hydroisomerization of *n*-pentane to isopentane over highly dispersed Pd-H$_4$SiW$_{12}$O$_{40}$/SiO$_2$

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Abstract

Pd-H$_4$SiW$_{12}$O$_{40}$ supported on SiO$_2$ with different loadings of H$_4$SiW$_{12}$O$_{40}$ were systematically characterized by X-ray diffractometry (XRD), infrared (IR) spectroscopy, and NH$_3$-temperature programmed desorption (TPD) and benzonitrile adsorption analyses. X-ray diffraction and infrared spectroscopy revealed that very few H$_4$SiW$_{12}$O$_{40}$ crystallites formed at less than 20 wt.% loading and that the Keggin structure was retained for all these catalysts. The density of acid sites on the top surface of catalysts determined by benzonitrile adsorption proved the average number of H$_4$SiW$_{12}$O$_{40}$ layers on SiO$_2$ to be 2.2, 2.6 and 4.0 at 10, 20 and 40 wt.% acid loading, respectively. NH$_3$ temperature programmed desorption showed that the acid strength increased markedly with the loading of H$_4$SiW$_{12}$O$_{40}$, attributed to suppressed interactions between the protons of H$_4$SiW$_{12}$O$_{40}$ and the OH groups on SiO$_2$. The selectivity to isopentane in skeletal isomerization of *n*-pentane was found to be highly sensitive to the loading of H$_4$SiW$_{12}$O$_{40}$, decreasing with increasing load, associated with the change in acid strength by the supporting on SiO$_2$. A catalyst with the composition 1 wt.% Pd-20 wt.% H$_4$SiW$_{12}$O$_{40}$ on SiO$_2$ exhibited very high selectivity (99.1%) and high activity.
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1. Introduction

Heteropolyacids exhibit strong acidity and high activity for various acid-catalyzed reactions [1–5], and several commercial processes have been established for acid-catalyzed reactions and oxidation reactions using heteropoly compounds [1,6,7]. As solid acids, heteropolyacids have relatively low surface area (around 6 m^2 g^{-1}). Supporting these heteropolyacids on oxidic carriers has been examined as a means of enhancing the density of acid sites available for reactions. SiO$_2$ has been reported to be a suitable support that disperses heteropolyacids while retaining the structure [1]. However, the acid strength has been also reported to decrease when supported in this way [8].

SiO$_2$-supported heteropolyacids have been shown to give high activities and selectivities for various reactions [9–13]. Tatibouet et al. [14] reported that H$_3$PMo$_{12}$O$_{40}$/SiO$_2$ selectively catalyzed the oxidation of methanol, and that this selectivity is closely related to the acid loading. Although the selectivity to dimethyl ether remained constant at high loadings, this selectivity disappeared at low loadings. The chemical state of heteropolyacids on SiO$_2$ has been

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characterized by solid-state nuclear magenetic resonance (NMR) spectroscopy, Raman spectroscopy, infrared (IR) spectroscopy, and X-ray diffractometry (XRD) [15–19]. The interaction between heteropolyacids and OH groups on the SiO_2 is considered to be responsible for the change in acid strength [8,15].

Recently, bifunctional catalysts consisting of a metal and a heteropolyacid have attracted much attention. Showa Denko has developed a bifunctional catalyst consisting of Pd, $H_4SiW_{12}O_{40}$ and SiO_2 for the selective oxidation of ethylene to acetic acid in the presence of water [20], proposing a mechanism that involves the hydration of ethylene on the acid sites and the subsequent oxidation of ethanol on Pd, which is different from the Wacker-type reactions [20].

Skeletal isomerization of alkanes has industrially important applications because branched alkanes are useful as clean high-octane fuels. This process is a refinery process that in fact produces significant quantities of the ideal component of reformulated gasoline: isoalkanes. There are also a number of reports detailing the hydroisomerization of *n*-pentane over bifunctional catalysts such as $Pt-SO_4^{2-}/ZrO_2$ [21], $Pt-Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [22], Pt-H-ZSM-5 [23] and $Pt-WO_3/ZrO_2$ [24].

In the present study, the catalytic performance of $Pd-H_4SiW_{12}O_{40}/SiO_2$ is evaluated with respect to the skeletal isomerization of *n*-pentane. The effects of the loading of $H_4SiW_{12}O_{40}$ and Pd on the catalytic activity and selectivity were systematically investigated, and the acid strength, dispersion of $H_4SiW_{12}O_{40}$, and in particular the density of acid sites on the catalyst surface was examined. The catalytic performance of $Pd-H_4SiW_{12}O_{40}/SiO_2$ for *n*-pentane isomerization is discussed in relation to the acidic property.

2. Experimental

2.1. Catalysts

Pd-free $H_4SiW_{12}O_{40}$ catalysts supported on silica ($H_4SiW_{12}O_{40}/SiO_2$) were prepared from an aqueous solution of $H_4SiW_{12}O_{40}$ (Nippon Inorganic Color Chemical Co.) and SiO_2 (Aerosil 300, $274 \, m^2 \, g^{-1}$) by incipient wetness impregnation as follows. The aqueous solution of $H_4SiW_{12}O_{40}$ at a concentration of $0.1 \, mol \, dm^{-3}$ was added drop-wise to SiO_2

at room temperature while stirring vigorously. The $H_4SiW_{12}O_{40}$ solution was added so as to achieve a ratio of about $2.0 \, cm^3 \, g^{-1}$ of SiO_2. The wet sample was then dried at 373 K in an oven. The loading of $H_4SiW_{12}O_{40}$ was changed from 10 to 40 wt.% by repeating this impregnation process. After impregnation, the sample was dried in an oven at 373 K overnight and then calcined at 573 K in air for 5 h. These samples are named $HSiW/SiO_2$.

Pd was added to $HSiW/SiO_2$ by impregnation using an aqueous solution ($0.03 \, mol \, dm^{-3}$) of $PdCl_2 \cdot 6H_2O$ (Wako Chemical Co). In order to dissolve the Pd compound in water, a small amount of HCl ($11.5 \, mol \, dm^{-3}$) was added. After drying at 373 K, the sample was calcined at 573 K in air for 5 h. The loading of Pd was adjusted to 2.0 wt.% for most samples. In the case of 20 wt.% $HSiW/SiO_2$, the loading of Pd was varied from 0.5 to 2 wt.%. These catalysts are named $Pd-HSiW/SiO_2$.

2.2. Catalytic reaction

Skeletal isomerization of *n*-pentane was performed in a flow reactor (Pyrex, 10 mm i.d.) at 523 K under atmospheric pressure. After placing 0.1 g of the catalyst in the reactor, the reactant gas (*n*-pentane:H_2:He = 6.1:69.4:24.5 vol.%) was fed at a rate of $24.1 \, cm^3 \, min^{-1}$. Prior to reaction, the catalysts were exposed to a flow of H_2 ($50 \, cm^3 \, min^{-1}$) at 573 K for 2 h. The composition of the gas at the outlet of the reactor was analyzed using a flame ionization detector gas chromatograph (Shimadzu GC-14B) equipped with a VZ-7 column.

2.3. Other measurements

Surface area was measured by the BET method using an automatic gas adsorption system (BELSORP-28, BEL, Japan). IR spectra of $HSiW/SiO_2$ and Pd-HSiW/ SiO_2 were obtained at room temperature using a Fourier transform infrared (FT-IR) spectrometer (FT/IR 230, JASCO). A sample disk was made by pressing the sample with KBr at the weight ratio of catalyst:KBr = 3.5:700. XRD patterns of the catalysts were recorded on a Rigaku Miniflex diffractometer at room temperature. NH_3-temperature programmed desorption (TPD) was performed on a Multitask TPD system (BEL, Japan) using 0.2 g of catalyst after

pretreatment at 523 K under He flow [25] as follows. The catalyst was exposed to NH_3 flow at 100 Torr for 20 min at 373 K, and the chamber was subsequently purged with He for 0.5 h at 373 K. The temperature of the sample was raised at a rate of $10\,K\,min^{-1}$ to 973 K, and the desorbed gases were analyzed using the integrated mass spectrometer.

Adsorption of benzonitrile was measured using a microbalance (improved TG-30, Shimadzu Co.) connected directly to an ultrahigh vacuum system [26]. About 15 mg of catalyst was set in a Pt pan and pretreated at 573 K for 2 h in a vacuum. Benzonitrile was then introduced to a total pressure of 0.16 Torr at 393 K. The amount of adsorption was determined after adsorption neared equilibrium longer than 1 h after the introduction of benzonitrile.

3. Results

3.1. Skeletal isomerization of n-pentane

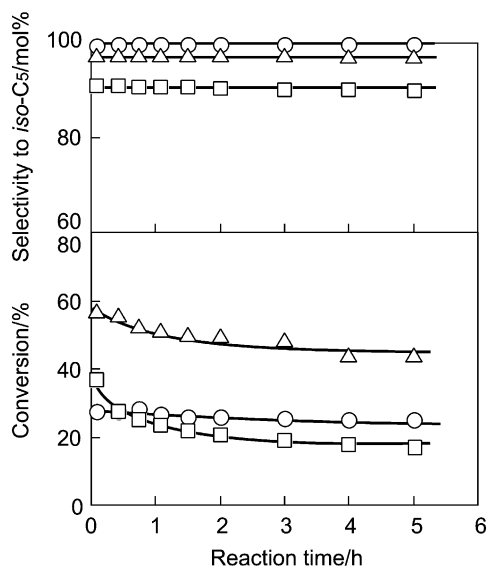Fig. 1 shows the progression of skeletal isomerization of n-pentane over 2 wt.% Pd-HSiW/SiO$_2$ for

Fig. 1. Time courses of skeletal isomerization of n-pentane over 2 wt.% Pd-H$_4$SiW$_{12}$O$_{40}$/SiO$_2$. Loading amounts of H$_4$SiW$_{12}$O$_{40}$: (○) 10 wt.%, (△) 20 wt.% and (□) 40 wt.%. $W/F = 27.6\,g\,h\,(mol$ of n-pentane$)^{-1}$; n-pentane:H$_2$:He = 6.1:69.4:24.5 (vol.%); reaction temperature: 523 K and catalyst: 0.10 g.

Fig. 2. The effect of loading amount of H$_4$SiW$_{12}$O$_{40}$ on skeletal isomerization of n-pentane. $W/F = 27.6\,g\,h\,(mol$ of n-pentane$)^{-1}$; n-pentane:H$_2$:He = 6.1:69.4:24.5 (vol.%); reaction temperature: 523 K and catalyst: 0.10 g.
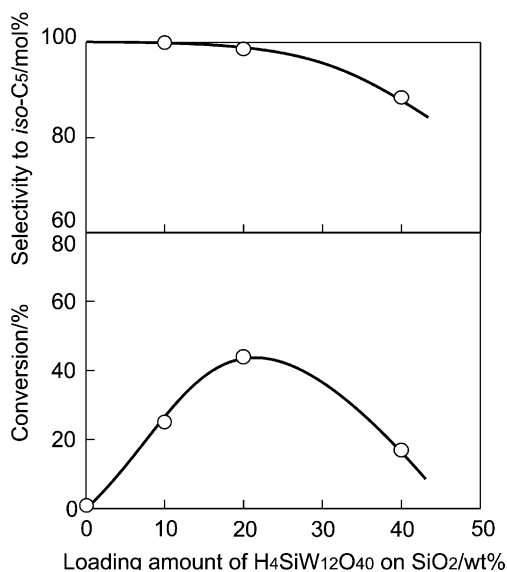
various H$_4$SiW$_{12}$O$_{40}$ loadings. The conversion decreased slightly in the initial stage of the reaction for all catalysts except the 10 wt.% acid loading. This conversion decrease was most prominent for the sample with 40 wt.% acid loading. The stationary catalytic activity and selectivity were obtained after 300 min of the reaction. The equilibrium conversion of n-pentane under these conditions is about 70% [27].

Fig. 2 shows the effect of H$_4$SiW$_{12}$O$_{40}$ loading on the conversion and selectivity to isopentane over 2 wt.% Pd-HSiW/SiO$_2$. The stationary conversion values peaked at around 20 wt.% H$_4$SiW$_{12}$O$_{40}$. The selectivity to isopentane decreased with increasing acid loading, the maximum of 99.8% occurring at 10 wt.% H$_4$SiW$_{12}$O$_{40}$.

Fig. 3 shows the effect of Pd loading on conversion and selectivity. The Pd-free HSiW/SiO$_2$ catalyst exhibited very low conversion. The addition of Pd to HSiW/SiO$_2$ significantly enhanced conversion up to saturation at 1.0 wt.% Pd. A selectivity higher than 97% was obtained for all Pd-20 wt.% HSiW/SiO$_2$ catalysts. The relevant data are summarized in Table 1.

Table 1
Catalytic data for *n*-pentane isomerization over Pd-$H_4SiW_{12}O_{40}/SiO_2$

	Conversion (%)	Selectivity (mol%)							
		C_1[a]	C_2[b]	C_3[c]	iC_4[d]	nC_4[e]	iC_5[f]	C_5[g]	C_6[h]
2.0 wt.% Pd-10 wt.% HSiW/SiO₂	25.1	0.0	0.0	0.0	0.1	0.0	99.8	0.0	0.1
2.0 wt.% Pd-20 wt.% HSiW/SiO₂	43.9	0.0	0.0	0.2	1.4	0.2	97.0	0.1	1.1
2.0 wt.% Pd-40 wt.% HSiW/SiO₂	17.0	0.0	0.0	0.8	5.1	0.6	89.9	0.1	3.5
20 wt.% HSiW/SiO₂	1.2	0.0	0.0	4.1	13.3	4.3	73.9	0.0	4.4
0.5 wt.% Pd-20 wt.% HSiW/SiO₂	31.1	0.0	0.0	0.0	0.7	0.1	98.6	0.0	0.6
1.0 wt.% Pd-20 wt.% HSiW/SiO₂	43.7	0.0	0.0	0.0	0.5	0.1	99.1	0.0	0.3
2.0 wt.% Pd-20 wt.% HSiW/SiO₂	43.9	0.0	0.0	0.2	1.4	0.2	97.0	0.1	1.1

$W/F = 27.6$ g h (mol of *n*-pentane)$^{-1}$; *n*-pentane:H_2:He = 6.1:69.4:24.5 (vol.%); reaction temperature: 523 K and catalyst weight: 0.10 g.
[a] Methane.
[b] Ethane.
[c] Propane.
[d] Isobutane
[e] *n*-butane.
[f] Isopentane.
[g] Pentenes.
[h] Hexanes.

3.2. Characterization of $H_4SiW_{12}O_{40}/SiO_2$ and Pd-$H_4SiW_{12}O_{40}/SiO_2$

The surface areas of HSiW/SiO₂ and 2 wt.% Pd-HSiW/SiO₂ are shown in Fig. 4, as a function of the loading of $H_4SiW_{12}O_{40}$. Both surface areas declined monotonically with increasing $H_4SiW_{12}O_{40}$ loading. The broken line in the figure is the surface area calculated from the composition of SiO₂ and $H_4SiW_{12}O_{40}$ by assuming the surface areas of 274 and 5 m² g⁻¹ for SiO₂ and bulk $H_4SiW_{12}O_{40}$,
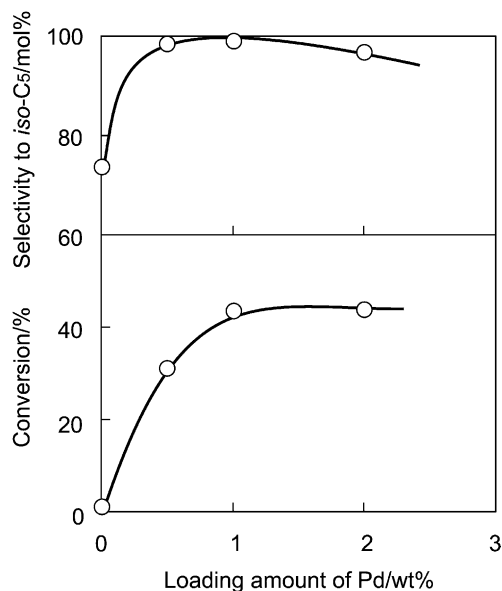

Fig. 3. Changes in the activity and selectivity as a function of loading amount of Pd for 20 wt.% $H_4SiW_{12}O_{40}/SiO_2$. *W/F* = 27.6 g h (mol of *n*-pentane)$^{-1}$; *n*-pentane:H_2:He = 6.1:69.4:24.5 (vol.%); reaction temperature: 523 K and catalyst: 0.10 g.

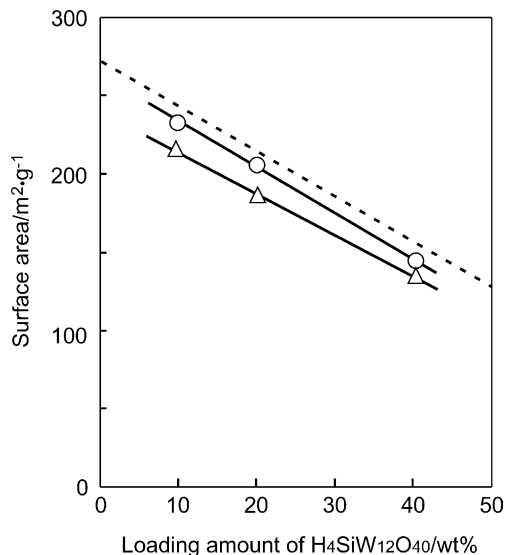

Fig. 4. Changes in the surface area as a function of loading amounts of $H_4SiW_{12}O_{40}$. Broken line: calculated line (see text); (○) $H_4SiW_{12}O_{40}/SiO_2$ and (△) 2 wt.% Pd-$H_4SiW_{12}O_{40}/SiO_2$.
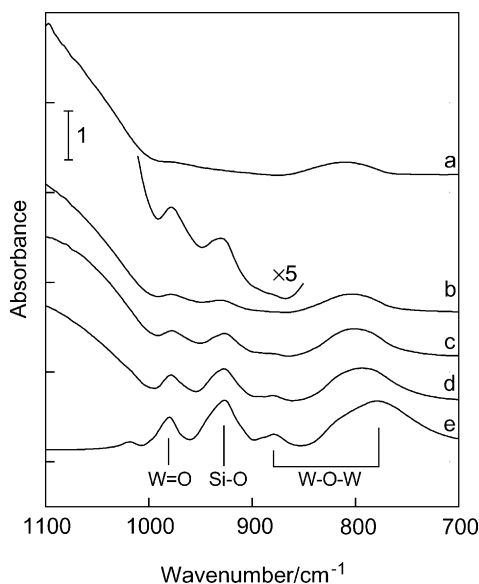
Fig. 5. IR spectra of 2 wt.% Pd-$H_4SiW_{12}O_{40}$/SiO_2. (a) SiO_2, (b) 2 wt.% Pd-10 wt.% $H_4SiW_{12}O_{40}$/SiO_2, (c) 2 wt.% Pd-20 wt.% $H_4SiW_{12}O_{40}$/SiO_2, (d) 2 wt.% Pd-40 wt.% $H_4SiW_{12}O_{40}$/SiO_2 and (e) $H_4SiW_{12}O_{40}$. Catalyst:KBr = 3.5:700 (in weight).

Fig. 6. XRD patterns of $H_4SiW_{12}O_{40}$/SiO_2 and 2 wt.% Pd-$H_4SiW_{12}O_{40}$/SiO_2. (A) $H_4SiW_{12}O_{40}$/SiO_2, (B) 2 wt.% Pd-$H_4SiW_{12}O_{40}$/SiO_2. (a) SiO_2, (b) 10 wt.% $H_4SiW_{12}O_{40}$/SiO_2, (c) 20 wt.% $H_4SiW_{12}O_{40}$/SiO_2, (d) 40 wt.% $H_4SiW_{12}O_{40}$/SiO_2, (e) $H_4SiW_{12}O_{40}$, (f) 2 wt.% Pd-10 wt.% $H_4SiW_{12}O_{40}$/SiO_2, (g) 2 wt.% Pd-20 wt.% $H_4SiW_{12}O_{40}$/SiO_2 and (h) 2 wt.% Pd-40 wt.% $H_4SiW_{12}O_{40}$/SiO_2. Arrows show the peaks due to the crystallites of $H_4SiW_{12}O_{40}$.

respectively. This calculated areas are in good agreement with the measured areas for HSiW/SiO_2. The surface areas of the Pd-HSiW/SiO_2 catalysts were slightly lower than those of HSiW/SiO_2. The surface areas of these catalysts therefore correspond to those of SiO_2 in these catalysts, suggesting that aggregation of SiO_2 is not important during preparation.

IR spectra for 2 wt.% Pd-HSiW/SiO_2 are illustrated in Fig. 5, together with those for SiO_2 and bulk $H_4SiW_{12}O_{40}$. $H_4SiW_{12}O_{40}$ gave peaks due to the Keggin structure at 980 cm^{-1} (ν(W=O)), 926 cm^{-1} (ν(Si–O)), 879 and 783 cm^{-1} (ν(W–O–W)). SiO_2 exhibited a broad peak at 808 cm^{-1} and a small peak at 980 cm^{-1}. All the 2 wt.% Pd-HSiW/SiO_2 catalysts produced peaks characteristic of the Keggin structure, and the intensity of these peaks varied according to the loadings of $H_4SiW_{12}O_{40}$. The peak at 783 cm^{-1} shifted with the loading of $H_4SiW_{12}O_{40}$ as a result of overlap with the SiO_2 peak (808 cm^{-1}). It is notable that even for 2 wt.% Pd-10 wt.% HSiW/SiO_2, the peaks due to W=O and Si–O were clearly detected. IR spectroscopy showed that the used Pd-20 wt.% $H_4SiW_{12}O_{40}$/SiO_2 also gave the peaks due to Keggin structure with the similar shape and intensity to those

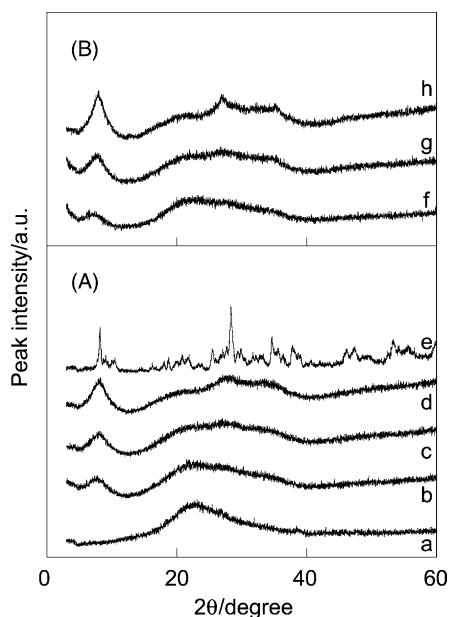in Fig. 5. This indicates that the Keggin structure was retained during the reaction.

The XRD patterns for 2 wt.% Pd-HSiW/SiO_2 and HSiW/SiO_2 are shown in Fig. 6. SiO_2 itself gave a broad peak at around $2\theta = 21°$ (Fig. 6a). Although all HSiW/SiO_2 catalysts were expected to be amorphous, broad peaks were detected at around $2\theta = 8.2°$ attributable to $H_4SiW_{12}O_{40}$. Similar results were obtained for 2 wt.% Pd-HSiW/SiO_2, although 2 wt.% Pd-40 wt.% $H_4SiW_{12}O_{40}$/SiO_2 produced small peaks due to the crystallites of $H_4SiW_{12}O_{40}$.

The adsorption of benzonitrile on 2 wt.% Pd-HSiW/SiO_2 and HSiW/SiO_2 is plotted as a function of the acid loading in Fig. 7. The broken line represents the total amount of protons present in Pd-HSiW/SiO_2 estimated from the loading of $H_4SiW_{12}O_{40}$. It was confirmed that only very small amounts of benzonitrile ($<1 \mu$mol g^{-1}) were adsorbed on bulk $H_4SiW_{12}O_{40}$ and SiO_2, as summarized in Table 2.
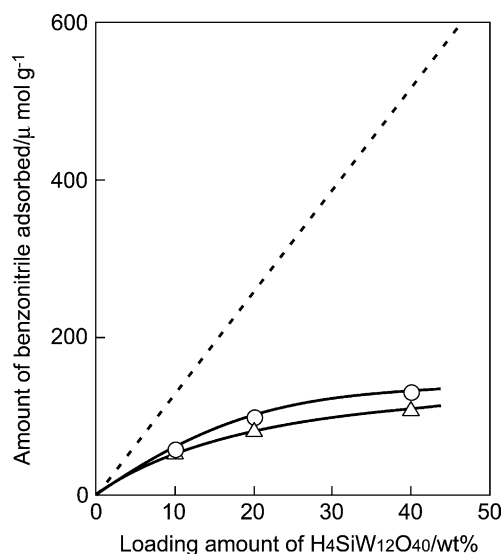
Fig. 7. Adsorption amounts of benzonitrile on $H_4SiW_{12}O_{40}/SiO_2$ and $Pd-H_4SiW_{12}O_{40}/SiO_2$ at 393 K. (○) $H_4SiW_{12}O_{40}/SiO_2$, (△) 2 wt.% $Pd-H_4SiW_{12}O_{40}/SiO_2$. Catalyst: 15 mg; broken line: total amount of protons calculated from the loading amount of $H_4SiW_{12}O_{40}$.

The adsorption of benzonitrile at 393 K on 2 wt.% Pd-HSiW/SiO₂ increased monotonically with the loading of $H_4SiW_{12}O_{40}$, whereas the opposite trend was observed at room temperature. It was confirmed that benzonitrile was adsorbed onto SiO₂ at room temperature but scarcely at 393 K.

Fig. 8 shows the NH₃-TPD patterns for HSiW/SiO₂. A sharp peak at about 800 K was observed for bulk $H_4SiW_{12}O_{40}$. When supported on SiO₂, the desorption temperature of $H_4SiW_{12}O_{40}$ decreased and the desorption peak became much broader. The

Table 2
Adsorption amount of benzonitrile ($\mu mol\, g^{-1}$) on $H_4SiW_{12}O_{40}/SiO_2$

	Loading amount of $H_4SiW_{12}O_{40}$ (wt.%)				
	0	10	20	40	100
Total H^{+}[a]	0	130	260	520	1300
NH₃[b]	0	171	293	559	1390
Benzonitrile[c]	<1	58	100	130	<1

[a] Calculated from the composition.

[b] Desorption amount in NH₃-TPD.

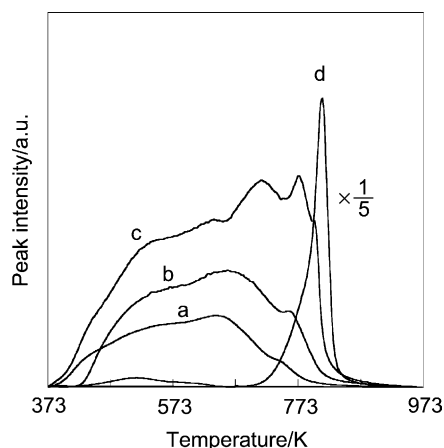[c] Adsorption pressure of benzonitrile: 0.16 Torr; adsorption temperature: 393 K and catalyst weight: 15 mg.

Fig. 8. NH₃-TPD profiles of $H_4SiW_{12}O_{40}/SiO_2$. (a) 10 wt.% $H_4SiW_{12}O_{40}/SiO_2$, (b) 20 wt.% $H_4SiW_{12}O_{40}/SiO_2$, (c) 40 wt.% $H_4SiW_{12}O_{40}/SiO_2$ and (d) $H_4SiW_{12}O_{40}$. Catalyst: 0.20 g. Adsorption of NH₃ (100 Torr) at 373 K for 10 min, and evacuation for 30 min. The temperature was raised at a rate of 10 K min⁻¹.

desorption amounts estimated from the peak areas correlate roughly with the loading of $H_4SiW_{12}O_{40}$, except for the 10 wt.% HSiW/SiO₂. As summarized in Table 2, the desorption amount of NH₃ from 10 wt.% HSiW/SiO₂ was greater than that of the total proton.

4. Discussion

4.1. Acidic property of $Pd-H_4SiW_{12}O_{40}/SiO_2$

Based on microcalorimetry measurements of the heat of adsorption of NH₃, Kozhevnikov and coworkers reported that the acid strength of $H_3PW_{12}O_{40}$ decreases significantly when supported on SiO₂ [8]. The present results confirm this observation, and this reduction in acid strength becomes more prominent with decreasing $H_4SiW_{12}O_{40}$ loading. Notably, the 10 wt.% $H_4SiW_{12}O_{40}/SiO_2$ catalyst did not give the NH₃ desorption peak at high temperature (∼800 K) observed for the parent $H_4SiW_{12}O_{40}$.

Mastihkin et al. and Lefebvre [15,16] proposed a model for the interaction between $H_3PW_{12}O_{40}$ and the surface of SiO₂ based on observations by solid-state NMR, wherein protons of $H_3PW_{12}O_{40}$ reacted with OH groups on SiO₂ to form $-OH_2^{+}\cdots H_2PW_{12}O_{40}^{-}$. This interaction would reduce the acid strength. Kozhevnikov et al. [28] claimed that the Keggin structure was retained on the SiO₂ surface, and this is

supported by the present IR data for Pd-HSiW/SiO$_2$ shown in Fig. 5.

If the interaction between H$_4$SiW$_{12}$O$_{40}$ and OH groups is essential, the degree of dispersion will influence the acid strength. In order to clarify the dispersion conditions, it is useful to determine the number of protons present on the top surface of the catalyst. The reactions catalyzed by heteropolyacids can be divided into surface reactions and bulk reactions [1,29,30], with non-polar molecules like hydrocarbons driving surface reactions and polar molecules such as alcohol driving bulk reactions. The catalytic activity in the skeletal isomerization of alkanes should be governed by the amount of acid exposed to the gas phase at the surface.

As base molecules such as NH$_3$ and pyridine interact with the acid sites of the bulk heteropolyacid [1,31], these molecules are not suitable for the measurement of acid sites on the top surface. However, these molecules are useful to measure the total amount of acid sites present in the catalyst. It is noted that the amount of acid sites estimated from the NH$_3$-TPD was greater than the expected one (Table 2). It is reasonable to consider that the OH groups became more acidic through the interaction with H$_4$SiW$_{12}$O$_{40}$ ($-OH_2^+ \cdots H_3SiW_{12}O_{40}^-$).

In the present study, the adsorption of various molecules was examined as a preliminary investigation to identify an appropriate agent for distinguishing acid sites on the top surface from the surface layers of the catalysts. It was observed that acetonitrile was absorbed into the bulk H$_4$SiW$_{12}$O$_{40}$. However, benzonitrile was not absorbed, and was instead adsorbed only on the surface (Table 2). This difference is reasonable because the adsorption capability was governed by the molecular size and basicity [32]. Benzonitrile was therefore selected as the base molecule for determining the amount of acid sites on the top surface and hence the dispersion of H$_4$SiW$_{12}$O$_{40}$ on SiO$_2$.

As demonstrated in Fig. 7 and Table 2, when benzonitrile was introduced at 393 K onto the catalysts, appreciable uptakes were observed for both the HSiW/SiO$_2$ and Pd-HSiW/SiO$_2$, but the uptakes were little for SiO$_2$ only or the bulk H$_4$SiW$_{12}$O$_{40}$. Therefore, it is concluded that benzonitrile is a suitable probe molecule to estimate the amount of acid sites on the top surface of supported heteropolyacid catalysts.

Based on the data in Table 2, the calculated ratios of the number of benzonitrile molecules adsorbed to the total number of protons for 10, 20 and 40 wt.% acid loading were 0.45, 0.38 and 0.25. Assuming that the number of adsorbed benzonitrile molecules corresponds to the number of protons on the top surface, the average number of layers of aggregates of H$_4$SiW$_{12}$O$_{40}$ is then 2.2, 2.6 and 4.0, respectively (Fig. 9). The model in Fig. 9 is consistent with the XRD results in Fig. 6. Considering the size of SiW$_{12}$O$_{40}{}^{4-}$ (about 1.0 nm) [1] and the surface area of SiO$_2$ (274 m^2 g^{-1}), the ideal monolayer of H$_4$SiW$_{12}$O$_{40}$ corresponds to 58 wt.% H$_4$SiW$_{12}$O$_{40}$ (corresponds to 202 μmol g^{-1}). Considering the number of OH groups present on SiO$_2$ (Aerosil 200; 39–92 μmol g^{-1}) [26], the formation of aggregates at higher loadings is probably due to the insufficient amount of OH groups.

To reveal more detailed structure of layers of H$_4$SiW$_{12}$O$_{40}$ on SiO$_2$, we should consider the influence of the acid strength on the interaction with benzonitrile. If benzonitrile is adsorbed only on protons directly attached to SiW$_{12}$O$_{40}{}^{4-}$, for example H$_3$SiW$_{12}$O$_{40}{}^-$ of $-OH_2^+-H_3SiW_{12}O_{40}^-$, the estimated number of layers will be less than 2.2 for 10 wt.% HSiW/SiO$_2$. On the contrary, if benzonitrile can also interact with Si–OH$_2^+$, the estimated number will be greater than 2.2 for 10 wt.% HSiW/SiO$_2$. While there is no evidence for the influence of the acid strength on the adsorption of benzonitrile at present, it should be elucidated in future.

4.2. Catalytic activity and selectivity

The activity and selectivity for the skeletal isomerization of *n*-pentane are strongly influenced by the loading amount of H$_4$SiW$_{12}$O$_{40}$ (Fig. 2 and Table 1). However, the change in conversion with acid loading differs from the change in benzonitrile adsorption (Figs. 2 and 7). The change in the acid amount (Fig. 7) is reasonable and is attributed to the aggregation of H$_4$SiW$_{12}$O$_{40}$. As this reaction can be classified as a surface reaction [1], the activity should be related to the amount of protons on the surface. The difference between the change in conversion and the change in acid amount on the surface is probably due to deactivation during the reaction. Significant deactiva-
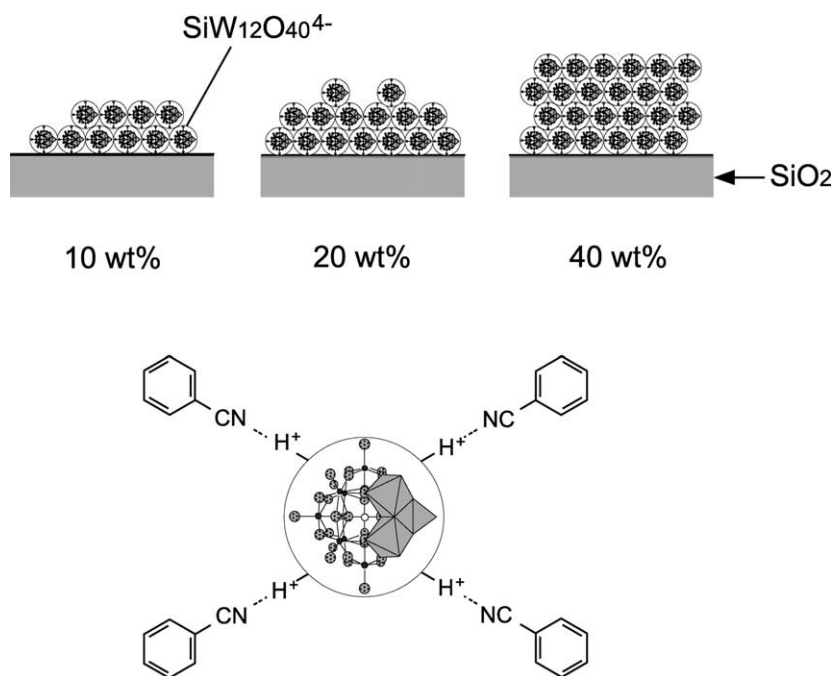
Fig. 9. Proposed models for Pd-$H_4SiW_{12}O_{40}$/SiO_2.

tion of 2 wt.% Pd-40 wt.% HSiW/SiO$_2$ would result in the observed variation in conversion.

The by-products, isobutane and propane (Table 1), are considered to be formed by β-scission of dimer intermediates (C10) on acid sites [33], and not by the hydrogenolysis of *n*-pentane at Pd sites. Thus, the acidic properties, particularly the acid strength, are considered to be a critical factor determining the selectivity. Considering the change in acid strength (Fig. 8), the higher selectivities at low loadings of $H_4SiW_{12}O_{40}$ are attributable to the reduced acid strength at these acid concentrations. Strong acid sites would preferentially accelerate the β-scission of intermediates compared to the skeletal isomerization of *n*-pentane.

The rate of this reaction with 6.1% *n*-pentane on 1.0 wt.% Pd-20 wt.% HSiW/SiO$_2$ at 523 K was 15.8 mmol g^{-1} h^{-1}, compared to 2.99 and 0.54 mmol g^{-1} h^{-1} reported for other bifunctional catalysts of 0.5 wt.% Pd-H-ZSM-5 with 10% *n*-pentane and 1 wt.% Pt-WO$_3$/ZrO$_2$ with 0.83% *n*-pentane at the same temperature in the literature [23,24]. Assuming that the rate is linearly proportional to the concentration of *n*-pentane, the relative catalytic activity would be 100:11:25 for 1 wt.% Pd-20 wt.% HSiW/SiO$_2$,

0.5 wt.% Pd-H-ZSM-5, and 1 wt.% Pt-WO$_3$/ZrO$_2$. The selectivity (99.1%) for isopentane over the present 1 wt.% Pd-20 wt.% HSiW/SiO$_2$ catalyst is the highest among these bifunctional catalysts. The results obtained in this study therefore demonstrate that 1 wt.% Pd-20 wt.% $H_4SiW_{12}O_{40}$/SiO$_2$ offers excellent catalytic performance for the hydroisomerization of *n*-pentane.

Finally, it is necessary to discuss the role of Pd sites on the skeletal isomerization. Since Pd-free HSiW/SiO$_2$ was much less active (Table 2), the critical role of Pd is clear. As was previously discussed [22], Pd activates alkanes to form the corresponding olefin, which is readily transformed to carbenium ion intermediates. In the absence of Pd, it is required that acid (proton) attacks directly to alkane to form carbenium ion intermediates. More stronger acid sites are necessary for the latter process.

Acknowledgements

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