Dehydration of *n*-butanol over highly dispersed heteropolyacid intercalation compounds

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Heteropolyacid is introduced in an intercalation compound of zinc aluminum carbonate hydroxide by an anion-exchanging technique. The acid is probably present as $H_{2.1}PW_{9.2}O_{33.3}^{4.2-}$ and is shown to be highly dispersed. The compound catalyzes dehydration of *n*-butanol with noticeably higher activity and selectivity to 1-butene than free Keggin type 12-heteropolyacid.

Keywords: Heteropolyacid; dehydration; intercalate; pyridine; butanol

1. Introduction

Heteropolyacids are well known as active acid catalysts for the hydration of olefins, dehydration of alcohol, esterification and so on [1–6]. It has been pointed out that the acid on supports such as silica, alumina, or activated carbon interacts strongly with the surface of the support, that the catalytic behavior is somehow different from that of a free heteropolyacid [1–6] and that the acid probably functions as a condensed solution on the surface of the support [7]. However, the different behavior is observed only in a low acid-content on these supports. Since the dispersion of heteropolyacid on these supports is still low, its catalytic property appears to reflect that of the original heteropolyacid [1–6]. Hence, we were interested in the catalytic activity of heteropolyacids highly dispersed on the support surface because the heteropolyacid would show different catalytic property from the condensed solution of the acid.

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In this study, a hydrotalcite-like layered compound was employed as a support for heteropolyacid in order to obtain the acid highly dispersed on a solid surface even in a high acid-content. The chemical formula of the layer compound can be represented as $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ having anion-exchanging ability. The carbonate anions in the compound are placed between the zinc-aluminum hydroxide layers to maintain charge neutrality [8] and the anion will be replaced with a tungstophosphate anion. Catalytic dehydration of *n*-butanol was carried out for characterization of the solid because alcohol dehydration is a typical acid-catalyzed reaction and the distribution of products provides information on the catalyst.

2. Experimental

Keggin type 12-heteropoly tungstophosphoric acid (PW_{12}), $H_3PW_{12}O_{40} \cdot nH_2O$, was synthesized by the method of Katsoulis and Pope [9]. The acid was used as a starting material. A hydrotalcite-like intercalation compound, zinc–aluminum carbonate hydroxide (Zn–Al), was prepared according to ref. [8]. The preparation of zinc–aluminum tungstophosphate hydroxide (PW / Zn–Al) was carried out as follows: at first, a sodium hydroxide aqueous solution was added to an aqueous solution of PW_{12} till the mixture reached pH 6 to avoid decomposition of the structure of Zn–Al which decomposes easily in strongly acidic solution. The powder of Zn–Al was then suspended in the solution and the mixture was kept at 80°C with stirring for 3 h. The precipitate was washed with decationized water and dried at 100°C for 5 h.

The chemical composition of these samples was determined with a Shimadzu sequential plasma spectrometer (ICPS-1000). As presented in table 1, the compositions of starting materials, PW_{12} and Zn–Al, were very consistent with the formulas of $H_3PW_{12}O_{40} \cdot nH_2O$ and $Zn_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, respectively. The sodium content of PW / Zn–Al was only 0.001 mmol g^{-1}, indicating that sodium is present as an impurity. The X-ray diffraction (XRD) patterns of the samples were recorded with a McScience XP_{18} spectrometer. The pattern of Zn–Al was identical with that of zinc aluminum carbonate hydroxide in ref. [10]. Adsorption of pyridine at

Table 1
Chemical composition of samples. In parentheses the values calculated for $2Zn_6Al_2(OH)_{16} \cdot 23.6H_2O \cdot H_2PW_9O_{33}$ are given

Sample	Composition (mmol g^{-1})			
	Zn	Al	P	W
PW_{12}	none	none	0.32	4.0
Zn–Al	6.9	2.3	none	none
PW / Zn–Al	3.2	1.0	0.24	2.2
	(3.14)	(1.05)	(0.262)	(2.36)

100°C was carried out by gravimetry using a Cahn 2000 microbalance. Infrared (IR) spectra of the samples dispersed in KBr wafers were recorded in air with a Perkin-Elmer Model 1760X FTIR spectrometer.

Dehydration of *n*-butanol over these samples was performed using a pulse microcatalytic reactor with a helium-flow rate of 10 ml min^{-1}. The reaction products were analyzed by gas chromatography with a PEG 1000 column (1 m). In order to compare the catalytic activity of heteropolyacid, 8.9 mg of PW_{12} and 11.8 mg of PW / Zn–Al (both samples include 0.0028 mmol of heteropolyacid) were placed in the catalyst bed. The amount of Zn–Al used was 20 mg.

3. Results and discussion

3.1. CHARACTERIZATION OF THE HETEROPOLYACID INTERCALATION COMPOUND

The absorption bands assignable to the stretching vibrations of P–O and W=O were observed in the IR spectrum of PW_{12} (fig. 1a) at 1080 and 983 cm^{-1}, respectively [11]. In the literature, the IR spectrum is reported as intense sharp bands at 1080 cm^{-1}, and at 983 cm^{-1} for PW_{12} [11], at 1085 cm^{-1} for $PW_{11}O_{39}^{7-}$ [12], and at ca. 1060 cm^{-1} and at ca. 950 cm^{-1} for $PW_9O_{34}^{9-}$ [13]. The bands were also observed in the spectrum of PW / Al–Zn (fig. 1b), however, the position was shifted to 1058 and 963 cm^{-1}, respectively. This shows that the structure of heteropolyacid in PW / Zn–Al is somehow different from that of the Keggin type material. Actually, the molar ratio of W / P in PW / Zn–Al was 9.2 (see table 1), indicating that the heteropolyacids in PW / Zn–Al are lacunary species and not Keggin type.

In order to estimate the number of acid sites, we measured the amount of pyridine irreversibly adsorbed on the intercalation compounds at 100°C. The amount of pyridine irreversibly adsorbed on PW / Zn–Al was 0.53 mmol g^{-1}, while that for

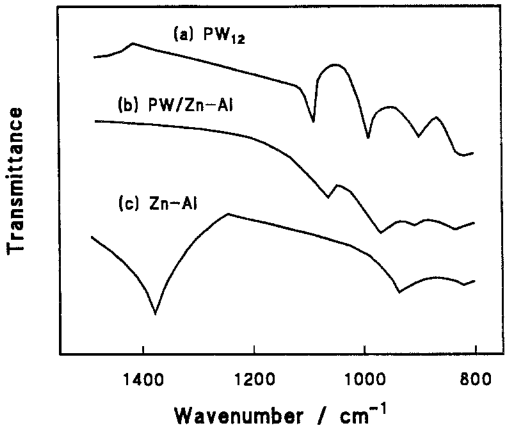

Fig. 1. IR spectra of samples. (a) PW_{12}, (b) PW / Zn–Al, (c) Zn–Al.

Zn–Al was 0.11 mmol g^{-1}. Pyridine would adsorb on weak acid sites or others on Zn–Al because Zn–Al did not exhibit catalytic activity toward the dehydration of *n*-butanol, which is a typical acid-catalyzed reaction as described in section 3.2. If the adsorption sites on Zn–Al are preserved after the modification of heteropolyacid, 0.04 mmol g^{-1} of pyridine can be adsorbed on these sites in PW/Zn–Al because it is calculated that PW/Zn–Al contains 36 wt% of $Zn_6Al_2(OH)_{16}$. However, the number is significantly smaller than that adsorbed on PW/Zn–Al, hence, the major part of pyridine on PW/Zn–Al is probably adsorbed on the acid sites newly generated by the modification of heteropolyacid to Zn–Al. Assuming that the acidic hydrogen atoms in heteropolyacid on PW/Zn–Al adsorb the rest of the pyridine (0.49 mmol g^{-1}), one can determine the molar ratio of H^+/P in PW/Zn–Al to be 2.1.

Although a strong IR absorption band was observed at 1380 cm^{-1} which is assignable to the C–O stretching vibration in carbonate anion in the spectrum of Zn–Al (fig. 1c) [14,15], no such band was present in the spectrum of PW/Zn–Al (fig. 1b), indicating that almost all carbonate anions in Zn–Al are removed by the process of anion exchanging. Hence, 0.50 mmol g^{-1} of carbonate ions in the support are estimated to be exchanged with tungstophosphate anions including 0.24 mmol g^{-1} of phosphorus atoms (table 1), suggesting that the valence of the tungstophosphate anion is 4.2– if the anion contains one phosphorus atom.

Under the anion-exchanging conditions, PW_{12} is converted to a tungstic acid and lacunary heteropoly anions such as PW_{11}, PW_9, and PW_8 [12]. A complete decomposition of PW_{12} forms a phosphoric acid. The valences of phosphoric acid and tungstic acid are 3– and 2–. If a coexistence of the exchanged anions is supposed – namely tungstic anion, tungstophosphate anions, and phosphoric anion – the following equations are presented (see table 1):

$$3x + my + 2z = \text{total valence}, \quad 0.00149\,\text{mol/g},$$

$$\text{(anion-exchangeable capacity plus proton number)} \tag{1}$$

$$x + y = \text{P content}, \quad 0.00024\,\text{mol/g}, \tag{2}$$

$$ny + z = \text{W content}, \quad 0.002\,\text{mol/g}.(3)$$

x, y, z, n, and $m > 0$, where x, y, and z are the content of phosphoric anion, tungstophosphoric anions, and tungstic anion, respectively, and n and $-m$ are W/P atomic ratio, and the valence per P atom in tungstophosphate anions; $n = (\sum n_i y_i)/y$, $m = (\sum m_i y_i)/y = 6.3$ as described below. One can deduce the following equation from eqs. (1) and (3):

$$3nx + (2n - m)z = 0.00149n - 0.0022m. \tag{4}$$

Since all the characterized tungstophosphate species with $m_i > 4$ have n/m ratio between 0.5 and 1.4 [12], one obtains the following relation:

$$2n - m \geqslant 0, \quad \text{and} \quad 0.00149n - 0.0022m < 0\,.$$

Here, the relation (4) does not hold for the assumption of coexistence, since all of n, x, $2n - m$, and z are more than 0 and/or equal 0. This leads to the conclusion that the exchanged anions are tungstophosphate anions, and that the anions are not a tungstic anion and phosphoric anion.

Since tungstophosphate anion is generally expressed as $H_aPW_bO_c^{d-}$, we can temporarily determine the tungstophosphate anion in PW/Zn–Al to be $H_{2.1}PW_{9.2}O_c^{4.2-}$ based on the results described above: $2c$ equals a plus 5 plus $6b$ plus d. We calculated the chemical composition of $2Zn_6Al_2(OH)_{16} \cdot 23.6H_2O \cdot H_{2.1}PW_{9.2}O_{33.3}$. Thus, it is believed that the tungstophosphoric anion in PW/Zn–Al is mainly present as $H_{2.1}PW_{9.2}O_{33.3}^{4.2-}$. The $PW_{9.2}O_{33.3}$ with $d = 6.3$ is reasonable, according to the experimental facts that no exchange was observed for Keggin ion type with $d < 4$ in Zn–Al [16].

The distance of the spacing, $d(001)$, for the intercalation compounds prepared can be determined from the XRD patterns. Since the main peaks were observed at 11.1, 22.5, and 34.2° in 2-theta for Zn–Al and 7.9, 18.3, and 31.0° for PW_9/Zn–Al, the distance is calculated as 0.76 nm for Zn–Al and 1.07 nm for PW_9/Zn–Al. The thickness of the zinc aluminum hydroxide sheets is estimated as ca. 0.4 nm based on the crystalline structure. Thus, the interlayer regions of Zn–Al probably expand from ca. 0.4 to 0.7 nm by the modification of the heteropolyacid. The thickness of $PW_{12}O_{40}$ is 1.0 nm [17] and that of $PW_{9.2}O_{33.3}$is expected to be ca. 0.7 nm because the lacunary $PW_{9.2}O_{33.3}$ is formed by elimination of about 3 WO_3 units from $PW_{12}O_{40}$ of the Keggin structure. Hence, the expanded spacing, ca. 0.7 nm, agrees with the thickness of $PW_{9.2}O_{33.3}$. No XRD peaks assignable to heteropolyacids were observed in the pattern of PW/Zn–Al although PW/Zn–Al contains 54 wt% of the acid, indicating that $H_{2.1}PW_{9.2}O_{33.3}^{4.2-}$ is highly dispersed in the interlayer regions.

3.2. DEHYDRATION OF *n*-BUTANOL

Dehydration of *n*-butanol over PW/Zn–Al and PW_{12} was investigated using a pulse microcatalytic reactor in order to characterize the catalytic activity of the heteropolyacid intercalation compounds. No significant changes in the IR spectra and XRD patterns were observed with the catalysts used in the reaction at 230 or 250°C, indicating that the catalysts are stable under these conditions. As reaction products 1- and 2-butenes and water were detected but no dibutyl ether was produced. With the GC column used, cis- and trans-butenes were not separated.

No reaction was observed over Zn–Al even at 250°C and a dehydration activity appeared only after the modification of Zn–Al with heteropolyacid, indicating that the intercalated tungstophosphate anions are active sites on PW/Zn–Al.

With a small dose of *n*-butanol almost all reactant was converted to butenes both on PW_{12} and PW/Zn–Al and the yield of butenes was constant at a large dose (fig. 2). The result shows that the formation rate of butenes does not depend on the pressure of the reactant. Thus, it is most probable that the decomposition of intermediates adsorbed on acid sites is the rate determining step. The number of acidic hydrogen in the PW_{12} catalyst (8.9 mg) is formally 0.0085 mmol and that in the PW/Zn–Al catalyst (11.8 mg) is estimated as 0.0056 mmol. Supposing that every acidic hydrogen works as an active site, the turn over numbers of PW/Zn–Al can be calculated as 1.1 at 230°C and 2.5 at 250°C at a large dose and those of PW_{12} are 0.4 and 0.8, respectively. Thus, the acid sites in heteropolyacid can function effectively on the intercalation compound, probably because the acid disperses highly on the intercalation compound.

In general, acid sites catalyze the isomerization of olefins as well as the dehydration of alcohols [18–20], and one can suppose that 2-butene is formed by acid-catalyzed isomerization of 1-butene produced by dehydration of *n*-butanol on other acid sites. If further transformation occurred, the selectivity to 1-butene would decrease with decrease in the amount of *n*-butanol injected because the acid sites escaping from the adsorption of *n*-butanol would catalyze the isomerization of 1-butene. However, the selectivity to 1-butene was almost constant regardless of the *n*-butanol dose. The selectivities produced over PW/Zn–Al were 67% at 230°C and 25% at 250°C, while those over PW_{12} were 33% at 230°C and 25% at 250°C. Thus, the selectivity could be directly related to the property of the acid sites in the catalysts. Since the heteropolyacid molecules in PW_{12} aggregate together, the density of the acid sites in PW_{12} will be considerably high. Moreover, three acidic hydrogen atoms are present on a heteropolyacid molecule in PW_{12}, while the number is probably two in the case of PW/Zn–Al. Hence, one can speculate that *n*-butanol interacting with a couple of acid sites at the same time would convert to 2-butene and this would be the reason for the lower selectivity of PW_{12}.

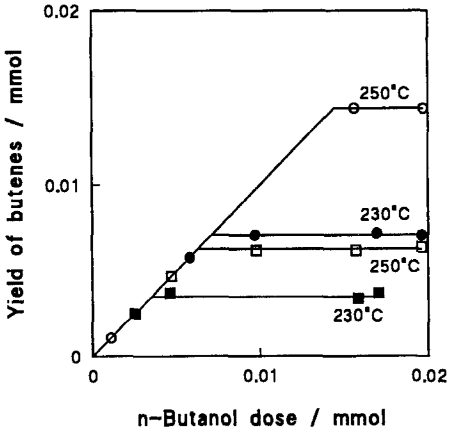

Fig. 2. Catalytic activity for dehydration of *n*-butanol. Circles: PW/Zn–Al, 11.8 mg; squares: PW_{12}, 8.9 mg.

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