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Hydration/hydrolysis by solid acids

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1. Introduction

Hydration and hydrolysis are important chemical processes to produce oxygen-containing organic compounds. Hydration usually includes the transformations of alkenes into alcohols or ethers, alkynes into carbonyl compounds, epoxides into glycols, and nitriles into amides. Amongst several hydrolysis reactions, the hydrolysis of esters of carboxylic acids is the most useful from the practical viewpoint. The hydration of alkenes, epoxides, and nitriles is usually catalyzed by proton to form the corresponding cabocations which react with water. Hydroxy ion also catalyzes the hydration of epoxides and nitriles through its direct nucleophilic attack to the carbon atom adjacent to the electronegative heteroatom of oxygen or nitrogen followed by protonation with water. The rates of hydrolysis of esters are also increased by acid or base, but there is an important difference. Acid is a catalyst (i.e., it is regenerated), whereas base is an reagent as exemplified by the saponification of esters.

In general, the reaction equilibrium of hydration becomes favorable at lower temperatures because they are essentially exothermic (10–20 kcal mol^{-1}). Epoxides and nitriles are relatively more reactive for hydration than alkenes. They can be readily hydrated at around 100°C to give high conversions in the presence of large excess of water. On the other hand, severe reaction conditions are often required to effect the hydration of alkenes, for example, 200–300°C and 25–70 atm in the vapor-phase hydration of ethene and propene. Both alkene hydration and ester hydrolysis are equilibrium reactions. The hydration is extremely unfavorable because the free energy change of the reaction is a very small negative. In contrast, an equilibrium constant of acid-catalyzed ester hydrolysis is near unity.

As for ester hydrolysis, acidic ion exchange resins, as well as mineral acids such as sulfuric acid and hydrochloric acid, have widely been employed as catalysts. Alkenes can be indirectly hydrated using concentrated sulfuric acid which irreversibly reacts with alkenes to afford monoalkyl sulfates and dialkyl sulfates followed by hydrolysis with excess water to produce the corresponding alcohols. In this indirect hydration of alkenes, sulfuric acid is used as a reagent, and the dilute acid produced in the hydrolysis process must be concentrated before reuse. As the indirect hydration of ethene needs highly concentrated sulfuric acid (95–98%) due to the relatively low reactivity of ethene, the direct hydration of ethene over a solid acid catalyst such as supported phosphoric acid has been developed in an earlier stage of petrochemical industry. Acrylonitrile is hydrated in the presence of concentrated sulfuric acid to form acrylamide sulfate followed by neutralization with ammonia. In this hydration, sulfuric acid actually works as a catalyst, but more than stoichiometric amounts of the acid are needed because of salt formation with the product acrylamide. Regarding the hydration of epoxide, a catalytic amount of sulfuric acid is often employed, but the acid must be removed from the product glycol by means of neutralization.

The processes for hydration and hydrolysis which use sulfuric acid pose several problems such as corrosion, toxicity, difficult reuse, and costly treatment of waste acid and salts. Sulfonic resin catalysts are actually very effective for hydrolysis, but they are thermally not so stable. In addition, supported phosphoric acid catalysts currently employed in the direct hydration of ethene, propene, and butene have the fatal disadvantage of the elution of phosphoric acid. The development of alternative effective acid catalysts, particularly insoluble, stable, readily recoverable solid acid catalysts, has been awaited for environmentally more benign hydration and hydrolysis processes not only in industries of commodity chemicals, but also in industries of fine chemicals.

In this monograph, recent progress in the field of the solid acids for hydration and hydrolysis is described, together with short historical reviews on each process. Particularly, much attention has been paid to the acid catalysis of heteropolyacid. The reason is that the present author has investigated for a long time the acid catalysis of heteropolyacid for several acid-catalyzed reactions, and has recently developed a new composite of silica-included heteropolyacid as an insoluble solid acid catalyst for ester hydrolysis.

2. Hydration of alkenes

2.1. General characteristics of alkene hydration

Hydration of alkene is reversibly catalyzed by acid to yield a secondary or tertiary alcohol through the addition of water to alkene which obeys Markovnikov's rule.

$$RCH = CHR' + H_2O = RCH(OH)CH_2R' \qquad (1)$$

Dehydrogenation and intermolecular dehydration of the product alcohol, as well as oligomerization of alkene, are involved as the side reactions to give the by-products of aldehyde or ketone, alkene oligomers and their hydration products of higher alcohols. Lower temperatures and higher pressures favor the equilibrium of the reaction because the hydration of alkene is exothermic, along with a decrease in the number of molecules. The enthalpy of hydration is -13 to -11 kcal mol^{-1} for simple alkenes [1]a,b, -12 to -7.7 kcal mol^{-1} for C_5 to C_7 acyclic alkenes including *n*-hexenes [1]d,f, and -3.3 to -8.8 for C_5 to C_6 cycloalkenes [1]e. The entropy change in alkene hydration in the gas phase is a large negative, and the free energy change of the reaction varies from negative to positive even at 50–100°C. Consequently the equilibrium conversion of alkene is very low. The empirical formulae for the equilibrium of alkene hydration are listed in Table 1 [1]. In the hydration of *n*-alkene, the equilibrium conversion decreases with increasing carbon number, but the reactivity of hydration is the lowest with ethene. An increasing molar ratio of water to alkene brings about a higher equilibrium conversion, but the concentration of alcohol becomes lower. Fig. 1 illustrates the change in equilibrium conversion for propene hydration in the gas phase and the liquid phase as a function of reaction temperature. The hydration in the gas phase is generally performed at around an equimolar ratio of steam to propene to give a propene conversion of less than 10%. Higher propene conversion (70–90%) is obtained in the liquid-phase hydration under high pressure at a mole ratio of water to propene between 20 and 40.

2.2. Catalysts for alkene hydration

A great number of catalysts, most of which include a wide variety of acidic substances, have been reported particularly for the hydration of simple alkenes such as ethene, propene, isobutene, and *n*-butenes [2–26,41,42]. They can be classified into water-soluble homogeneous catalysts for liquid-phase hydration and heterogeneous catalysts for gas-phase and liquid-phase hydration (Table 2).

Among the water-soluble catalysts, heteropolyacid is the most efficient as will be

Table 1
Equilibrium constants of alkene hydration

Reaction	Empirical formula
$C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$	$\log K_p = 2100/T - 6.195$
$C_3H_6(g) + H_2O(g) = CH_3CH(OH)CH_3(g)$	$\log K_p = 1950/T - 6.060$
$C_3H_6(g) + H_2O(l) = CH_3CH(OH)CH_3(l)$	$\log K_c = 2040/T - 5.08$
$n\text{-}C_4H_8(g) + H_2O(g) = CH_3CH_2CH(OH)CH_3(g)$	$\log K_p = 1845/T - 6.395$
$C_nH_{2n}(g) + H_2O(g) = C_nH_{2n+1}OH(g),$	$-\Delta G = 5320 - 815n - 17.2T + 0.5nT$ (cal)

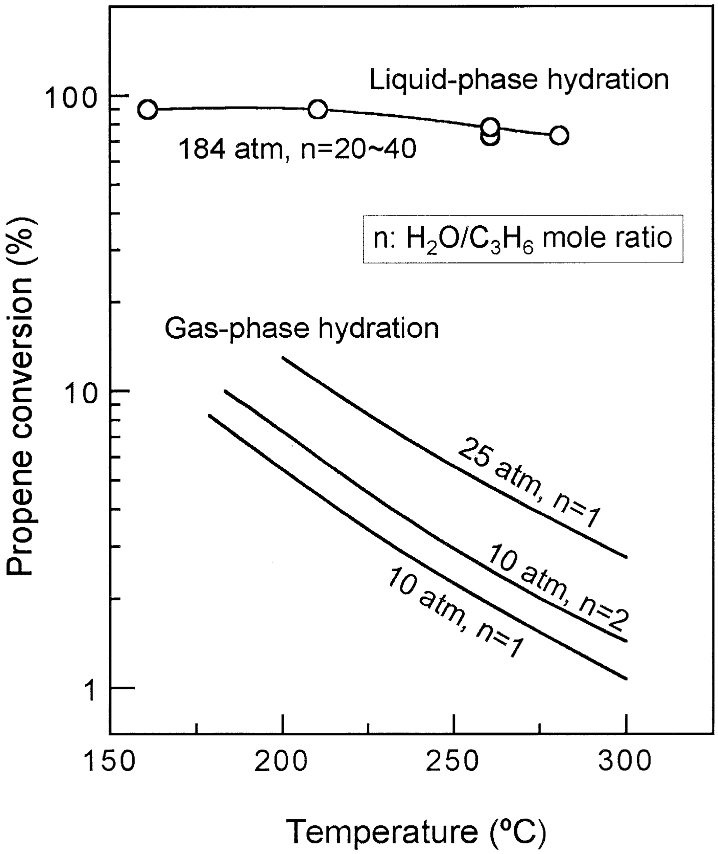


Fig. 1. Equilibrium of propene hydration.

described in detail in Section 2.5. Heteropolyacid has been commercially applied to the hydration of propene in the liquid phase [5]a[27].

Supported phosphoric acid catalyst shows high selectivity. It has preferably been used for industrial hydration of ethene, propene, and *n*-

Table 2
Catalysts for alkene hydration

Homogeneous catalysts (aqueous solution)	sulfuric acid [2]; perchloric acid [3]; phosphoric acid [4]; $CuCl_2$ [4]; heteropolyacid [5]; heteropolyacid + other acids [6]; sulfates of Al, Cr, Fe, Cu, Co [7]; sulfates + sulfuric acid [8]a; Sb chloride [8]b,c; NH_4Cl [9]a; $(NH_4)_2SO_4$ [9]b; $Hg(NO_3)_2$ [9]c; Mo compounds [10]a; Be compounds [10]b; perchlorates of Fe, Hg, Zr, Cr [10]c; Re_2O_7 [10]d; *p*-toluenesulfonic acid [10]e
Heterogeneous catalysts	
1.	Mineral acids: phosphoric acid supported on silica, alumina, and activated carbon [11], heteropolyacid or its soluble salts [12]; silicophosphoric acids ($H_2Si(PO_4)_2$, $Si_3(PO_4)_4$) [13]
2.	Metal salts: silica-supported or non-supported sulfates of Al, Cr, Fe, Cu, Co [14]; phosphates of B, Al, Cr, Zr, Fe, Mn [15]
3.	Sulfonic acid type resins: poly(styrene-divinylbenzene) type [11]b, [16]; Nafion-H [17]
4.	Zeolites and clays: Cr^{3+}-exchange zeolite [18]; acid-treated and metal ion-exchanged montmorillonite [11]b, [19]; ZSM-5, Ferrierite [29,30]
5.	Metal oxides: tungsten oxides (WO_3 and W_2O_5) and those doped with ZnO or Cr_2O_3 [11]b, [20]; $Al(OH)_3$ [21]a; SiO_2–Al_2O_3 [21]b; zirconium tungstate [22]; MoO_3–ZrO_2 [23]; TiO_2–SiO_2 [24]; TiO_2–ZnO [25]; hydrated Nb_2O_3 [41]; mixed oxides [26]; Ta_2O_5 [42]

butenes in the gas phase [11]. The catalytic efficiency of the supported phosphoric acid greatly depends on the property of support because in the presence of steam phosphoric acid appears to exist as liquid layers inside the pores of the support even at high temperatures [28]. Silica or diatomaceous earth with large pore volumes is suitable for supporting phosphoric acid. An appropriate loading of phosphoric acid is usually in the range of 55 to 75 wt%. The supported phosphoric acid catalyst has the disadvantage that the acid is vaporized or eluted from the support during the process, which causes a decline in catalytic activity and corrosion of equipment. A continuous feed of phosphoric acid to the catalyst bed is, therefore, needed to assure stable operation.

Water-insoluble metal oxide catalysts can be applied to the liquid-phase hydration under high pressure, although they are less active than the supported phosphoric acid. Tungsten oxides such as WO_3 and W_2O_5 are effective oxide catalysts with high selectivity. In general, metal oxide catalysts are susceptible to hydrothermal treatment, and they often deteriorate or dissolve when used in the liquid phase at high temperatures.

Sulfonated cation exchange resins are commonly employed to catalyze the hydration of reactive isoalkenes [16]. The resin catalysts are ordinarily used for the liquid-phase hydration operated at about 100°C because of low thermal durability. The resin catalyst is also commercially applicable for the fixed-bed hydration of propene in the gas–liquid mixed phase at 130–150°C through an appropriate reactor design to be able to suppress the overheat of the catalyst bed [16]b,c.

Acidic zeolites and metal ion-exchanged zeolites work as hydration catalysts in the gas phase [18,29]. Recently acidic ZSM-5 has industrially been applied as a catalyst to the hydration of cyclohexene [30].

Table 3 summarizes the reaction conditions for the hydration of simple alkenes over several typical catalysts.

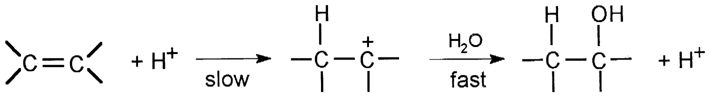
2.3. Reaction mechanism of alkene hydration

The reaction mechanism for alkene hydration in homogeneous aqueous acidic media is expressed as Scheme 1, where the protonation of alkene to yield a carbenium ion intermediate is rate determining [31]. The evidence is based on the fact that in the hydration of 2-methyl-1-butene and 2-methyl-2-butene which afford the same product alcohol, alkene isomerization is not observed [31]a, namely capture of the carbe-

Table 3
Hydration of simple alkenes

Catalyst	Alkene	Reaction type	Temperature (°C)	Pressure (atm)	H_2O/alkene (mole ratio)	Alkene conv. (%)	Selectivity (mole %)	Ref.
H_3PO_4/SiO_2	ethene	gas phase, fixed-bed	290	70	0.6	4.7	97	[11]
H_3PO_4/SiO_2	propene	gas phase, fixed-bed	180	10	1.0	5.7	96	[11]
W_2O_5	propene	gas–liquid phase, fixed-bed	270	250	15	47	98.8	[20]
Resin [a]	propene	gas–liquid phase, fixed-bed	130–150	65–100	12.5–15.0	75	96.5	[16]c
Resin [a]	isobutene	liquid phase, suspension	95–120	–	–	50–60	–	[16]b
Heteroplyacid	propene	liquid phase, homogeneous	240–270	150–200	large excess	60–70	99	[5]a

[a] Poly(styrene-divinylbenzene) sulfonic acid type resin.



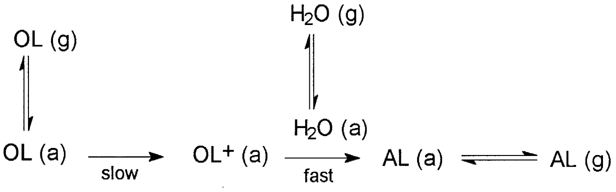
Scheme 1.

nium ion intermediate by water is fast relative to deprotonation. Specific acid catalysis is proposed for the hydration of aliphatic alkenes (e.g., isobutene) [31]h, where the rate depends on acidity function H_0 exhibiting a solvent-isotope effect $(k(H_3O^+)/k(D_3O^+))$ of 1.4 [31]i. Hydration of styrenes is, however, a general acid catalyzed reaction exhibiting a solvent-isotope effect of 2-4 [31]e,g. Regarding the pathway to the carbenium ion intermediate, an alkene-proton π-complex is assumed as a transition state [31]a–c. On the other hand direct protonation without complex formation is also observed with aliphatic alkenes [31]h, [32] and styrenes [31]d–f, [33]. As described in Section 2.5, heteropolyacid catalyzes the hydration of propene and isobutene in a dilute aqueous solution (10^{-3} M) several times more efficiently than sulfuric acid at the same acid concentration. This is probably due to the stabilization of the carbenium ion intermediate by heteropoly anion [27,34].

The hydration of alkene over supported phosphoric acid in the gas phase proceeds according to a mechanism similar to that for the hydration in an aqueous solution, because phosphoric acid exists as liquid layers inside the pores of the support even at high temperatures [28,35]. As for metal oxides and metal salts catalysts, the hydration follows a surface reaction mechanism expressed by the Langmuir–Hinshellwood equation (Scheme 2) [12]a, [14]a, [15]f. In the hydration with D_2O over the solid catalysts, the unreacted alkene contains no deuterium [36]; this means that the formation of the carbenium ion from the adsorbed alkene is rate-determining. The hydration activity over metal sulfates correlates with the electronegativity of the metals [37]. The hydration activity over solid acid s correlates with their surface acidity estimated by Hammett indicators [14]a. These facts suggest that the surface acid sites of solid catalysts are responsible for the hydration of alkene. Solid acid catalysts having an acid strength of between −8.2 and −3.0 in terms of H_0 are effective for the hydration of ethene [38], and an acid strength of between −3.0 and +1.5 is strong enough to effect the hydration of propene [14]a. Strong acid sites with an H_0 smaller than −8.2 enhance the oligomerization of alkene.

2.4. Processes for alkene hydration

The processes for alkene hydration can be classified into four groups according to the type of catalysis: fixed-bed catalysis in the gas phase, trickle-bed catalysis in the gas and liquid phases, suspension catalysis in the aqueous phase, and homogeneous catalysis in the aqueous phase. The preferred physical properties and forms of



OL: alkene, OL+: carbenium ion, AL: alcohol
(g): gaseous state, (a) adsorbed state

Scheme 2.

catalysts should be chosen to fit each reaction system and reactor type.

Amongst these four processes, the fixed-bed gas-phase process is usually conducted at relatively lower pressures. The catalyst to be used in this process must therefore be active at relatively lower reaction temperatures. Phosphoric acid supported on silica, diatomaceous earth, or montmorillonite with a large pore volume is preferably applied as a catalyst for the fixed-bed gas-phase process [39]; the acid loading is normally 55–75 wt%. The supported phosphoric acid is liable to vaporize from the support under the reaction conditions, hence the acid is continuously supplied to the catalyst bed during the operation. In the presence of water, metal oxide catalysts such as silica-alumina, zeolites, and tungsten oxides are generally less active than the supported phosphoric acid. A block flow diagram for the fixed-bed gas-phase ethanol process using a supported phosphoric acid catalyst is given in Fig. 2 [40]a,b.

The hydration with gaseous alkene and liquid water is conducted under the conditions of a high temperature and a high pressure in a continuous manner over a water-insoluble solid catalyst packed into a column. Liquid water is trickled down over the catalyst bed, and gaseous alkene flows either upward or downward in the catalyst bed. The reaction occurs over the catalyst between the liquid water and the alkene dissolved in it. The equilibrium favors the product, and the conversion of alkene is much higher than in the gas-phase hydration. Insoluble and heat-durable metal oxide catalysts such as tungsten oxides have extensively been studied for this type of hydration. Since these metal oxide catalysts are active usually at 200–300°C and 150–250 atm, catalyst deactivation is often caused by crystal growth or dissolution under such severe hydrothermal reaction conditions. An industrial process for the hydration of propene over a sulfonated cation exchange resin catalyst has been developed [16]b,c: a block

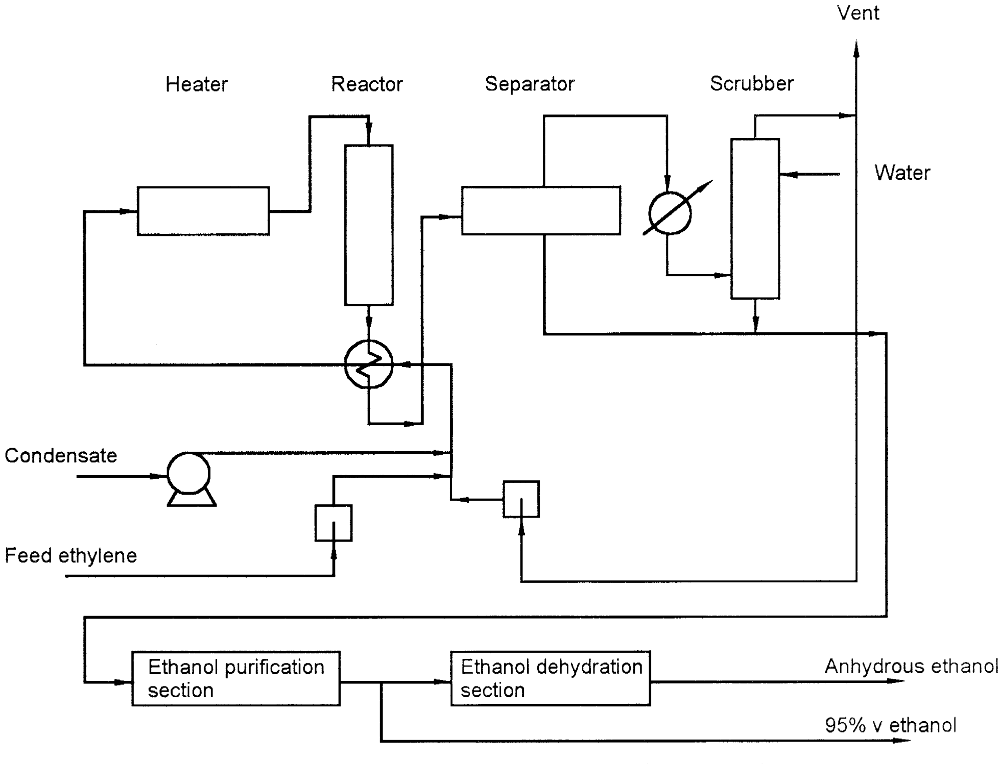


Fig. 2. Fixed-bed gas phase hydration of ethene (Shell process).

flow diagram is shown in Fig. 3 [40]e. This resin catalyst process is conducted at a relatively low temperature of between 130 and 150°C, and water is supplied to the catalyst bed in a divided manner in order to avoid overheating of the catalyst.

In the suspension catalysis, the catalyst is suspended as fine particles in water, and the reaction takes place between water and the dissolved alkene. Insoluble solid catalysts, such as WO_3 and $Al(OH)_3$, can be applicable to this type of hydration. The yield of alcohol per unit weight of catalyst is much better in the suspension catalysis than in the fixed-bed catalysis. The suspension process has some disadvantages, such as a relatively rapid catalyst deterioration and abrasion of equipment.

The alkene hydration by homogeneous catalysis is conducted in an aqueous solution of an acid catalyst. If the catalyst is stable and not corrosive, this type of process will be the best for the hydration of simple alkenes because the conversion is very high, and an azeotrope of the product alcohol and water can be readily separated by distillation from the catalyst solution. Heteropolyacid is very soluble in water, and it becomes a catalyst suitable for the hydration of propene, isobutene and *n*-butene in the aqueous phase. Aqueous sulfuric acid and phosphoric acid are both less active and less selective than heteropolyacid. A block flow diagram of the hydration of propene with heteropolyacid is given in Fig. 4 [40]f. Certain metal sulfates and chlorides are also active for alkene hydration in an aqueous solution [7–9], but they have not practically been applied because they are often corrosive and readily decomposed through hydrolysis. The features of some typical industrial hydration processes are listed in Table 4.

2.5. Liquid-phase alkene hydration catalyzed by heteropolyacid

Heteropolyacid (referred to as HPA) is defined as a condensate of different kinds of oxoacids. Amongst various heteropolyacid, the Keggin-type acid [43] (Fig. 5) is the most popular. It is well known that ‘heteropoly blue’ in

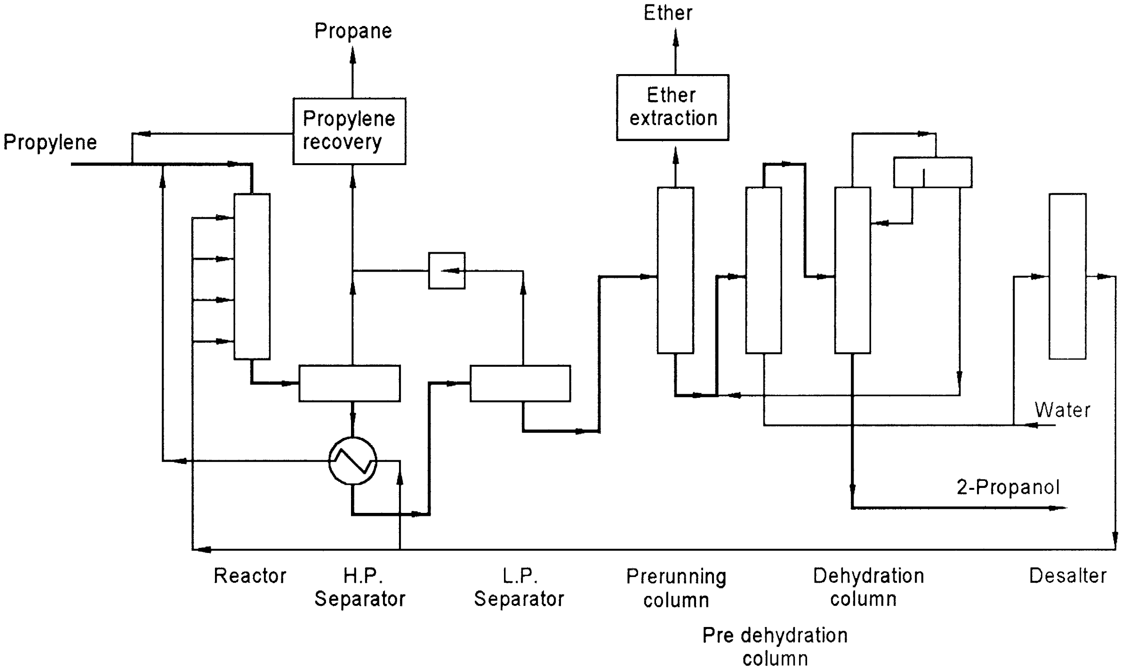


Fig. 3. Fixed-bed gas–liquid phase hydration of propene (Deutsche Texaco process).

Table 4
Typical industrial processes of simple alkene hydration

Process:	Shell [40]a,b	Veba [40]c	Veba [40]d	Deutsche Texaco [16]b[40]e	Tokuyama [27,40]f
Alcohol	ethanol	ethanol	2-propanol	2-propanol	2-propanol
Catalyst	supported H_3PO_4 fixed-bed (gas phase)	supported H_3PO_4 fixed-bed (gas phase)	supported H_3PO_4 fixed-bed (gas phase)	sulfonic acid ion-exchange resin fixed-bed (gas–liquid phase)	heteropolyacid solution (liquid phase)
Reaction conditions					
temperature	290	230–250	170–190	130–160	240–280
pressure (kg/cm^2)	70	70	25–45	83–103	150–200
H_2O/alkene (mole ratio)	0.6	–	–	12.5–15.0	large excess
Alkene conversion (%)	4.2	–	6	75	60–70
Selectivity for alcohol	97	97	97	93.4	99
Consumption					
alkene (t/t)	–	–	–	0.746	0.72
steam (t/t)	–	3.5	5	3.8	3.5

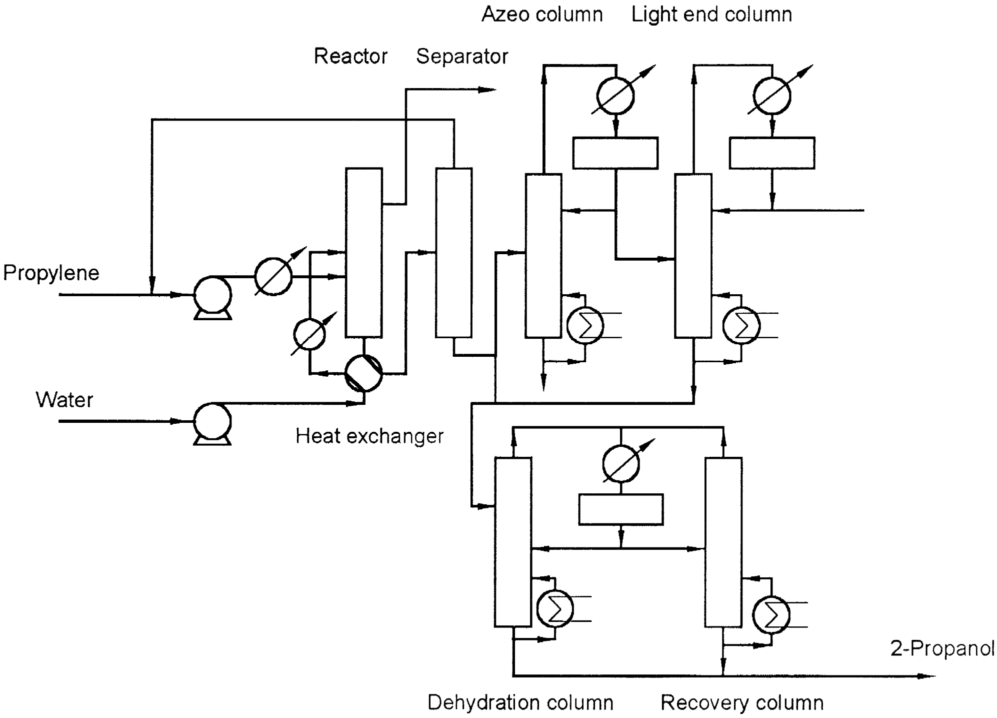


Fig. 4. Homogeneous liquid phase hydration of propene (Tokuyama process).

the colorimetric determination of phosphorus is due to the formation of reduced heteropolymolybdate anions. It is also frequently used as an oxidizing agent for the organic compounds separated by thin layer chromatography. The chemistry of heteropolyacid has long been studied extensively [44–46], but its debut in the field of catalyst chemistry and technology is rather recent; the importance of the Keggin structure was first suggested in 1959 in a Sohio patent for the oxidation of methacrolein [47]. It should be noted, however, that heteropolyacid is now commercially applied mainly in Japan as a practical catalyst material to several petrochemical processes including the direct hydration of propene for the manufacture of 2-propanol (the first industrial application of heteropolyacid molecular catalysis in 1972) [48,49], the oxidation of methacrolein to methacrylic acid in 1982 [50], the chemical separation of isobutene as *t*-butyl alcohol from the spent butane–butene fraction in 1984 [51], the oligomerization of tetrahydrofuran to the polymeric diols in 1985 [52], and the hydration of *n*-butenes in 1989 [53]. Most of the pioneering work has been done since the 1970's mainly by Russian and Japanese research groups [5,54–58] both on the

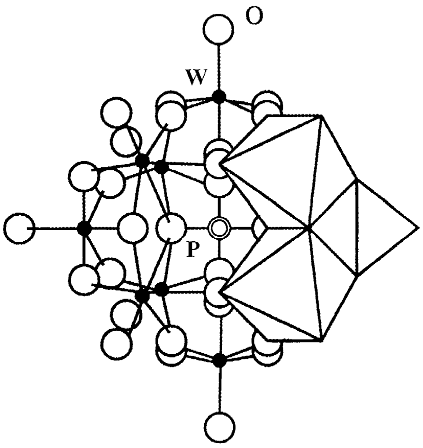


Fig. 5. A schematic Keggin structure of $PW_{12}O_{40}^{3-}$ anion. From M. Misono, Catal. Rev., 29 (1987) 271 (fig. 1, partly modified), Marcel Dekker.

homogeneous molecular catalysis of heteropolyacid and the heterogeneous catalysis of heteropolyacid crystal bulk. Their work on heteropolyacid catalysis revealed the essential role of the Keggin structure of heteropolyacid both in acid catalysis [5,49] and oxidation catalysis [59]. In addition to its practical usefulness, heteropolyacid is now attracting much academic interest as a potential catalyst material because it possesses the dual catalytic functions of strong acidity and high oxidizing ability.

Izumi and Mizutani have first pointed out that HPA exhibits high catalytic activity and selectivity for the hydration of alkene, rendering it applicable as a commercial catalyst to the manufacture of 2-propanol [48]. The liquid-phase hydration of isobutene, for example, is catalyzed by an aqueous HPA under atmospheric pressure much more efficiently than nitric acid at the same proton concentrations and the same ionic strengths [60] (Fig. 6). Other simple oxoacids such as sulfuric acid and perchloric acid show completely the same activity as nitric acid at the same proton concentration.

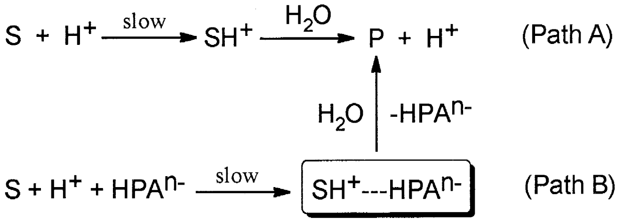
The rate of hydration in aqueous nitric acid is believed to be directly proportional to the proton concentration [61], but the rate of hydration in aqueous HPA shows higher order (ca. 1.5) dependence on the proton concentration. In a relatively narrow range of HPA concentration, the rate appears to be proportional to the acid concentration [56]. The activation energy of the hydration is lowered by 4 kcal mole^{-1} when HPA is used for nitric acid (Fig. 7).

HPA is completely dissociated in aqueous solution [62]. For instance, $H_4SiW_{12}O_{40}$ is a tetrabasic acid whose four protons are quite equivalent [62]a. Although HPA is fairly susceptible to alkali [63,64], $H_3PW_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$ decompose even in a weakly acidic aqueous solution (Eqs. (2), (3)) [64,65].

$$PW_{12}O_{40}^{3-} + 3H_2O = PW_{11}O_{39}^{7-} + WO_4^{2-} + 6H_2O \tag{2}$$

$$SiMo_{12}O_{40}^{4-} + H_2O = SiO_{2\,aq.} + 3MoO_4O_{13}^{2-} + 2H^+ \tag{3}$$

However, according to the measurements of conductivity and pH [62,66,67], even $H_3PW_{12}O_{40}$, which is somewhat sensitive to hydrolysis, can exist intact in an acidic aqueous solution (pH = 1.0–1.5), if a certain oxygen-containing organic substance such as *t*-butyl alcohol, acetone, or dioxane is added. In addition, it has also been confirmed by X-ray diffraction [68] and ^{16}O-NMR [69] studies that $SiW_{12}O_{40}^{4-}$ anion holds its Keggin structure in an aqueous solution. It is therefore probable that HPA dissociates completely without deterioration during the hydration of butene in acidic (pH < 1.0) aqueous solutions exemplified by Figs. 6 and 7. In the alkene hydration catalyzed by ordinary protonic acids, the rate depends merely on the proton concentration (specific acid catalysis) [70], and the formation of a carbenium ion from H_3O^+ and an alkene molecule controls the rate. The fact that HPA exhibits higher catalytic activity than nitric acid under the same proton concentration and same



S: alkene, P: alcohol, HPA: heteropoly anion

Scheme 3.

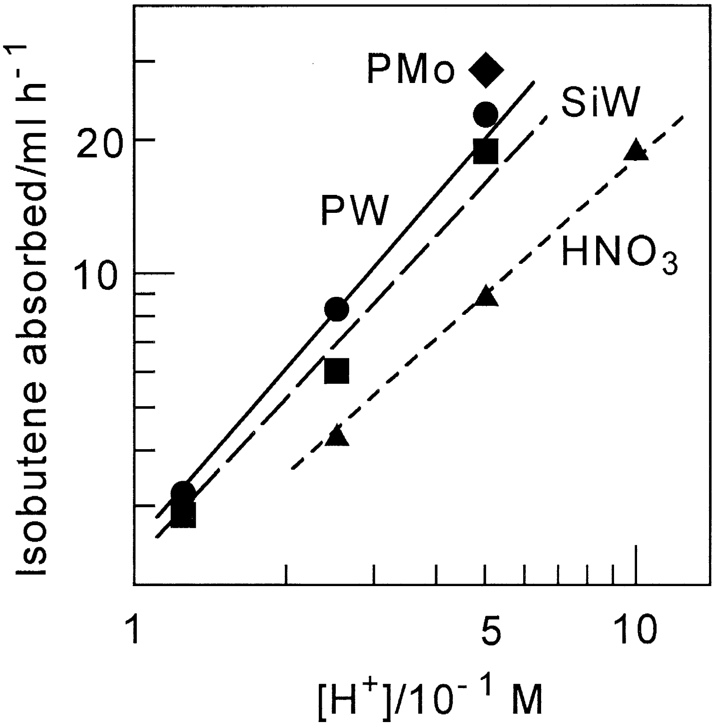


Fig. 6. Dependence of the rate of isobutene hydration on proton concentration at 39°C. PW: $H_3PW_{12}O_{40}$; PMo: $H_3PMo_{12}O_{40}$; SiW: $H_4SiW_{12}O_{40}$; ionic strength: 1.00 M (HNO_3, PW, PMo), 1.25 M (SiW).

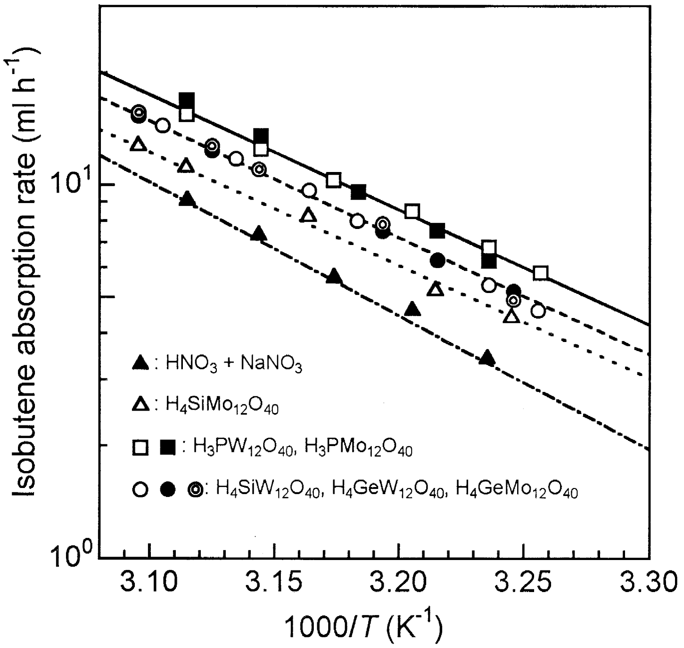


Fig. 7. Temperature-dependence of the rate of isobutene hydration. [H$^+$]: 0.25 M.

ionic strength suggests that heteropoly anion plays an important role in accelerating the reaction.

Izumi and coworkers proposed a parallel reaction mechanism as shown in Scheme 3 for the HPA-catalyzed alkene hydration, which involves path A by the specific acid catalysis and another path B via the carbenium ion being stabilized by heteropoly anion [60].

Since the activities of proton and heteropoly anion are both regarded as constant in a dilute aqueous solution at a constant ionic strength, the overall reaction rate of the isobutene hydration according to the parallel reaction mechanism can be expressed as Eq. (4):

$$v = k_A p_b[H_3O^+] + k_B p_b[H_3O^+][HPA^{n-}] \tag{4}$$

where k_A and k_B denote the rate constants of paths A and B, respectively, p_b the partial pressure of isobutene, and $[HPA^{n-}]$ the concentration of heteropoly anion. The compatibility of Eq. (4) with the experimental data is elucidated by a good linear relationship between $v/\{p_b[H_3O^+]\}$ and $[HPA^{n-}]$, as depicted in Fig. 8. The kinetic result thus suggests that heteropoly anion may stabilize the intermediate carbenium ion through mutual strong interaction to lower the activation energy, resulting in enhancement of hydration rate.

The existence of the interaction between heteropoly anion and carbenium ion is directly supported by the studies on the structural analysis of *O*-alkylated HPA compounds and the NMR analysis of the HPA-catalyzed ethanol dehydration. Knoth and coworkers [71] prepared *O*-alkylated HPA compounds according to the following reaction:

$$\begin{aligned} &R_3O^+BF_4^- + (n - C_6H^{13})_4N_3PMo_{12}O_{40} \\ &= (n - C_6H^{13})_4N_2(RO)PMo_{12}O_{39}R \\ &= CH_3, C_2H_5 \end{aligned} \tag{5}$$

where a bridged oxygen atom of HPA was alkylated to form an *O*-alkylated HPA compound. The bond distance between the alkyl carbon and the oxygen atom of HPA was determined to be 0.164 nm, which is much longer than the ordinary C–O covalent bond of 0.143 nm. This long C–O bond distance suggests that

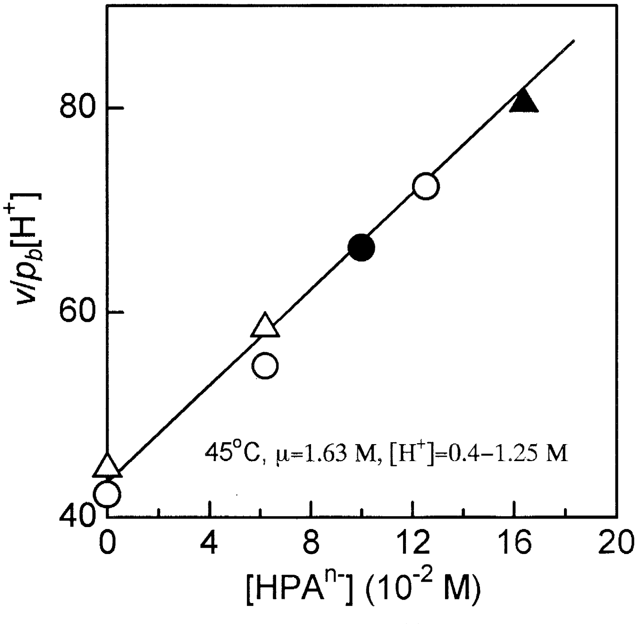


Fig. 8. Validity of Eq. (4).

the interaction between alkyl carbon and HPA oxygen is rather ionic. More directly, in the dehydration of ethanol inside the bulk of $H_3PW_{12}O_{40}$ crystal, Misono and coworkers [72] confirmed the existence of ethyl cation directly bound to the bridged oxygen of $PW_{12}O_{40}^{3-}$ anion through solid-state ^{13}C MAS NMR spectroscopy.

As indicated in Fig. 7, the catalytic activity of HPA for isobutene hydration varies depending on the kind of HPA. This difference in catalytic activity is mostly associated with the difference in proton activity or acid strength of aqueous HPA. The relative acid strengths of different HPA can be estimated by measuring the relative base strengths of their conjugate bases, namely the basicities of heteropoly anions. According to Barcza and Pope [73], the basicity of heteropoly anions can be accurately determined by measuring the degree of heteroconjugation (hydrogen bonding) of chloral hydrate ($Cl_3CH(OH)_2$) with heteropoly anions in an organic medium by means of NMR spectroscopy: the variation of chemical shift for the chloral hydrate protons correlates with the basicity of heteropoly anions. The change in chemical shift of the hydroxy protons of chloral hydrate with the change in the concentration of heteropoly anions has been measured in $C_6D_5NO_2$ solutions [74], and the result is shown in Fig. 9. Since $PW_{12}O_{40}^{3-}$ anion is the weakest base, $H_3PW_{12}O_{40}$ should correspond to the strongest acid of the various HPA in Fig. 9. The order of acid strength of HPA is therefore expressed as follows: $H_3PW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiW_{12}O_{40} = H_4GeW_{12}O_{40} > H_4SiMo_{12}O_{40} > H_4GeMo_{12}O_{40}$.

This order of acid strength for HPA explains fairly well the difference in the catalytic activity of HPA in isobutene hydration (Fig. 7). Judging from the relative basicity of conjugate anions, the acid strength of $H_3PW_{12}O_{40}$ is almost comparable to that of perchloric acid, but the catalytic activity of the HPA is much higher owing to the nature of heteropoly anions as mentioned above.

A commercial technology of separating isobutene from the butane–butene fraction

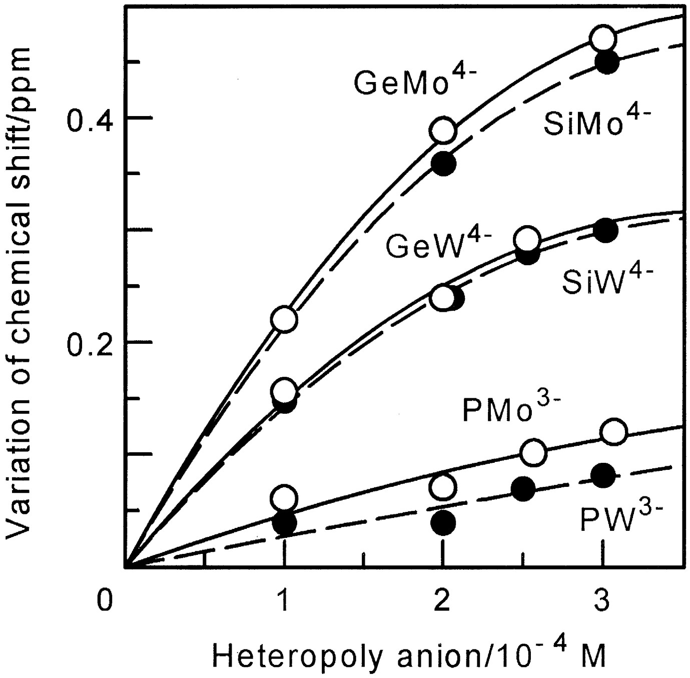


Fig. 9. Heteroconjugation of chloral hydrate protons with heteropoly anion in $C_6D_5NO_2$ at 30°C.

through direct hydration of isobutene into *t*-butyl alcohol has recently been developed using an extraordinarily concentrated aqueous solution of HPA (0.1–0.5 M) [51]. In the isobutene hydration with a concentrated aqueous HPA, HPA also shows higher catalytic activity than nitric and perchloric acids (Fig. 10), and the reaction rate is expressed only by the second term of Eq. (4) at a HPA concentration of more than 0.5 M; i.e. the reaction path B in Scheme 3 becomes dominant [51]. Although this hydration process can be operated at a relatively low reaction temperature (ca. 80°C) to give high conversions owing to high catalytic activity and also it can minimizes unfavorable side reactions such as isobutene oligomerization, careful attention must be paid to suppress the deterioration of HPA because aqueous HPA at high concentrations is liable to be decomposed [75,76].

The vapor-phase alkene hydration over the heteropolyacid supported on silica, celite, and carbon has ever been examined [12], but in this process a large amount of ether is produced, in addition to the elution of heteropolyacid from the support. Commercial processes by the supported heteropolyacid in the vapor phase, therefore, have not been developed.

2.6. Alkene hydration catalyzed by zeolites

Chromium and rare-earth-exchanged Y-type zeolites [18]h,i and highly siliceous zeolites of ZSM series [29]a were first examined for the hydration of C_2–C_5 alkenes under moderate pressures in the vapor phase.

The hydration over various proton-exchanged zeolites with different framework structures has been investigated for 1-butene in the liquid phase [29]b. At 250°C and 65 atm, and with a water/1-butene mole ratio of 4.4, the alcohol yields per gram of catalyst follow the pattern: mordenite > ZSM-5 > offretite = omega = Y. In particular, mordenites with intermediate Al contents (7 < Si/Al < 9) enable 75% of the

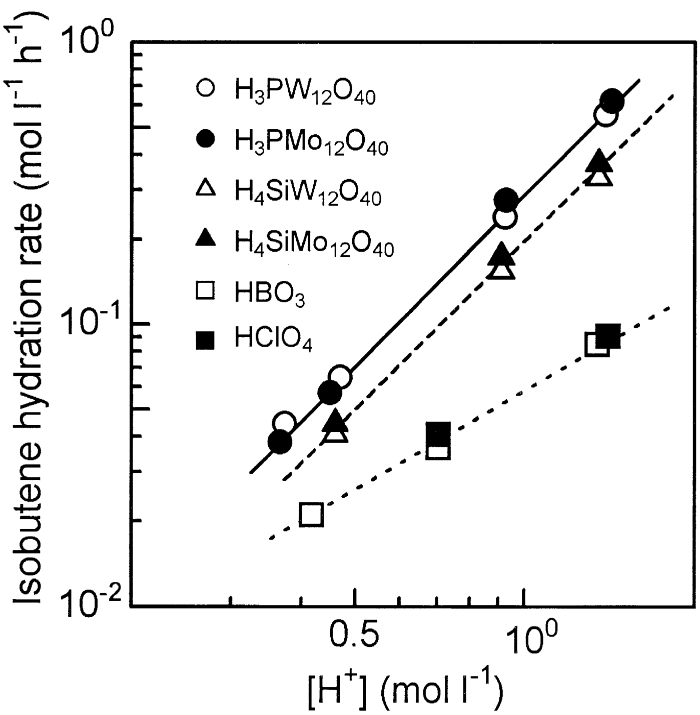


Fig. 10. Dependence of the rate of isobutene hydration on proton concentration at 40°C. From A. Aoshima et al., Nippon Kagaku Kaishi, (1987) 977 (fig. 2, partly modified), The Chemical Society of Japan.

thermodynamic equilibrium to be reached with 100% selectivity; 1-butene equilibrium conversion is 4.39 mol% at 250°C. Overdealumination of mordenite, as well as more severe reaction conditions, leads to the formation of dimer by-products. Zeolites exhibiting a hydrophobic character have a very good activity but hydrophobicity does not appear to play a decisive role in the process. It is found that the activities per protonic site are correlated with the aluminum content of the catalyst regardless of its framework structure. It is proposed that, as in aqueous acid media, the hydration activity of zeolites is a direct function of their protonic acid strength.

Proton-exchanged ferrierite-type zeolites efficiently catalyzes the hydration of ethene in the vapor phase. At 200°C and atmospheric pressure, and with a water/ethene mole ratio of 3.8, the order of activity is ferrierite $>$ mordenite $>$ Y $>$ ZSM-5. A ferrierite with a SiO_2/Al_2O_3 molar ratio of 16.3 is the best, and gives 80% of the thermodynamic equilibrium to be reached with 99% selectivity [29]c,e. High catalytic efficiency of ferrierite-type zeolites for alkene hydration has been confirmed by the studies on the vapor-phase hydration at a high pressure of 5 atm (Table 5) [29]d,h. At 5 atm, pentasil- and ferrierite-type zeolites are more active than mordenite- and Y-type zeolites, and the difference in activity among zeolites with different framework structures can not be simply explained in terms of the number of acid sites or acid strength. Regarding the hydration of ethene and propene, higher hydrophobicity of the acid sites of pentasil- and ferrierite-type zeolites appears to be responsible for higher hydration activity because a rapid supply of alkene molecules to the acid sites becomes possible.

According to a recent study [29]j on the vapor-phase hydration of ethene over proton-exchanged ferrierite catalysts under practical reaction conditions (260°C, 70 atm, $H_2O/C_2H_4 = 1.0$, GHSV $= 1500$ h^{-1}), ferrierite is more active (C_2H_4 conversion $= 19.9\%$) than a silica-supported phosphoric acid (C_2H_4 conversion $= 8.1\%$), but the selectivity to ethanol is as low as 51.4%: selectivities to diethyl ether, acetaldehyde, and ethylene oligomers are 44.8%, 0.16%, and 3.6%, respectively. In addition, the zeolite catalyst is deactivated by coking.

Recently, a commercial liquid-phase hydration process using a high-silica zeolite catalyst has successfully been developed for the conversion of cyclohexene to cyclohexanol [30]. Cyclohexene has become commercially available by the partial hydrogenation of benzene catalyzed by a zinc-promoted ruthenium catalyst with high activity and selectivity in an aqueous phase [30]e; benzene conversion = 14–52%, cyclohexene selectivity = 70–90% [30]d. The hy-

Table 5
Alkene hydration over various zeolites [a] (from K. Eguchi et al., Appl. Catal., 34 (1987) 276, partly cited from table 1, Elsevier)

Zeolite	Si/Al	Ethene hydration, 200°C		Propene hydration, 150°C		1-Butene hydration, 150°C	
	atomic ratio	Yield (%)	Selec. (%)	Yield (%)	Selec. (%)	Yield (%)	Selec. (%)
Pentasil	11.7	2.16	72.8	3.53	94.4	2.10	95.7
	20.2	1.53	81.3	0.50	99.9	1.17	97.3
	24.9	1.44	81.1	0.30	100	0.39	84.6
Mordenite	5.1	0.26	100	0.10	93.0	0.44	95.6
	7.5	0.42	98.3	0.10	92.8	0.12	86.7
	10.1	0.61	95.4	0.19	94.6	0.84	78.0
Ferrierite	8.4	1.68	84.5	4.10	98.1	1.27	99.2
Erionite–Offretite	3.7	0.57	95.7	0.23	94.6	1.09	96.6
Y	2.6	0.04	100	0.13	100	1.08	92.0
Equilibrium conversion (%)	4.04			7.58		2.21	

[a] H_2O/alkene = 1.0, W/F = 7.5 g-cat h mol^{-1}.

dration of cyclohexene is, therefore, more economical for the production of cyclohexanol as a starting material of adipic acid than the conventional cyclohexane oxidation process in which a mixture of cyclohexanol and cyclohexanone is produced. Table 6 summarizes the catalytic efficiency of various zeolites for the hydration of cyclohexene in the liquid phase [30]b. Highly siliceous zeolites with a SiO_2/Al_2O_3 mole ratio of higher than 20 exhibit high hydration activity because cyclohexene molecules are readily accessible to the active sites competing with water molecules owing to the hydrophobic property of the zeolites. ZSM-5 and ZSM-11, both of which possess the channels formed by 10-membered rings, show high selectivities to cyclohexanol of more than 99%, while mordenite built by 12-membered rings forms a considerable amount of dicyclohexyl ether. These facts appear to indicate the shape selectivity of zeolite. The reaction rate over the ZSM-5 with crystal sizes of more than 1.0 μm is proportional to the external surface area of the primary crystal particles (external diffusion controlling), whereas the rate over the ZSM-5 with crystal sizes of less than 0.1 μm depends on the acid amount of zeolite (activation energy = 20.9 kcal mol^{-1}).

This reaction system consists of three phases; an oil phase, an aqueous phase, and a solid phase (catalyst). The reaction rate and the equilibrium composition of the oil phase depend on the adsorption capacity of catalyst for cyclohexene and cyclohexanol, and also depend on their distribution ratios between the oil and the aqueous phases. The ZSM-5 catalyst deactivates during the hydration of cyclohexene in the liquid-phase. The deactivation is mainly caused by the acidity loss due to the increase in the non-framework aluminum formed under the hydrothermal condition. The deactivated catalyst can be completely regenerated by treating it with dilute aqueous alkali (0.3 M) at 80°C for 1 h, followed by ion exchange with nitric acid (1 M) [30]c.

2.7. Other solid acids for alkene hydration

2.7.1. Zirconium tungstate

Tungsten oxides, particularly partially reduced oxides such as W_2O_5, catalyze the ethene hydration, but their activities are not so high. Amorphous zirconium tungstate $ZrW_{2-8}O_{0.5-3.5}$ (referred to as ZrW) shows high catalytic activity for the hydration of ethene [22]. ZrW is an

Table 6
Catalytic efficiency of various zeolites for cyclohexene hydration [a] (from Y. Fukuoka et al., Nippon Kagaku Kaishi, (1989) 522, table 1, partly modified, The Chemical Society of Japan)

Zeolite	SiO_2/Al_2O_3 (mole ratio)	Crystal size (mm)	Time (h)	Composition of oil phase (wt%)			
				Anol [b]	MCP [c]	DCHE [d]	Select.(%) [e]
ZSM-5	25	0.6	2	12.8	0.084	0.008	99.3
	30	1.0	2	9.0	0.070	trace	99.3
ZSM-11	25	1.0	2	11.5	0.045	0.018	99.0
ZSM-35	15	2.0	72	0.3	trace	trace	100
	10	0.7	4	0.3	trace	0.01	96
Mordenite	33	0.5	4	8.2	trace	2.72	74
	45	0.5	4	4.1	trace	1.67	70
	94	0.5	4	3.4	trace	4.25	43
ZSM-12	35	1.0	16	6.7	0.024	2.16	74
Y	5	0.5	72	0.3	trace	0.005	98

[a] Cyclohexene/water/catalyst = 2.4/2.7/1.0 (wt ratio), 120°C, in an autoclave.
[b] Cyclohexanol.
[c] Methylcyclopentenes.
[d] Dicyclohexyl ether.
[e] Selectivity to cyclohexanol.

acidic binary-metal oxide, and is known as an inorganic ion-exchanger in the field of analytical chemistry. ZrW is insoluble in water and is expected to be an alternative for the problematic supported phosphoric acid catalyst. ZrW can be prepared in various compositions with different W/Zr mole ratios, provided the ratio is above unity. The ZrW having a composition of W/Zr = 2.0 is the most active for the hydration of ethene.

An active ZrW catalyst with a W/Zr ratio of 2.0 is prepared by mixing aqueous Na_2WO_4 (0.3 M, 2.5 dm^3) and $ZrOCl_2$ (0.3 M, 1.25 dm^3) at room temperature to give a white gel-like precipitate, followed by adding aqueous HCl (11.3 M, 1.25 dm^3). The cake separated by filtration is treated with HCl (0.1 M, 5 dm^3), and this washing with aqueous HCl is repeated two or three times, then the cake is calcined at 450°C for 7 h. The ethene hydration activity of this catalyst in the vapor phase at atmospheric pressure is shown in Table 7, together with the results for the other ZrW and supported phosphoric acid. The ZrW obtained through a procedure of HCl washing is the most active. The reaction data are kinetically well interpreted by assuming that the hydration of ethene over the ZrW catalyst is controlled by the surface reaction between adsorbed reactants with preferential adsorption of water. The heat values of adsorption are 39 and 8.5 kcal mol^{-1} for water and ethene, respectively, and an apparent activation energy is 30 kcal mol^{-1}.

Commercial processes for the vapor-phase hydration of ethene over a supported phosphoric acid catalyst are usually carried out at 60–80 atm. Fig. 11 illustrates the efficiency for the hydration of ethene over an active ZrW catalyst under high pressure conditions. At each pressure, the yield of ethanol (moles of C_2H_5OH formed per mole of C_2H_4 fed) increases with temperature, passing through a maximum, and then decreases owing to equilibrium limitation. The maximum yield increases with pressure shifting toward higher temperature. The discrepancy between the observed yield under the equilibrium limitation and the theoretical yield that is calculated according to Ewell's method [78] becomes greater at a higher pressure. This is ascribed partly to the by-products. However, the amount of the by-products is not so great as to correspond to the discrepancy. The ZrW has the maximum pore-size distribution at a radius of around 1.3 nm, which is estimated from the measurement according to the methanol adsorption method [79]. Under the present reaction conditions, this pore size appears to be small enough to cause capillary condensation of water vapor on the catalyst surface. Thus it is probable that at a space velocity of 2300 h^{-1} the reaction is still also kinetically controlled even at higher temperatures and retarded by the increasing condensation of water at higher pressures. The reverse effect of pressure observed below ca. 250°C (kinetic control region) can be elucidated also in terms of the increasing condensation of water vapor with the increase in pressure.

The by-products in the ethene hydration at high pressures include acetaldehyde, diethyl ether and butenes. Oily substances such as ethylene oligomers are not detected over the ZrW catalyst. The formation of acetaldehyde is illustrated in Fig. 12. At each pressure acetaldehyde

Table 7

Catalytic activity of zirconium tungstate for the ethene hydration at atmospheric pressure in the vapor phase (from H. Momose et al., J. Catal., 77 (1982) 25, table 1, partly modified, Academic Press)

Catalyst	W/Zr (mole ratio)	Reaction temp. (°C)	EtOH concn. (wt%)
Zirconium tungstate			
ZrW-I without HCl washing	1.0	220	0.38
ZrW-I with HCl washing	1.0	220	0.60
ZrW-II without HCl washing	2.0	220	0.74
		245	0.70
ZrW-II with HCl washing	2.0	220	0.90
		245	0.81
ZrW-III with HCl washing	3.0	220	0.80
Silica-supported H_3PO_4		220	0.45
		245	0.59

[a] Concentration of ethanol in the liquid sample under the conditions of H_2O/C_2H_4 (mole ratio) = 1.0 and SV = 2300 h^{-1}.

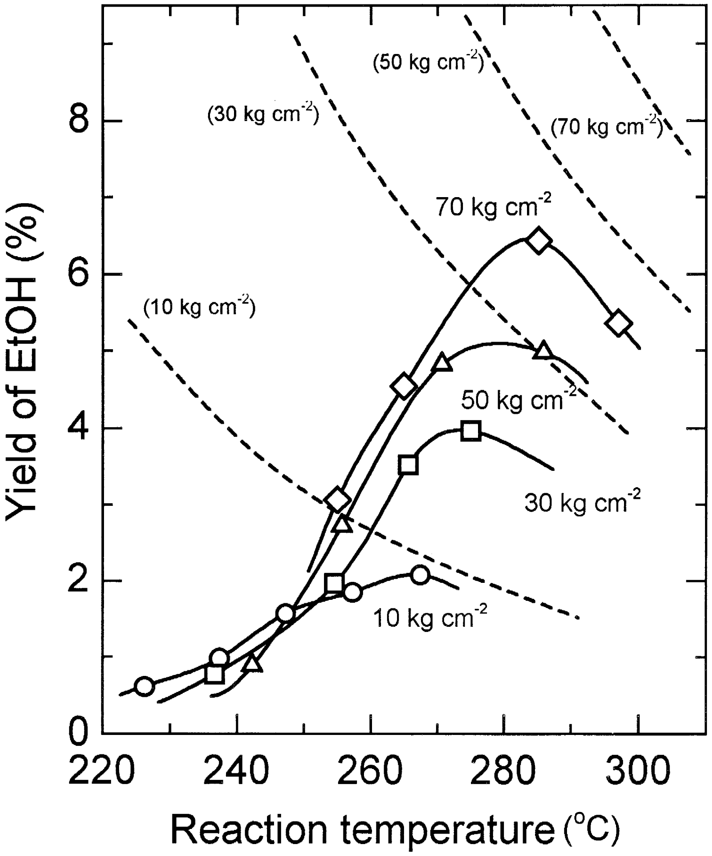


Fig. 11. Effects of reaction temperature and pressure on the yield of ethanol. H_2O/C_2H_4 mole ratio: 1.0; SV: 2300 h^{-1}. From H. Momose et al., J. Catal., 77 (1982) 555 (fig. 2, partly modified), Academic Press.

increases significantly above the temperature where the yield of ethanol becomes maximum. This fact suggests that acetaldehyde is formed by the dehydrogenation of ethanol over the ZrW catalyst which may be expected to reveal dehydrogenation activity like that of tungsten oxide catalysts. Also the fact that the acetaldehyde formation is suppressed with increasing pressure supports the dehydrogenation mechanism. However, the amount of hydrogen in the off-gas stream is too small to be detected. Another experiment indicates that the ZrW undergoes reduction with ethanol to a certain degree. The reaction, therefore, involves the stoichiometric oxidation of ethanol to acetaldehyde with the ZrW catalyst. In fact a significant amount of acetaldehyde is detected just after the start of the reaction. However, its steady formation is attained within several hours on-stream, which means the occurrence of the catalytic dehydrogenation of the product ethanol during the reaction. In every run the equilibrated amount of diethyl ether is formed. The equilibration of the intermolecular dehydration of ethanol into diethyl ether is ascertained by the facts that the equilibrium constant calculated from the product composition depends only on the reaction temperature and the constant does not change with the prior addition of the ether to the feeds. The equilibrium constant of the dehydration is 2.6 at 280°C. Butenes, which are formed by ethene dimerization, consist of *trans*-2-butene as a major component, and *cis*-2-butene and 1-butene as minor components. The total yield of butenes increases noticeably with temperature (0.1–0.4 mol% of C_2H_4 fed). At a constant

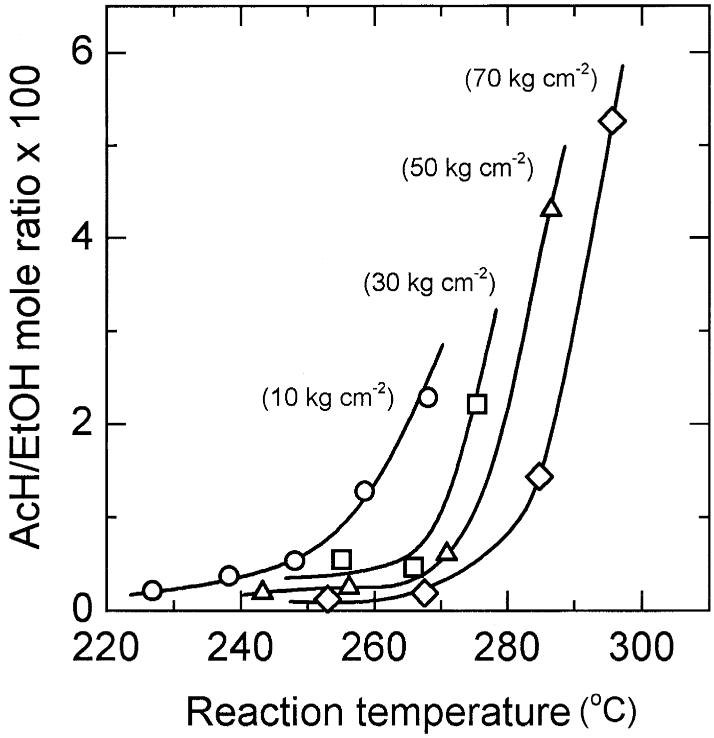


Fig. 12. Effects of reaction temperature and pressure on the ratio of acetaldehyde to ethanol. H_2O/C_2H_4 mole ratio: 1.0; SV: 2300 h^{-1}. From H. Momose et al., J. Catal., 77 (1982) 556 (fig. 5, partly modified), Academic Press.

temperature, a higher H_2O/C_2H_4 ratio reduced the dimerization reaction.

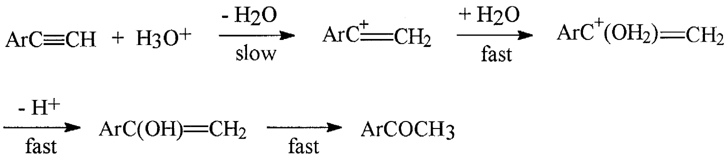
2.7.2. Niobic acid and hydrated tantalum oxide

Niobic acid ($Nb_2O_5 \cdot nH_2O$) has a strong acidic property ($H_0 < -5.6$) when heated in air even at moderate temperatures (100–300°C). It efficiently catalyzes several water-participating reactions such as dehydration and esterification [41]. Niobic acid preheated in vacuo at 200–220°C is active for the vapor-phase hydration of ethene. Its activity at a steady state is higher than that of supported phosphoric acid under the reaction conditions of 220°C and partial pressures of 7.3 kPa for water and 48 kPa for ethene. Its activity is further enhanced when treated with HF, H_2SO_4, and H_3PO_4 [41]b,e. The niobic acid calcined at 300°C is more active than acidic ion exchange resins, silica-alumina and titania-silica for the hydration of dicyclopentadiene to the corresponding alcohol, tricyclo[5,2,1,$0^{2,6}$]-3-decene-8(or 9)ol at 170°C (conversion = 17%) [41]f.

The physical property and structure of tantalum are very similar to those of niobium. The hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$, $n = 2.1$ at 120°C) displays a strong acid property ($H_0 < -8.2$) in its amorphous form. The liquid-phase hydration of isobutene in methyl cellosolve as a solvent is effectively catalyzed by a hydrated tantalum oxide preheated at 200°C to give 23% yield of *t*-butyl alcohol with 100% selectivity (150°C, 5.5 atm, isobutene 2.90 g, water 19.35 g, solvent 57.76 g, catalyst 2.5 g) [42].

3. Hydration of alkynes

Before the advent of the Wacker process, acetaldehyde was produced via the hydration of ethyne. As the hydration of ethyne needs a toxic mercury sulfate catalyst, various alternative cat-



Scheme 4.

alysts have been studied. On the other hand, reactive acetylenic compounds with electron donating groups, such as alkynylethers, are readily hydrated to afford the corresponding carbonyl compounds in the presence of protons.

3.1. Catalysts for alkyne hydration

Mercury sulfate is the most active catalyst for the hydration of alkynes. It had been commercially applied to produce acetaldehyde from ethyne as an 1–2% solution dissolved in 18–25% aqueous sulfuric acid. Other catalysts include phosphates of Cu, Zn, B, [80], Zn^{2+}, Cd^{2+}, or Cu^{2+} ion-exchanged zeolites [81] for the vapor-phase hydration, chlorides of Ru, Rh and Zn [83], and ion-exchange resins containing Hg^{2+} and Fe^{3+} [82]. The resin catalysts effectuate the hydration of ethyne efficiently at room temperature [82]b. Heteropolyacid is also an active catalyst for alkyne hydration as described below.

3.2. Reaction mechanism of alkyne hydration

According to a study [84] on the hydration of phenylacetylene in an aqueous sulfuric acid and acetic acid, the reaction mechanism of acetylene hydration in the liquid-phase is expressed by Scheme 4, which is similar to that of the hydration of alkene. Hg^{2+} appears to accelerate the nucleophilic addition of water to the acetylenic carbon through the Hg π-complex formation (Scheme 5) [85].

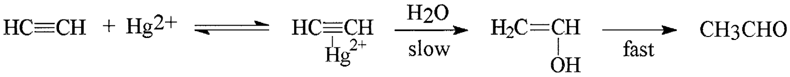
The hydration of acetylene in an aqueous HCl solution of $RuCl_3$ or $RhCl_3$ proceeds via the *syn*-addition of coordination water to the acetylene molecule coordinated to the metal [83]b. Methyl vinyl ketone and allyl alcohol are obtained from vinylacetylene and cyclic allene with Hg^{2+}, respectively [86].

3.3. Hydration of acetylene by heteropolyacid

An acetylenic compound such as phenylacetylene is effectively hydrated in the presence of heteropolyacid to afford acetophenone [87]:

$$PhC{\equiv}CH + H_2O = PhCOCH_3 \qquad (6)$$

The catalytic activity of HPA for the reaction of Eq. (6) is compared with those of typical conventional acids of sulfuric and perchloric acids (Table 8) at a reaction temperature of 60°C, where ethanol is used as a solvent in order to keep the reaction medium homogeneous. All of the HPA catalysts tested are much more active for the hydration than H_2SO_4 and $HClO_4$. In the case of H_2SO_4, the reaction rate is nearly proportional to the catalyst concentration, and the addition of a neutral salt of Na_2SO_4 lowers the rate. In contrast, the rate in the presence of heteropolyacid catalyst ($H_3PW_{12}O_{40}$) shows approximately second-order dependence on the catalyst concentration. The addition of a neutral salt of heteropolyacid ($Na_4SiW_{12}O_{40}$) increases the rate, although the neutral salt alone is quite inactive for the hydra-



Scheme 5.

Table 8
Hydration of phenylacetylene [a]

Catalyst $(10^{-1}$ M)		Salt added $(10^{-2}$ M)		Specific rate $k/10^{-2}$ cat. mol^{-1} h^{-1}
$H_3PW_{12}O_{40}$	(0.61)			2.90
	(1.20)			5.94
	(1.73)			10.6
	(1.20)	$HgHPW_{12}O_{40}$	(0.018)	25.3
$H_3PMo_{12}O_{40}$	(1.18)			6.51
$H_4SiW_{12}O_{40}$	(0.90)			2.94
	(0.90)	$Na_4SiW_{12}O_{40}$	(2.51)	5.19
	(0.90)	$Na_4SiW_{12}O_{40}$	(5.03)	5.89
H_2SO_4	(3.65)			0.173
	(5.13)			0.191
	(5.16)	Na_2SO_4	(12.2)	0.122
	(3.57)	$HgSO_4$	(0.018)	2.11
$HClO_4$	(3.54)			0.271

[a] 60°C, phenylacetylene 9.2 mmol, H_2O 550 mmol, EtOH 14 ml.

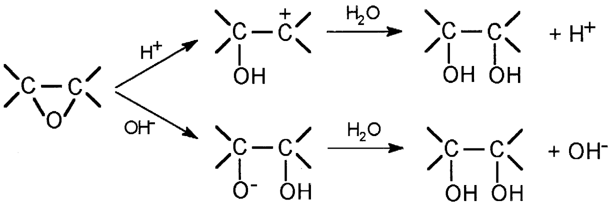
tion. The activation energies observed with $H_3PW_{12}O_{40}$ and H_2SO_4 are 24.2 and 27.5 kcal mol^{-1}, respectively, in a temperature range of 55 to 70°C. These results suggest that the reaction may be catalyzed by proton in essence, but heteropoly anions may play an important role in accelerating the reaction, in contrast to the ineffective sulfate anion. The heteropoly anion probably interacts with a protonated phenylacetylene molecule forming a stable complex, just as discussed in the hydration of alkene. As expected, the addition of an Hg salt brings about an increase in the reaction rate. In this case, the $H_3PW_{12}O_{40}$–$HgHPW_{12}O_{40}$ system is also more active than the H_2SO_4–$HgSO_4$ system at the same Hg^{2+} concentration.

3.4. Hydration of acetylene by zeolites

Zn^{2+}, Cd^{2+}, Cu^{2+} and Ag^{+} containing zeolites have been investigated as catalysts for the vapor-phase hydration of acetylene [81]a, but the relatively high concentration of crotonaldehyde in the product and the formation of polymers on the catalyst prevent their use at higher conversions for longer periods. The acidic OH groups on the zeolite surface appear to be responsible for the unfavorable polymer formation which causes deactivation [81]b. Cd^{2+}-exchanged clinoptilolite zeolite, which has no acidic OH groups on the surface [81]c, catalyzes the acetylene hydration at 190°C forming acetaldehyde without deactivation during 750 min (catalyst 8 g, acetylene 40 ml min^{-1}, water (vapor) 100 ml min^{-1}, and N_2 60 ml min^{-1}); prior to the reaction the catalyst is pretreated in a N_2 stream at 400°C for 1 h, followed by adsorption of excess ammonia at 25°C and desorption of ammonia at 270°C in a N_2 stream for 1 h [81]b. Unlike the Cd^{2+}-exchanged clinoptilolite zeolite, Cd and Zn forms of X- and Y-faujasites, A-zeolite and mordenite deactivate rapidly [81].

4. Hydration of epoxides

As shown in Scheme 6, the hydration of epoxides is accelerated in the presence of either acid or base. The catalysts for epoxide hydration are listed in Table 9. In the hydration of ethylene oxide and propylene oxide to form the corresponding glycols, excess water has to be used to suppress the polymerization of the oxides. The liquid-phase hydration using sulfuric acid is carried out at 50–70°C under atmospheric pressure, but the acid catalyst must be neutralized before separating the product glycol. Industrial processes for the hydration of epoxide



Scheme 6.

Table 9
Catalysts for epoxide hydration

Catalyst	Reaction temp. (°C)	H_2O/epoxide(mole ratio)	Conversion [a] (%)	Selectivity [b] (%)	Reference
Etylene oxide to ethylene glycol					
Amberlite IR 120	127–193	–	Yield = 70–90%		[88]d
Nafion XR(6%)/SiO_2	50–110	10	94	94	[88]e
$(CH_3)_4N^+I^-$–$NaHCO_3$	100–200	1.0	Y = 97%		[89]a
K_2MoO_4–KI	140	1.1	100	92.6	[90]a
$AlPO_4$–$Cu(NO_3)_2$	266	–	90.4	57.4	[90]b
$Ph_4Sb^+Cl^-$ [c]	120	2.0	98	79.6	[92]
Propylene oxide to propylene glycol					
$Ph_3P(CH_3)+I^-$	155	2.1	98.3	90.9	[89]b
Cyclohexene oxide to *trans*-1,2-cyclohexanediol					
Nafion-H [d]	r.t.	2.8	Y = 73		[91]
Phenyloxirane to phenyl-1,2-ethanediol					
$Nb_2O_5 \cdot nH_2O$ [e]	100	excess	Y = 100		[93]
Glycidol to glycerin					
KU-2-M	60–100	6.2–7.8	90–95	99.5	[88]f

[a] Epoxide conversion.
[b] Monoglycol selectivity.
[c] CO_2 5 atm.
[d] in THF.
[e] Calcinated at 300°C.

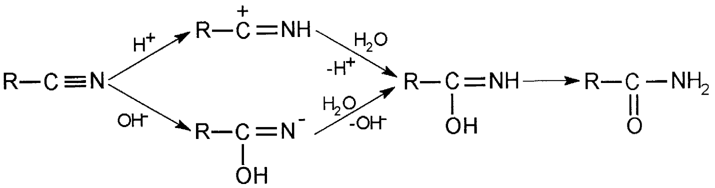
are, therefore, usually performed with large excess of water in the absence of catalyst at 140–230°C and 20–40 atm to give a high selectivity to glycol (ca. 90%). The use of solid catalysts appears favorable, since the reaction can be performed at lower temperatures and lower water-to-epoxide mole ratios to reduce evaporation loads, in addition to easy separation of the product from the catalyst. The catalytic hydration of epoxide has been studied using acidic ion-exchange resins [88], tetra-alkylammonium [89]a and tetra-phenylphosphonium salts [89]b, aluminum phosphate [90]b, Nafion-H [88]e[91], organoantimony compounds [92], and niobic acid [93].

Nafion-H, a perfluorinated resinsulfonic acid catalyst, effectively catalyzes epoxide ring-opening reactions, combining the high acidity required with the advantages of a solid catalyst [91]. It provides a very simple work-up and product isolation upon completion of the reactions. The catalyst can be readily regenerated for further use without loss of activity. The method allows the reactions to be carried out under mild conditions, without heating of the reaction mixtures. Generally high yields are obtained. For example, cyclohexene glycol is obtained in a yield of 78% by the hydration of cyclohexene oxide over Nafion-H at room temperature in dry tetrahydrofuran as a solvent [91].

5. Hydration of nitriles

5.1. Catalysts for nitrile hydration

Nitrile is hydrated to the corresponding amide with acid or base (Scheme 7), but the selectivity to amide is generally low because the amide once formed undergoes hydrolysis changing into carboxylic acid. Aromatic nitrile is selectively hydrated with alkali in the presence of hydrogen peroxide [94]. Many studies on the hydration of nitrile have been done since metallic and ionic copper, as well as copper oxide, have been found very effective to catalyze the hydration of aromatic nitriles [95,96]. The hydration of acrylonitrile is practically very important, but the problem is that the unsaturated bond of acrylonitrile is readily hydrated (Michael addition) to



Scheme 7.

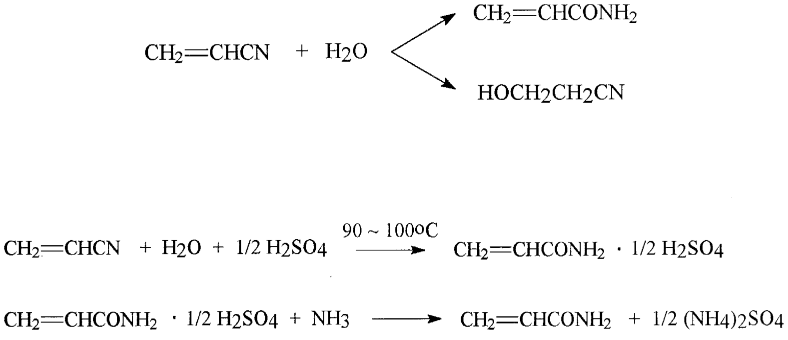
give 3-hydroxypropionitrile. Industrially the hydration of acrylonitrile have long been carried out via a non-catalytic two-step process which involves the hydration with hydrochloric acid [97] or sulfuric acid [98] followed by neutralization with ammonia (Scheme 8).

Recently various types of catalysts have been proposed for the selective hydration of nitrile as shown in Table 10. Particularly, copper systems [100] and manganese oxide systems [101]a, [108,109] are very effective. The copper catalysts include Raney Cu, Ullmann Cu, and supported metallic Cu. They are employed as an aqueous suspension or a fixed bed in the liquid phase under the reaction conditions of 70–120°C [99]c. Basic supports, such as 4-vinylpyridine polymer, MgO and ZnO, are preferable for supporting copper [106]. The hydration of 2-cyanopyridine is catalyzed by a copper complex such as $[Cu(en)_2]Cl_2$ [107]. Manganese oxides, particularly δ- and γ-type oxides which have large surface areas, are very active for the hydration of nitriles [101]a, [108,109]. Nickel works efficiently for the hydration of aromatic nitriles and acetonitrile, but in the hydration of acrylonitrile cyanohydrins are formed as by-products [107]. Hydorxy complexes of Pd, Rh, Pt and Ir, as well as other metal complexes of Co and Ru, are also effective for the hydration of nitriles [99]e, [110]. The hydration of nicotinonitrile is catalyzed by hydroxy ion-exchanged anionic resin catalysts [111].

5.2. Reaction mechanism of nitrile hydration

The hydration of nitriles proceeds according to Scheme 9. Both proton and hydroxy ion work catalytically, but they also promote the hydrolysis of the amide formed: proton interacts with the nitrile nitrogen atom to accelerate the polarization of the carbon–nitrogen bond, and hydroxy ions behave as a nucleophile to react with the nitrile carbon atom.

The mechanism of the hydration with copper and nickel metals has not completely been elucidated. It has been reported that the addition of a basic substance such as pyridine enhances the catalytic activity of the metal, whereas an acidic

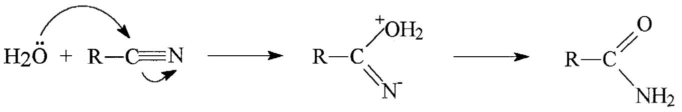


Scheme 8.

Table 10
Catalysts for nitrile hydration

Catalyst	Reaction temp. (°C)	Conversion (%)	Selectivity (%)	Reference
Acrylonitrile to acrylamide:				
Cu + $CuCl_2$	125	65.3	–	[100]a
Cu + Cu salt ($CuSO_4$,$Cu(NO_3)_2$ etc.)	120	71.5	–	[100]g
Cu reduced with HCHO and H_2	100	80.5	92.7	[100]b
Cu reduced with Zn	110		Yield = 96%	[100]h
Cu–Cr (H_2 reduction)	135	72.5	87.9	[100]c
Cu silicate + Mg,Cr	70	72	99.7	[100]d
Cu–Fe–Mn reduced with Zn	85	80.8	98.5	[100]e
Cu–Mg silicate reduced with H_2	70		STY = 68–92 g amide/kg-cat./h	[100]f
Cu + $Ni(OAc)_2$ reduced with Al	170	98.1	98.9	[100]i
Cu + Rh reduced with Al	100	98.7	99.6	[100]j
MnO_2	70	65	100	[101]a[108]
Cu^{2+}-exchanged Amberlite IRC-50	125		Y = 16%	[105]a
Amberlite IRA-400 + HCHO	23–42		Y = 75% for $HOCH_2CH_2CN$	[105]b
Ru/C	135		Y = 50.8%	[102]a
$RhCl_3(EtCN)_3$ + $HgCl_2$	70		70 mol-amide/mol-Rh/h	[102]b
Fe oxide, Zn oxide	135		Y = 76.7%	[103]d
Cr oxide + Ni,Zn,Co,Sn,	96	98	98.2	[103]c
Acetonitrile to acetamide:				
Na_2PdCl_4	77	23	100	[102]e
$Zn(OAc)_2$	225		Y = 72.3%	
Benzonitrile to benzamide:				
$PhCO_2NH_4$	250	92	89.3	[104]a
Methacrylonitrile to methacrylamide:				
LiOH	200	35.2	93	[104]b
Acetone cyanohydrin to 2-methyl-2-hydroxypropionamide:				
MnO_2	80	92	81	[101]d
Succinonitrile to 3-cyanopropionamide:				
$Nb_2O_5 \cdot nH_2O$	150	70	83	[112]

substance deactivates [107]. The basic sites on the metal surface are probably responsible for the dissociation of water to form hydroxy ions, or for promotion of the polarization of the carbon–nitrogen bond of nitrile. Regarding the catalysis of metal oxides such as MnO_2, CuO and NiO, the surface hydroxy groups of the oxide catalysts may play an important role in the hydration of acrylonitrile, but the strong basicity of the surface hydroxy group promotes unfavorable Michael addition to form 3-hydroxypropionitrile and eventually bis-2-cyanoethyl ether (Scheme 10) [99]c. In the catalysis of the Pd hydroxy complex, the hydra-



Scheme 9.

Scheme 10.

tion proceeds via *syn*-addition of the hydroxy ligand to the coordinated acrylonitrile molecule [108].

6. Hydrolysis of esters

For liquid-phase hydrolysis of esters, there are only a few solid acid catalysts which are acceptable for both activity and stability. Because most inorganic solid acids are generally hydrophilic, water covers their surface to reduce acid strength and to prevent the adsorption of organic substances. Acidic ion-exchange resins, such as Amberlite IR-100 and Amberlyst-15, are often employed for ester hydrolysis, but their application is limited to the reactions when operated at relatively low temperatures of less than 100°C because of low thermal stability. Unlike silica-alumina and Y-type zeolite, a high-silica zeolite of H-ZSM-5 keeps its strong acidity in aqueous media owing to hydrophobicity. H-ZSM-5 is, therefore, applicable to the hydrolysis of ethyl acetate [113], although its activity is not necessarily high due to its meager acidity. A layer compound of zirconium phosphonate has recently been reported as an active solid acid catalyst for the hydrolysis of ethyl acetate when a sulfonic group is introduced into the phosphonate moiety [114]. Insoluble acidic alkali metal salts of the Keggin-type heteropolyacids, such as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, work as efficient acid catalysts for ester hydrolysis in the liquid phase [115]. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is much more active than H-ZSM-5, for it shows higher acid strength ($H_0 > 0.8$) than H-ZSM-5 ($H_0 > 1.5$) in both aqueous and alcoholic reaction media.

6.1. Cation exchange resin catalysts

Cation exchange resins having sulfonic acid groups are typical of insoluble solid acid catalysts. They have widely been applied to the hydrolysis of esters. Amberlite IR-100 and IR-120 have first been studied as catalysts for the hydrolysis of methyl, ethyl and amyl acetates in water and aqueous acetone media [116,117]. The catalytic activity of the acidic resins may reasonably be expected to be parallel to that of homogeneous strong acids. Differences, however, arise due to diffusion effects and other factors mostly related to the differences in solvent composition in the proximity of the resin matrix, compared with the composition in the bulk of the solution [118–120]. Catalytic activity of macroreticular-type sulfonic resins has been compared with that of gel-type resins for the hydrolysis in the gas–solid and gas–liquid phases [121]. Strong enhancement of catalytic activity by the co-presence of protons and metal cations with large electronegativity, such as Bi^{3+}, Fe^{3+}, and Ga^{3+}, has been observed with the hydrolysis of ethyl acetate over Amberlyst-15 [122]. The influence of the molecular size of ester on the rate of reaction in the resin catalysis is generally attributed to the steric factors involved. The effects of variation of the acyl and alkyl groups in a series of esters on the kinetics of their hydrolysis have been investigated [123].

6.2. Zeolite catalysts

Silica-alumina and acidic Y-type zeolite, which are insoluble in water, are generally considered to be inactive as solid acid catalysts in aqueous solutions at relatively low temperatures because water covers their surface to prevent the adsorption of organic substrates owing to their hydrophilic nature. On the other hand, high-silica zeolites, such as dealuminated mordenite [124] and ZSM-5 [125] are known to be hydrophobic. These zeolites are expected to show high activity as solid acid catalysts in aqueous solutions. The hydrolysis of ethyl ac-

Table 11
Hydrolysis of ethyl acetate catalyzed by solid acids [a] (from S. Namba et al., J. Catal., 72 (1981) 18, table 2, Academic Press)

Catalyst	Si/Al atomic ratio	Acidity (meq g^{-1})	Hydrolysis activity [b] (10^{-3} min^{-1} g^{-1})
H-ZSM-5	47	0.47	1.75
H-M [c]	5.5	0.01	0.03
H-M [c]	7.4	0.13	0.49
H-M [c]	8.7	0.20	0.77
H-Y	2.4	0.01	0.04
SA [d]	5.7	0.01	0.04
SA [d]	2.6	0.01	0.04
Sulfonic resin [e]	–	1.17	4.44

[a] 5.0% aqueous ethyl acetate, 60°C.
[b] Specific rate.
[c] H-Mordenite.
[d] Silica-alumina.
[e] Amberlite 200C.

etate over various kinds of zeolites was first investigated in detail by Namba and Yashima [113]. As shown in Table 11, the hydrolysis activities of high-silica zeolites (H-ZSM-5, dealuminated H-mordenite) are moderate, while the activities of silica-alumina, non-dealuminated mordenite, and HY zeolite are all very small. Particularly, the activity of an H-ZSM-5 (Si/Al = 47) is high and about 40% of that of Amberlite 200C, a gel-type sulfonated resin. The H-ZSM-5 has the acid sites whose acid strength is $-5.6 < H_0 < -3.0$ in water, whereas HY and silica-alumina are much less acidic in water (Table 12). The higher Si/Al atomic ratios provide more hydrophobic property on the catalyst surface, which, therefore, show better affinity for the ester than water. However, too high a Si/Al ratio results in the decrease in the activity, because the acid sites decreased in number. The Si/Al ratio that gives the highest hydrolysis activity appears to be 20–47 for H-ZSM-5, 9–20 for H-mordenite, and about 3 for Y zeolite [113,126]. According to a study on acidic and hydrophobic properties of H-ZSM-5 and dealuminated H-mordenite zeolites with different Si/Al ratios by means of ammonia adsorption, ammonia TPD and water adsorption [126], the amount of adsorbed water is proportional to the Al/Si ratio of zeolite, and the following sequence for both acid amount and acid strength is afforded: H-mordenite > dealuminated H-mordenite > H-ZSM-5. However, at the same Si/Al ratio, H-ZSM-5 is more active than H-mordenite for the hydrolysis of ethyl acetate. Higher hydrophobicity or higher acid strength *in water* is responsible for higher catalytic efficiency of H-ZSM-5.

On the basis of the effectiveness of hydrophobic H-ZSM-5 zeolite for ester hydrolysis, the hydrolysis of water-insoluble esters catalyzed by a modified lipophilic H-ZSM-5 has been reported [127]. An effective catalyst is obtained by treating a high-silica H-ZSM-5 (Si/Al = 39) with octadecyltrichlorosilane in toluene under reflux; about one molecule of the octadecylsilyl group is attached per unit cell of the zeolite. In a toluene–water solvent (1:1 volume ratio) under reflux, the alkylsilane-treated H-ZSM-5 catalyst shows a notable activity for the hydrolysis of insoluble, hydrophobic esters, such as heptyl, octyl, dodecyl acetates, and

Table 12
Acid strength of aluminosilicates in water [a] (from S. Namba et al., J. Catal., 72 (1981) 17, table 1, Academic Press)

Silicates	Proton exchange degree (%)	Si/Al atomic ratio	H_0 $+3.3$	$+1.5$	$+0.8$	-3.0	-5.6
H-ZSM-5	100	47	+	+	+	+	−
H-M	96	5.5	+	+	+	−	−
H-M	98	7.2	+	+	+	±	−
H-Y	80	2.4	+	±	−	−	−
H-Y	93	3.8	+	+	±	−	−
SA	–	5.7	+	±	−	−	−
SA	–	2.6	+	−	−	−	−

[a] +: acidic color, ±: slightly acidic color, −: basic color.

methyl and ethyl esters of decanoic acid. The relative hydrolysis activity of the modified zeolite to the non-alkylated H-ZSM-5 is as much as 4–60. The reaction proceeds over the catalyst suspended in the toluene–water interface, while the non-alkylated H-ZSM-5 stays in suspension in the water phase. In the case of the hydrolysis of benzyl acetate, phenyltrichlorosilane is preferable to octadecyl-trichlorosilane as a modifying agent.

6.3. Heteropolyacid catalysts

6.3.1. Acidic cesium salt of 12-tungstophosphoric acid

Heteropolyacid is an active catalyst for the hydrolysis of ester, but the separation of heteropolyacid from the product is not easy. Heteropolyacid is strongly adsorbed on activated carbon. The heteropolyacid entrapped in carbon, therefore, appears to be applicable as a solid acid catalyst to the liquid-phase reactions in polar reaction media [128], but in water the heteropolyacid entrapped partly dissolves out. Recently, the acid catalysis of insoluble acidic alkali metal salts of the Keggin-type heteropolyacids with large surface areas has extensively been studied [129–133].

Acidic alkali metal salts of the Keggin-type heteropolyacids are prepared by adding a required amount of aqueous alkali metal carbonate (0.47 M) to aqueous heteropolyacid (0.75 M) at room temperature. The precipitate obtained is aged in water for 20 h at room temperature, followed by evaporation at 45°C in vacuo (25 Torr), and calcination at 300°C for 3 h in vacuo (25 Torr).

Amongst various acidic alkali metal salts of the Keggin-type heteropolyacids, an acidic Cs salt of 12-tungstophosphoric acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is considerably durable against hydrothermal treatment. Table 13 demonstrates significant water-durability of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Its catalytic activity for the benzylation of benzene [133] as a test reaction does not change even after hydrothermal treatment at 120°C for 6 days, during which the Keggin structure is completely retained. This result suggests that acidic salts of heteropolyacid may be applicable as effective solid acid catalysts to several types of water-involving organic reactions, such as the hydrolysis of ester in the liquid phase. In fact, water-insoluble acidic Cs heteropolytungstates, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$, exhibit higher catalytic activity than a comparative inorganic solid acid of H-ZSM-5 in terms of both specific rate per unit catalyst weight and turnover frequency for the hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol in the liquid phase (Table 14). In the hydrolysis of ethyl acetate, a small amount of water ($AcOEt/H_2O = 3.88$ mole ratio) is used in order to avoid colloidal dispersion of the salts as described below. These acidic Cs salts are stable and insoluble during the reaction. Amberlyst-15, an organic solid acid, is two or three times more active than the acidic Cs salts of heteropolytungstic acids with respect to the catalytic activity per unit weight, but its turnover frequency that denotes the specific rate per unit acid amount is much lower than those of the Cs salts.

Fig. 13 illustrates the changes in hydrolysis activity and surface area with the Cs content in terms of x in the formula of $Cs_xH_{3-x}PW_{12}O_{40}$. The hydrolysis activity decreased monotonously with increasing Cs content or decreasing acidity, whereas the surface area increased abruptly

Table 13
Effect of hydrothermal treatment on catalytic property of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (from Y. Izumi et al., Chem. Lett., (1993) 826, Table 1, The Chemical Society of Japan)

Hydrothermal treatment	Catalytic activity for benzylation of benzene [a]	
	$PhCH_2Cl$ conversion (%)	Ph_2CH_2 yield (%)
None	90	48
120°C, 6 days [b]	100	53

[a] Benzene/$PhCH_2Cl$/catalyst = 100/5/0.02 mmol, benzene reflux 2 h.

[b] Treated in an autoclave; the catalyst recovered was calcined at 300°C for 3 h prior to reuse for benzylation.

Table 14
Catalytic activity of solid acids in water-involving organic reactions (from Y. Izumi et al., Chem. Lett., (1993) 826, table 2, The Chemical Society of Japan)

Solid acid	Surface area (m^2 g^{-1})	Acid amount (mequiv. g^{-1})	Hydrolysis [a]		Esterification [b]	
			Activity [c]	TF [d]	Activity [c]	TF [d]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	02	0.156 [h]	2.04	13.1	0.52	33.3
$Cs_{2.5}H_{1.5}SiW_{12}O_{40}$	49	0.468 [h]	4.56	9.7	–	–
$Cs_3HSiW_{12}O_{40}$	83	0.305 [h]	1.76	5.8	–	–
Amberlyst-15 [e]	–	4.9 [i]	7.80	1.6	1.64	3.5
H-ZSM-5 [e,f]	–	0.234 [h]	0.43	1.8	0.03	1.3
SiO_2-Al_2O_3 [e,g]	–	–	0	0	–	–

[a] Ethyl acetate/water/catalyst = 1080/27.8/0.1 mmol, 60°C.
[b] Acetic acid/ethanol/catalyst = 100/100/0.1 mmol, 60°C.
[c] Specific rate (10^{-3} min^{-1} g^{-1}).
[d] Turnover frequency (min^{-1}).
[e] 321 mg.
[f] Si/Al = 70.
[g] Si/Al = 6.25.
[h] Calculated value based on chemical composition.
[i] Determined by titration.

from less than 10 to 130 m^2 g^{-1} at above $x = 2.0$. $CsH_2PW_{12}O_{40}$, as well as the parent free acid $H_3PW_{12}O_{40}$, dissolved during the hydrolysis reaction, and $Cs_2HPW_{12}O_{40}$ partly dissolved. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, however, remained as an insoluble solid without forming a colloidal

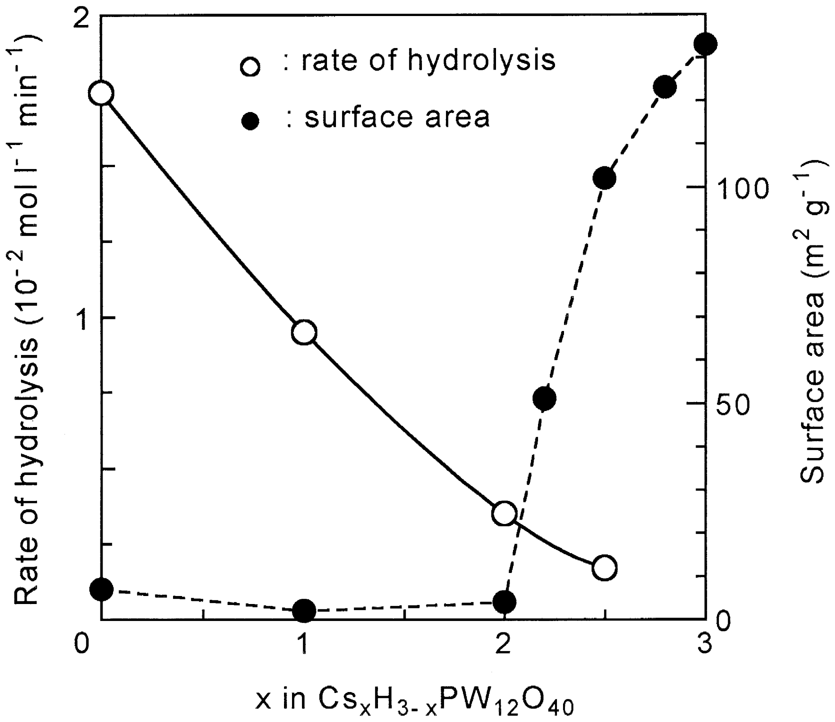


Fig. 13. Changes in the catalytic activity of ethyl acetate hydrolysis and surface area with Cs content of $Cs_xH_{3-x}PW_{12}O_{40}$. AcOEt = 9.5 g, H_2O = 0.5 g, catalyst = 0.1 mmol, 60°C. From Y. Izumi et al., Microporous Materials, 5 (1995) 257 (fig. 1), Elsevier.

solution. The activity was related directly to the bulk acidity of the salt. This catalytic behavior in the hydrolysis was quite different from that observed with the liquid-phase Friedel–Crafts reactions over $Cs_xH_{3-x}PW_{12}O_{40}$ ($x = 0$ to 3) whose catalytic efficiency was greatly dependent on surface area because the reactions proceeded exclusively on the surface owing to lower polarity of the reaction media [134]. Other acidic salts of heteropolyacid such as $(NH_4)_2HPW_{12}O_{40}$, $Cs_2H_2SiW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PMo_{12}O_{40}$, and $K_{2.5}H_{0.5}PW_{12}O_{40}$ which worked as efficient and insoluble solid acid catalysts for the liquid-phase Friedel–Crafts reactions [134], were unfavorable for the hydrolysis of ethyl acetate because they partly dissolved in the course of the reaction.

Table 15 indicates qualitative estimation of acid strength for the solid acids used in the liquid media relevant to the reactions listed in Table 14. Both $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Cs_{2.5}H_{1.5}SiW_{12}O_{40}$ show relatively higher acid strengths than H-ZSM-5 in each liquid medium, which corresponds well to their higher turnover frequency than that of H-ZSM-5; in a non-polar solvent $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ shows a higher acid strength of less than -13.16 in terms of H_0 [135]. Thus these two acidic Cs salts of heteropolytungstic acids may be useful as solid acid catalysts to be able to replace ion-exchange resins for the acid-catalyzed water-involving organic reactions which depend on strong acidity or high temperatures.

6.3.2. *Silica-included acidic cesium salt of 12-tungstophosphoric acid*

The salt of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ above-mentioned consists of relatively uniform very fine crystal particles with ca. 10 nm diameter. In the hydrolysis of ethyl acetate with a low concentration of water, the salt particles could be separated by filtration as large-size aggregates from the liquid medium. However, if applied to the hydrolysis under the commonly employed reaction condition using a large excess of water, i.e. in a highly polar reaction medium, the salt particles formed a colloidal solution, and so became inseparable. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ can be supported on a porous material such as silica gel, but the salt supported is easily removed from the support when put into water or alcohol.

In order to make the salt recoverable from water, a composite in which $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ crystallites are tightly included with silica matrix has been developed by means of a sol-gel technique which involves the hydrolysis of ethyl orthosilicate [136]. Silica-included $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is prepared through the hydrolysis of ethyl orthosilicate conducted at 40°C for 1 h, then at 80°C for 3 h in the presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ dispersed in ethanol. The hydrogel obtained is dehydrated slowly at 45°C in vacuo (25 Torr), followed by extraction with water at 80°C for 10 h to remove the non-trapped salt and organics, and finally calcined at 300°C for 3 h in vacuo (25 Torr). The ratios of

Table 15
Acid strength of solid acid in polar liquid media [a] (from Y. Izumi et al., Chem. Lett., (1993) 827, table 3, The Chemical Society of Japan)

	Water			Water–AcOEt [b]			AcOH–EtOH [c]		
$pK_a =$	+1.5	+0.8	−3.0	+1.5	+0.8	−3.0	+1.5	+0.8	−3.0
Solid Acid									
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	+	±	−	+	−	−	+	+	−
$Cs_{2.5}H_{1.5}SiW_{12}O_{40}$	+	±	−	−	−	−	+	+	−
H-ZSM-5	+	−	−	−	−	−	−	−	−

[a] Qualitative estimation by Hammett indicators, +: acidic color, −: basic color, ±: border line.

[b] 95 wt% AcOEt.

[c] An equimolar mixture of AcOH and EtOH.

$SiO_2/Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $H_2O/(EtO)_4Si$, and $EtOH/(EtO)_4Si$ are the most important criteria to effect better inclusion. Higher SiO_2 content brings about smaller leakage of the salt. Higher water content accelerates much the hydrolysis of $(EtO)_4Si$ to cause more leakage of the salt, probably due to the formation of a rough silica network [137]. Ethanol is necessary to make ethyl orthosilicate and water miscible with each other. In this method, the salt to be included promotes the hydrolysis of ethyl orthosilicate by its own acid catalysis. According to an observation by scanning electron microscopy on a silica-included $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ composite with a silica content of 1.2 in terms of the calculated weight ratio, the fine crystal particles of the salt appeared to be included in a silica matrix holding their original morphology. The composite was a porous material with a large surface area of 364 $m^2\ g^{-1}$.

Table 16 lists the catalytic efficiency of silica-included $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for the hydrolysis of ethyl acetate with excess water; the activity of non-modified $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is given for comparison. Silica itself is inactive for the hydrolysis. At a silica weight ratio of less than 1.2, considerable leakage of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as colloid from the silica composite is observed during the reaction, but the leakage can be effectively suppressed when the ratio is increased to 8. The silica composites are comparable with the non-modified salt in catalytic activity. They are less active than Amberlyst-15, but more active than H-ZSM-5 on the basis of the rate per unit catalyst weight. However, the values of their turnover frequency are larger than those of Amberlyst-15 and H-ZSM-5. This means that the silica-included $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ shows higher acid strength in water than the resin and the zeolite. A silica composite with a silica weight ratio of 8 was readily recoverable by simple filtration, and it could be reused for the hydrolysis reaction repeatedly without deactivation. Fig. 14 depicts the thermal stability for the composite and the original salt $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. The composite is less stable

Table 16
Hydrolysis of ethyl acetate catalyzed by silica-included $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [a] (frm Y. Izumi, Microporous Materials, 5 (1995) 259, table 2, Elsevier)

$SiO_2/Cs_{2.5}PW$ [b]	Surface area ($m^2\ g^{-1}$)	Catalytic activity		Leakage [e] (%)
		Rate [c]	TOF [d]	
0.0 [f]	105	2.80	17.9	–
1.2	598	3.06	17.7	>1
2.0	–	1.94	12.4	0.77
4.0	–	2.78	17.8	0.62
8.0	364	2.07	13.2	0.20
SiO_2 [g]	865	0.0	0.0	–
Amberlyst-15 [h]	–	4.9 [j]	3.9	–
H-ZSM-5 [i]	–	0.23 [j]	8.1	–

[a] $H_2O = 9.5$ g, AcOEt = 0.5 g, catalyst = 0.05 mmol on the basis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, 60°C. Catalyst was prepared under the conditions of $H_2O/(EtO)_4Si = 5$, $EtOH/(EtO)_4Si = 1.3$ (mole ratio), and calcined at 300°C for 3 h.

[b] Weight ratio of SiO_2 to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ calculated from the amounts of reagents charged at the preparation.

[c] First-order specific rate per unit weight of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ($10^{-3}\ min^{-1}\ g^{-1}$).

[d] Turnover frequency (min^{-1}).

[e] Leakage of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ during the hydrolysis reaction (3 h), estimated by UV spectrometry.

[f] Non-modified $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

[g] Prepared by hydrolysis of $(EtO)_4Si$.

[h] 160 mg, dried at 100°C.

[i] 160 mg, calcined at 300°C.

[j] First-order specific rate per unit weight.

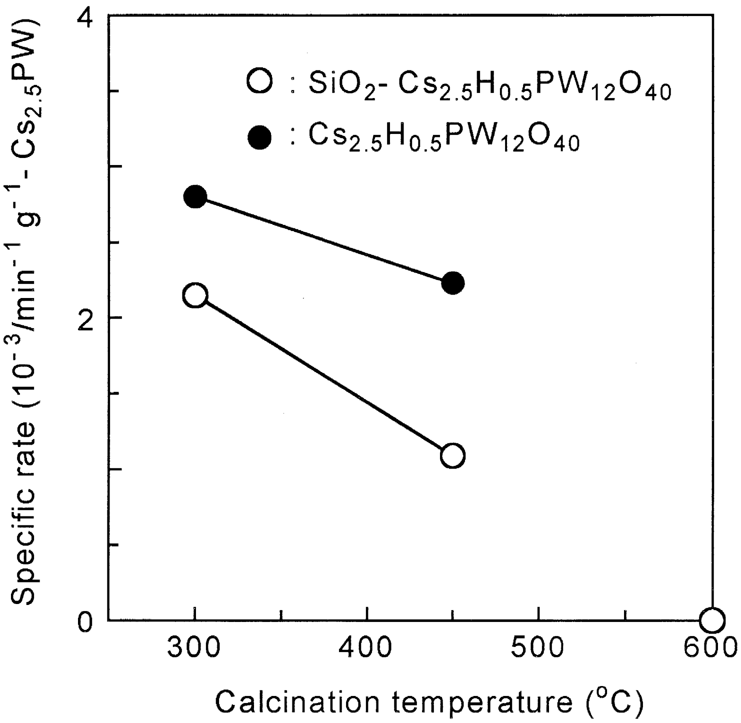


Fig. 14. Effect of calcination temperature on hydrolysis activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and silica-included $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. AcOEt = 0.5 g, H_2O = 9.5 g, catalyst = 0.05 mmol on the basis of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, 60°C for 6 h. From Y. Izumi et al., Microporous Materials, 5 (1995) 259 (fig. 5), Elsevier.

than the salt itself, but it works as a solid acid catalyst even after being treated at 450°C, although there is a gradual deactivation due to the reduction in surface area. IR spectroscopy indicates that the Keggin structure of $PW_{12}O_{40}^{3-}$ anions is retained completely inside the composite until 450°C, showing its characteristic absorption bands; P–O: 1080 cm^{-1}, W = O: 985 cm^{-1}, $W{-}O{-}W_{corner}$: 887 cm^{-1}, $W{-}O{-}W_{edge}$: 807 cm^{-1}. No IR absorption bands characteristic of $SiW_{12}O_{40}^{4-}$ anion are observed, which suggests that the substitution of Si for P in the Keggin anion does not occur in the course of silica inclusion.

6.3.3. *Silica-included 12-tungstophosphoric acid*

In place of silica inclusion of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, an attempt to immobilize $H_3PW_{12}O_{40}$ itself into silica matrix has been done for the purpose of obtaining more easily an insoluble, recoverable solid heteropolyacid catalyst. The method for immobilization is almost the same as for silica inclusion of the cesium salt, except for pre-calcination before extraction with hot water and a lower final calcination temperature (150°C). Compared with

Table 17
Compositions of silica-included $H_3PW_{12}O_{40}$ (from Y. Izumi, Microporous Materials, 5 (1995) 260, table 3, Elsevier)

SiO_2 /HPW [a] (wt ratio)	HPW content (wt%)		
	calc. [b]	found 1 [c]	found 2 [d]
1.0	50.0	49.8	12.3
3.0	25.0	25.7	11.9
5.0	16.7	16.1	15.6
8.0	11.1	10.4	11.1

[a] Weight ratio of SiO_2 to $H_3PW_{12}O_{40}$ calculated from the amounts of reagents charged at the preparation.
[b] Calculated from SiO_2 /HPW wt ratio.
[c] Determined through ICP analysis before extraction with water at 80°C.
[d] Determined through ICP analysis after extraction with water at 80°C.

the salt inclusion, a higher weight ratio of silica to $H_3PW_{12}O_{40}$ is necessary to effect better inclusion, since $H_3PW_{12}O_{40}$ is freely soluble in water. Table 17 lists the compositions of silica-included $H_3PW_{12}O_{40}$. As for the composites with silica to acid weight ratios of less than 5, considerable leakage of the acid is observed after the extraction with hot water, but the acid leakage can be somewhat reduced when the ratio is increased to 8. $H_3PW_{12}O_{40}$ included in silica forms relatively uniform crystallites with 10 nm diameter on average according to scanning electron microscopy. Silica-included $H_3PW_{12}O_{40}$ is also a porous composite with a large surface area of more than 500 $m^2\ g^{-1}$.

Table 18 summarizes the catalytic efficiency of silica-included $H_3PW_{12}O_{40}$ with different silica contents for the hydrolysis of ethyl acetate. As expected, the activity of silica-included $H_3PW_{12}O_{40}$ is much higher than silica-included $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ on the basis of unit weight of

Table 18
Hydrolysis of ethyl acetate catalyzed by silica-induced $H_3PW_{12}O_{40}$ [a] (from Y. Izumi, Microporous Materials, 5 (1995) 260, table 4, Elsevier)

SiO_2/HPW [b]	Surface area ($m^2\ g^{-1}$)	Catalytic activity		Leakage [e] (%)
		Rate [c]	TOF [d]	
3.0 [f]	–	2.5	24	2.13
5.0 [f]	623	3.5	34	1.79
8.0 [g]	581	1.9	18	0.62
12 [g,h]	869	2.1	20	0.32

[a] $H_2O = 9.5$ g, AcOEt = 0.5 g, catalyst = 0.05 mmol on the basis of $H_3PW_{12}O_{40}$, 60°C. Catalyst was calcined at 150°C for 3 h prior to use.

[b] Weight ratio of SiO_2 to $H_3PW_{12}O_{40}$ calculated from the amounts of reagents charged at the preparation.

[c] First-order specific rate per unit weight of $H_3PW_{12}O_{40}$ (10^{-2} min^{-1} g^{-1}).

[d] Turnover frequency (min^{-1}).

[e] Leakage of $H_3PW_{12}O_{40}$ during the hydrolysis reaction (3 h), estimated by UV spectrometry.

[f] Catalyst was prepared under the conditions of $H_2O/(EtO)_4Si = 3$ and $EtOH/(EtO)_4Si = 0.2$ (mole ratio).

[g] Catalyst was prepared under the conditions of $H_2O/(EtO)_4Si = 5$ and $EtOH/(EtO)_4Si = 0.7$ (mole ratio).

[h] Re-inclusion of a composite with a silica to acid weight ratio of 8.

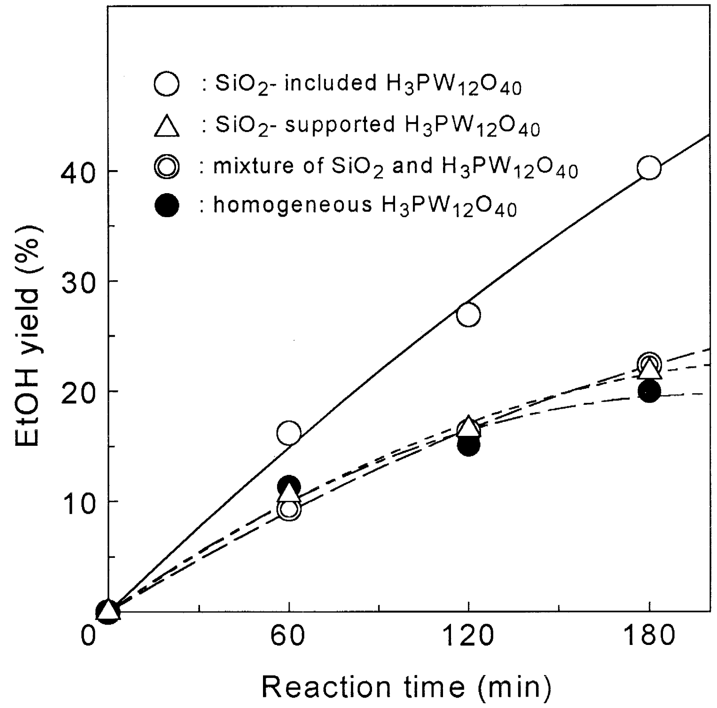


Fig. 15. Effect of silica inclusion on catalytic activity of $H_3PW_{12}O_{40}$. SiO_2/acid = 8.0, net weight of the acid introduced = 0.05 mmol, AcOEt = 0.5 g, $H_2O = 9.5$ g, 60°C. From Y. Izumi et al., Microporous Materials, 5 (1995) 261 (fig. 7), Elsevier.

Table 19
Hydrolysis of ethyl benzoate by silica-included $H_3PW_{12}O_{40}$ and Amberlyst-15 [a] (from Y. Izumi, Microporous Materials, 5 (1995) 261, table 5, Elsevier)

Catalyst	Turnover (min^{-1})
$SiO_2-H_3PW_{12}O_{40}$ [b]	3.26
Amberlyst-15 [c]	0.51

[a] $H_2O = 9.0$ g, $PhCO_2Et = 1.0$ g, catalyst = 0.05 mmol on the basis of $H_3PW_{12}O_{40}$ (0.144 g as the total), 100°C, 24 h.

[b] Catalyst was prepared under the conditions of $SiO_2/H_3PW_{12}O_{40} = 12$ (wt ratio), $H_2O/(EtO)_4Si = 10$ (mole ratio), $EtOH/(EtO)_4Si = 0.7$ (mole ratio), and calcined at 150°C for 3 h.

[c] 0.65 g; the resin was partially dissolved.

composite, when compared at the same silica content. Leakage of $H_3PW_{12}O_{40}$ during the hydrolysis reaction can be suppressed as low as 0.3%, if the silica to acid weight ratio is increased to 12 by additional silica inclusion for a composite having a silica weight ratio of 8.

Fig. 15 shows the hydrolysis activities of four different $H_3PW_{12}O_{40}$ catalyst systems; a silica-included $H_3PW_{12}O_{40}$ with a silica weight ratio of 8, silica-supported $H_3PW_{12}O_{40}$, a physical mixture of silica and $H_3PW_{12}O_{40}$, and homogeneous $H_3PW_{12}O_{40}$, where the content of $H_3PW_{12}O_{40}$ is kept the same for all catalyst systems. The catalytic activities of the supported and the mixed systems are almost the same as for homogeneous acid, because the $H_3PW_{12}O_{40}$ supported or mixed is dissolved completely into the reaction medium. Interestingly, the catalytic activity of the silica-included acid is much higher than the homogeneous acid. Probably $H_3PW_{12}O_{40}$ is entrapped in the silica network as a highly concentrated aqueous solution: the silica network appeared to be narrow enough to prevent the Keggin anion (ca. 1 nm diameter) from migrating outside the silica network.

Table 19 denotes the catalytic activities of silica-included $H_3PW_{12}O_{40}$ and Amberlyst-15 for the hydrolysis of ethyl benzoate at 100°C. The silica composite is much more active than the resin catalyst in terms of turnover frequency on the basis of protons. In addition, the silica composite catalyst shows no migration of its active catalyst components during the reaction, while the thermally unstable resin catalyst is partially dissolved in the reaction medium.

6.4. Zirconium phosphonate catalysts

Zirconium phosphonates, $Zr(O_3PR)_2$, are a new type of layer compounds typically synthesized in amorphous forms under aqueous conditions by the reaction of a soluble salt of Zr^{4+} and a phosphonic acid or an organophosphonic acid [114]. The crystalline zirconium phosphonates are obtained by treating the amorphous phosphonates with aqueous HF. Zirconium phosphate (R = OH) is almost inactive as a solid acid catalyst for the hydrolysis of esters. On the other hand, a zirconium phosphonate containing sulfonic groups, $Zr(O_3PCH_2SO_3H)_2$, behaves as a strong solid acid showing higher catalytic activity than Nafion-H for the hydrolysis of ethyl acetate at 68°C [114]a. This strongly acidic zirconium phosphonate has a large ion-exchange capacity of 5.79 meq g^{-1}, but it poses a problem that it is swollen or dissolved in

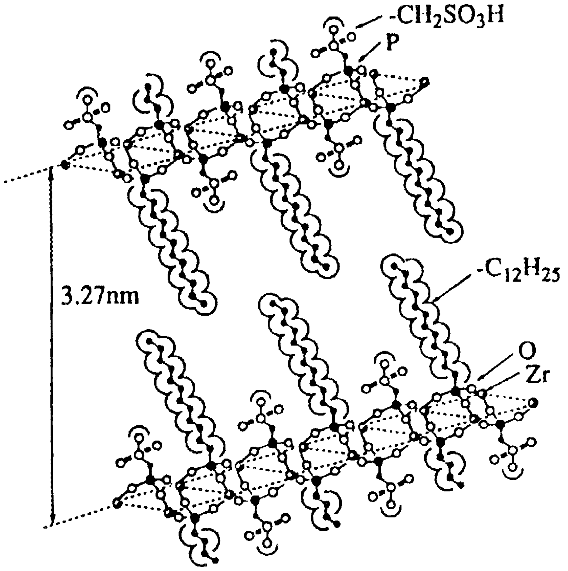


Fig. 16. Ideal structure of $Zr[(O_3PCH_2SO_3H)_{0.5}(O_3PC_{12}H_{25})_{0.5}]_2$. From K. Segawa et al., Shokubai, 37 (1995) 626 (fig. 5), Catalysis Society of Japan.

water owing to its hydrophilicity. This difficulty has been overcome by designing an insoluble composite zirconium phosphonate which includes an acidic function and a hydrophobic function in the single-crystal phase, for example $Zr[(O_3PCH_2SO_3H)_x(O_3PC_{12}H_{25})_{1-x}]_2$, where $x = 0.1 - 0.7$. An ideal pendant structure of a layered composite zirconium phosphonate has been proposed as shown in Fig. 16 [114]c. The composite materials show higher catalytic activity of the hydrolysis than $Zr(O_3PCH_2SO_3H)_2$ because they become accessible to any reactant molecules, and their hydrophobicity improves.

7. Subject Index

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