Chem. Rev. **2002,** *102,* 3641–3666

Water-Tolerant Solid Acid Catalysts

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Received February 13, 2002 (Revised Manuscript Received June 12, 2002)

Contents

I. Introduction

Solid acid catalysts have served as important functional materials for the petroleum refinery industry, such as in the cracking processes, and for the production of chemicals.[1] At present, about 180 industrial processes using solid acids are in operation, featuring acids such as zeolites, oxides, mixed oxides including heteropoly acids, and phosphates.[1a] In contrast, a significant number of acid-catalyzed reactions, such as Friedel–Crafts reactions, esterification, hydration, and hydrolysis, are still carried out using conventional acids, such as H_2SO_4 and $AlCl_3$. However, processes involving conventional acids are typically associated with problems of high toxicity, corrosion, catalyst waste, use of large amounts of catalyst, and difficulty of separation and recovery. Because solid acids are environmentally friendly with respect to corrosiveness, safety, less waste, and ease of separation and recovery, replacement of these liquid acids with solid acids is desirable in the chemical industry.

For reactions in which water participates as a reactant or product, such as hydrolysis, hydration, and esterification, only a few solid acids are acceptable in terms of their activity, stability, and insolubility. A difficulty in the use of solid acids is the severe poisoning of the acid sites by water, and in fact, most solid acids lose their catalytic activities in aqueous solutions. Development of new water-tolerant solid acids would have a major impact in industrial applications.

The use of an aqueous solution of reactant has interesting advantages. For example, formalin (aqueous formadehyde) is cheap, easy to handle, and stable even at room temperature. However, the use of formalin is strongly restricted owing to the low reactivity caused by the existence of a large amount of water. Catalysts efficient for the activation of formaldehyde in water are desirable.

Toshio Okuhara was born in 1949 in Hokkaido, Japan. He received his Bachelor's, Master's, and Doctor's degree from the Department of Chemistry at Hokkaido University in 1973, 1975, and 1978, respectively. He began his academic career at the Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo in 1979. In 1986, he did postdoctoral work at the University of Texas at Austin with Professor J. M. White. He is presently a professor at the Graduate School of Environmental Earth Science, Hokkaido University. His research interests are solid catalysts for the purification of water, organic reaction in water, selective oxidation of alkanes, and synthesis of clean gasoline.

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10.1021/cr0103569 CCC: $39.75

Advantages of catalytic reactions in aqueous systems include low cost, inflammability, nontoxicity, availability, and safety. Recent developments of Lewis acids and water-soluble organometallic catalysts have attracted much attention. Although water is probably an environmentally friendly solvent in several cases, it may require more energy in the separation step. It must also be mentioned that the recycling of aqueous organic solvent is less desirable than that of pure organic liquid.

The scope of this review will cover the state of the art of water-tolerant solid acids, including zeolites, heteropoly compounds, oxides, mixed oxides such as MoO_3-ZrO_2, phosphates, and polymer resin–silica composites. Much attention has been focused on zeolites and heteropoly compounds due to the extensive data that were accumulated for their water-tolerant catalysis, as well as acidic and hydrophobic properties. Additionally, biphasic reaction systems containing an aqueous phase are also briefly described. Furthermore, organometallic catalysts that are active in water and new hydrophobic porous materials are introduced. Although oxidation reactions using solid catalysts in water are important and interesting, these reactions will not be within the scope of this review.

II. Zeolites

1. Organic Reactions in Water Catalyzed by Zeolites

In 1981, Namba et al.[2] first reported an example of an acid-catalyzed reaction in water using solid acids. Zeolites with Si/Al ratios >8.7 were found to be active for hydrolysis of ethyl acetate in excess water at 333 K. Figure 1 shows first-order plots of this reaction over various zeolites and Amberlyst-200. H-ZSM-5 (Si/Al = 46.6) showed a higher activity than H-mordenites, whereas the activity was less than that of a cation-exchange resin (Amberlite 200C). Several cation-exchange resins are also active for the reaction in water[2] but are thermally and mechanically less stable.

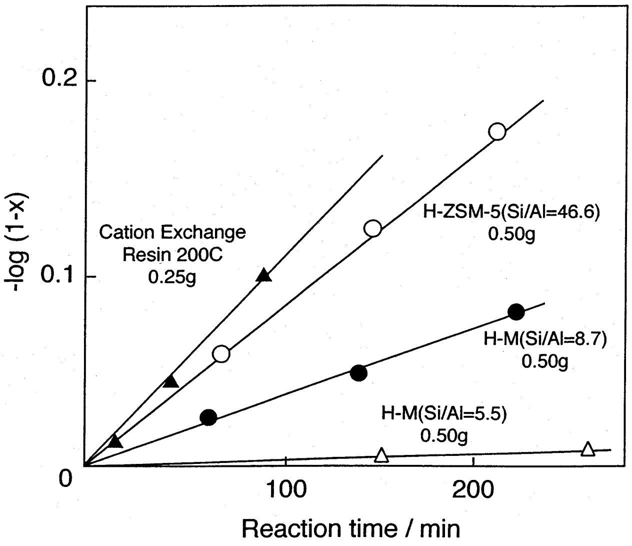


Figure 1. First-order plots for hydrolysis of ethyl acetate in excess water at 333 K over various solid acids.

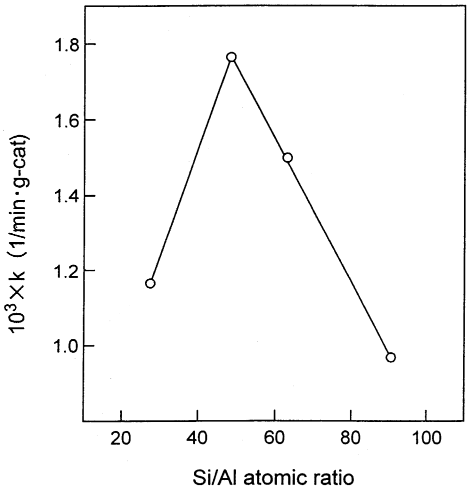


Figure 2. Effects of Si/Al ratio of H-ZSM-5 on activity for hydrolysis of ethyl acetate in water at 333 K.

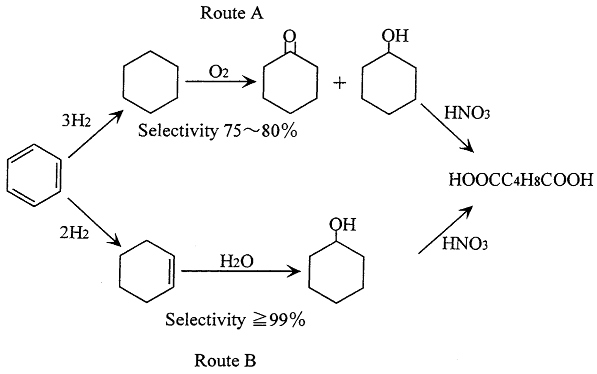


Figure 3. Scheme of benzene to adipic acid.

Figure 2 shows the influence of the Si/Al ratio of H-ZSM-5 on the rate constant. The maximum activity was observed at Si/Al = 47. As will be described below, as the Si/Al ratio increases, the surface of the zeolite becomes more hydrophobic and possesses stronger affinity for ethyl acetate and the number of acid sites decreases.

Esterification is an important acid-catalyzed reaction in the chemical industry.[1] However, it has been shown that the byproduct water deactivates the solid acid catalysts during the reaction. Thus, the high-silica zeolites, which were hydrophobic, were expected to show high catalytic activities for this reaction. As a matter of fact, high-silica zeolites were efficient for esterification of acetic acid with ethanol.[3] On the other hand, for esterification of acetic acid with 2-butanol, the activity of H-ZSM-5 was much lower than that of the cation-exchange resin.[3] Presumably, the reaction was suppressed because of the limited diffusion of the bulky reactant into the pores; the reaction took place only on the external surface of the crystallites.

Asahi Kasei has commercialized the hydration process of cyclohexene using high-silica H-ZSM-5 zeolite[4] (route B in Figure 3), combining a partial hydrogenation of benzene. The process has been operated successfully since 1990 with the scale of 60000 tons/year. In contrast, the case of conventional H_2SO_4 process (Figure 4) involves a biphasic system, the oil (cyclohexene) and the aqueous phase contain-

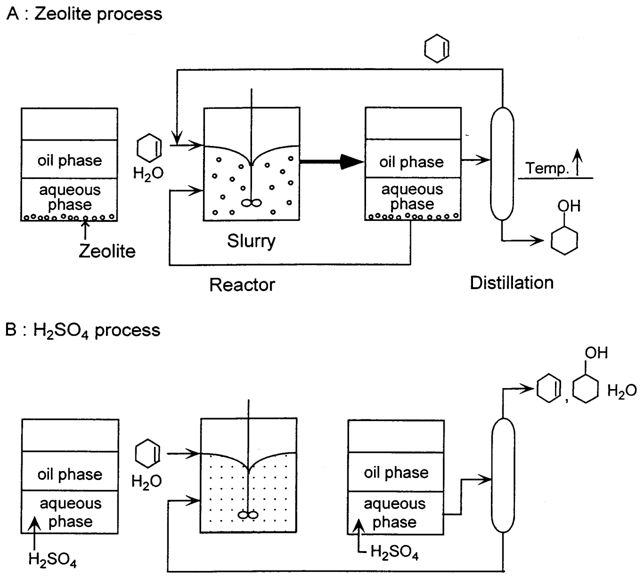


Figure 4. Processes of hydration of cyclohexene.

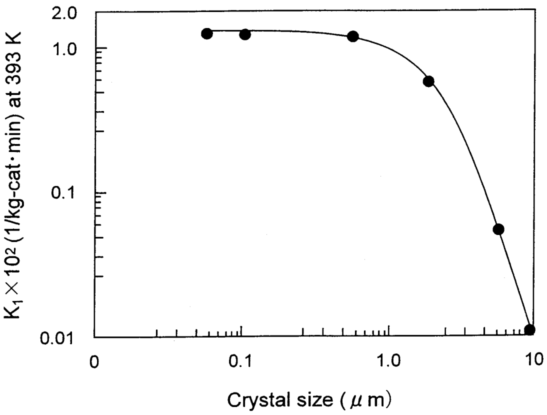


Figure 5. Effect of crystallite size of H-ZSM-5 on rate of liquid-phase hydration of cyclohexene at 393 K.

ing H_2SO_4. The product cyclohexanol is concentrated in the acidic aqueous phase. If the aqueous phase is distilled to separate the product, the reverse reaction proceeds due to the presence of H_2SO_4. Thus, it is impossible to recover the product by simple distillation. Another disadvantage of the H_2SO_4 process is the corrosion of the equipment.

When a zeolite is used as solid catalyst, and because the zeolite is present in the aqueous phase and the aqueous phase is neutral, the product cyclohexanol is exclusively distributed in the organic phase (cyclohexene phase), as illustrated in Figure 4. The slurry formed by the zeolite system consisting of solid and two phasic liquids and cyclohexanol can be recovered readily by distillation of the oil phase. This is a critical advantage of the zeolite process.

Although ion-exchange resins such as Nafion and Amberlyst (see below) can also serve as catalysts for this reaction, temperatures >373 K are required to obtain a commercially acceptable reaction rate with these resins. These are less stable under these reaction conditions and thus cannot be used as the commercial catalyst for this reaction.

The activity and selectivity of various zeolites for the hydration of cyclohexene are summarized in Table 1.[5,6] It was found that various zeolites having Si/Al ratios >10 were active. Because zeolites with higher Si/Al ratios are more hydrophobic (see the next section), hydrophobicity is essential for the activity of zeolites. Another interesting finding is that zeolites with 10-membered ring pores showed high selectivities (>99%) to cyclohexanol, whereas those with 12-membered ring pores, such as mordenite, produced large amounts of dicyclohexyl ether. Considering the differences in the molecular sizes or cross-sectional areas of cyclohexanol and dicyclohexyl ether, the difference of the selectivity depending on the zeolites can be attributable to shape selectivity,[5-7] therefore suggesting that this reaction took place in the pores of the zeolites.

A simulation using molecular dynamics for simple Lennard-Jones particles in silicalite, as a function of the adsorbate diameter, showed unexpected behavior[8] in which the diffusion coefficient exhibited a peak when the diameter of the adsorbate approached the channel diameter of H-ZSM-5. The pore width of H-ZSM-5 and the molecular size of cyclohexene are comparable, so it is reasonable to expect specific interactions between the molecule and the wall of the zeolite. The interaction would be in favor of both the diffusion of cyclohexene into the pores and the reaction with water in the pores.

The relationship between the crystallite size of H-ZSM-5 and its catalytic activity is shown in Figure 5.[9] The catalytic rate constant remained nearly

Table 1. Activity and Selectivity of Various Zeolites for Hydration of Cyclohexene

					composition of oil phase (wt %)			
catalyst	channel system[a]	Si/Al	crystal size (μm)	time (h)	cyclohexanol	methylcyclopentenes	dicyclohexyl ether	selectivity for cyclohexanol (%)
ZSM-5	$\underline{10}$***	12.5	0.62	2	12.8	0.084	0.008	99.3
		15	1.02	2	9.0	0.070	trace	99.3
ZSM-11	$\underline{10}$***	12.5	1.0	2	11.5	0.045	0.018	99.0
ZSM-35	$\underline{10}$*	7.5	2.0	72	0.3	trace	trace	100
		5	0.7	4	0.3	trace	0.01	96
mordenite	$\underline{12}$*** ↔ $\underline{8}$*	5	0.5	4	0.2	trace	trace	100
		16.5	0.5	4	8.2	trace	2.72	74
		22.5	0.5	4	4.1	trace	1.67	70
		47	0.5	4	3.4	trace	4.25	43
ZSM-12	$\underline{12}$*	17.5	1.0	16	6.7	0.024	2.16	74
Y	$\underline{12}$***	2.5	0.572	72	0.3	trace	0.05	98

[a] Underlined: the number of oxygen atoms that constitute the rings of the pores. Number of asterisks: the number of dimensions of the channel. Reaction conditions: cyclohexane/water/catalyst weight ratio = 2.4/2.7/1.0. Temperature: 393 K.

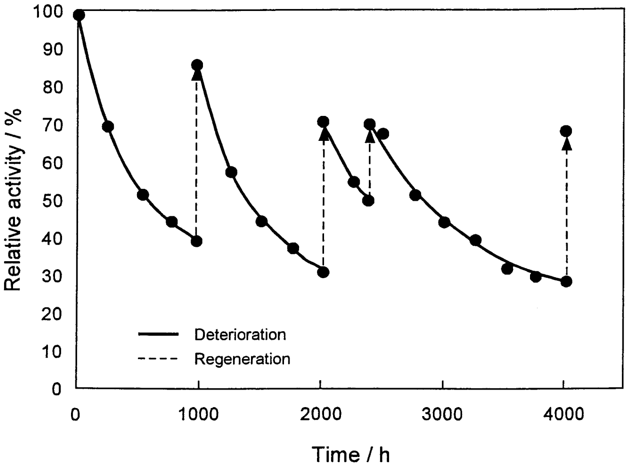


Figure 6. Regeneration and deterioration of H-ZSM-5 for liquid-phase hydration of cyclohexene.

constant for particles within the sizes from 0.05 to 0.4 μm and decreased for particles with larger crystallite sizes, thus indicating that smaller crystallites are favorable for catalytic activity. From this crystallite-size relationship, Kono et al.[9] have suggested that the reaction occurred within the pores. On the contrary, we believe that the relationship does not indicate the reaction occurring within the pores; if the reaction did occur on the external surface, the reaction rate should increase as the crystallite size decreases. The fact that the reaction rate decreases for large crystallites can be explained as the restriction of internal diffusion.

The deactivation characteristics of H-ZSM-5 were examined using catalysts with different crystallite sizes (0.7 and 0.05 μm).[4,9] The larger crystallites of H-ZSM-5 exhibited higher degrees of deactivation, which is probably due to the accumulation of hydrocarbons with higher boiling points in the zeolite pores and the dealumination from the zeolite lattice to decrease the active sites. Attempts by Asahi Kasei to regenerate the activity by calcination in air or O_2 at elevated temperatures were unsuccessful and resulted only in the removal of aluminum from the zeolite by the steam formed. Subsequently, a method involving wet oxidation using hydrogen peroxide[4,9] was adopted, as shown in Figure 6. The activity was mostly fully recovered using the H_2O_2 treatment, suggesting that dealumination was slight during the wet oxidation process.

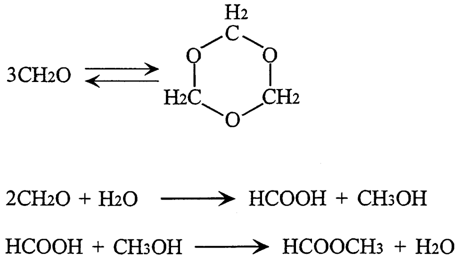


Figure 7. Reaction paths of HCHO in water.

Reaction of the framework Al ions with water and H^+ resulted in the release of aluminum from the zeolite as aluminum cations or aluminum hydroxides. However, the catalytic activity was fully recovered by mixing the deactivated H-ZSM-5 with an aqueous sodium hydroxide solution to form a 10 wt % slurry, heating at 353 K with stirring, and treating with 1 M nitric acid.

Gas-phase hydrations of olefins have been examined using various zeolites,[10] in which, as shown in Table 2, pentasil and ferrierite zeolites showed high activities. Although yields of the reaction decreased as the Si/Al ratios increased, as in the case of the pentasil zeolites, strong specific activities (per acid site) were observed for high Si/Al ratios. Furthermore, as will be described below, the acid strengths for mordenite were higher than that for pentasil zeolite. Therefore, it can be suggested that hydrophobicity rather than the acid strength influences the activities of these zeolites. Additionally, it was reported that, as the reaction approached equilibrium, water condensed in the pores and the activities of these catalysts appeared to be partly limited by the diffusion processes.

Trioxane, a raw material for polyacetal copolymer, is synthesized from formalin (aqueous formaldehyde) using sulfuric acid. Because the equilibrium concentration is low (4−5%), isolation of trioxane is carried out by distillation at 373−393 K. However, under these conditions, the resulting formic acid (byproduct) solution causes corrosion of the equipment. Attempts by Asahi Kasei to use zeolites for the trioxane synthesis[11] are presented in Figure 7. The reaction was carried out in a glass tube reactor equipped with a water condenser, to which formalin (65% w/w) and zeolite were introduced at 373 K. As summarized in Table 3, which lists the activities of various zeolites for the synthesis of trioxane using formalin (65% w/w)

Table 2. Gas-Phase Hydration of Alkenes over Various Zeolites[a]

		ethene hydration, 473 K		propene hydration, 423 K		1-butene hydration, 423 K	
zeolite	Si/Al atomic ratio	yield (%)	selectivity (%)	yield (%)	selectivity (%)	yield (%)	selectivity (%)
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
equiliblium conversion (%)		4.04		7.58		2.21	

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

Table 3. Synthesis of Trioxane from Formalin over Zeolites[a]

catalyst	Si/Al	crystal size (μm)	concn of catalyst (wt %)	trioxane in the effluent (wt %)	productivity of trioxane (g of trioxane·g of catalyst^{-1}·h^{-1})	selectivity (%) trioxane	selectivity (%) formic acid	selectivity (%) methyl formate
*H-β	28	0.05	1.0	20.5	9.7	96.4	2.4	1.2
**H-ZSM-5	36	0.2	0.5	18.7	17.7	83.2	10.0	6.8
Amberlyst			10.0	19.7	0.93	96.5	1.5	2.0

[a] Conditions: amounts of formalin in the bottoms, 20 g; concentration of feed formalin, 65 wt %; feed rate of formalin, 95 g·h^{-1}; temperature, 373 K; pressure, atomospheric.

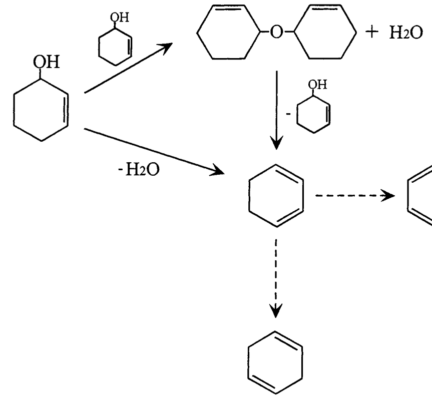


Figure 8. Reaction scheme of dehydration of 2-cyclohexen-1-ol.

at 373 K, zeolites with the Si/Al ratio >8 were active. Among the high-silica zeolites, β-zeolite (Si/Al = 14) was ~10 times more active than Amberlyst-15 on the unit per catalyst weight basis. Therefore, similarly as above, these results also indicate that hydrophobicity plays an important role in controlling the catalytic activity for this reaction.

Treatment of H-ZSM-5 with 4-methylquinoline, which is adsorbed only on the external surface,[12] did not result in any changes in the catalytic activity. In contrast, treatment with pyridine, which is adsorbed also on the inner surface in the pores, effectively decreased the activity. These results indicate that the reaction takes place within the pores. Furthermore, the acidic sites on the external surface would most likely become strongly poisoned with water molecules. As the crystallite size of H-ZSM-5 (Si/Al = 60) decreased, catalytic activity greatly increased, and at the same time, the selectivity to trioxane also increased. The size of trioxane is comparable to the width of the pore, so diffusion of trioxane is probably restricted in the pores, and thus an increase in the crystallite size would cause a decrease in the selectivity.

1,3-Cyclohexadiene is a useful raw material for polymers and has been produced by gas-phase dehydration of 2-cyclohexen-1-ol over Al_2O_3 or phosphates. However, the use of these catalysts typically imparts various byproducts, such as benzene and cyclohexene (by disproportionation of 1,3-cyclohexadiene), and 1,4-cyclohexadiene by isomerization (Figure 8).[13,14] For liquid-phase dehydration of 2-cyclohexene-1-ol, using copper sulfate[15] exhibited low activities, whereas using H_2SO_4[16] caused polymerization of 1,3-cyclohexadiene. The activity and selectivity for dehydration of 2-cyclohexen-1-ol over various solid acid catalysts are summarized in Table 4. H-ZSM-5 (Si/Al = 14) and Amberlyst-15 afforded cyclohexadiene with yields >40%, along with significant amounts of dicyclohexenyl ether. Al_2O_3 and TiO_2 were inactive, probably due to their weak acidity. Heteropolyacids were highly active, but the yield of cyclohexadiene was only 10% due to the formation of polymers. A relatively high yield of 1,3-cyclohexadiene was obtained using H-ZSM-5, whereas H-β and mordenite with 12-membered pores afforded mainly dicylohexenyl ether; therefore, the diffusion of the bulky dicyclohexenyl ether was probably restricted from the pores of H-ZSM-5. When the acidic sites on the external surface of H-ZSM-5 were poisoned with 4-methylquinoline, the rate of formation of dicyclohexenyl ether was greatly suppressed, but that of cyclohexadiene remained almost unchanged. This indicated that cyclohexadiene is formed on the acidic sites within the pores, and dicyclohexenyl ether is mainly produced on the acidic sites located on the external surface.[14]

Dehydration of 2-cyclohexen-1-ol was carried out with solid acids in a biphasic system, which consisted of the organic reactant and water.[14] It was expected

Table 4. Activity and Selectivity for Dehydration of 2-Cyclohexen-1-ol over Various Catalysts[a]

catalyst	Si/Al	crystal size (μm)	conversion of 2-cyclohexen-1-ol (%)	selectivity (%) 1,3-cyclohexadiene	selectivity (%) dicyclohexenyl ether	selectivity (%) dimer$^+$	yield of 1,3-cyclohexadiene (%)
H-ZSM-5	14	0.05	95.0	49.0	49.0	2.0	46.6
H-ZSM-5	60	3.1	5.1	20.3	79.7	0	1.0
H-Y	2.8	0.2	55.7	1.6	98.4	0	0.9
H-mordenite	10	0.1	66.3	3.2	85.5	3.3	2.1
H-β	14	0.05	72.0	7.8	80.9	5.5	5.6
γ-Al_2O_3			0	0	0	0	0
TiO_2			0	0	0	0	0
Amberlyst-15			96.5	44.2	27.2	22.1	42.6
$H_3PMo_{12}O_{40}$			100	10.6	0	22.0	10.6
$H_3PW_{12}O_{40}$			100	4.4	0	5.4	4.4

[a] Reaction conditions: 2-cyclohexen-1-ol/catalyst wt ratio = 5/1; temperature, 353 K; time, 1 h.

Table 5. Activity and Selectivity of Various Zeolites in the Dilute Aqueous Solution of 2-Cyclohexen-1-ol[a]

			selectivity (%)			
catalyst	Si/Al	conversion of 2-cyclohexen-1-ol (%)	1,3-cyclohexediene	dicyclohexenyl ether	dimer$^+$	yield of 1,3-cyclohexadiene (%)
H-ZSM-5	14	84.1	91.8	0	8.1	77.2
H-*β*	14	30.0	10.0	0	0	3.0
H-mordenite	28	20.0	8.0	0	0	1.6
H-Y	3.3	3.0	0	0	0	0
Amberlyst-15		37.6	96.5	0	3.3	36.3

[a] Reaction conditions: water/2-cyclohexen-1-ol/catalyst wt ratio = 400/0.48/1; concentration of 2-cyclohexen-1-ol in solution = 0.12 wt %; temperature, 373 K; time, 1 h.

Table 6. Deterioration of Various Catalysts[a]

			yield (%)		
catalyst		Si/Al	1,3-cyclohexadiene	dicyclohexenyl ether	dimer$^+$
H-ZSM-5	initial	14	67.0	24.1	6.4
	reused	14	54.0	20.2	2.0
H-*β*	initial	14	6.3	48.2	1.0
	reused	14	1.2	10.9	0.1
H-mordenite	initial	28	1.6	25.6	1.7
	reused	28	0.2	3.0	0
H-Y	initial	3.3	1.4	50.2	0.7
	reused	3.3	0.9	33.8	0.2

[a] Reaction conditions: water/2-cyclohexen-1-ol/catalyst wt ratio = 26/10/1; temperature, 373 K, Time: 1 h.

that the formation of dicyclohexenyl ether byproduct would become suppressed with the dilution of the reactant with water and the extraction of the cyclohexadiene product into the organic phase. As shown in Table 5, H-ZSM-5 (Si/Al = 56) resulted in higher yields of 1,3-cyclohexadiene than other zeolites, such as H-mordenites, and Amberlyst-15. For H-ZSM-5, the yield and selectivity of 1,3-cyclohexadiene reached 77 and 92%, respectively. As listed in Table 6, the activity of H-ZSM-5 in the second run was ~80% that of the first run. However, the activities of mordenite and H-*β* significantly decreased in the second run. To improve selectivity, the reaction was carried out using diluted 2-cyclohexen-1-ol (0.12% w/w) solution. Using H-ZSM-5, the yield and selectivity of cyclohexadiene reached 77.2 and 91.8%, respectively, whereas the yields using Amberlyst and other zeolites were <36%. An interesting approach in the use of zeolite as a water-tolerant solid acid was described by Ogawa et al.;[17a] high activity for hydrolysis of water-insoluble dodecyl acetate in a biphasic system was afforded by octadecyltrichlorosilane-treated H-ZSM-5, which floated at the interface between water and toluene. Hydration of terpene was catalyzed by zeolites.[17b,c]

2. Hydrophobicity of Zeolites

Because water covers the surface of the solid acids and prevents the adsorption of organic materials, hydrophobic surfaces are preferable for conducting organic reactions in water. This section will discuss surface structures with hydrophobic characteristics and the adsorption of water on the surfaces. Upon evacuation at elevated temperatures, the surface of SiO_2 becomes highly hydrophobic. Young et al.[18] have studied the interactions between the SiO_2 surface and water vapor at 298 K by means of thermogravimetry and IR spectroscopy and have concluded that water molecules are adsorbed on the surface silanol groups (Si−OH) but not on Si−O−Si groups. It can therefore be reasoned that the hydrophobic character of the dehydroxylated SiO_2 surface is due to the nonpolar Si−O−Si groups. Because the pores of zeolites, which consist mainly of silica, are constructed with tetrahedral SiO_4, ideal pores do not possess silanol groups and should be highly hydrophobic.

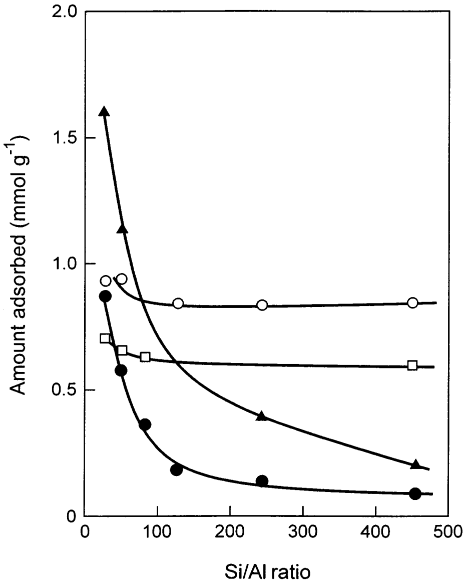


Figure 9. Amounts of water, methanol, benzene, and *n*-hexane adsorbed on H-ZSM-5 as a function of SiO_2/Al_2O_3 ratio: (●) water; (▲) methanol; (□) benzene; (○) *n*-hexane.

However, if some Si^{4+} atoms become partly substituted by Al^{3+} atoms, a negative charge would result on the oxygen atom of AlO_4. Ordinarily, counterions such as alkaline and alkaline earth ions, as well as protons, can compensate for the charge and have affinity for water. Accordingly, the amount of water adsorbed on a series of H-ZSM-5 was proportional to the aluminum content;[19] the Al content related to the number of OH groups, which would interact with water.

Nakamoto and Takahashi[20] investigated the differences in the hydrophobic nature of H-ZSM-5 using various Si/Al ratios and solvents. Figure 9 shows the adsorbed amounts of water, methanol, benzene, and *n*-hexane on H-ZSM-5s at 373 K with various Si/Al ratios. For H-ZSM-5 with Si/Al ≥200, the amount of water adsorbed was much less than that of other organic compounds. The adsorption amounts de-

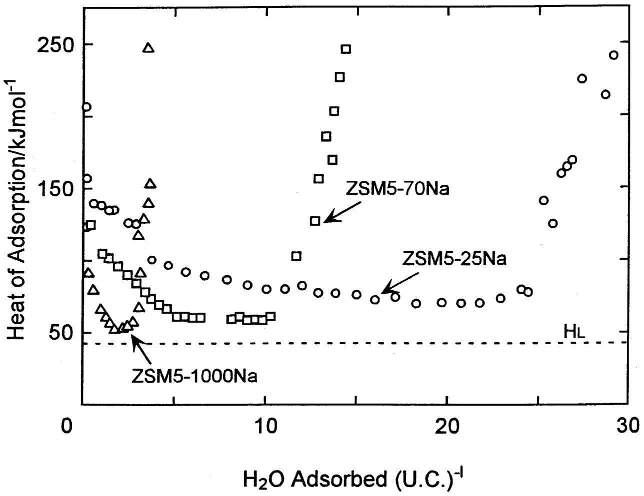


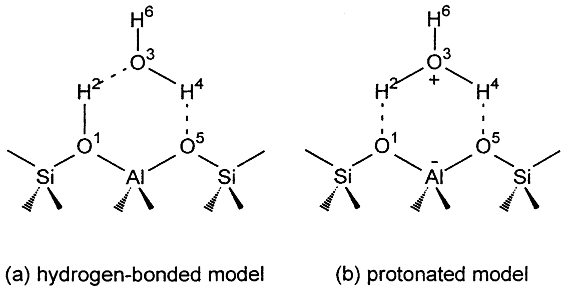
Figure 10. Heat of adsorption of water on various Na-ZSM-5s. Si/Al = 12.9 (25 Na), 46.3 (70 Na), and 685 (1000 Na).

creased in the following order: *n*-hexane > benzene ≫ methanol > water. Water and methanol showed similar tendencies in the adsorption; that is, the adsorption gradually decreased as the Si/Al ratio increased. Under these conditions (373 K and low relative pressure, 0.06), dipole−dipole interaction and hydrogen bonding were suggested as the main contributors to the adsorption. For zeolites consisting of Al and Si, the lattice has a negative charge, and thus exchangeable cations are located within the pore. Because of this ionic interaction, the surface acquires a polar character, and therefore molecules having dipole or quadrupole are strongly adsorbed by specific interactions with the surface.

Assuming that 1-propanol rather than water is preferentially adsorbed on the hydrophobic surface, the degree of hydrophobicity was quantified by measuring the adsorption amount of 1-propanol.[11] H-ZSM-5 and β-zeolite with high Si/Al ratios showed large adsorption capacities for 1-propanol, thus indicating that these zeolites are highly hydrophobic.

Specific interactions between water molecules and protons associated with the framework aluminum have been studied. A cluster of four water molecules was formed around each hydronium ion on H-ZSM-5 at 298 K.[21] Similarly, four water molecules were adsorbed to each Al atom, forming $H_9O_4^+$ in mordenites with Si/Al ratios >5.[22] In contrast, at 308 K and with a relative pressure of water of 10^{-6}, only one water molecule was adsorbed on one hydronium ion on H-ZSM-5 (Si/Al = 36).[23]

On the basis of measurements of the heat of immersion of water on zeolites, Tsutsumi et al.[24,25] claimed that the surface consists of siloxane bondings and is hydrophobic in the region of low Al content. As shown in Figure 10, the heat of adsorption of water exhibited sharp increases at certain amounts of adsorption.[24,25] These sharp increases are due to the formation of water clusters, which can form only when the zeolites have hydrophobic surfaces and adequate pore size. Considering the pore width of H-ZSM-5, the water clusters are presumably dodecahedral, consisting of 20 water molecules.



(a) hydrogen-bonded model (b) protonated model

Figure 11. Possible structures of adsorbed water.

Table 7. Observed IR Bands Due to Adsorbed Water on H-ZSM-5

assignment	monomer	dimer	polymer
ν(OH)	3701	3600	3429
	~3550	3366	
	2872[a]	3213	
	2460[a]		
	~1700[a]	~1700	
δ(HOH)			1659
δ(OH)	1350		
γ(OH)	875		

[a] (A, B, C) triplet.

Adsorption of water on the protonic sites of H-ZSM-5 was investigated by means of IR spectroscopy. Lercher et al.[23] showed that at equilibrium pressure below 10^{-4} mbar, the most significant adsorption sites were Lewis acid sites. At higher equilibrium pressures, strong Brønsted acid sites (bridging hydroxyls) become important in the adsorption process. At these bridging hydroxyl groups, one water molecule is adsorbed at lower pressures, whereas larger clusters are formed at higher pressures. IR spectra showed bands at 2885 and 2463 cm^{-1}, which are characteristic for hydroxonium ions.

In the adsorption of water on zeolites, two models have been suggested: a hydrogen-bonded model and a protonated model, as shown in Figure 11. Zecchina et al.[26] inferred by using IR spectroscopy that the 1:1 hydrogen-bonded structure transferred with the reaction of water to dimeric $H_5O_2^+$ and polymeric $H_2O_5^+$ $n(H_2O)$ species. A study using $H_2{}^{18}O$ demonstrated that the water adsorbed on H-ZSM-5 has such a hydrogen-bonded structure.[27] Kondo et al.[28] observed that the monomeric hydrogen-bonded H_2O converted to the protonated dimer species at 373 K by increasing the equilibrium pressure of H_2O. They also showed that protonated polymeric water was formed by further increasing H_2O pressure at the expense of dimeric species. Table 7 lists the IR bands that are associated with the adsorbed water on H-ZSM-5.[28]

3. Acidic Property of Zeolites

The acidic sites of zeolites can be generally expressed as shown in Figure 12.[29,30] Upon removal of ammonia by the calcinations, ammonium ion-exchanged zeolites changed to the acid form having Brønsted acid sites. Additional thermal treatment resulted in the condensation of two Brønsted acid sites to form one Lewis acid site. Furthermore, the hydroxyl groups that are present on the surface of

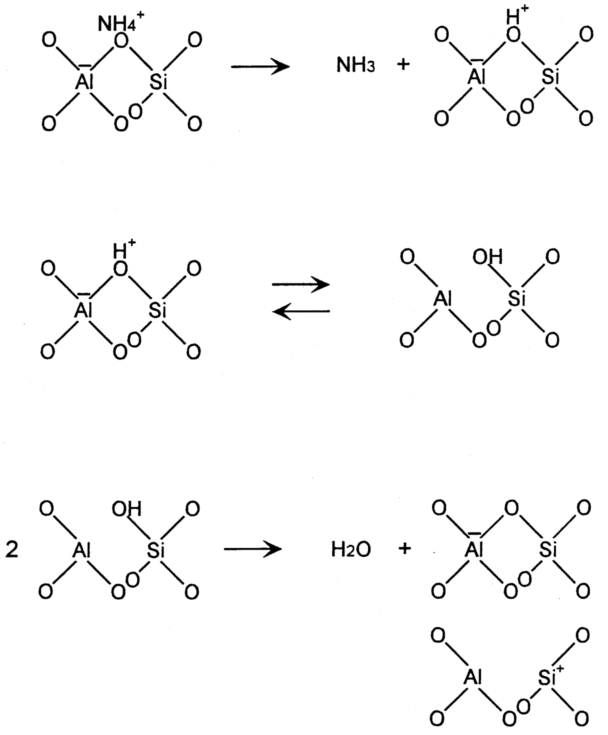


Figure 12. Generation of acidic sites of zeolites.

zeolites can be regarded as another type of Brønsted acid site.

The acid strength of solid acids can be measured using an indicator method,[31] IR spectroscopy of base molecules,[32] temperature-programmed desorption (TPD) of base molecules,[33] or microcalorimetry;[34] each method has its advantages and disadvantages. Niwa and Katada[33] proposed a method for determining the strength of zeolite acidity using NH_3-TPD (temperature-programmed desorption), in which they concluded that the acidic strength is not influenced by the number of acid sites but rather by the structure. They claimed that the strength of acidic site of zeolite is not directly reflected in the temperature of the peak maximum, because the maximum temperature is affected not only by strength but also by the W/F (contact time of carrier gas). Readsorption of NH_3 influences the maximum temperature; the peak tends to move to lower temperatures with decreasing concentration of the acidic sites. On the basis of their proposal to theoretically calculate the heat of adsorption, they showed that for H-mordenite and H-ZSM-5, the values of the obtained heat and those determined by microcalorimetry[35] were comparable. Microcalorimetry of NH_3 adsorption showed that the sequence of acid strength was mordenite (145) > H-ZSM-5 (130) > beta (120) > Y (110), where the figures in parentheses are the adsorption heats of ammonia in kilojoules per mole. Other studies have reported values of 150 $kJ\ mol^{-1}$ for H-ZSM-5 [36] and 130 $kJ\ mol^{-1}$ for HY.[37]

The Si/Al ratio has been shown to be a critical factor in determining acid strength as well as hydrophobicity. Nishimiya and Tsutsumi[38,39] have reported on the influence of the Si/Al ratio of various zeolites on the acid strength, which were estimated by calorimetry using ammonia. As shown in Figure 13, the highest value of the initial heat of adsorption was 170 $kJ\ mol^{-1}$ for HM-20, which corresponded to that of a solid superacid, $SbF_5-SiO_2-Al_2O_3$. For faujasite, ferrierite, and mordenite, the initial heat of adsorption of ammonia increased as the Si/Al ratio increased. A similar trend was observed for H-ZSM-5 compounds; however, for H-ZSM-1000H (Si/Al = 685), because it is highly hydrophobic, decrease of the heat of adsorption of NH_3 was observed.[40] The acid strength of zeolite in water was measured using Hammett indicators[2]. H-ZSM-5 in water exhibited acid sites with acid strength of $-5.6 < H_0 < -3.0$ (Table 8), whereas HY was much less acidic. The detailed relationship between acid strength and/or hydrophobicity and the structure of zeolite has yet to be elucidated.

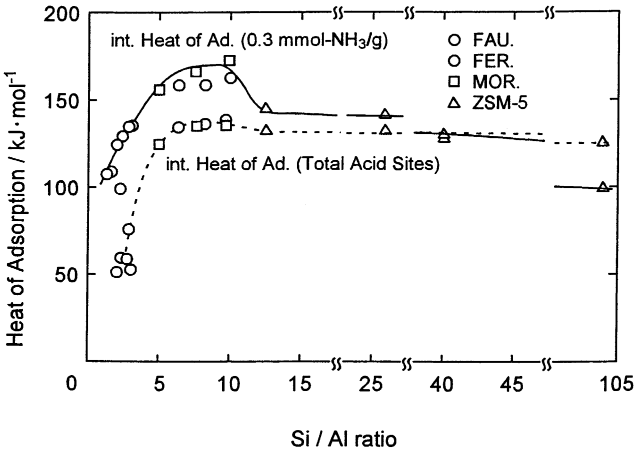


Figure 13. Heat of NH_3 adsorption as a function of Si/Al ratio of various zeolites.

Table 8. Acid Strength of Aluminosilicates in Water[a]

silicate	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	+	+	±	−	−

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

On the basis of a systematic study of the shift induced by bases with proton affinities, the following order in the acid strength has been proposed; H-mordenite (Si/Al = 5) ~ H-β (Si/Al = 12.5) ~ H-ZSM-5 (Si/Al = 14) > H-Y (Si/Al = 3).[41,42] CO has been widely used as a probe molecule, because interaction of the dipole molecule (CO) with acidic centers shifts the CO stretching from that of the free CO (2143 cm^{-1}).[43,44] Knozinger has reviewed the IR spectroscopic probes of the acid strength of zeolites.[45] Not only the shift of CO but the shift of ν(OH) upon the CO adsorption is consistent with relative acid strength of zeolite.[45]

III. Heteropolyacid

1. Acidity of Liquid Heteropolyacids

Although the acid form of heteropolyacid is highly soluble in water, the acidic salts with large cations

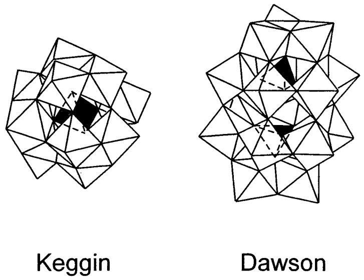


Figure 14. Structures of Keggin- and Dawson-type heteropoly anions.

such as Cs^+ are often water-insoluble. In water, the former act as excellent liquid acids, and the latter solid acids were active also in water. In this section, the catalysis using heteropolyacids will be initially presented, followed by the introduction of heterogeneous catalysis using solid heteropoly compounds. Heteropolyacid, which includes the popular Keggin-type, is defined as a condensate of different types of oxoacids. Structures of typical heteropoly anions (Keggin and Dawson structures) are illustrated in Figure 14. In water, all protons of these heteropolyacids are dissociated.[46,47] The order of acid strength of the CH_3CN solution of acids was estimated as $H_3PW_{12}O_{40}$ (heteropolyacid) > CF_3SO_3H > *p*-toluenesufonic acid (PTS) > H_2SO_4 > CF_3COOH > ClC_6H_4COOH.[48] In addition, the enthalpy of interaction of a proton with pyridine was determined to be −32.7 kcal mol^{-1} for solid $H_3PW_{12}O_{40}$,[49] which was comparable to that for $H_3PW_{12}O_{40}$ dissolved in acetonitrile. The acid strength of a concentrated $H_3PW_{12}O_{40}$ solution in acetic acid was measured using ^{13}C NMR spectroscopy with mesityl oxide as an indicator.[50]

Among the heteropolyacids, the order of acid strength was $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4GeW_{12}O_{40} > H_6P_2W_{18}O_{62} > H_5BW_{12}O_{40} > H_6CoW_{12}O_{40}$, which was determined in acetonitrile using the Hammett indicator test.[51] When the stepwise dissociation constants of the heteropolyacids in acetone or acetic acid were compared with those of inorganic acids,[46] heteropolyacids were significantly stronger than typical inorganic acids, including H_2SO_4, HBr, HCl, HNO_3, and $HClO_4$. The differences in the acid strength between the heteropolyacids and typical inorganic acids can be simply explained within the framework of electrostatic theory taking into account the size and charge of the anions.[52] Heteropoly anions are larger than the inorganic acids, so the strength of bonding between the proton and heteropoly anions should be lower, which implies that the dissociation constants should be higher as compared to the usual acids. Furthermore, greater degrees of delocalization of the charge of the anion would lower the effective negative charge on its individual basic proton-accepting centers and, thus, weaken the attraction of the proton to the anion. As a result, heteropolyacids $H_{8-x}XM_{12}O_{40}$, are much stronger than $H_{8-x}XO_4$. It should be pointed out that degradation of $PW_{12}O_{40}{}^{3-}$ to the corresponding oxoanions in water takes place, even in the low-pH region.[53]

2. Aqueous Organic Reactions Catalyzed by Liquid Heteropolyacids

Heteropolyacids have been commercially utilized, mainly in Japan, for several petrochemical processes. The direct hydration of propene for the manufacture of 2-propanol was the first industrial application of heteropolyacid in 1972.[54−58] Subsequent examples include the chemical separation of isobutylene as *tert*-butyl alcohol from spent butane−butene fractions in 1984[57] and the hydration of *n*-butenes[58] in 1989.

On the basis of studies on the hydration of isobutylene in aqueous heteropolyacid solution, Izumi et al.[59] reported that the reaction order is higher than unity and that the activation energy is lower than that for mineral acids. It was proposed that the heteropolyacids accelerated the reaction, not only by their strong acidity but also by stabilizing a protonated intermediate through coordination to the polyanions, as shown in Figure 15. Kozhevnikov et al.[60] proposed that the activity of liquid acids, including heteropolyacids, could be explained by a combination of stronger acidity, solubility, and ionic effects. The rate constant (k) is expressed by eq 1, and H_0 is the acidity function of the catalyst solution.

$$\log k = 1.04H_0 - 3.46 \tag{1}$$

The hydration of isobutylene was industrialized by Asahi Kasei for the separation of isobutylene from a mixture of isobutylene and butenes.[57] Excellent activity and selectivity of heteropolyacids were obtained at concentrations >50% w/w. As shown in Figure 16, high activity was due to strong acidity, increased solubility of butenes, and formation of a complex with a carbenium ion intermediate.[57,59,61] The reaction rate was proportional to the concentrations of proton, heteropolyanion, and isobutylene. The 10-fold increased activity (compared with that of mineral acids) was presumably due to the combination of the above three factors, in the order listed. Furthermore, the heteropolyacid process was highly selective; formation of isobutylene oligomers was <0.1%, and conversion of *n*-butene was <0.05%; in contrast, 4−8% and 0.4−0.8%, respectively, were observed for the H_2SO_4 process.

The above heteropolyacid process can be regarded as environmentally friendly due to its high selectivity, easy separation, and use of only the reactants

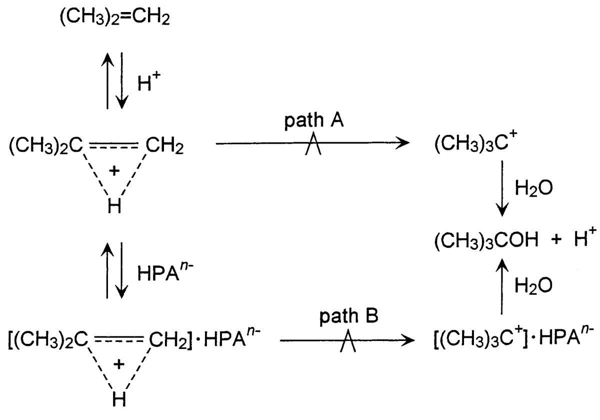


Figure 15. Reaction paths for hydration of isobutylene.

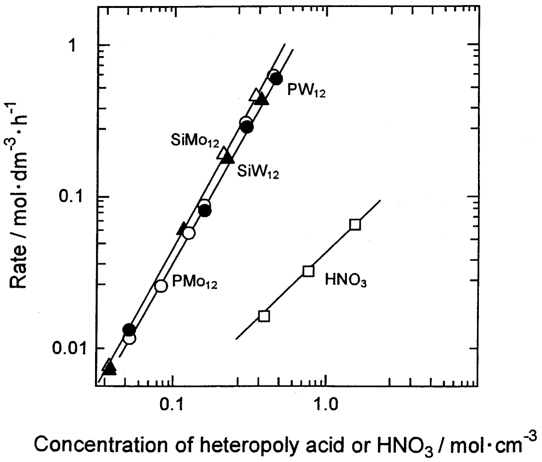


Figure 16. Reaction rates for hydration of isobutylene catalyzed by various solids.

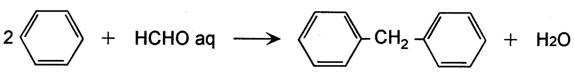
and catalyst.[62] Furthermore, the lifetime of a heteropoly catalyst can be >10 years, and the investment for a heteropoly catalyst facility is roughly half that of a sulfuric acid facility. Sulfuric acid is corrosive, and the process also requires extraction and decomposition of the sulfuric ester. The ion-exchange resin process requires a water−acetic acid mixture as the solvent to improve the contact between the reactant and the catalyst and, therefore, causes potential problems, such as corrosion caused by acetic acid and hydrolysis of butyl acetate.[62]

Acetal resins are formed by the polymerization of formaldehyde and, presently, as engineering thermoplastics, the annual demand in the world is ~400000 tons/year.[63] The major problem in the production of acetal resins is the high energy consumption that is required to obtain a reactant, monomeric trioxane. In the commercial process, trioxane is obtained by heating aqueous formaldehyde in the presence of H_2SO_4, as shown by Figure 7.

Asahi Kasei has reported a method for the synthesis of trioxane using heteropolyacids, which is more advantageous than using conventional acid, such as H_2SO_4.[63] Table 2 compares the results of reactions using heteropolyacids and H_2SO_4 at 373 K. For selectivity of 96%, conversion by $H_4SiW_{12}O_{40}$ was 27%, whereas conversion by H_2SO_4 was 20%. The improvement using heteropolyacid is attributable to the increase in the solubility of formalin in the presence of heteropolyacid, which can be explained as the interaction of heteropolyacids with the ether linkage of the oligooxymethylene glycol. There are reviews for liquid-phase reactions with heteropoly compounds.[64,65]

3. Biphasic System Consisting of Aqueous Phase

A biphasic reaction system can be regarded as an environmentally friendly process if the product and catalyst can effortlessly separate into the different phases. Heteropolyacids, such as $H_3PW_{12}O_{40}$, are exceptionally active for the synthesis of diphenylmethane ($C_6H_5CH_2C_6H_5$, denoted $PhCH_2Ph$) from benzene and formalin (aqueous formaldehyde), as shown in eq 2, in a biphasic system. Furthermore, the direct use of formalin is economical, the byproduct is ideally only water, and the catalyst can be recycled by simple drying of the aqueous phase at room temperature.[66]



(2)

As shown in Table 9, conversion of formaldehyde was >93% for $H_3PW_{12}O_{40}$ and $Sc(CF_3SO_3)_3$.[66] It should be emphasized that only $H_3PW_{12}O_{40}$ afforded $PhCH_2Ph$ (in 35.3% yield, under these conditions). $Sc(CF_3SO_3)_3$ efficiently catalyzed the dimerization of formaldehyde to HCOOMe but was inactive for the formation of $PhCH_2Ph$. *p*-Toluenesulfonic acid (PTS) was also active for the dimerization of formaldehyde but did not produce $PhCH_2Ph$. Reactions using inorganic acids, such as H_2SO_4, H_3PO_4, and HNO_3, and CF_3COOH did not afford $PhCH_2Ph$.

Although $H_3PW_{12}O_{40}$ recovered by drying of the aqueous phase showed activity, the conversion of formaldehyde and yield of aromatics were somewhat reduced with repeated runs (Table 10). The reduced activity would be due to the residual carbonaceous species on the heteropoly catalyst. IR spectroscopy of $H_3PW_{12}O_{40}$ confirmed that the Keggin structure was unchanged even after the five runs.

Condensation of formaldehyde has been carried out using heteropolyacid.[67] Although high activities were observed for $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ for the formation of methylglycolate and methyl methoxyacetate from pure formaldehyde, the presence of water in the reaction system significantly decreased the catalytic activity. Phase transfer polymerization of tetrahydrofuran (THF) has been in operation as an organic biphasic reaction consisting of THF and

Table 9. Conversion and Selectivity of Diphenylmethane Synthesis from Benzene and Formalin with Various Liquid Acids[a]

				selectivity[b,c] (mol %)							
catalyst	mmol	conversion[b] (mol %)	yield[d] (mol %)	CO	HCOOMe	CH_3OH	HCOOH	$PhCH_2Ph$	$(PhCH_2)_2CH_2$	$PhCH_2OMe$	MB[e] (%)
$H_3PW_{12}O_{40}$	4.2	93.2	35.3	3.3	35.1	5.4	5.3	38.7	11.4	0.8	97.0
$Sc(CF_3SO_3)_3$	2.1	95.1	0.0	0.2	83.0	12.3	4.6	0.0	0.0	0.0	100.0
PTS[f]	12.6	82.2	4.1	4.2	71.8	7.2	6.3	5.9	1.5	3.0	79.8
HNO_3	12.6	24.4	0.0	10.0	90.0	0.0	0.0	0.0	0.0	0.0	100.0
H_3PO_4	4.2	18.7	0.0	0.2	68.8	12.0	19.0	0.0	0.0	0.0	100.0
H_2SO_4	6.3	33.7	0.0	0.6	92.0	4.0	4.0	0.0	0.0	0.0	101.0

[a] Reaction conditions: benzene, 40 cm^3 (450 mmol); formalin, 6.72 cm^3 (HCHO, 90 mmol; H_2O, 222 mmol, methanol 18.2 mmol), 160 °C, and 2 h. [b] On the basis of HCHO. [c] $PhCH_2Ph$, diphenylmethane; $(PhCH_2)_2CH_2$, dibenzylbenzene; $PhCH_2OMe$, methyl benzyl ether. [d] $PhCH_2Ph$ (on the basis of HCHO). [e] Mass balance; 100 × total amount of products and remaining HCHO)/(the initial amount of HCHO). [f] *p*-Toluenesulfonic acid.

Table 10. Recycled $H_3PW_{12}O_{40}$[a]

run	conversion[b] (%)	total yield of aromatics[b] (mmol)	selectivity[c] (mol %) PhCH$_2$Ph	TON[d]
1	83.5	31.4	79.1	4.5
2	74.7	23.8 (75.6)	76.2	2.9
3	72.2	21.1 (68.4)	73.4	2.4
4	64.1	17.8 (56.7)	70.6	1.7
5	63.1	17.6 (56.1)	66.7	1.6

[a] Reaction conditions: benzene, 40 cm^3 (450 mmol); formalin, 6.72 cm^3 (HCHO, 90 mmol; H_2O, 222 mmol; methanol, 18.2 mmol); $H_3PW_{12}O_{40}$, 4.2 mmol; 160 °C; 30 min. Between the runs, the aqueous phase of $H_3PW_{12}O_{40}$ was dried in the ambient atmosphere. The recovered solid $H_3PW_{12}O_{40}$ was reused without any treatment. [b] Total yields of PhCH$_2$Ph, (PhCH$_2$)$_2$CH$_2$, and PhCH$_2$OMe. Figures in parentheses are the percentages of the yield compared to that of the first run. [c] Selectivity to PhCH$_2$Ph among the aromatic products on the basis of HCHO. [d] Turnover number defined as (mol of PhCH$_2$Ph)/(mol of catalyst).

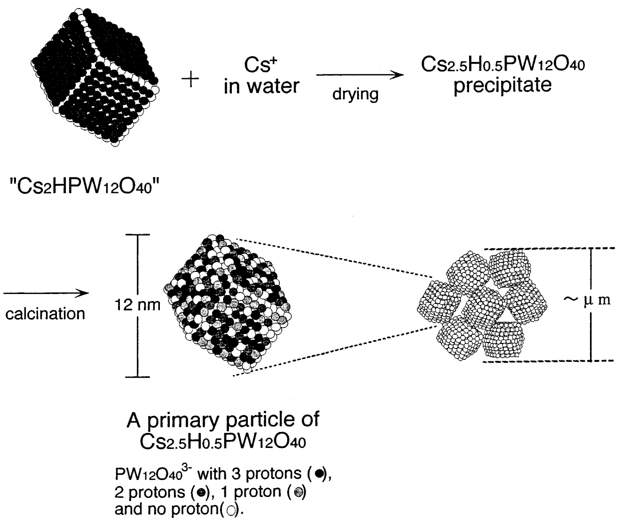


Figure 17. Microstructure of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

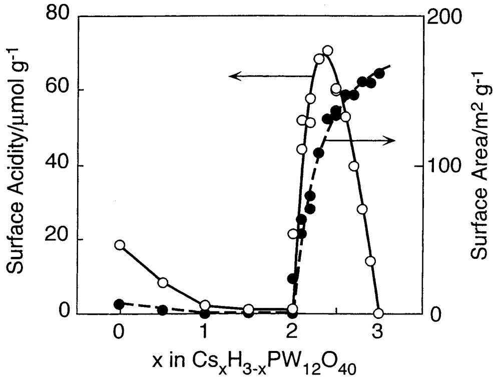


Figure 18. Surface area and surface acidity of $Cs_xH_{3-x}PW_{12}O_{40}$ as a function of Cs content, x.

THF−heteroplyacid phase.[68] Heteropolyacids also catalyze the cyclotrimerization of propionaldehyde to 2,4,6-triethyl-1,3,5-trioxane, in which the catalyst and product separate into two phases, and thus the recovered catalyst could be recycled.[69]

4. Solid Heteropoly Compounds That Are Active in Water

i. Microstructure

One of the characteristics of a solid heteropolyacid compound is its strong acidity. Although the acid form itself is a useful solid acid, the number of acidic sites on the surface is relatively small because of the low surface area (~5 m^2 g^{-1}). The acid forms are highly soluble in water. Substitution of the proton by an alkaline cation exhibits interesting effects on the surface area and pore structures, as well as on the solubility. Salts with large monovalent ions, such as Cs^+, are insoluble in water and possess high surface areas.[70,71] Partial substitution for proton by Cs^+ ions resulted in unique changes in the surface area and hence in the amount of acidic site on the surface (see below). The amount of acidic site on the surface showed a maximum for $Cs_xH_{3-x}PW_{12}O_{40}$ compounds with $x = 2.5$.[70] Because $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated Cs2.5) showed significantly higher activities than $H_3PW_{12}O_{40}$ and other solid acid catalysts for various acid-catalyzed reactions,[47,72−83] Cs2.5 is presently utilized as a solid acid.

A schematic model for the microstructure of the Cs2.5 is shown in Figure 17.[83] During the preparation process by a titration method, Cs3 crystallites are initially formed, followed by the epitaxial adsorption of $H_3PW_{12}O_{40}$ on the surface of Cs3. The resulting precipitate, which exhibited an XRD pattern similar to that of Cs3,[83] has a composition of $Cs_2HPW_{12}O_{40}$.

Subsequent drying resulted in aggregates of the small crystallites in forming larger secondary particles. In the case of low amounts of Cs, the ultrafine particles were thickly covered by $H_3PW_{12}O_{40}$, which was deposited upon evaporation of water, in which $H_3PW_{12}O_{40}$ possibly acted as the cement. In the case of higher amounts of Cs and lower amounts $H_3PW_{12}O_{40}$ deposited on Csx, the hydrogen form formed very thin films or small islands on Csx and, therefore, a high surface area of the ultrafine particles can be retained. After the thermal treatment, they are converted to particles having nearly uniform composition. The close-packed aggregates of the primary crystallites have voids with average widths of 4 nm, which is consistent with that of Csx.[83]

The arrangement of the primary structure together with Cs^+ ions is the basis of the secondary structure, which corresponds to the microcrystallites. Aggregates of the microcrystallites create tertiary structures, which correspond to the secondary particles. High surface areas are usually associated with salts with large cations (classified as group B salts) due to the smaller sizes of the primary particles, thus providing favorable properties for catalytic activity. Furthermore, these salts are relatively stable to heat, which is also important for solid catalysts.

Figure 18 shows the dramatic changes in surface areas as a function of the Cs content in Csx. Remarkably, the surface area increased as the Cs content (x in Csx) increased from $x = 2$ (1 m^2·g^{-1}) to $x = 3$ (156 m^2·g^{-1}) and decreased as Cs content increased from $x = 0$ (6 m^2·g^{-1}) to $x = 2$. It is important to note that the number of acidic sites on the surface (surface acidity) showed a maximum at $x = 2.5$ (Figure 18).[83]

As shown in Figure 19, the pore sizes of Cs2.5 had bimodal distributions in the range from micropore to mesopore.[83,84] It can be assumed that the mesopores

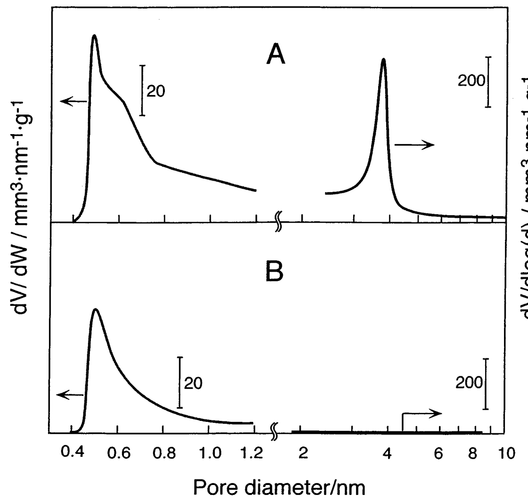
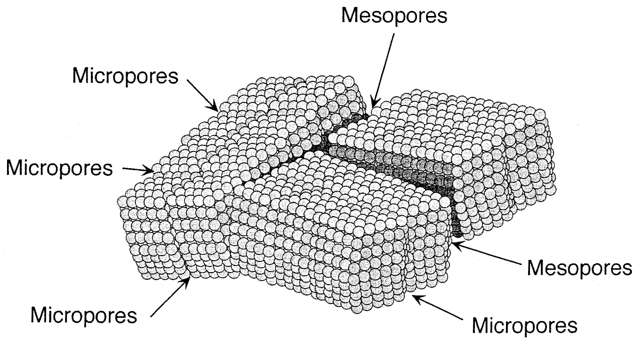


Figure 19. Pore-size distributions of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (A) and $Cs_{2.1}H_{0.9}PW_{12}O_{40}$ (B).

Bimodal distribution of Cs2.5



Unimodal distribution of Cs2.1

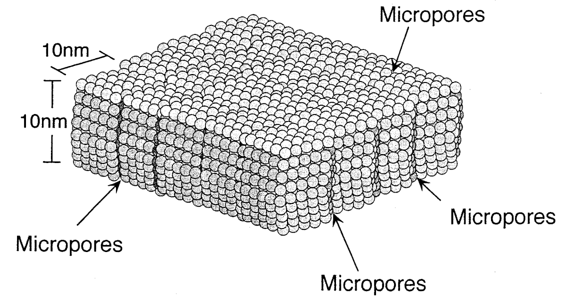


Figure 20. Model of pores of $Cs_xH_{3-x}PW_{12}O_{40}$.

(~4 nm) correspond to the voids between the primary particles (crystallites; ~10 nm in size) and the micropores correspond to the spaces between the crystal planes formed by misaligned fragments (Figure 20).[85−87] Mizuno and Misono[88] examined the pore structure of Cs3 by estimating the surface area using three different methods: particle-size distribution measured by transmission electron microscopy (TEM), pore-size distribution measured by N_2 adsorption (assuming cylindrical pores), and Brunauer−Emmett−Teller (BET) calculations. All three results were in good agreement with each other, thus suggesting that Cs3 is composed of fine primary particles, as observed by TEM, with intercrystallites, not intracrystallite pores. Considering the size and shape of the Keggin anion and the structure of Cs3, there should not be any open pores in the crystal in which an N_2 molecule (0.36 nm in diameter) can pass through.

Studies have shown that $Cs_{2.1}H_{0.9}PW_{12}O_{40}$ possesses only ultramicropores.[84−86,89] Adsorption of various molecules such as N_2 [molecular size (MS) = 0.36 nm], *n*-butane (MS = 0.43 nm), isobutane (MS = 0.50 nm), benzene (MS = 0.59 nm), 2,2-dimethylpropane (MS = 0.62 nm), and 1,3,5-trimethylbenzene (MS = 0.75 nm) revealed that the pore width of $Cs_{2.1}H_{0.9}PW_{12}O_{40}$ was in the range between 0.43 and 0.50 nm. These intriguing materials, including the recently synthesized $Rb_{2.1}H_{0.9}PW_{12}O_{40}$ with 0.60 nm micropores,[87] can serve as shape-selective catalysts.[84,87]

ii. Acidity of Solid Heteropoly Compounds

The acid strengths of typical solid acids are summarized in Table 11. Microcalorimetry of NH_3 adsorption and TPD of NH_3 revealed that the acid strengths of the heteropoly compounds follow the order $H_3PW_{12}O_{40}$ > $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ > H-ZSM-5 (Si/Al = 40) > $SiO_2−Al_2O_3$.[70,72,83] The high acid strength of anhydrous $H_3PW_{12}O_{40}$, which is stronger than those of zeolites such as H-ZSM-5, allows its classification as a superacid.[90,91]

Figure 21 lists the results of calorimetry of NH_3 for $H_3PW_{12}O_{40}$ and Cs2.5 evacuated at 473 K.[83] The initial heats of NH_3 sorption were about 195 and 170 kJ·mol^{-1} for $H_3PW_{12}O_{40}$ and Cs2.5, respectively. The amounts of adsorbed NH_3 that exhibited heats of sorption >160 kJ·mol^{-1} were about 1.05 and 0.13 mmol·g^{-1} for $H_3PW_{12}O_{40}$ and Cs2.5, respectively. These values were similar to the overall proton concentration of $H_3PW_{12}O_{40}$ (1.04 mmol·g^{-1}) and Cs2.5 (0.155 mmol·g^{-1}).

Table 11. Acid Strength of Various Solid Acid Catalysts

catalyst	$-\Delta H_{ads}(NH_3)^a$ (kJ·mol^{-1})	$T_{des}(NH_3)^b$ (K)
$H_3PW_{12}O_{40}$	195	850
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	165	830
H-ZSM-5	150	670
$SiO_2−Al_2O_3$	145	600

[a] Initial heat of NH_3 adsorption (absorption). [b] Desorption temperature of NH_3.

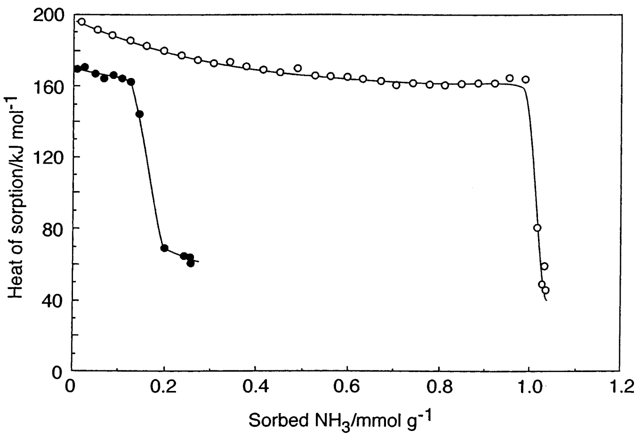


Figure 21. Differential heats of sorption of NH_3: (○) $H_3PW_{12}O_{40}$; (●) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.

The surface acidity (the number of protons on the surface) of Csx ($2 < x < 3$) was directly measured by IR spectroscopic studies of CO adsorption at 110 K.[92] Adsorbed CO on Cs2.5 exhibited three bands: a band at 2165 cm^{-1} attributable to CO adsorbed on acidic protons sites, a band at 2154 cm^{-1} due to CO on Cs^+ ion, and a band at 2139 cm^{-1} corresponding to physisorbed CO. Adsorbed CO on Cs3 did not exhibit either the band at 2165 cm^{-1} or a broad band in the OH stretching region. Direct correlations were observed between the intensity of the first band (2165 cm^{-1}, CO on proton site) and the catalytic activity for alkylation reactions.[91,92]

iii. Hydrophobicity

Because hydrophobicity is the property of “lacking affinity” for water and is characteristic of oils, fats, waxes, etc.,[93] the ratio of the adsorption amount of water and that of a hydrocarbon can quantify the degree of hydrophobicity of the surface. Figure 22 shows the ratio of adsorption area (adsorption amount × molecular cross section) of benzene to that of water [r(B/W)] as a function of the relative pressure of the adsorbates.[94] Ratios of r(B/W) = 10.6 and 22.5 were obtained for SiO_2 and H-ZSM-5(H) at $p/p_0 = 0.04$, respectively. The r(B/W) value for H-ZSM-5(L) was smaller than those of SiO_2 and H-ZSM-5(H) (Si/Al = 628). Low r(B/W) values for $SiO_2-Al_2O_3$ and Al_2O_3 (1.1 and 1.0, respectively, at $p/p_0 = 0.04$) indicate that these compounds are relatively less hydrophobic. Although the r(B/W) ratios for Cs2.5 and H-ZSM-5(L) were comparable to each other, r(B/W) for Cs3 (7.2 at $p/p_0 = 0.04$) was higher than that of H-ZSM-5(L). Using the ratios, the hydrophobicity of the heteropoly compounds follow in the order H-ZSM-5 (Si/Al = 628) > Cs3 > H-ZSM-5 (Si/Al = 40) > Cs2.5 > $SiO_2-Al_2O_3$ > Al_2O_3. The r(B/W) values imply that the hydrophobicity of the surface of Cs2.5 is similar to that of H-ZSM-5 (Si/Al = 40); presumably this hydrophobic nature corresponds to the high catalytic activity of Cs2.5 as a water-tolerant catalyst.

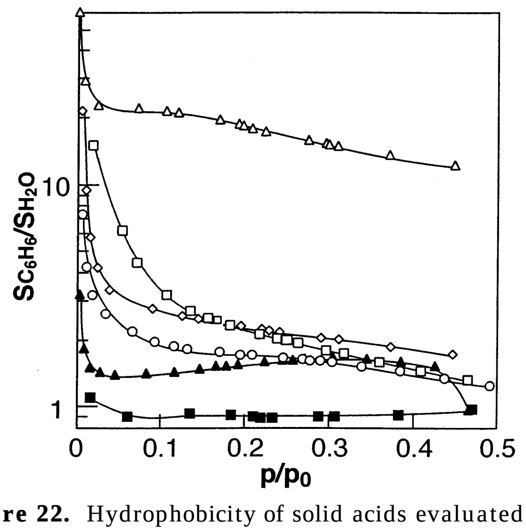


Figure 22. Hydrophobicity of solid acids evaluated from adsorption of benzene and water: (○) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$; (□) $Cs_3PW_{12}O_{40}$; (△) H-ZSM-5 (Si/Al = 628); (◇) H-ZSM-5 (Si/Al = 40); (■) Al_2O_3; (▲) $SiO_2-Al_2O_3$. S_W and S_B are adsorption areas of H_2O and benzene, respectively.

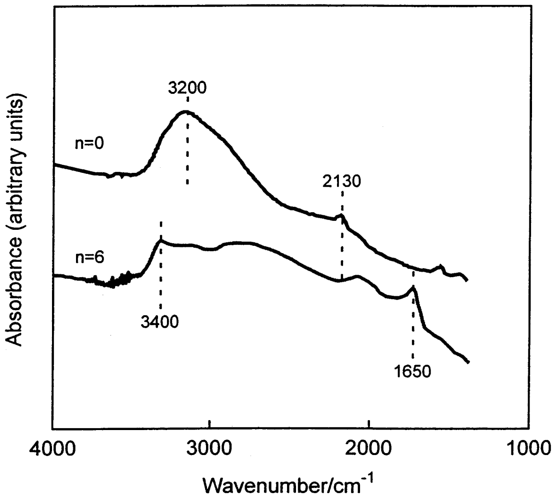


Figure 23. IR spectra of $H_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}{\cdot}6H_2O$.

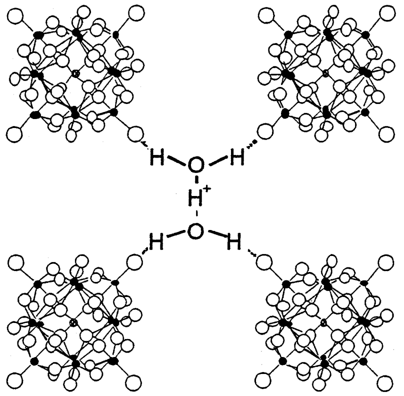


Figure 24. Structure of $H_3PW_{12}O_{40}{\cdot}6H_2O$.

Koyano et al.[95] and Zecchina et al.[96] have independently reported IR spectroscopic studies of $H_3PW_{12}O_{40}$ nH_2O. Figure 23 shows the IR spectra of anhydrous$H_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ $6H_2O$, as reported by Koyano et al.[95] As shown in Figure 24, the hexahydrate includes $H_5O_2^+$; observed IR bands (3400 and 1650 cm^{-1}) for the hexahydrate were assigned as $H_5O_2^+$ ($H_2O{\cdots}H^+{\cdots}OH_2$). The anhydrous sample exhibited a broad peak at 3200 cm^{-1}, which is identified as isolated acidic protons bonded to the peripheral oxygens of the polyanion. Solid-state ^{31}P, ^1H, and ^{17}O NMR provided further insight toward the states and dynamics of the protons and water molecules of $H_3PW_{12}O_{40}{\cdot}nH_2O$.[97] NMR studies indicated that the protons exist in three forms: (a) as protons attached to the polyanion, (b) as H_3O^+, and (c) as $H_5O_2^+$. Moreover, weak interactions existed between H_3O^+ and $H_2O_5^+$ to the polyanion by hydrogen bonding.

iv. Organic Reactions in Water

An important feature of Cs2.5 is its high activity for acid-catalyzed reactions, even in the presence of large excesses of water. The catalytic activity of Cs2.5 for hydrolysis of ethyl acetate in excess water was compared with those of typical solid acids.[98] The activity of Cs2.5 (per weight) was 3 and 35 times higher than those of H-ZSM-5 (Si/Al = 40) and H-ZSM-5 (Si/Al = 628), respectively. $SiO_2-Al_2O_3$ and Al_2O_3 were inactive under similar reaction conditions.

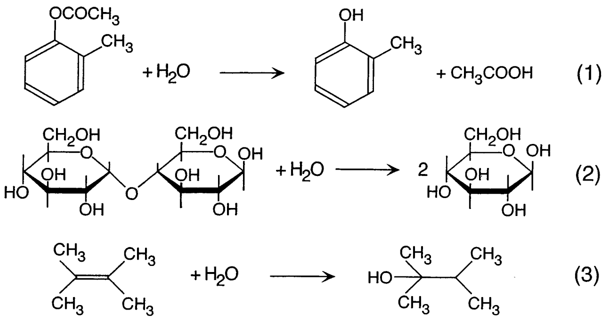


Figure 25. Organic reactions used as water-tolerant reactions.

Table 12. Catalytic Activities of Solid and Liquid Acids for Hydrolysis of 2-Methylphenyl Acetate[a]

catalyst	reaction rate per wt (μmol·g^{-1}·min^{-1})	reaction rate per acid amount [mmol (acid-mol)$^{-1}$·min^{-1}]
solid acids		
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	10.7	71.3
H-ZSM-5 (Si/Al = 40)	0.0	0.0
$SO_4^{2-}-ZrO_2$	0.4	2.0
H-Y	0.0	0.0
H-mordenite	0.0	0.0
Nb_2O_5	0.5	1.7
$SiO_2-Al_2O_3$	0.0	0.0
γ-Al_2O_3	0.0	0.0
TiO_2-SiO_2	0.0	0.0
organic resins		
Amberlyst-15	32.7	6.9
Nafion-H	44.5	55.6
liquid acids		
H_2SO_4	55.3	2.7
PTS	27.7	4.8
$H_3PW_{12}O_{40}$	5.6	5.6
$Sc(OTf)_3$	14.4	7.2

[a] 2-Methylphenyl acetate, 4.03 mmol; H_2O, 3.3 mol at 353 K.

It should be noted that the specific activity of Cs2.5 (per unit of acid amount) was 7 times higher than that of the two H-ZSM-5s catalysts. It would seem that the hydrophobicity and strong acidity of Cs2.5 are responsible for its high activity.

Another feature of Cs2.5 is its mesopores (see Figure 19), which bulky reactants can access. Three types of reactions, as shown in Figure 25, were used as tests for organic reactions in water:[98-102] (1) hydrolysis of 2-methylphenyl acetate, (2) hydrolysis of maltose (oligosaccharide), and (3) hydration of 2,3-dimethyl-2-butene. The catalytic activities of various solid and liquid acid catalysts for hydrolysis of 2-methylphenyl acetate (Figure 25, reaction 1) are summarized in Table 12.[99,101] It should be emphasized that Cs2.5 exhibited significantly superior activity against other solid acids. Although the activity of Cs2.5 (per unit of weight) was less than that of liquid acids, such as H_2SO_4 and PTS, the specific activity of Cs2.5 (per unit acid amount) was ~15-fold higher than those of the liquid acids. Due to the hydrophobic character of the Cs2.5 surface, as described above, the acidic protons most likely were shielded from the poisoning effects of water.

The catalytic performance of Cs2.5 was also evaluated for the hydration of alkenes in a solid−liquid system with large excesses of water (Table 13) (Figure 25, reaction 3).[100,102] For hydration of 2,3-dimethylbut-2-ene, Cs2.5 was again superior as compared to other inorganic solid acids (H-ZSM-5 and $Nb_2O_5 \cdot nH_2O$) and the parent $H_3PW_{12}O_{40}$ (used as a homogeneous acid). Although Amberlyst-15 was somewhat more active than Cs2.5 (Cs2.5 was more active on the basis of the acid amount), Nafion was essentially inactive. For Cs2.5, the selectivity to 2,3-dimethylbutan-2-ol was 99%. Despite possessing a larger amount of acidic sites, the lower catalytic activity (per unit weight) of homogeneous $H_3PW_{12}O_{40}$ compared with Cs2.5 indicates that the hydrophobic surface of Cs2.5 is arranged very efficiently. On the other hand, the activity of H-ZSM-5 for the hydration of cyclohexene was notably superior to that of Cs2.5,[102] as was also reported by Ishida et al.[4] As described in the preceding section, the excellent activity of H-ZSM-5 for cyclohexene hydration is due to specific interactions between the reactant and the pore surface of the zeolite.

Table 13. Catalytic Activities of Solid Acids for Acid-Catalyzed Reactions in Excess Water

catalyst	reaction rate (μmol·g^{-1}·h^{-1}) reaction 2[a]	reaction rate (μmol·g^{-1}·h^{-1}) reaction 3[a]
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	51.0	10.5
H-ZSM-5 (Si/Al = 40)	1.7	5.7
$SO_4^{2-}-ZrO_2$	0	0
H-mordenite	0	0
HY	0.4	0
Nb_2O_3	3.0	0.1
SiO_2-Al_2O	0	0
SiO_2-TiO_2	6.3	0
γ-Al_2O_3	4.6	0
Amberlyst-15	95.0	14.0
Nafion-H	52.0	1.8

[a] Reaction temperatures are 373 and 343 K for reactions 2 and 3 in Figure 25, respectively.

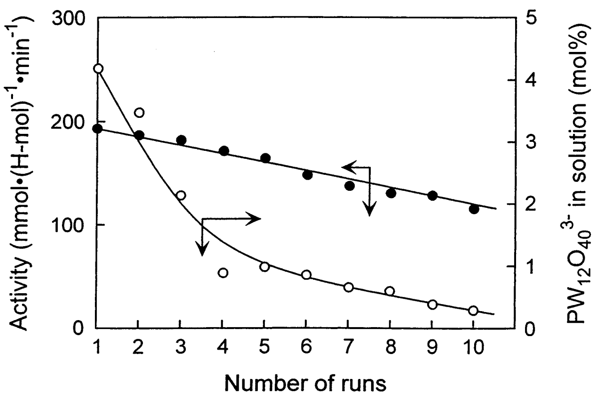


Figure 26. Changes of (●) specific activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for hydrolysis of ethyl acetate and (○) amount of heteropoly species released from the catalyst with repeated reactions.

The catalytic activity of Cs2.5 was essentially retained upon repeated use of the catalyst (Figure 26). However, spectroscopic measurements indicated the presence of $PW_{12}O_{40}^{3-}$ species in the reaction solution; for example, the UV spectrum of the supernatant of the Cs2.5 suspension after hydrolysis of ethyl acetate exhibited an absorption band near 265 nm, which is attributable to Keggin-type $PW_{12}O_{40}^{3-}$

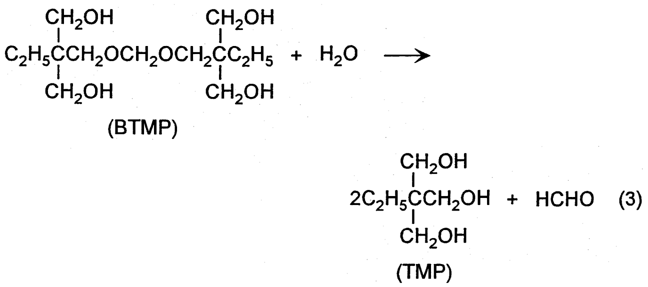
ions.[99,103] The amounts of the released heteropoly anions are listed in Figure 26. The amount of discharged heteropoly species was substantial for the first few runs and decreased with subsequent runs. Less than 1% of the heteropoly anions of Cs2.5 was detected in the solution during the 10th run; the total amount of polyanion lost through 10 runs of the reaction reached 14% of the starting amount of Cs2.5.

When Cs2.5 was thermally treated in hot water, changes in its surface structure and acidity were observed.[103] After the catalyst was stirred in water at 353 K for 72 h, catalytic activity for hydrolysis of ethyl acetate decreased to ~85% of that before the water treatment. Calorimetry of ammonia sorption showed that the acidic property was changed by the hot water treatment. The initial heat of adsorption, corresponding to the acid strength, decreased slightly with water treatment (165 $kJ \cdot mol^{-1}$ before water treatment; 160 $kJ \cdot mol^{-1}$ after water treatment). In contrast, the amounts of adsorbed NH_3 on Cs2.5, which corresponds to the acid amounts, were estimated as 0.15 and 0.12 $mmol \cdot g^{-1}$, before and after water treatment, respectively. The decrease in the catalytic activity with the water treatments is thus explained by the decrease in the acid amount.

ICP emission and atomic absorption spectrometry, as well as ion chromatography, have revealed that Cs was not dissolved as free Cs^+ ions but instead involved in the released Keggin-type clusters following water treatment; in other words, in water, the Cs salt is not dissociated and the Keggin-type clusters are not collapsed. The primary Cs*x* particles at the entrance of the mesopores are released into water by the water treatment, which broadens the entrance. Protons would be somewhat preferentially released during this process, due to interactions between the protons and the water molecules, and would explain the decrease in the acid amount.

High resistance of Cs2.5 to water was demonstrated in the synthesis of *N*-adamantylacrylamide from acrylonitrile and 1-adamantanol.[104,105] The use of Cs2.5 resulted in 97% yield with selectivity of 93%. Although HY zeolites showed some activity, the yield and selectivity were less than those of Cs2.5. H-ZSM-5 was even less active, which was probably due to the limited adsorption of this bulky alcohol into the constrained pores. Although the yields decreased by the addition of water for all catalysts, Cs2.5 retained high activitiy (84%), demonstrating that the water tolerancy of Cs2.5 was realized in the Ritter-type reaction.

Recently, a unique reaction involving the hydrolysis of bistrimethylolpropane monoformal (eq 3) in water at 348 K was reported, in which protons in the surface layer of acidic cesium salts of $H_3PW_{12}O_{40}$ were much more active than protons in homogeneous solution.[106]



$$\underset{\text{(BTMP)}}{C_2H_5\underset{CH_2OH}{\overset{CH_2OH}{C}}CH_2OCH_2OCH_2\underset{CH_2OH}{\overset{CH_2OH}{C}}C_2H_5} + H_2O \longrightarrow \underset{\text{(TMP)}}{2C_2H_5\underset{CH_2OH}{\overset{CH_2OH}{C}}CH_2OH} + HCHO \quad (3)$$

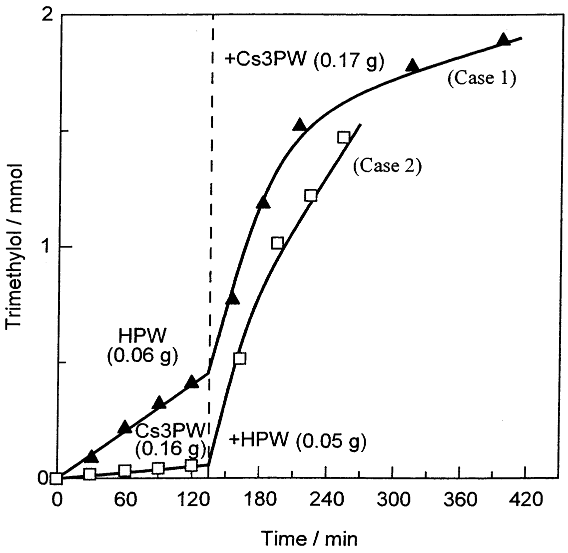


Figure 27. Time courses of hydrolysis of bistrimethylolpropane monoformal. Temperature, 348 K; solvent, water.

As shown in Figure 27, when inactive Cs3 was added to a reaction solution containing $H_3PW_{12}O_{40}$, an instantaneous 6-fold increase in the reaction rate was observed. Concurrently, the pH of the solution increased after the addition of Cs3 (decrease in proton concentration). Addition of $H_3PW_{12}O_{40}$ to a reaction solution containing Cs3 similarly enhanced catalytic activity significantly. The UV spectra of the liquid phase of the $H_3PW_{12}O_{40}$ + Cs3 system, measured after separation of the solid, showed that the concentration of heteropoly anion in the solution also decreased by the addition of Cs3. The activity of the liquid was very low, but the separated solid was very active. These results indicated that the active phase was formed on the surface of Cs3 by the adsorption (absorption) of ployanions and protons.

Silica-entrapped heteropoly compounds were prepared through the hydrolysis of ethyl orthosilicate at 313 K in the presence of $H_3PW_{12}O_{40}$ or $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, dissolved or dispersed in ethanol. A nitrogen adsorption isotherm showed that the resulting $Cs_{2.5}H_{0.5}PW_{12}O_{40}$–silica was a porous material with a large surface area of 364 $m^2\ g^{-1}$.[107,108]

Table 14 shows the catalytic activity for the hydrolysis of ethyl acetate in the presence of silica-entrapped $H_3PW_{12}O_{40}$ with different silica contents. In the case where the silica to heteropolyacid weight ratio was 12, the leakage of $H_3PW_{12}O_{40}$ was suppressed to as low as 0.3%. When the silica-entrapped $H_3PW_{12}O_{40}$ was prepared from a mixture of water, 1-butanol, $H_3PW_{12}O_{40}$, and tetraethyl orthosilicate at 353 K, the resulting porous silica-entrapped $H_3PW_{12}O_{40}$ had micropores of 0.55 nm and a surface area of 554 $m^2\ g^{-1}$.[109] The hydration of isobutylene at 353 K was performed by bubbling isobutylene at a rate of 20 $cm^3\ min^{-1}$ into a flask (50 cm^3) containing water (9.0 g), 1,4-dioxane (9.0 g), and catalyst (0.5–1.0 g). For hydration, the activity of silica-entrapped $H_3PW_{12}O_{40}$ (11% w/w) was higher than those of

Table 14. Hydrolysis of Ethyl Acetate Catalyzed by Silica-Included $H_3PW_{12}O_{40}$[a]

SiO_2/HPW[b] (wt ratio)	surface area ($m^2 \cdot g^{-1}$)	catalytic activity rate[c]	catalytic activity TOF[d]	leakage[e] (%)
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

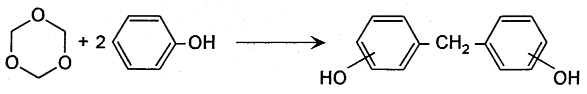
[a] H_2O = 9.5 g, AcOEt = 0.5 g, catalyst = 0.05 mmol on the basis of $H_3PW_{12}O_{40}$, 333 K. Catalyst was calcined at 423 K for 3 h prior to use. [b] Weight ratio of SiO_2 to $H_3PW_{12}O_{40}$ calculated from the amounts of reagents charged at the preparation. [c] First-order specific rate per unit weight of $H_3PW_{12}O_{40}$ (10^{-2} $min^{-1} \cdot g^{-1}$). [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 condition of $H_2O/(EtO)_4Si$ = 3 and $EtOH/(EtO)_4Si$ = 0.2 (molar ratio). [g] Catalyst was prepared under the conditions of $H_2O/(EtO)_4Si$ = 5 and $EtOH/(EtO)_4Si$ = 0.7 (molar ratio). [h] Re-inclusion of a composite with a silica-to-acid weight ratio of 8.

Table 15. Catalytic Performance of Heteropoly Compounds for Synthesis of Acetic Acid[a]

catalyst	STY[b]	selectivity (%) HOAc[c]	selectivity (%) HAc[d]	selectivity (%) CO_2
$Pd-H_4SiW_{12}O_{40}$	93.1	78.5	5.5	14.2
$Pd-Se(0.02)-H_4SiW_{12}O_{40}$	240	86.4	8.1	5.1
$Pd-Te(0.05)-H_4SiW_{12}O_{40}$	200	85.5	8.9	5.2
$Pd-Sb(0.05)-H_4SiW_{12}O_{40}$	150	80.0	9.8	10.1
$Pd-Bi(0.02)-H_4SiW_{12}O_{40}$	155	80.2	8.8	10.6
$Pd-Sn(0.1)-H_4SiW_{12}O_{40}$	140	79.6	5.8	14.4
$Pd-Ag(0.1)-H_4SiW_{12}O_{40}$	132	78.4	5.9	15.5
$Pd-Cr(0.05)-H_4SiW_{12}O_{40}$	97	72.2	0.9	25.6
$Pd-Zn(0.05)-H_4SiW_{12}O_{40}$	94	70.6	1.1	27.8

[a] Reaction conditions: reaction pressure = 5 kg/cm^2G; reaction temperature = 423 K; GHSV = 3000/h; gas component ($C_2H_4/O_2/H_2O$/inert gas = 50/7/30/13). [b] STY, space time yield (g/L of catalyst·h). [c] HOAc, acetic acid. [d] HAc, acetaldehyde.

homogeneous $H_3PW_{12}O_{40}$ and Amberlyst-15. Silica-entrapped $H_3PW_{12}O_{40}$ is envisioned as providing concentrated solution of water and dioxane entrapped within the pores of the silica network. Because the reaction rate depends on the concentrations of both protons and heteropoly anions, a concentrated $H_3PW_{12}O_{40}$ solution probably catalyzes the hydration more effectively than the diluted homogeneous system. A microporous composite is favorable for molecular shape selective reactions, and accordingly, silica-entrapped $H_3PW_{12}O_{40}$ afforded bisphenol F in the reaction of phenol with trioxane with a selectivity of 48% (eq 4). Similar selectivities were observed for reactions involving H-ZSM-5 and H-mordenite.



(4)

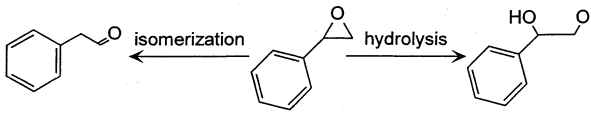
Showa Denko has developed a one-stage process of acetic acid production from a mixture of ethylene, water, and O_2 by the direct oxidation of ethylene. Currently, this process has the capacity of 100000 tons/year of acetic acid in Oita, Japan.[110] As shown in Table 15, which lists the catalytic performances of heteropoly compounds for this reaction, $Pd-H_4SiW_{12}O_{40}$ promoted by Se or Te was highly efficient. When only Pd was supported on silica, partial oxidation was not observed. A catalyst containing only $H_4SiW_{12}O_{40}$ on silica afforded ethanol but did not produce any oxidation products. The combination of metallic Pd and heteropolyacid is thus indispensable. Addition of Se or Te was effective in suppressing complete oxidation to CO_2, thus enhancing the selectivity. It can be presumed that the reaction proceeds in two steps: (1) hydration of ethylene to ethanol catalyzed by the heteropolyacid (acid catalysis) and (2) oxidation of ethanol to acetic acid on the Pd site, which is different from Wacker-type oxidation. This novel process has several advantages, such as the production of significantly lower amounts of wastewater and byproducts and freedom from corrosion.[110]

IV. Oxides and Phosphates

1. Niobic Acid

Niobium oxide is a water-insoluble solid, of which the structure and chemical property have been described in the literature.[111] Niobic acid (hydrated niobium oxide, $Nb_2O_5 \cdot nH_2O$) has been reported to possess high acid strengths.[111,112] Generally, hydrated niobium oxide crystallizes at 853 K, and its strong acid character vanishes following heat treatment above 800 K.[111,112]

Sugi et al. have reported on the Nb_2O_5-catalyzed hydrolysis of phenyloxirane (eq 5) in water under mild conditions.[113,114] Whereas typical solid acids, such as zeolites and ion-exchange resins, were used for this reaction,[115,116] the catalytic activities were not satisfactory for industrial application. The results are summarized in Table 16. When the reaction was performed in water at reflux temperature, niobic acid exhibited the highest activity among the solid acids. Aluminosilicate catalysts, such as H-ZSM-5 and $SiO_2-Al_2O_3$, while effectively enhancing isomerization, showed lower activities than that of niobic acid. The selectivity to the diol (III) was higher using niobic acid than using aluminosilicates or Nafion.



(II) (I) (III)

(5)

As shown in Figure 28, the activity and the ratio of hydrolysis to isomerization (H/I) depended on the calcination temperature of niobium oxide in a mixture of dioxane and water (90:10 v/v). Because activity significantly decreased after calcination above 723 K and, in contrast, the H/I ratio steadily decreased with the calcination temperature, it can be suggested that the structural changes of the surface occurred after the calcination above 723 K.

Niobic acid can also catalyze dehydration of alcohol and esterification.[117,118] In addition, niobic acid that was pretreated at 473 K has shown activity for hydration of ethylene, in which the activity was higher than that of phosphoric acid supported on

Table 16. Hydrolysis of Phenyloxirane with Some Solid Acid Catalysts[a]

catalyst (calcination temp, K)	solvent volume H_2O/dioxane[b] (mL/mL)	yield (%)		
		phenyloxirane (I)	phenylacetaldehyde (II)	phenyl-1,2-ethanediol (III)
niobic acid (573)	10/90	0.0	11.4	88.6
	50/50	0.0	0.5	99.0
	100/0	0	0	100
$SiO_2-Al_2O_3$[c] (773)	10/90	3.9	34.8	61.2
$SiO_2-Al_2O_3$[d] (773)	10/90	8.0	36.4	55.7
H-ZSM-5 (773)	10/90	0.3	83.2	16.5
H-silicalite (773)	10/90	63.7	33.8	2.5
H-Nafion	10/90	0.0	25.7	74.3

[a] Reaction time, 3 h; substrate volume, 0.5 mL; catalyst amount, 500 mg; total solvent volume, 100 mL. [b] Mixture of water and 1,4-dioxane was used as solvent. [c] High-alumina type (SiO_2/Al_2O_3 = 3). [d] Low-alumina type (SiO_2/Al_2O_3 = 6).

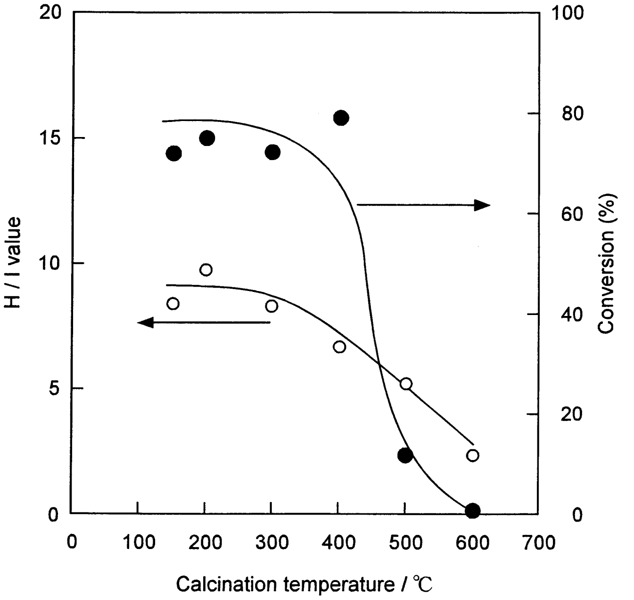
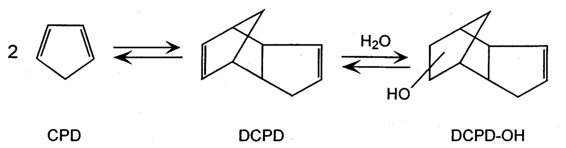


Figure 28. Effect of calcination temperature on activity and selectivity for hydrolysis of phenyloxirane over niobic acid. I/H shows the ratio of the yield of hydrolysis to that of isomerization. Reaction was performed in dioxane with 10 vol % water at 323 K for 6 h.

silica.[117,118] For the hydration of dicyclopentadiene, niobic acid (eq 6)[119] showed more activity than SiO_2-

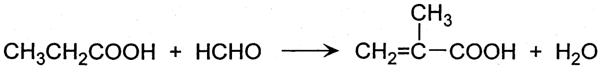


(6)

Al_2O_3, SiO_2-TiO_2, and Nafion-H. However, the activity of niobic acid considerably dropped after treatment at 673 K due to the decrease of the acidic sites.

Reaction of isobutyraldehyde with isobutylene to yield 2,5-dimethyl-2,4-hexadiene, an important intermediate in the synthesis of agrochemicals, was carried out using niobic acid catalyst[120] and subsequently was commercialized.[121] Niobic acid catalysis yields better results that those of SO_4^{2-}/ZrO_2, $SiO_2-Al_2O_3$, and WO_3/TiO_2. Comparison of the catalytic activity and selectivity of niobic acid with those of H_2SO_4 (16% w/w) demonstrated that niobic acid was more selective while affording a similar conversion.

Recently Spivey et al.[122] reported on a method to synthesize methacrylic acid (MAA) from propionic acid (PA) and formaldehyde (eq 7). Nb_2O_5/SiO_2 (20%



$$CH_3CH_2COOH + HCHO \longrightarrow CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}COOH + H_2O \quad (7)$$

w/w), which was prepared from SiO_2 and NbF_5, exhibited high yields of MAA (71% based on charged formaldehyde), as compared to yields afforded by the catalytic activity of Ta_2O_5/SiO_2 or V−Si−P oxide. Hydrated Ta_2O_5 was found to catalyze esterification and aldol condensation for acetone.[123]

2. MoO_3–ZrO_2

Okuhara et al.[124] reported that MoO_3/ZrO_2 calcined at 1073 K was highly active in the hydrolysis of ethyl acetate in excess water and esterification of acetic acid with ethanol. As shown in Figure 29, the effects of the calcination temperature on the conversion of hydrolysis of ethyl acetate or esterification of acetic acid are unique. When MoO_3-ZrO_2 was calcined at temperatures below 773 K, the conversions were less than 7 and 15% for hydrolysis and esterification,

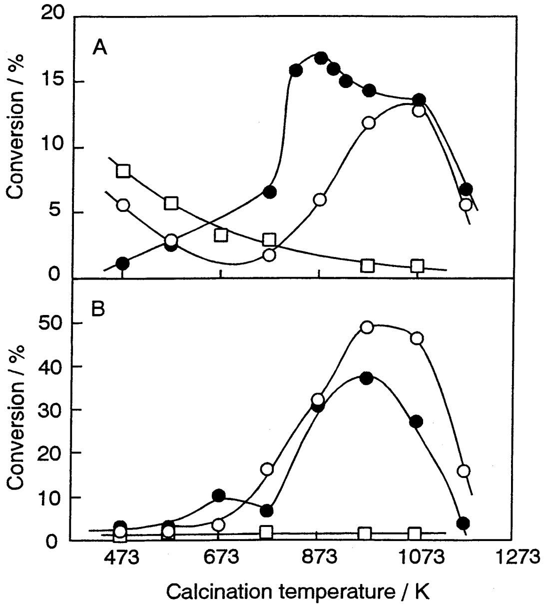


Figure 29. Conversions of hydrolysis (A) and esterification (B) over MoO_3-ZrO_2 as a function of the calcination temperature: (○) 9 at % MoO_3-ZrO_2; (●) 23 at % MoO_3-ZrO_2; (□) ZrO_2.

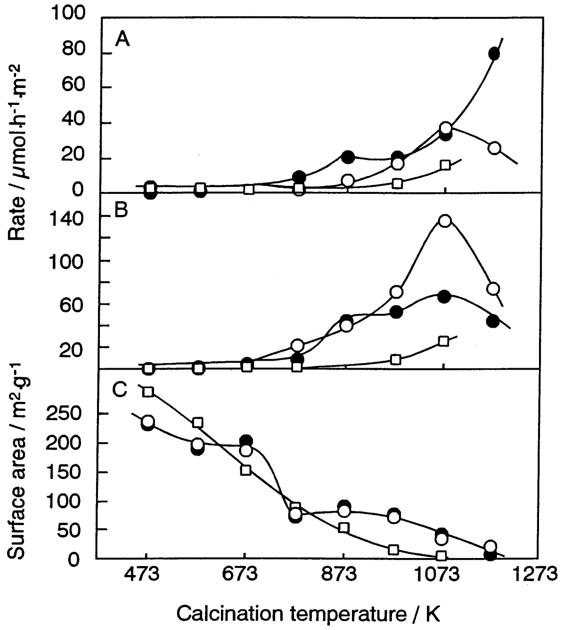


Figure 30. Specific rates of hydrolysis (A) and esterification (B) and changes in the surface area (C) as a function of the calcination temperature: (○) 9 at % MoO_3-ZrO_2; (●) 23 at % MoO_3-ZrO_2; (□) ZrO_2.

respectively. For calcination temperatures below 573 K, MoO_3-ZrO_2 (9% atom/atom) showed less activity for hydrolysis than the activity of ZrO_2 itself. However, the activity of MoO_3-ZrO_2 significantly improved as the calcination temperatures was increased to 873−1073 K.

As shown in Figure 30, the specific rates for the two reactions are presented as a function of the calcination temperature. The results show that the specific rates (per surface area) increased as the calcination temperature increased up to 1073 K. These changes are consistent with the hydrophobicity measurements, which were evaluated by adsorption of water, but not with the density of acidic site as measured by NH_3 adsorption.[124] Adsorption of water demonstrated that MoO_3-ZrO_2, which was calcined at high temperatures, possessed higher hydrophobic surfaces as compared with $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, H-ZSM-5 (Si/Al = 40), and other oxides. It should be pointed out that the changes in the density of acidic site were not consistent with changes in the catalytic activity, and therefore the activities of MoO_3-ZrO_2 for the water-participating reactions are related to the hydrophobicity of the surface, as well as the acidic properties.

As shown in Table 17, the catalytic activities of MoO_3-ZrO_2 were compared with those of other typical solid acids. The acid amounts of MoO_3-ZrO_2 and WO_3-ZrO_2, as measured by NH_3-TPD, are also shown in Table 17. For the esterification, the following order in the activity was obtained: $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ > Nafion−SiO_2 > MoO_3-ZrO_2 (9% atom/atom) > H-ZSM-5 > WO_3-ZrO_2 (9% atom/atom) > MoO_3-ZrO_2 (23% atom/atom) > WO_3-ZrO_2 (23% atom/atom) > Nb_2O_5 > $SiO_2-Al_2O_3$. This demonstrates that the activity of MoO_3-ZrO_2 (9% atom/atom) is comparable to that of the commercial water-tolerant catalyst, H-ZSM-5. For the hydrolysis of ethyl acetate, the activities of MoO_3-ZrO_2 and WO_3-ZrO_2 followed those of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, H-ZSM-5, and Nafion−$SiO_2$.

Table 17. Catalytic Activities for Hydrolysis of Ethyl Acetate and Esterification of Acetic Acid with Ethanol

catalyst	acid amount (mmol·g^{-1})	surface area (m^2·g^{-1})	rate constant[a] A	rate constant[a] B
Nafion−SiO_2	0.12[b]	344	4.5	9.4
H-ZSM-5 (Si/Al = 40)	0.40[c]	400	3.5	3.2
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.15 (0.06)[d]	128	3.5	10.2
$Nb_2O_5 \cdot nH_2O$	0.31[e]	131	1.0	0.6
$SiO_2-Al_2O_3$	0.35[f]	539	0.0	0.1
9 at % MoO_3-ZrO_2[g]	0.12[c]	36	1.4	3.5
23 at % MoO_3-ZrO_2[g]	0.07[c]	43	1.6	1.8
9 at % WO_3-ZrO_2[g]	0.16[c]	47	1.5	2.2
23 at % WO_3-ZrO_2[g]	0.13[c]	33	1.2	1.0

[a] A, hydrolysis of ethyl acetate, 10^{-3} min^{-1}·g^{-1}; B, esterification of acetic acid and ethanol, 10^{-3} mol^{-1}·dm^3·min^{-1}·g^{-1}. Reaction conditions: for hydrolysis, 5 wt % aqueous solution 30 cm^3 at 343 K and 0.8 g of catalyst; for esterification, acetic acid 1 cm^3, ethanol 1 cm^3 in toluene (5 cm^3) at 343 K, and 0.8 g of catalyst. [b] From ref 12. [c] Measured by NH_3-TPD. [d] Total amount. The figure shows the number of acid site on the surface (ref 6). [e] From ref 6. [f] From ref 6. [g] Calcined at 1073 K.

Desorption peaks of NH_3 were around 473 K for MoO_3-ZrO_2 (23% atom/atom) and also for MoO_3-ZrO_2 (9% atom/atom) and were nearly independent of the calcination temperature. Typical strong solid acids gave peaks of NH_3 desorption at about 600 K ($SiO_2-Al_2O_3$), 650 K (H-ZSM-5), 700 K (mordenite), and 830 K ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$).[70] Considering that the temperature of the desorption peak is related to the acid strength, the acid strengths of MoO_3-ZrO_2 were significantly lower than those of typical solid acids (listed above).

3. Zirconium Tungstate

For ethylene hydration, partially reduced tungsten oxide, such as W_2O_5, has shown some, although not high, catalytic activity,[125] and amorphous zirconium tungstate $ZrW_{2-8}O_{0.5-3.5}$ has shown high catalytic activity. Zirconium tungstate with a composition of W/Zr = 2 provided the highest activity. Because of the high activity, and also because it is insoluble in water, zirconium tungstate holds promise as an alternative for the problematic phosphoric acid catalyst.

4. Zirconium Phosphate

Zirconium phosphonates, $Zr(O_3PR)_2$, are layered compounds that are synthesized in amorphous forms under aqueous conditions by the reaction of a soluble salt of Zr^{4+} and phosphonic or organophosphoric acid. Segawa et al.[126] have synthesized several types of zirconium phosphonates, $Zr(O_3PR)_2$, either as a single component, with one type of R, or as composite zirconium phosphonates, with two different R groups, where R could be $-OH$, $-CH_3$, $-C_6H_5$, $-C_{12}H_{25}$, $-C_{22}H_{45}$, $-CH_2COOH$, $-C_2H_4COOH$, or $-CH_2SO_3H$. The idealized structure of composite crystalline $Zr[O_3PCH_2SO_3H]_{0.5}(O_3PC_{12}H_{25})_{0.5}]_2$ is illustrated in Figure 31. In such compounds, two different tetra-

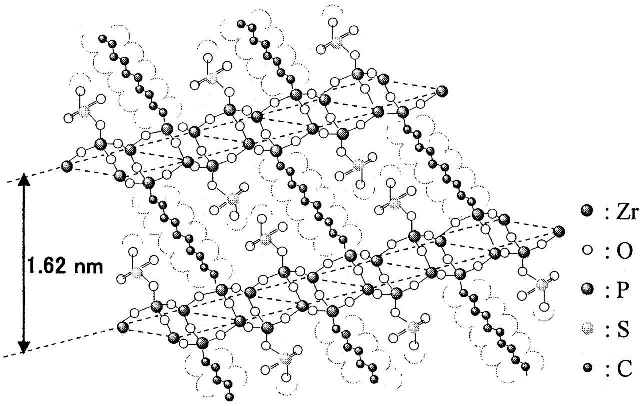


Figure 31. Structure of $Zr[(O_3PCH_2SO_3H)_{0.5}(O_3PC_{12}H_{25})_{0.5}]_2$.

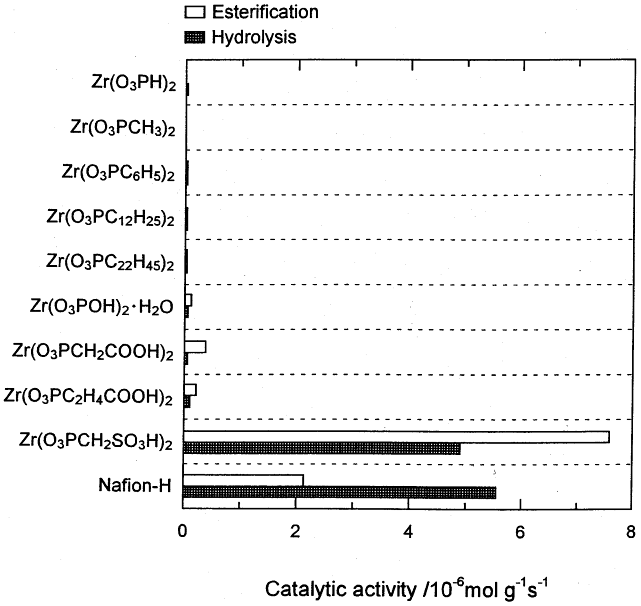


Figure 32. Catalytic activities of zirconium phosphates for hydrolysis and esterification.

hedral phosphonate groups are bonded to the plane of zirconium atoms. The interlayer *d* spacing of *n*-alkyl zirconium phosphonates increases linearly with the carbon number, suggesting that the *n*-alkyl groups are uniformly distributed between each pair of Zr atom planes and that the interlayer *d* spacing abides by the bulkiness of *n*-alkyl groups. Although ion-exchange capacity was not associated with pure alkyl zirconium phosphonates, replacing R with $-OH$, $-CH_2COOH$, $-C_2H_4COOH$, or $-CH_2SO_3H$ groups increased the ion-exchange capacity in direct proportion to the number of acid hydrogens in the replacing groups.

Figure 32 shows the catalytic activities for the hydrolysis of ethyl acetate in water at 341 K and esterification of acetic acid with ethanol at 343 K. Zirconium phosphonates (R = OH) were essentially inactive as solid acid catalyst. On the other hand, $Zr(O_3PCH_2SO_3H)_2$ exhibited high catalytic activity, in comparison to the other zirconium phoshonates with their relatively lower activities. The activity of $Zr(O_3PCH_2SO_3H)_2$ was higher than that of the hydrogen form of Nafion. However, $Zr(O_3PCH_2SO_3H)_2$ is problematic in terms of swelling or dissolution. As shown in Figure 32, the results suggest that, even when the acid functions are present (R = $-OH$, $-CH_2COOH$, or $-C_2H_4COOH$), the reactant molecules are not accessible, because the *d* spacings are smaller than those of alkyl zirconium phosphonates.

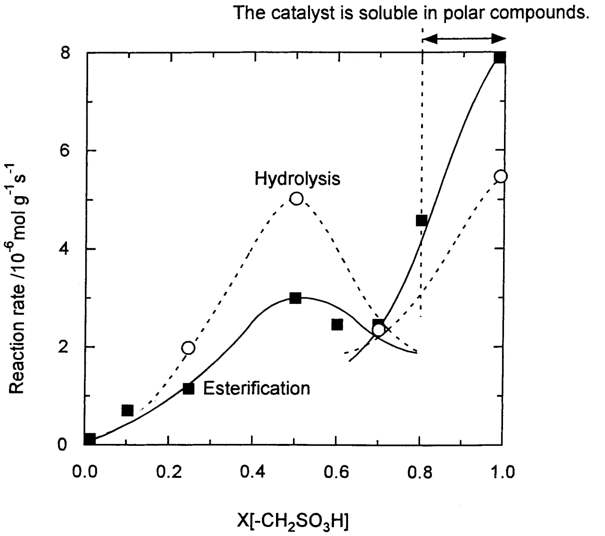


Figure 33. Catalytic activities of $Zr[(O_3PCH_2SO_3H)_x(O_3PC_{12}H_{25})_{1-x}]_2$.

To overcome the problem of water solubility or swelling for $Zr(O_3PCH_2SO_3H)_2$, a second functional group was introduced to achieve catalytic advantages in certain applications. $Zr[(O_3PCH_2SO_3H)_x(O_3PC_{12}H_{25})_{1-x}]_2$, having a $-CH_2SO_3H$ group for acidic function and a $-C_{12}H_{25}$ group for hydrophobic function, was prepared,[127,128] and the layered structure was confirmed using XRD studies. As shown in Figure 33, for the catalytic esterification of acetic acid in ethanol as the solvent, or aqueous hydrolysis of methyl acetate, the composite material showed higher catalytic activities than single-function zirconium phosphonates. For $Zr[(O_3PCH_2SO_3H)_x(O_3PC_{12}H_{25})_{1-x}]_2$ with $x > 0.8$, the reaction proceeded under somewhat homogeneous reaction, because the catalyst is water-soluble or soluble in polar compounds. In contrast, at $x < 0.7$, the zirconium phosphonate catalyst is insoluble.

5. Lanthanum Phosphate

Biodegradable salts, such as carboxymethoxysuccinic acid (CMOS), $CH_2(COOH)CH(COOH)OCH_2COOH$, are useful as phosphorus-free detergent builders. Aqueous solutions of $Ca(OH)_2$ can afford the Ca salt of CMOS from maleic anhydride with glycolic acid. The addition of Na_2CO_3 was required to obtain the precipitates of $CaCO_3$ and the Na salt of product. Besides $Ca(OH)_2$, lanthanum salts of CMOS were obtained by the reaction of sodium glycolate with disodium maleate in the presence of lanthanum trichloride in water.[129] The reaction scheme, as proposed by Nippon Shokubai, is illustrated in Figure 34. After the reaction, La^{3+} must be separated from the reactant solution, such as by using ion-exchange resins, thus indicating that the steps of the separation were not avoided in these homogeneous systems. Because La^{3+} forms a stable chelate compound with a 1:2 ratio, the amount of product formed was only 2 times that of the La^{3+} (in molar ratio). The product

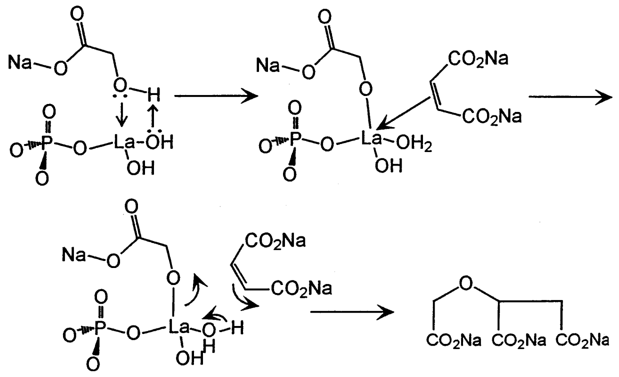


Figure 34. Reaction scheme of methoxycarboxysuccinic acid from sodium salts of glycolic and maleic acid.

Table 18. Etheration of Glycolic Acid with Maleic Acid

catalyst	composition (mol ratio, pH[a])	con-version (%)	selec-tivity (%)	yield (%)
LP-1	$La/PO_4 = 0.95$ (pH 1.5)	0	0	0
LP-2	$La/PO_4 = 0.99$ (pH 12)	30.7	71.0	21.8
LP-3	$La/PO_4 = 2.09$ (pH 12)	46.1	71.3	33.1
YP-1	$Y/PO_4 \approx 1$ (pH 12)	28.1	71.2	19.7
CP-1	$Ca/PO_4 \approx$ (pH 12)	0	0	0
$Ca_3(PO_4)_2$		0	0	0
$Mg_3(PO_4)_2$		0	0	0
$AlPO_4$		0	0	0
$FePO_4$		0	0	0

[a] Reaction conditions: [glycolic acid] = [maleic acid] = 0.5 mol·dm^{-3}, pH 12.5, catalyst 10% (to glycolic acid). [b] pH at the preparation.

La^{3+} chelate is then transformed to the corresponding Na salt of the carboxylate or carboxylic acid. Overall, this method using metal ions is not suitable as an industrial process.

Nippon Shokubai Co. has attempted to synthesize CMOS using solid acid catalysts.[130,131] Table 18 presents the results for the reaction using various solid acids at 363 K. Whereas lanthanum phosphate (LP-1, $La/PO_4 = 0.95$) prepared at pH 1.5 was inactive, LP-2, $La/PO_4 = 0.99$, prepared at pH 12, showed activity. Furthermore, the lanthanum phosphate with the La/PO_4 ratio of 2.09 was more active than that with the ratio of 0.99 when the phosphates were prepared at pH 12. It should be emphasized that the separation of the solid phosphate was straightforward, and the dissolution of La^{3+} was <1 ppm. Although commercial $La_2(CO_3)_3$ and LaF_3 were inactive, $La_2(CO_3)_3$ and LaF_3 prepared at pH 12 were active.[130,131]

6. Niobium Phosphate

Dehydration of fructose to 5-(hydroxymethyl)-2-furaldehyde (abbreviated HMF) was carried out using niobium phosphates. An aqueous solution of fructose (6% w/w) was refluxed in the presence of the solid catalysts (Figure 35).[132] Reactions of this type have attracted much attention because of the demand of renewable resources, such as biomass, as substitutes for mineral raw materials.

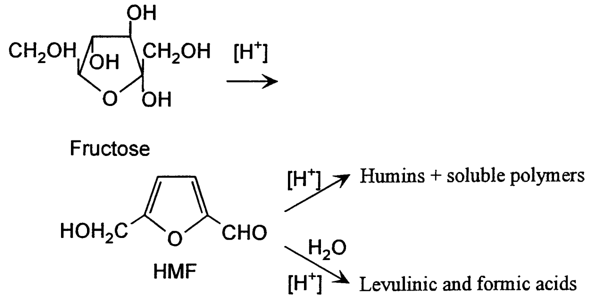


Figure 35. Reaction paths for oxidation of fructose.

Table 19. Solubilities of Oxides and Hydroxides in Water at Room Temperarure

species	solubility (g·dm^{-3})	species	solubility (g·dm^{-3})
$Mg(OH)_2$	9.8×10^{-3}	Sb_2O_3	1.6×10^{-4}
$Al(OH)_3$	9.5×10^{-3}	$La(OH)_3$	1.2×10^{-3}
$Sc(OH)_3$	9.5×10^{-7}	La_2O_3	$0.4-1.5 \times 10^{-3}$
$Ti(OH)_3$	4.3×10^{-9}	$Ce(OH)_3$	6.6×10^{-4}
$Ti(OH)_4$	8.4×10^{-11}	$Ce(OH)_4$	4.7×10^{-9}
V_2O_5	7×10^{-3}	$Pr(OH)_3$	4.3×10^{-4}
$Cr(OH)_2$	1.5×10^{-5}	Pr_2O_3	2.01×10^{-4}
$Cr(OH)_3$	9.1×10^{-7}	$Pt(OH)_2$	3.1×10^{-10}
$Mn(OH)_2$	2.55×10^{-3}	$Nd(OH)_3$	9.0×10^{-5}
$Fe(OH)_2$	4.8×10^{-4}	Nd_2O_3	1.94×10^{-3}
$Fe(OH)_3$	2.71×10^{-8}	$Sm(OH)_3$	1.1×10^{-4}
$Co(OH)_2$	$8-22 \times 10^{-4}$	$Eu(OH)_3$	2×10^{-4}
$Co(OH)_3$	2.2×10^{-3}	$Gd(OH)_3$	8.4×10^{-5}
$Ni(OH)_2$	7.5×10^{-5}	$Tb(OH)_3$	3.4×10^{-4}
$Ni(OH)_3$	$\sim 10^{-8}$	$Dy(OH)_3$	3.2×10^{-4}
Cu_2O	1.9×10^{-3}	$Er(OH)_3$	1.53×10^{-4}
CuO	1.4×10^{-5}	$Tm(OH)_3$	1.3×10^{-4}
$Zn(OH)_2$	1.0×10^{-2}	$Yb(OH)_3$	5.3×10^{-5}
$Ga(OH)_3$	5.72×10^{-8}	$Lu(OH)_3$	1.2×10^{-4}
GeO (brown)	1.8×10^{-2}	$Hf(OH)_4$	2.3×10^{-7}
GeO (yellow)	0.44	$Au(OH)_3$	5.3×10^{-10}
$Sr(OH)_2$	7.4	Hg_2O	1.2×10^{-13}
$Y(OH)_3$	1.35×10^{-4}	HgOH	2.9×10^{-10}
$Zr(OH)_4$	9.9×10^{-9}	HgO (red)	5.1×10^{-2}
$Nb(OH)_5$	$\sim 10^{-11}$	HgO (yellow)	5.2×10^{-2}
MoO_3	1.9×10^{-2}	$Tl(OH)_3$	5.6×10^{-10}
$Ru(OH)_3$	2.1×10^{-8}	Tl_2O_3	2.97×10^{-7}
$Ru(OH)_4$	2.4×10^{-7}	$Pb(OH)_2$	1.07×10^{-3}
$RuO_2 \cdot xH_2O$	6.5×10^{-26}	$Pb(OH)_4$	6.22×10^{-12}
$Pd(OH)_2$	4.1×10^{-9}	PbO (red)	5.04×10^{-4}
AgOH	0.024	$Th(OH)_4$	9.5×10^{-7}
$Cd(OH)_2$	1.5×10^{-3}	UO_2	8.1×10^{-6}
$In(OH)_3$	3.19×10^{-7}	$UO_3 \cdot H_2O$	1.13×10^{-4}
$Sn(OH)_2$	1.82×10^{-3}	$Am(OH)_3$	1.3×10^{-4}
$Sb(OH)_3$	5.1		

Commercial niobium phosphate [NP1, CBMM (Companhia Brasileira de Metalurgia e Mineracao)] was treated at 528 K for 6 h under high vacuum (denoted NP2). Additionally, two kinds of niobium phosphate (P/N1 and P/N2) were prepared; P/N1 was obtained by the stirring of niobic acid (CBMM) and H_3PO_4, followed by calcination, and P/N2 was prepared from P/N1 and NaCl.[132] When P/N1 and P/N2 were used, a high selectivity toward HMF was observed, with no detectable amounts of levulinic and formic acid. This is in contrast with the results of ion-exchange resins[133] or zeolites.[134] Turnover numbers are higher than those previously reported for other heterogeneous catalysts in this reaction.[135] When the acidities were measured by adsorption of acetonitrile,[132] the Lewis strength of these sites was lower than that of alumina, vanadium pentoxide, and vanadyl pyrophosphate. Other solid catalysts, such as zeolites,[136] ion-exchange resins,[137] and heteropoly compounds,[138] have been tested for this reaction; however, their catalytic performances were less than satisfactory. In addition to activity, the insolubility of the solid acids in water is also indispensable for water-tolerant catalysts. For reference, the solubilities of the oxides and hydroxides are summarized in Table 19.[139,140]

V. Organic–Inorganic Composites

1. Polymer Resin–Silica Composites

Two main classes of ion-exchange resins are the styrene-based sulfonic acids (Amberlyst- and Dow-type resin) and the perfluorosulfonic acid-based catalyst (Nafion). Some reviews[141−144] have described the catalytic properties of these ion-exchange resins.

Cation-exchange resins with strong acidity have been used as solid acids in many processes.[141−144] Although methyl *tert*-butyl ether (MTBE) will be phased out in the United States, synthesis of MTBE is an application of the resins.[145] Other examples are dehydration of *tert*-butyl alcohol to isobutylene, alkylation of phenol, bisphenol A synthesis, hydration of propene, decomposition of cumene hydroperoxide, and hydrolysis of ester. One of the main differences between the styrene-based and perfluorinated resin sulfonic acids is in their acid strengths. It is generally accepted that perfluorinated resin sulfonic acids are strong acids with values of the Hammett acidity function (H_0) from −11 to −13, whereas that of Amberlyst-15 is −2.2. Another important difference between the resins is the number of acid sites, which is ~5-fold greater for the styrene-based systems. Interaction of H_2O, alcohol, and pyridine with Nafion has been studied by means of IR specroscopy.[146]

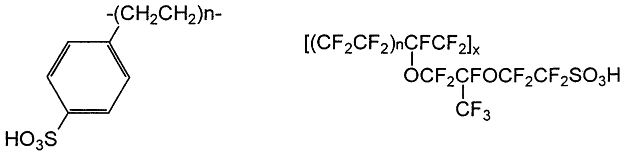
To increase the acceccibility for acid sites of Nafion resin-based catalysts, a new class of solid acid catalyst that is based upon a high surface area Nafion−silica nanocomposite has been prepared.[145−147] Nafion resin−silica nanocomposites with high surface areas can now function in nonswelling solvents. Table 20 summarizes the physical properties of three cation-exchange resins (the original table[145] contains some errors), and the open structure is shown in Figure 36.

Nafion−silica nanocomposites have shown higher catalytic activity than that of Amberlyst-15 for the esterification of cyclic olefins with saturated and unsaturated carboxylic acids.[147] Esterification of dicyclopentadiene with acrylic acid was catalyzed effectively using Nafion−silica (13% w/w) composite catalyst. The product was obtained in 91% yield using the composite, whereas yields of <5% were obtained using Amberlyst-15. Because of the low-polarity adjustments (that suppress the swelling of Nafion), the Nafion composites showed higher activities as compared to the native Nafion itself. The hydration of cyclohexene with water was studied using Nafion-based catalysts;[148] however, only traces of product were obtained. For nitration of benzene, Nafion−silica composite was found to be a better catalyst than Nafion itself.[147]

Table 20. Physical Properties of Some Cation-Exchange Resins

catalyst	surface area ($m^2 \cdot g^{-1}$)	pore volume ($mL \cdot g^{-1}$)	capacity (mequiv of $H^+ \cdot g^{-1}$)	max operating time	H_0
Amberlyst-15	50	0.35	4.8	120	−2.2
Nafion-NR50	0.02	*a*	0.9	280	−12
Nafion−silica nanocomposite	200	0.7	0.15	280	>−12

[a] Nonporous.


Sulfonated Polystyrene

Perfluorinated resin sulfonic acid

Figure 36. Structure of polymer resins.

Table 21. Catalytic Activities of Solid Acids for Hydrolysis of Ethyl Acetate

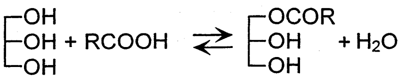
catalyst	acid amount ($mmol\ g^{-1}$)	surface area ($m^2\ g^{-1}$)	conversion[a] (%)	specific rate[b]
Aciplex−SiO_2	0.46[c]	1.3	27.4	0.42
Nafion−SiO_2	0.12[c]	344	11.5	0.68
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	0.15	105	11.2	0.53
H-ZSM-5	0.43	400	15.1	0.25
SiO_2−Al_2O_3	0.35	560	0	0

[a] At 2 h. Catalyst weight = 0.2 g. [b] mol (acid-mol)$^{-1}$ min^{-1}. The ion-exchange capacities were used as the acid amounts. [c] Ion-exchange capacities of polymer−SiO_2 composites.

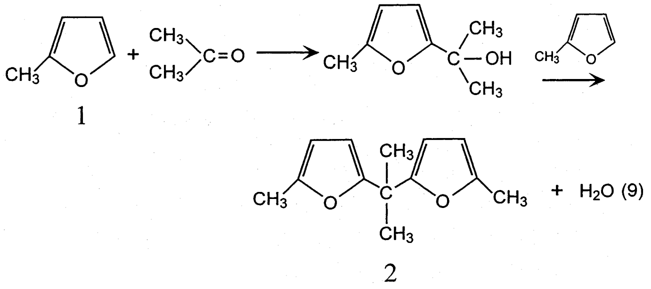
Okuyama et al.[149] reported on the effectively catalyzed hydrolysis of ethyl acetate using a new silica composite of the perfluorocarbonsulfonic acid resin, Aciplex (Asahi Chemical Co.), as shown in Table 21. The Aciplex−silica composite showed higher activity than typical solid acids, such as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, H-ZSM-5, and SO_4^{2-}−ZrO_2 for hydrolysis of ethyl acetate in excess water and esterification of acrylic acid with 1-butanol. In contrast, the Aciplex−silica composite was less active than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ for N-alkylation of acrylonitrile with 1-adamantanol. Overall, Aciplex−silica composite was superior in activity to Nafion−silica composite for all of the above reactions and in thermal stability. The acid strength of the Aciplex−silica composite, as estimated from an initial heat of adsorption of ammonia (~160 kJ mol^{-1}), was similar to that of Nafion−SiO_2. The activity of the Aciplex−silica composite for the reaction of benzene and formaldehyde (anhydrous) was also higher than that of other solid acids, such as zeolites (HY, H-ZSM-5, and β-zeolite), heteropoly compounds, and the other polymer resins (Nafion-H, Nafion−silica composite, and Amberlyst-15). However, addition of water to the reactant mixture significantly decreased the activity of Aciplex−silica.[150]

2. Mesoporous Organic Composites

Sulfonic acid bearing MCM-41 (mesoporous silica) was prepared via silylation and used for esterification of lauric acid with glycerol[151,152] (eq 8). One-pot

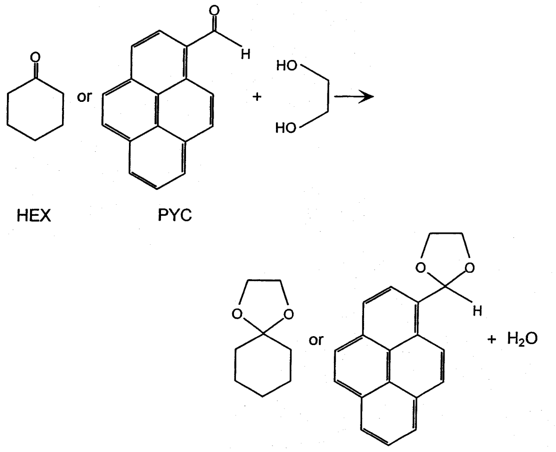

(8)

synthesized MCM-41 silicas containing both methyl and sulfonic acid ligands were active for the reaction.[153] Higher monoglycerol yields were obtained with lauric acid rather than oleic acid. Condensation (eq 9) as well as alcohol dehydration reactions were catalyzed using MCM-41 that are functionalized with sulfonic acid groups via silylation, coating, or co-condensation.[154−156]



(9)

Various attempts to introduce organic functional groups as active sites or hydrophobic sites have been carried out. Corma et al.[157] tried grafting organic silanes to ultrastable Y, but modifications within the pores proved to be difficult. Cauvel et al.[158] also examined the grafting of organosilane to Y zeolite; however, modification occurred only on the surface. Davis et al.[159] reported the synthesis of an organic-functionalized molecular sieve (OFMS), in which organic groups are immobilized on the wall of the pores through the covalent bond of Si−C. This OFMS exhibited shape selectivity in the synthesis of acetal (eq 10). Although the reaction of cyclohexanone with ethylene glycol proceeded using OFMS, reaction of the bulky aldehyde, pyrenecarboxaldehyde (PYC), did not take place, indicating the reactant shape selectivity.



(10)

Recent interests for functional materials having hydrophibicity are the mesoporous silicates with organic groups as skeletals of the structure.[160−166] Features applicable to water-tolerant catalysts are expected.

VI. Lewis Acids and Organometallic Catalysts

Small amounts of water can decompose a Lewis acid, such as $AlCl_3$, Lewis-promoted organic reactions are generally carried out under strict anhydrous conditions. It was reported that scandium triflate [$Sc(CF_3SO_3)_3$, denoted $Sc(OTf)_3$] and yttrium triflate [$Y(OTf)_3$] functioned as homogeneous catalysts in water.[167−171] Kobayashi et al.[171] have found that $Yb(OTf)_3$ accelerated the hydroxymethylation of silyl enol ether with formalin to give the correponding ketone (eq 11), in which the less nucleophilic counteranions, such as OTf^- or ClO_4^-, were effective in the acceleration. Yb salts with the less nucleophilic anions are more cationic and thus show high Lewis acidities. On the other hand, the Yb salts with the more nucleophilic anions, such as Cl^-, OAc^-, NO_3^-, and SO_4^{2-}, gave only low yields. Lanthanide(III) triflates promoted the nitration of various simple aromatic compounds with high yields.[172]

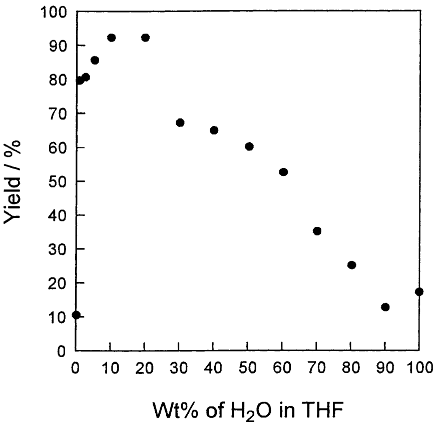
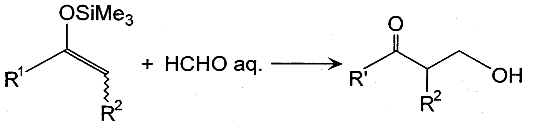


Figure 37. Influence of water content in THF on product yield of the reaction of 1-methylsiloxycyclohexane with benzaldehyde catalyzed by $Yb(OTf)_3$.

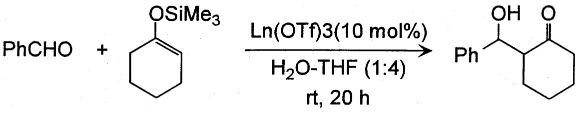


(11)

Lanthanide triflates are more soluble in water than in organic solvents, such as dichloromethane. Typically, the reaction is quenched with water and the products are extracted into an organic solvent. Because lanthanide triflates are partitioned in the aqueous layer, removal of the water is the single step to recover the catalyst. As for the active sites, protons are probably formed according to eq 12. Effects of water on the yield of the reaction between 1-methylsiloxycyclohexane and benzaldehyde (eq 13) in the presence of $Yb(OTf)_3$ (10% mole/mole) in THF are shown in Figure 37. Highest yield was obtained when

$$\begin{tikzcd} Yb(OTf)_3 + m\,H_2O \arrow[r, shift left] & Yb(H_2O)_m^{3+} + 3OTf \arrow[l, shift left] \arrow[d, shift left] \\ & Yb(H_2O)_{m-1}(OH)^{2+} + H^+ \arrow[u, shift left] \end{tikzcd}$$

(12)

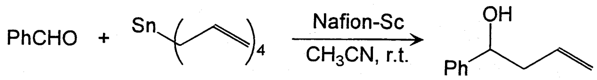


(13)

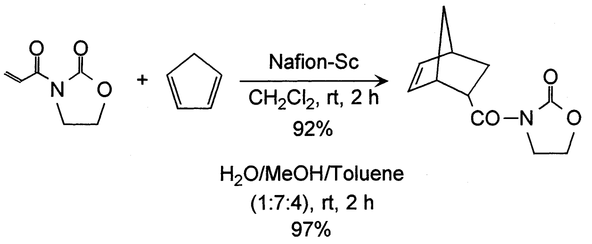
the ratio of water/THF was 10−20% w/w. Further increases in the amount of water resulted in decreases in the yields, and at 100% water, only 18% of the product was isolated.

Kobayashi et al.[173] prepared a new type of catalyst, “Lewis acid-surfactant-combined catalyst (LASC)”, in which colloidal particles are created by LASCs in the presence of the reactants in water. Scandium trisdodecyl sulfate was employed as the catalyst for the aldol reaction of benzaldehyde with silyl enol ether in water. Under neat conditions, without any solvents, the aldol reaction of benzaldehyde was accelerated by LASC. Although scandium trisdodecyl sulfate is only slightly soluble in water, stable dispersions were formed upon the addition of the aldehyde using stirring and vigorous mixing. Remarkably, the yield became higher in water, thus illustrating the advantage in the use of water.

Use of polymer-supported catalysts offers several advantages, such as separation and isolation, as well as reuse of the catalyst. A polymer-supported scandium catalyst was applied under aqueous conditions. Nafion−Sc, which was prepared by treatment of $ScCl_3 \cdot 6H_2O$ in acetonitrile under reflux conditions, was active for the allylation reactions of carbonyl compounds with tetraallyltin (eq 14).[173] A Diels−Alder reaction was accelerated by Nafion−Sc in H_2O-CH_3OH−toluene at room temperature.[174] Nafion−Sc also worked efficiently for an imino Diels−Alder reaction to afford the corresponding adducts in high yields (eq 15). Nafion−Sc was recovered simply by filtration and washing with a suitable solvent, with minimal loss of activity. In the reaction of benzaldehyde with tetraallytin (eq 14) in H_2O−MeOH−toluene (1:7:4) at room temperature, the yields were 91% (15 h), 81% (48 h), and 93% (40 h) for the first, second, and third runs, respectively. Details of the property and catalysis of water-tolerant Lewis acid are described by Kobayashi in his review.[175]



(14)



(15)

Bosnich et al.[176] have prepared water-tolerant Diels−Alder catalysts, $[Ti(Cp^*)_2(H_2O)_2]^{2+}$, from $[Ti(Cp^*)_2Cl_2]$ and $AgCF_3SO_3$, where Cp* is the pentamethylcyclopentadinyl anion. Yamamoto et al.[177,178] have claimed that tris(pentafluorophenyl)boron is an efficient, air stable, and water-tolerant Lewis acid catalyst for aldol-type and Michael reactions of silyl enol ethers with carbonyl compounds. Fringuelli et al.[179] have reported that classical Lewis acids, such as $AlCl_3$, $TiCl_4$, and $SnCl_4$, believed to be unusable as catalysts in aqueous medium, efficiently catalyzed regio- and stereoselective azidolysis and iodolysis of α,β-epoxycarboxylic acids in water at pH 4.0 and 1.5, respectively. Katritzky et al.[180] showed that, in the presence of bismuth(III) chloride−metallic aluminum, alkyl halide can react with *N*-(alkylamino)-benzotriazoles in THF−water mixtures to afford the corresponding homoalkylated amines in high yields.

Kuntz found the water-soluble metal complex with hydrophilic ligand.[181] The reaction proceeded in a biphasic system, in which the product was extracted into the organic phase. Ruhrchemie commercialized the hydroformylation process of butyraldehyde production using a water-soluble Rh catalyst (1000000 tons/year, 1984).[182−184] Various water-soluble ligands have been extensively tested, but only TPPTS [tri-(*m*-sulfonyl)triphenylphosphine, vulgo triohenylphosphine, trisulfonated] has proven itself in terms of price, handling, and the ratio of price and performance.[183] The hydration process of butadiene to octadienol was commercialized using a water-soluble Pd complex (5000 tons/year).[184,185] A review about water-soluble metal complexes[186] would be informative for this field. The following advantages are associated for biphasic system using organometallic catalysts: (i) selectivity is high due to the constant concentration of reactant and product, (ii) simple separation of product is possible, and (iii) the process is safe and environmentally friendly. The following reports[187−196] should be added to survey the water-tolerant metal complexes.

Recently, organic zeolites have been synthesized by Aoyama et al.[197,198] as a new type of catalyst that can be active in water.

VII. Closing

Design, preparation, and evaluation of water-tolerant solid catalysts are gradually driving the more hazardous homogeneous processes to heterogeneous processes with environmental as well as economic benefits. Recent developments and the evolution of these novel functional materials, designed at the molecular level, promise the creation of excellent catalysts and improvement of processes at present and in the near future.

VIII. Acknowledgments

I gratefully acknowledge Professor K. Tanabe, Y. Sumida (Nippon Sholubai), and H. Ishida (Asahi Kasei) for providing new information and fruitful discussion. I sincerely thank T. Echizen and K. Kobayashi for their help in preparing the manuscript.

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CR0103569