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Nanostructured Catalysts

Water-Tolerant, Highly Active Solid Acid Catalysts Composed of the Keggin-Type Polyoxometalate $H_3PW_{12}O_{40}$ Immobilized in Hydrophobic Nanospaces of Organomodified Mesoporous Silica**

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Since the discovery of mesoporous silica,[1–3] new organic–inorganic nanocomposites based on mesoporous silica materials have been extensively investigated in the development of functional materials in various fields.[4] The grafting of organic groups onto the pore walls of the silica[5] has provided novel materials for catalysis,[6] heavy-metal ion adsorption,[7] photocontrollable molecular storage,[8] gas separation,[9] and molecular recognition.[10–12] Since the chemical functionalities of these materials have been ascribed mainly to the organic moiety, a promising strategy toward new functions is to design an inorganic–organic cooperative mechanism in nanostructured materials.[11,12]

Solid acid catalysts have served as important functional materials in about 180 industrial processes in the petroleum refinery industry and in the production of chemicals.[13] In contrast, a significant number of acid-catalyzed reactions, such as Friedel–Crafts reactions, esterification, and hydrations, are still carried out by using conventional acids, such as H_2SO_4 and $AlCl_3$. In particular, for the reactions in which water participates as a reactant or product, such as hydrolysis, hydration, and esterification, only a few solid acids show acceptable performances.[14–16] The development of new water-tolerant solid acids is expected to have a major impact in industrial applications as well as in scientific aspects. One of the major difficulties concerned with the use of solid acids is the severe deactivation of the acid sites by water, and in fact, most solid acids lose their catalytic activity in aqueous solutions.

We have overcome this difficulty by designing acid catalysts comprising polyoxometalate (hetero-polyacid) molecules and organografted mesoporous silica. We found that the acidic protons in the hydrophobic environment of organomodified mesoporous silica show extremely high catalytic activity for ester hydrolysis in water.

Figure 1 illustrates the concept of the nanostructured catalyst. Two kinds of organic groups, *n*-octyl and 3-aminopropyl, were grafted onto the pore walls of mesoporous silica SBA-15.[3] The aminopropyl groups immobilize the $H_3PW_{12}O_{40}$ polyoxometalate anions on the pore walls, while the octyl groups (ca. 1 nm in length) form hydrophobic regions around the polyanions. It was found that water and reactant molecules can penetrate into the nanospaces through the remaining spaces at the centers of the SBA-15 pores. In the preparation of the catalyst, first alkyl groups and then 3-aminopropyl groups (AP groups) were grafted on SBA-15 (pore diameter 7.5 nm, BET surface area 458 m^2g^{-1}) to obtain organomodified materials, denoted by C_n-AP-SBA, where *n* is the number of carbon atoms of the alkyl group. After neutralization of the amino groups with hydrochloric acid,

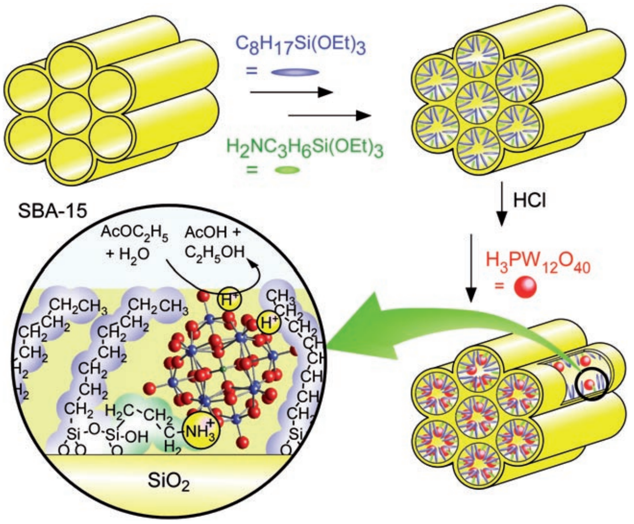

Figure 1. Schematic illustration outlining the preparation and structure of the catalysts. Octyl and 3-aminopropyl groups were subsequently grafted on the pore walls of mesoporous silica SBA-15, followed by immobilization of $H_3PW_{12}O_{40}$ polyoxometalate molecules in the nanospaces. Water and reaction substrates can penetrate the centers of the nanospaces to approach the vicinity of the acidic protons surrounded by the hydrophobic octyl groups.

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the materials were immersed into aqueous solutions of $H_3PW_{12}O_{40}$ and then washed with water to load $H_3PW_{12}O_{40}$ into the nanospaces. In this process, the 3-ammoniumpropyl groups, -$(CH_2)_3NH_3^+$, immobilize the $[PW_{12}O_{40}]^{3-}$ polyanions, leaving some portion of the acidic protons on the anions. These catalysts are denoted by, for example, PW/C_8-AP-SBA. Infrared spectra and ICP analysis confirmed that the Keggin structure of the polyoxometalate anions was maintained in the catalysts. X-ray diffraction confirmed that the catalysts maintained the nanostructure of SBA-15. The N_2 adsorption isotherms demonstrated that the parent SBA-15 and PW/C_8-AP-SBA had mesopores with 7.5- and 5.5-nm diameters, respectively, thus supporting the model in Figure 1 (see the Supporting Information).

Table 1 lists the catalytic activities of the catalysts for ethyl acetate hydrolysis. For comparison, Table 1 also summarizes the catalytic activities of various acid catalysts in the literature for the same reaction conditions. In the first instance, we carried out the reaction using catalysts with different alkyl chain lengths. The octyl-grafted catalyst showed the highest activity. For catalysts comprising ethyl, dodecyl, and octadecyl groups, the corresponding catalytic activities were 0.18, 0.21, and 0.18 times lower than those of the octyl-grafted catalyst. We then focused on the octyl-grafted catalyst (polyoxometalate loading: 13 wt%). To evaluate the catalytic activity per acidic proton, the amount of acidic protons was measured by irreversible pyridine adsorption. The results indicate that the catalyst had 91×10^{-6} mol g^{-1} of acidic protons, which corresponds to 2.0 acidic protons per polyoxometalate anion, thus suggesting that one polyanion is immobilized by one aminopropyl group.

Table 1: Activity of catalysts for ethyl acetate hydrolysis in water.

Catalyst	State of catalysts[a]	Acidity of catalysts[b]	Catalytic activity	
			Per cat. weight[c]	Per acidic protons[d]
PW/C_8-AP-SBA	solid	0.091 (2.0)[e]	25.1	275
$H_3PW_{12}O_{40}$	liquid	1.0 (3)	78.7	78
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$[f]	solid	0.15 (0.5)	30.1	200
Nafion-H resin[f]	solid	0.8	161.9	202
SO_4^{2-}/ZrO_2[f]	solid	0.35	25.5	127
H-ZSM-5 zeolite[f]	solid	0.39	27.6	70
γ-Al_2O_3[f]	solid	0.47	0	0
HY zeolite[f]	solid	2.6	0	0
H_2SO_4[f]	liquid	19.8	992	46

[a] Liquid, homogeneous catalysis; solid, heterogeneous acid catalysis. [b] Acid amount (10^{-3} mol g^{-1}). [c] In μmol $g_{cat.}^{-1}$ min^{-1}. [d] In mmol mol_{acid}^{-1} min^{-1}. [e] The figures in parentheses are molar ratios of the acidic protons to $[PW_{12}O_{40}]^{3-}$ polyanions. [f] Reference [15].

As shown in Table 1, the octyl-grafted catalyst showed a high activity of 275 mmol mol_{acid}^{-1} min^{-1}. To our knowledge, this activity is the highest observed in solid acid catalysts. Most inorganic solid acid catalysts do not work in water solvent; the exceptions include: H-ZSM-5, a hydrophobic zeolite, and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, which is also believed to have hydrophobic surfaces. Some ion-exchange resins do show activity in water. Our catalyst exceeded these other catalysts in activity per acidic proton. What is notable here is that our catalysts showed much higher activity than either the $H_3PW_{12}O_{40}$ or H_2SO_4 liquid acid catalysts. PW/C_8-AP-SBA showed a catalytic activity (per acidic proton) six times higher than H_2SO_4.

To obtain information about the hydrophobicity of the catalysts, water adsorption isotherms in the gas phase were measured (Figure 2). The corresponding nitrogen adsorption isotherms at 77 K (see the Supporting Information) showed clear capillary condensation and considerable adsorption amounts for all materials, indicating that the materials had considerable volumes of nanospaces even after organografting and the introduction of polyoxometalate molecules into the nanospaces. Pristine SBA-15 showed a large water uptake at $P/P_o \approx 0.7$ owing to capillary condensation of water, thus indicating that the nanospaces of SBA-15 were readily filled with liquid water. On the other hand, the organomodified materials, C_8-AP-SBA, showed no water condensation, demonstrating that the nanospaces were highly hydrophobic in nature. After the introduction of polyoxometalate molecules into the nanospaces of C_8-AP-SBA, the material PW/C_8-AP-SBA showed water condensation at $P/P_o = 0.8$–0.9, which is larger than that for pristine SBA-15 ($P/P_o \approx 0.7$). The water adsorption amount coincided with the pore volume of PW/C_8-AP-SBA determined by N_2 adsorption (0.15 cm^3 g^{-1}). This result shows that aqueous reaction mixtures can penetrate into the nanospaces of the polyanion-immobilized material PW/C_8-AP-SBA, while the nanospaces were still highly hydrophobic compared to those of pristine SBA-15. This point is important to allow the reactant molecules ready access to the acidic sites in the hydrophobic nanospaces of the catalysts.

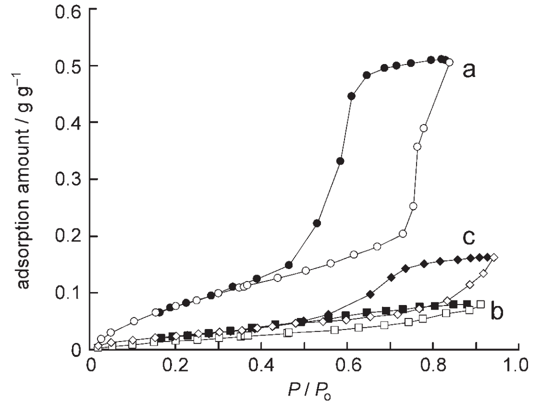

Figure 2. Water adsorption isotherms for the catalyst and its precursors. a) SBA-15. b) Octyl- and aminopropyl-grafted SBA-15 (C_8-AP-SBA). c) $H_3PW_{12}O_{40}$-loaded catalyst PW/C_8-AP-SBA. Open and solid symbols represent adsorption and desorption data, respectively.

The polyanions are about 1 nm in diameter and have lengths similar to the octyl groups, as illustrated in Figure 1. It is thereby reasonable that the acidic protons catalyze the reaction at the interfaces between the liquid water phase and the hydrophobic organic layers in the nanospaces. The hydrophobic environment around the acidic protons at the interfaces is considered to contribute to the exceptionally high activity of the protons compared to other solid acid catalysts. This model can explain the fact that the octyl-grafted catalyst is much more active than catalysts with different alkyl chain lengths: The polyanions are buried completely within the thick hydrophobic layer in the case of catalysts with longer alkyl groups. For catalysts with shorter alkyl groups, the polyanions are exposed to the water phase to a much greater extent, such that the protons lose their catalytic activity. The mesoporous silica nanostructure affords suitable conditions for the highly active reaction, such as the large area interfaces between the water and the hydrophobic organic layers, active sites on the polyanions immersed in the hydrophobic layers, and the nanospaces at the center of the mesopores, thus enabling the efficient diffusion of reactant molecules and water to the active sites.

The catalyst showed high stability during reactions in water. After a reaction time of 12 h for the batch ester hydrolysis, the leaching of the polyanions was only 2 % of the loaded polyanions. The long reaction time yielded acidic proton turnover numbers of 187 after 12 h and 348 after 24 h, thus demonstrating that no deactivation of the catalyst occurred on this time scale.

In conclusion, we have achieved a solid acid catalyst highly active in aqueous media. The catalyst comprises inorganic active species ($H_3PW_{12}O_{40}$ polyoxometalate molecules) surrounded by hydrophobic alkyl groups in the nanospaces of mesoporous silica. The acidic protons in the hydrophobic environment showed the highest activity for the ester hydrolysis reaction. The mesoporous silica nanostructure afforded paths for the efficient approach of reactant molecules and water to the active sites. This study indicates that a promising strategy for novel functional materials is to design an organic–inorganic cooperative function on the basis of the mesoporous silica nanostructure.

Experimental Section

Further details of the experimental procedures and the characterization results of the catalysts are provided in the Supporting Information. Mesoporous silica (SBA-15) was prepared according to literature methods (BET surface area 458 $m^2 g^{-1}$; mesopore diameter 7.5 nm).[3] The organografting was carried out by heating SBA-15 at reflux with an excess amount of $C_nH_{2n+1}Si(OC_2H_5)_3$ in freshly distilled toluene for 48 h to obtain "C_n-SBA". Then 3-aminopropyl (AP) groups were grafted on "C_n-SBA" by reaction with 3-aminopropyltriethoxysilane using procedures similar to those above to obtain "C_n-AP-SBA". By using a CHN analyzer (Perkin-Elmer 2400II), the amounts of grafted alkyl groups and AP groups were determined, and the surface densities of the organic groups (in molecules per nm^2) were calculated: C_2-AP-SBA: ethyl 1.8, AP 1.9; C_8-AP-SBA: octyl 1.8, AP 1.2; C_{12}-AP-SBA: dodecyl 0.76, AP 1.3; C_{18}-AP-SBA: octadecyl 0.70, AP 1.3. The most active catalyst was prepared by the following procedure: C_8-AP-SBA was immersed in dilute hydrochloric acid (pH 4.0). The obtained material was immersed in an aqueous solution of $H_3PW_{12}O_{40}$. The solid was then washed in warm water (333 K) for 5 min, followed by drying in vacuum to obtain PW/C_8-AP-SBA. The loading amount of $H_3PW_{12}O_{40}$ was 13 wt % (determined by ICP analysis).

Nitrogen adsorption was carried out at 77 K using a BELSORP-Mini (Japan BEL Co., Osaka, Japan). Water adsorption was measured using a CAHN microbalance placed in a custom-built glass high-vacuum system. The amount of acid was measured by pyridine chemisorption.

The catalytic hydrolysis of ethyl acetate was carried out as follows: An aqueous solution of ethyl acetate (3.7 g, 5 wt %) was heated to 333 K in a glass vial (5 cm^3). The catalyst (40 mg) was then added to the solution to initiate the reaction. The catalytic activity was then measured by GC analysis of the solution after 2 h.

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