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Development of catalyst materials for acid-catalyzed reactions in the liquid phase

Y. Izumi *, K. Urabe, M. Onaka

School of Engineering, Department of Applied Chemistry, Nagoya University Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Abstract

Silica-included tungstophosphoric acid and its Cs salt, zinc ion-exchanged smectite clays, and montmorillonite K10 could be effectively applied as insoluble, readily recoverable solid acid catalysts to the hydrolysis of ethyl acetate, liquid-phase Friedel–Crafts reactions, and the synthesis of alkylporphyrin derivatives, respectively. They are expected to be alternatives to the environmentally problematic homogenous acid catalysts such as sulfuric acid, aluminum chloride, and boron trifluoride.

Keywords: Acid catalyst; Liquid phase; Silica-included tungstophosphoric acid

1. Introduction

Aluminum chloride, boron trifluoride, and sulfuric acid are widely used as efficient acid catalysts for many homogeneous liquid-phase reactions such as Friedel–Crafts reactions, esterification, hydration, and hydrolysis. However, these acids pose several problems of high toxicity, corrosion, spent acid disposal, use of more than stoichiometric amounts, and difficult separation and recovery. The research work on solid acid catalysts that has been done to replace the problematic homogeneous acids plays a key role for the development of environmentally benign chemical processes. In this context, several solid acids which include ion-exchange resin, zeolite [1], clay montmorillonite [2–5], silica-alumina, sulfate-doped metal oxides [6], and heteropolyacids and their salts [7–14] have been investigated.

Recently we reported that silica-included heteropoly compounds [12,14], Zn^{2+}-exchanged smectite clays [15], and montmorillonite K10 could be effectively applied as insoluble, readily recoverable solid acid catalysts to the hydrolysis of ethyl acetate, liquid-phase Friedel–Crafts reactions, and the synthesis of alkylporphyrin derivatives [16–19], respectively. In this paper the outline of the above works are described.

2. Experimental

2.1. Ester hydrolysis catalyzed by silica-included heteropolyacid

Silica-included heteropoly compounds were prepared through the hydrolysis of ethyl orthosilicate, conducted at 40°C for 1 h and then 80°C for 3 h in the presence of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ or $H_3PW_{12}O_{40}$ dispersed or dissolved in ethanol. The hydrogel obtained was

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* Corresponding author.

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dehydrated slowly at 45°C in vacuo (25 Torr). In the case of salt inclusion, the dried gel was extracted with water at 80°C for 10 h to remove the non-trapped salt and organics, and finally calcined at 300°C for 3 h in vacuo (25 Torr). As for acid inclusion, the dried gel obtained was calcined at 150°C for 3 h in vacuo (25 Torr) to fasten the silica network, then extracted with water at 80°C for 3 h, and finally calcined at 150°C for 3 h in vacuo (25 Torr). The hydrolysis of ethyl acetate was performed at 60°C in a 30 ml flask containing reactants and suspended catalyst powder (60 mesh pass) with vigorous stirring for 3–6 h. The product ethanol was determined by gas chromatography using a PEG Unisole 30T column (2 m) and acetonitrile as an internal standard.

2.2. *Friedel–Crafts alkylation and acylation catalyzed by Zn^{2+}-exchanged clays*

Zn^{2+}-exchanged montmorillonite was prepared by a common cation exchange method. Prior to use, the clay catalyst was vacuum-dried under 0.5 Torr at 120°C for 3 h. The alkylation of benzene with benzyl chloride and the acylation of *p*-xylene with benzoyl chloride were carried out in a 30 ml flask containing the clay catalyst (60 mesh pass) and the reactants with vigorous stirring under a stream of nitrogen to remove the HCl liberated in the course of the reaction. The products recovered were diphenylmethane and 2,5-dimethylbenzophenone for the benzylation and the benzoylation, respectively. They were determined by gas chromatography using a silicone SE-30 column (2 m) and *n*-tridecane as an internal standard.

2.3. *Alkylporphyrin synthesis catalyzed by montmorillonite K10*

Montmorillonite K10 was purchased from Aldrich. The clay (1 g) was activated at 120°C and 0.5 Torr for 3 h in a 200 ml flask. To the flask were added CH_2Cl_2 (100 ml), aldehyde (1 mmol) and pyrrole (1 mmol) at room temperature, and the mixture was agitated for 1 h. Solid *p*-chloranil (0.75 mmol) was added, and the mixture was refluxed at 45°C for 1 h. Solid materials were removed through a Celite pad and washed with AcOEt or CH_2Cl_2 (60 ml). The combined filtrate containing free base porphyrin was condensed and adsorbed on Florisil (2 g). The adsobate was placed on the top of an alumina column (100 g) and developed with hexane–AcOEt or hexane–CH_2Cl_2. The porphyrin fraction was collected, condensed, charged on an alumina (100 g) column, and purified again. The purified porphyrin was dried at 80°C and 0.5 Torr for 6 h.

3. Results and discussion

3.1. *Silica-included heteropoly compounds for ester hydrolysis*

Only a few solid acid catalysts which are acceptable in both activity and stability have

Table 1
Hydrolysis of ethyl acetate catalyzed by silica-included $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ [a]

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

[a] $H_2O = 9.5$ g, AcOEt = 0.5 g, catalyst = 0.05 mmol with respect to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, 60°C; catalyst was prepared under the conditions of $H_2O/(EtO)_4Si = 5$, $EtOH/(EtO)_4Si = 1.3$ (mole ratio), and calcined at 300°C for 3 h.
[b] Weight ratio of SiO_2 to $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ calculated from the amounts of reagents charged at the preparation.
[c] First-order specific rate per unit weight of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (10^{-3} min^{-1} g^{-1}).
[d] Turnover frequency (min^{-1}).
[e] Leakage of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ during the hydrolysis reaction (3 h), estimated by UV spectrometry.
[f] Non-modified $Cs_{2.5}H_{0.5}PW_{12}O_{40}$.
[g] Prepared by hydrolysis of $(EtO)_4Si$.
[h] 160 mg, dried at 100°C.
[i] 160 mg, calcined at 300°C.
[j] First-order specific rate per unit weight.

Table 2
Hydrolysis of ethyl acetate catalyzed by silica-included $H_3PW_{12}O_{40}$ [a]

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

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

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

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

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

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

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

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

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

been known for the liquid-phase hydrolysis, hydration, and esterification reactions. Acidic ion-exchange resins such as Amberlyst-15 are often employed, but their use is limited to the reactions operated at relatively low temperatures of less than 100°C, because of low thermal stability. A high-silica zeolite of H-ZSM-5 keeps its strong acidity in aqueous media owing to hydrophobicity, so it is applicable to the hydrolysis of ethyl acetate [20] and to the hydration of butene [21] and cyclohexene [22], but its hydrolysis activity is not necessarily high due to its meagre acidity. A layer compound of zirconium phosphonate has been reported as an active solid acid catalyst for the esterification of acetic acid with ethanol when a sulfonic group is introduced into the phosphonate moiety [23].

We have reported that insoluble acidic alkali metal salts of the Keggin-type heteropolyacids, such as $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, worked as efficient acid catalysts not only for Friedel–Crafts alkylation and acylation reactions [11], but also for the esterification and hydrolysis in the liquid phase [12]. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was much more active than H-ZSM-5 for the hydrolysis of ethyl acetate and the esterification of acetic acid with ethanol, because it showed higher acid strength ($H_0 > 0.8$) than H-ZSM-5 ($H_0 > 1.5$) in both water and alcohol. Unfortunately, however, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ readily disperses in water or in alcohol forming a colloidal solution because it consists of very fine crystal particles (ca. 10 nm in average), consequently the salt becomes inseparable by means of simple filtration. We recently showed that the cesium salt could be transformed into a readily separable solid acid, a new type of mesoporous material, by including it into the silica network through a sol–gel technique which involved the hydrolysis of ethyl orthosilicate, and that the composite obtained was effectively applied as an active, insoluble, readily recoverable solid acid catalyst to the hydrolysis of ethyl acetate [12] (Table 1).

Very recently we found that even 12-tungstophosphoric acid itself, which is freely soluble in water, could also be entrapped effectively in silica matrix to be a water-insoluble and readily separable microporous solid acid catalyst effective for the hydrolysis of ester [14] (Tables 2 and 3). Interestingly, the silica-included $H_3PW_{12}O_{40}$ showed much higher hydrolysis activity than the same amount of aqueous $H_3PW_{12}O_{40}$. Probably $H_3PW_{12}O_{40}$ was entrapped in the silica network as a highly concentrated aqueous solution during the reaction: the

Table 3
Hydrolysis of ethyl benzoate catalyzed by silica-included $H_3PW_{12}O_{40}$ and Amberlyst-15 [a]

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

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

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

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

silica network appeared to be narrow enough to prevent the Keggin anion (ca. 1 nm diameter) from migrating into the aqueous medium.

Thus the silica-included heteropoly compounds were much more active for the hydrolysis of ethyl acetate and ethylbenzoate than the resin catalyst and acidic ZSM-5 zeolite in terms of turnover frequency, which suggests that they worked as stronger solid acid catalysts in aqueous reaction media.

3.2. Zn^{2+}-exchanged smectite clays for Friedel–Crafts alkylation and acylation

Recently, K10 (acid treated montmorillonite)-supported metal salts were reported [24] as efficient solid Friedel–Crafts alkylation catalysts that reduced the problems associated with the standard Friedel–Crafts reactions using $AlCl_3$. Very recently, we found that Zn^{2+}-exchanged smectite clays, particularly Zn^{2+}-exchanged nontronite ($Zn_x[Fe_2](Si_{4-x}Al_x)O_{10}(OH)_2$) and montmorillonite, showed much higher catalytic activity for the alkylation than $ZnCl_2$/K10 montmorillonite (Table 4) [15].

Interestingly, it has recently been reported that montmorillonite K10-supported zinc chloride very much enhanced the benzylation of benzene with benzyl alcohol in the presence of an equimolar amount of benzyl chloride [25]. We confirmed this peculiar catalytic performance of clay using Zn^{2+}-exchanged montmorillonite (Zn-Mont) (Fig. 1). Since benzyl chloride is a very active alkylating agent for the alkylation of benzene, the reaction was accomplished after 30 min over Zn-Mont whereas benzyl alcohol was much less reactive. However, benzyl alcohol reacted with benzene preferentially when benzyl chloride was present.

Table 4
Alkylation of benzene with benzyl chloride over clay catalysts [a]

Catalyst	Benzyl chloride conversion (%)	Diphenylmethane selectivity (%)
Zn^{2+}-montmorillonite	40	58
Zn^{2+}-beidellite	40	64
Zn^{2+}-nontronite	100	71
Na^{+}-montmorillonite	7.4	14
H^{+}-montmorillonite	8.6	5.8
K10	12	36
$ZnCl_2$/K10	45	32

[a] Reaction temperature 30°C, catalyst 63 mg, $BzCl/C_6H_6 = 10$ (mole ratio), reaction time 2 h.

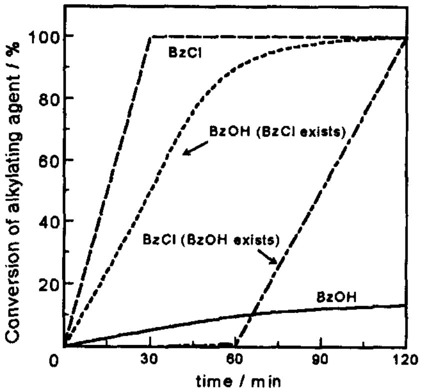


Fig. 1. Benzylation of benzene with benzyl chloride (– – –) and benzyl alcohol (—). Catalyst: Zn^{2+}-montmorillonite 6.3 mg, 80°C, benzene 100 mmol, alkylating agent 5 mmol; competitive alkylation (- -,– · –): BzOH 5 mmol; BzCl 1 mmol.

The activity of Zn-Mont for the alkylation of benzene with benzyl alcohol in the presence of a small amount of benzyl chloride was proportional to the zinc content of the clay, which suggests that the zinc ion bound to the clay should be a catalytic site. Only smectite clays with zinc ions showed high catalytic activity for the benzylation with benzyl alcohol, while other silicate catalysts such as Zn^{2+}-exchanged zeolite and silica-alumina could not activate benzyl alcohol. In addition, Zn-Mont pretreated with hydrogen chloride efficiently catalyzed the alkylation similarly with benzyl alcohol without benzyl chloride. Moreover, Zn-Mont also catalyzed the acylation of p-xylene with benzoic acid anhydride either in the presence of benzoyl chloride or by the pretreatment with hydrogen chloride.

As for the alkylation with benzyl alcohol in the presence of benzyl chloride, the alcohol is preferentially adsorbed on the clay prior to benzyl chloride, where the hydroxy group of benzyl alcohol exchanges with the chloride ligand attached to the zinc ion of the clay to be transformed into a reactive benzyl chloride molecule, leaving a hydroxylated zinc ion. The benzyl chloride formed quickly reacts with benzene to form the product and the concurrently evolved hydrogen chloride reacts with the hydroxylated zinc ion to regenerate the catalytic site. Thus the less active benzyl alcohol changes to very active benzyl chloride on the chloride-containing zinc sites of the clay. The enhancement of the acylation with benzoic acid anhydride is rationalized by a similar mechanism which involves preferential adsorption of the anhydride followed by the transformation of the less active anhydride into reactive acyl chloride.

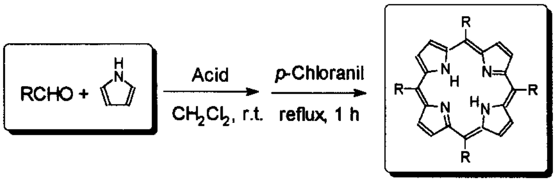
3.3. Nanospace of K10 montmorillonite for alkylporphyrin synthesis

Porphyrin and its derivatives have recently attracted much interest, since they are useful intermediates for bioactive substances, liquid crystals, and synthetic enzymes. However the synthesis of porphyrin is not necessarily easy. The reason why porphyrin synthesis is so difficult is that immediately after 4 molecules of aldehyde and 4 molecules of pyrrole were alternatively condensed, the chain formed must be closed into a precursor cyclic compound, porphyrinogen, or the reaction proceeds toward the undesirable linear polymer formation. Once porphyrinogen is formed, its dehydrogenation into porphyrin is readily performed with an oxidant. An earlier method involves the propionic acid-catalyzed condensation of aldehyde and pyrrole followed by the oxidation with air. This method was improved by another method which involves the condensation catalyzed by BF_3 ehtherate and the oxidation with a quinone-type oxidant, chloranil, to give higher yield. However the best yield reported so far is at most 50% even for readily obtainable tetraphenylporphyrin (R = phenyl. in the scheme shown below). For tetraalkylporphyrin (R = alkyl), the yield remains less than 20%. Since tetraalkylporphyrin is more versatile than tetraphenylporphyrin from the viewpoint of transformation into various types of derivatives, its effective synthetic methods have long been awaited.

Table 5
Tetraalkylporphyrin synthesis catalyzed by montmorillonite K10 [a]

R	Catalyst	Time (h)	Yield (%)
n-Pentyl	K10	1	46
	Fe-Mont	40	4
	SiO_2-Al_2O_3	1	trace
	H-Y	2	0
	BF_3-Et_2O	1	20
	CF_3CO_2H	1	15
$-(CH_2)_5Cl$	K10	1	40
	CF_3CO_2H	1	13
	BF_3-Et_2O	1	21

[a] Aldehyde 1 mmol, pyrrole 1 mmol, catalyst 1 g, in CH_2Cl_2.



We recently found that montmorillonite K10 was much more effective than BF_3 etherate and trifluoroacetic acid for the synthesis of tetrapentylporphyrin and tetrachloropentylporphyrin (Table 5). In addition, the work-up procedure in the clay-catalyzed method became much easier than in the conventional homogeneous reaction, since the porphyrin produced readily desorbed from clay into liquid phase and the by-product linear polymer remained on the clay surface. Thus a large scale porphyrin synthesis, for example gram-order synthesis, became possible with good reproducibility.

Interestingly, the other acidic silicates such as amorphous silica-alumina and Ca^{2+}-exchanged zeolite were all ineffectual for the porphyrin synthesis. In addition, the well-ordered laminated structure of montmorillonite was not suitable as a reaction medium, but the random delaminated mesoporous structure of K10 with pore sizes between 2 and 5 nm [26] was preferable for the porphyrin formation.

4. Conclusion

Silica-included 12-tungstophosphoric acid and its acidic cesium salt have several advantages as solid acid catalysts over the commonly employed homogeneous acid catalysts and resin catalysts in applying to the reactions in aqueous media, since they are insoluble, readily separable, thermally stable, and they show high catalytic activity owing to large surface areas and strong acidity.

Zinc ion-exchanged smectite clays efficiently catalyze the Friedel–Crafts reactions in which alcohol and carboxylic acid anhydride can be used as effective alkylation and acylation reagents, respectively, in place of alkyl halide and acyl halide which produce undesirable hydrogen chloride.

Montmorillonite K10 catalyzes the synthesis of alkylporphyrin derivatives from aliphatic aldehyde and pyrrole more efficiently than the conventional homogeneous acids such as BF_3 etherate. The mesopores of K10 possibly provides a favorable reaction medium for the formation of porphyrin molecules. In addition, the work-up of the clay-catalyzed method becomes much easier than the conventional procedures using homogeneous acid catalysts.

It is expected that silica-included tungstophosphoric acid and its Cs salt, zinc ion-exchanged smectite clays, and montmorillonite K10 will find wide applications to various types of acid-catalyzed liquid-phase organic reactions including those in aqueous media as environmentally benign solid acid catalysts which are replaceable for the problematic aluminum chloride, sulfuric acid, and ion-exchange resin catalysts.

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