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Silica-Supported Heteropoly Acid Catalyst for Liquid-Phase Friedel-Crafts Reactions

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Silica-supported Keggin-type heteropoly acids such as 12-tungstophosphoric, molybdophosphoric, and tungstosilicic acids efficiently catalyzed Friedel-Crafts alkylation and acylation reactions of aromatic hydrocarbons with 1-octene, benzyl chloride and benzoyl chloride in the liquid phase. The catalytic activity of heteropoly acid was generally enhanced when supported on silica. Silica-supported tungstosilicic acid worked as an insoluble heterogeneous catalyst even to the acylation of *p*-xylene with benzoyl chloride or benzoic anhydride, though deactivation was observed during repeated use. Considering that supported *p*-toluenesulfonic acid, an ordinarily used typical strong protonic acid, was far less active than the supported heteropoly acid, the high catalytic efficiency revealed by heteropoly acid appears to be due to a unique property of heteropoly anion which can stabilize alkyl and acyl cations as the reaction intermediates.

Several types of insoluble heterogeneous acid catalysts have recently been proposed for liquid-phase Friedel-Crafts reactions, in order to replace the conventional homogeneous catalysts such as $AlCl_3$ and sulfuric acid which often pose difficult operational problems of corrosion, removal from products, and requirement of stoichiometric catalyst amount. These heterogeneous catalyst systems include metal ion-exchanged aluminosilicates[1,2] and sulfate-doped metal oxides.[3] Concerning the acylation with acyl halides, however, there have not been developed such heterogeneous catalysts as can endure long-term use, yet.

Keggin-type heteropoly acid, which has been known to catalyze several organic reactions much more effectively than the ordinary protonic acids,[4] has also been explored as a Friedel-Crafts catalyst in the non-supported[5,6] or supported[7] state. The present study aims to inspect the applicability of supported heteropoly acids as heterogeneous catalysts for liquid-phase Friedel-Crafts reactions through the examination on the optimal conditions of catalyst preparation and through the re-examination on a problem of deterioration of heteropoly acid which has previously been pointed out concerning the acylation using acyl halides.[6]

Experimental

Catalyst. Each supported heteropoly acid catalyst was prepared by impregnating a support in the form of powders (115 mesh pass) with an aqueous solution of heteropoly acid followed by drying at 60—70 °C. The catalyst was calcined at a given temperature under reduced pressure (3 kPa) prior to use for the reaction. The Keggin-type heteropoly acids employed were of commercially available purity; tungstophosphoric ($H_3PW_{12}O_{40}\cdot 25H_2O$), molybdophosphoric ($H_3PMo_{12}O_{40}\cdot 9.3H_2O$), and tungstosilicic ($H_4SiW_{12}O_{40}\cdot 23.8H_2O$) acids. Silica A (Fuji Davison B, surface area 585 $m^2\,g^{-1}$, pore volume 0.774 $cm^3\,g^{-1}$), silica B (Fuji Davison ID, 105 $m^2\,g^{-1}$, 1.08 $cm^3\,g^{-1}$), and active carbon (Kraray GC, 1656 $m^2\,g^{-1}$, 0.34 $cm^3\,g^{-1}$) were used as catalyst supports.

Reaction Procedure. The organic reagents used were all purified by distillation. A suspension mixture of liquid organic substrates and solid catalyst granules in a flask was heated under reflux at atmospheric pressure. In the alkylation and acylation reactions using benzyl chloride and benzoyl chloride, the hydrogen chloride evolved during the reaction was removed by a continuous flow of nitrogen.

Analysis. The reaction products were determined by GLC (SE 30 and Unisole 30T columns) using internal standards. After the recation, the structural change of the supported heteropoly acid or of the heteropoly acid dissolved out during the reaction was examined through IR measurement using a Jasco IR-810 spectrophotometer.

Results and Discussion

Alkylation. Among the heteropoly acid catalysts tested, supported tungstophosphoric acid was most active for the alkylation of benzene with 1-octene. Only less than 5 mol% of a by-product dioctylbenzene was formed even at complete conversion of olefin, provided that an excess of benzene was used at a low reaction temperature of 35 °C. The isomers of 3- and 4-phenyloctanes were formed in addition to the major product of 2-phenyloctane (50—80 mol%).

Figure 1 demonstrates a remarkable influence of pretreatment temperature of catalyst on the catalytic activity of silica A-supported tungstophosphoric acid. The maximum conversion of 1-octene was attained when the catalyst was treated at 150 °C. The pretreatment at 100 °C gave only a meager activity. This is probably due to the remains of the crystal water of heteropoly acid which may reduce its acid strength. Indeed, according to the measurement by Hammett indicators, hydrous heteropoly acid ($H_3PW_{12}O_{40}\cdot 25H_2O$) showed an acid strength of $H_0 \geqq -3.0$, but it became more acidic ($H_0 \geqq -8.2$) when dehydrated by calcination at above 150 °C. Since it was confirmed from IR measurement that the Keggin structure of tungstophosphoric acid had still been completely retained even after 300 °C treatment, the reduction in catatytic

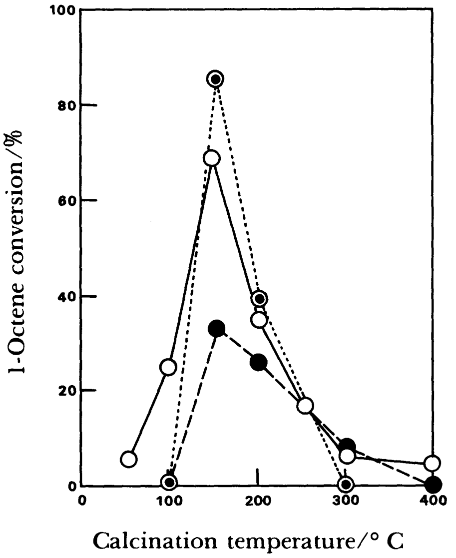

Fig. 1. Alkylation of benzene with 1-octene catalyzed by 12-tungstophosphoric acid (35 °C, 2 h). ○: Supported on silica A (15 wt%, 0.01 mmol); ●: supported on silica B (15 wt%, 0.01 mmol); ⊙: non-supported (0.03 mmol); benzene: 30 mmol; 1-octene: 3 mmol.

activity of supported heteropoly acid caused by calcination at 300 °C may be due to decrease in effective surface area of the exposed crystallites of heteropoly acid through aggregation. In this context, it was observed that the surface area of non-supported tungstophosphoric acid was decreased on heating from 8.3 $m^2 g^{-1}$ (150 °C) to 4.2 $m^2 g^{-1}$ (300 °C), though the degree of activity decrease was more drastic (Fig. 1). A similar decrease in surface area on heating has already been pointed out by Misono et al.[8] about non-supported molybdophosphoric acid.

Lower dispersion of heteropoly acid on silica B support which has a relatively small surface area (105 $m^2 g^{-1}$) brought about lower catalytic activity in comparison with high surface area silica A support (585 $m^2 g^{-1}$). Tungstophosphoric acid, even in non-supported state, reasonably catalyzed the reaction, but its efficiency could be enhanced obviously when supported on silica A.

The catalytic activity increased monotonously with the loading of heteropoly acid even beyond high levels of 25 and 30 wt% over silica B and silica A supports, respectively, without any dissolution and deterioration of heteropoly acid (Fig. 2). According to our previous study on the vapor-phase alkylation of benzene with ethene over silica (319 $m^2 g^{-1}$)-supported tungstophosphoric acid catalysts,[4e] a ceiling of activity increase was observed at a lower loading of 15—20 wt% (Fig. 2, a broken line). Since the vapor-phase alkylation proceeded exclusively on the outer surface of the supported heteropoly acid, a loading of more than 15 wt% did not bring about a substantial increase in activity because of crystal growth of supported heteropoly aicd. Therefore, the activity increase beyond 25 wt% loading observed even with a smaller surface area silica B support (105 $m^2 g^{-1}$) in the present liquid-phase alkylation reaction suggests that the reaction may involve a 'bulk-type reaction,' namely, the reaction occurs not only on the surface but also inside the bulk of the crystallites of heteropoly acid on the support.

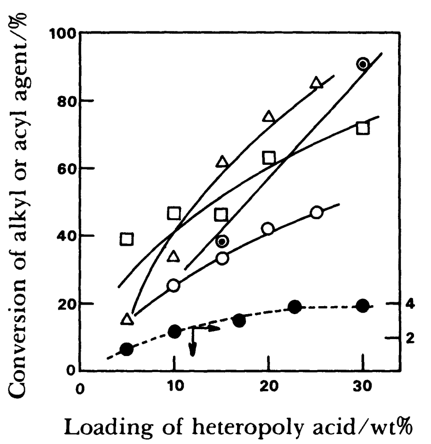

Fig. 2. Effect of loading of heteropoly acid on catalytic activities. ○: Alkylation of benzene with 1-octene by 12-tungstophosphoric acid (0.01 mmol) on silica B (35 °C, 2 h); ⊙: alkylation of benzene with 1-octene by 12-tungstophosphoric acid (0.01 mmol) on silica A (35 °C, 1 h); ●: vapor-phase alkylation of benzene with ethene over silica-supported 12-tungstophosphoric acid (200 °C),[4e] △: alkylation of toluene with benzyl chloride by 12-molybdophosphoric acid (0.02 mmol) on silica B (75 °C, 2 h); □: acylation of *p*-xylene with benzoyl chloride by 12-tungstosilicic acid (0.01 mmol) on silica B (138 °C, 1 h).

Table 1. Benzylation of Benzene with Silica-Supported Acid Catalysts (80 °C, 2 h)[a]

Acid	Benzyl chloride conversion/%
$H_3PMo_{12}O_{40}$	72.2
$H_3PW_{12}O_{40}$	27.2
$H_4SiW_{12}O_{40}$	17.3
p-$CH_3C_6H_4SO_3H$	0

a) Support: silica B; acid: 0.02 mmol; loading: 15 wt%; pretreatment: 300 °C, 3 h; benzene: 100 mmol; benzyl cloride: 5 mmol.

In contrast to the case of alkylation with olefin, silica B-supported molybdophosphoric acid catalyzed the alkylation of aromatic hydrocarbons with benzyl chloride most efficiently (Table 1). Neither dissolution nor deterioration of the supported heteropoly acid was observed during the reaction. Since the acid strength of molybdophosphoric acid is weaker than that of tungstophosphoric acid,[4d] higher catalytic efficiency of molybdophosphoric acid in this acylation may reflect its stronger affinity to benzyl chloride compared with other heteropoly acids. *p*-Toluenesulfonic acid, a typical conventional protonic acid, was inactive for this reaction. It is, therefore, suggested that heteropoly acid may exhibit Lewis acid-like catalytic function through an stabilizing effect by heteropoly anion[4d] on the benzyl cation as a reaction intermediate, although heteropoly acid itself is a protonic acid in nature.

Figure 3 illustrates the effect of pretreatment temperature of supported molybdophosphoric acid on the catalytic activity of benzylation of toluene. The maximum conversion appeared when the catalyst was preheated at 300 °C, but deactivation of catalyst occurred at higher pretreatment temperatures above 300 °C mainly because of decomposition of the heteropoly acid.

The benzylation activity increased with increasing loading of heteropoly acid beyond 25 wt% on silica B support without any dissolution and deterioration of heteropoly acid (Fig. 2), indicating that the benzylation involved a bulk-type reaction, also (vide supra). Other active alkyl halides such as bromocyclohexane could be favorably applied as an alkylating agent in the presence of the supported molybdophosphoric acid catalyst, but the catalyst was almost inactive for the alkylation reactions using primary alkyl halides.

Acylation. Figure 4 shows the result of the acylation of *p*-xylene with benzoyl chloride using silica-supported molybdophosphoric acid catalyst which was calcined beforehand at different temperatures. The catalysts which underwent milder thermal pretreatment were active, in particular (a solid line). However, the reaction proceeded still more even when the solid catalyst was removed out of the reaction medium in the course of the reaction (a broken line). In addition, molybdophosphoric acid was found almost decomposed after the reaction. These results unambiguosly indicate that the real active catalyst species was not the heteropoly acid on the support, but any other soluble species which might be formed during the reaction between heteropoly acid and benzoly chloride. Yamaguchi et al.[6] have also reported similar possibility of deterioration of non-supported molybdophosphoric acid when employed as a catalyst in the liquid-phase acylation of chloro-

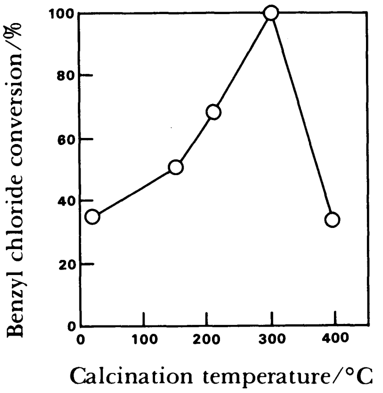

Fig. 3. Alkylation of toluene with benzyl chloride catalyzed by supported 12-molybdophosphoric acid (75 °C, 2 h). Heteropoly acid: 0.02 mmol; support: silica B (15 wt% loading); toluene: 100 mmol; benzyl chloride: 10 mmol.

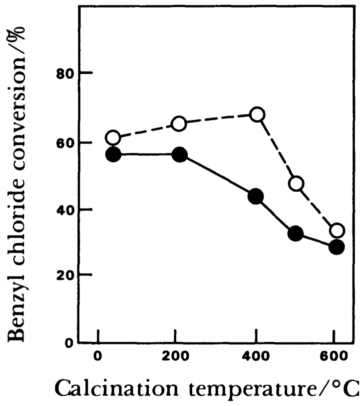

Fig. 4. Acylation of *p*-xylene with benzoyl chloride catalyzed by supported 12-molybdophosphoric acid (138°, 1 h). Heteropoly acid: 0.01 mmol; support: silica B (15 wt% loading); *p*-xylene: 30 mmol; benzoyl chloride: 3 mmol. The broken line denotes the final conversion of the reaction performed for more one hour successively after the catalyst was removed.

Table 2. Acylation of *p*-Xylene with Benzoyl Chloride Catalyzed by Supported Heteropoly Acid (138 °C, 1 h)[a)]

Calcination temperature/°C	Benzoyl chloride conversion/%[b)] Tungstosilicic acid	Tungstophosphoric acid
Not treated	6.4 (6.4)	0 (0)
100	11.9 (11.5)	— —
200	49.0 (47.4)	11.0 (10.6)
300	46.0 (47.3)	33.2 (33.6)
400	40.7 (39.4)	17.0 (16.0)
500	0 (0)	20.2 (21.2)
600	0 (0)	0 (0)

a) Support: silica B; loading: 15 wt%; net amount of heteropoly acid: 0.01 mmol; *p*-xylene: 30 mmol; benzoyl chloride: 3 mmol. b) The values in parentheses denote the final conversions of the reaction which was performed for more one hour successively after the catalyst was removed.

benzene with *o*-chlorobenzoyl chloride.

In contrast to molybdophosphoric acid, however, it was found that tungstosilicic acid and tungstophosphoric acid were both hardly soluble and remained unchanged in the reaction medium of the acylation of *p*-xylene with benzoyl chloride, still holding their Keggin structures. Thus the supported tungstosilicic and tungstophosphoric acids proved to effectively catalyze the acylation as heterogeneous and insoluble catalysts, particularly when calcined at between 200—500 °C (Table 2). In these cases, the reaction did not proceed any more if each solid catalyst was filtrated off out of the reaction medium.

The benzoylation activity increased with increasing loading of tungstosilicic acid beyond 30 wt% on silica B support without any dissolution and deterioration of heteropoly acid (Fig. 2), indicating that the benzoylation involved a bulk-type reaction, also.

In a polar reaction medium as met in the acylation of chlorobenzene, however, even silica-supported tungstosilicic acid was gradually migrated and deteriorated in the course of the reaction like as supported molybdophosphoric acid. Thus the silica-supported tungstosilicic acid appears to be effectively applicable as an insoluble acid catalyst for an acylation reaction in which a large excess of less polar aromatic hydrocarbon is applied, as exemplified by a reaction medium which consists of benzene and benzoyl chloride in a mole ratio of between 10:1 and 3:1.

Table 3. Deactivation of Silica-Supported Tungstosilicic Acid in Acylation of *p*-Xylene with Benzoyl Chloride[a)]

Repeated run number	Benzoyl chloride conversion/%
0	100
1	100
2	91
3	62
4	41
5	0

a) Support: silica B; loading: 15 wt%; net amount of heteropoly acid: 0.04 mmol; *p*-xylene: 30 mmol; benzoyl chloride: 3 mmol; reaction conditions: 138 °C, 3 h.

Table 3 represents the deactivation of silica-supported tungstosilicic acid catalyst in the course of the acylation reaction which was repeated several times by separating organic liquid from catalyst followed by the addition of fresh reactants whenever the reaction was performed for 3 h. A rapid decline in catalytic activity was observed from the second repeated run, but the total catalytic turnover was as much as about 300 per mole of heteropoly acid. The deactivation is probably caused by strong adsorption of the product benzophenone onto the catalyst, because it was confirmed from a separate experiment that the acylation was considerably retarded if the reaction was started in the presence of benzophenone. The detailed examination on catalyst deactivation and its regeneration are in progress.

Benzoic anhydride was also favorably employed as an acylating agent over the silica-supported tungstosilicic acid, but the acylation with benzoic acid did not proceed over this catalyst. Active carbon-supported tungstosilicic acid could catalyze the acylation, although its activity was limited to about a half of silica B-supported catalyst because of the reduction in acid strength.

p-Toluenesulfonic acid was quite inactive also for this acylation reaction. This fact again indicates a peculiar function of heteropoly anion to be able to stabilize the intermediate acyl cation.

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