

Acidic Alkali Metal Salts and Ammonium Salts of Keggin-type Heteropolyacids
as Efficient Solid Acid Catalysts for Liquid-phase Friedel-Crafts Reactions

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Acidic salts of the Keggin-type heteropolytungstic acids prepared through partial neutralization with alkali metal carbonates or ammonium hydroxide had relatively large surface areas, and showed high catalytic efficiency as insoluble solid acid catalysts in Friedel-Crafts alkylation and acylation using benzyl chloride, benzoyl chloride, benzoic anhydride, benzoic acid, acetic anhydride, and acetic acid as electrophiles.

Aluminum chloride is widely used as an efficient homogeneous catalyst for the liquid-phase Friedel-Crafts alkylation and acylation using alkyl halides, acyl halides, carboxylic acids and anhydrides. Several insoluble solid acids catalysts relevant to Friedel-Crafts reactions have recently been developed to replace conventional problematic homogeneous catalysts; those include Nafion-H, zeolite,¹⁾ clay montmorillonite,²⁾ $\text{SiO}_2\text{-Al}_2\text{O}_3$, sulfate-doped metal oxides,³⁾ and heteropolyacids and their salts.^{4,5)} As for heteropolyacids, we have reported efficient catalysis of silica-supported heteropolyacids for alkylation and acylation in less polar reaction media,⁴⁾ and Misono and Okuhara demonstrated high catalytic activity of insoluble acidic Cs salt of 12-tungstophosphoric acid having a large surface area of $157 \text{ m}^2 \text{ g}^{-1}$ for alkylation in nonpolar reaction media.⁵⁾ In this report, we wish to present high catalytic activity of insoluble, acidic alkali metal salts and ammonium salts of the Keggin-type heteropolytungstic acids for alkylation and acylation in polar reaction media.

Acidic alkali metal salts and ammonium salts of heteropolyacids were prepared from aqueous heteropolyacids and alkali metal carbonates or ammonium hydroxide, followed by calcination at 300°C 3 h under a reduced pressure. The reaction was performed in a Pyrex flask (30 ml) containing a vigorously stirred suspension of catalyst powder (60 mesh pass) and reactants under a stream of nitrogen gas to remove the HCl liberated in the course of the reaction. The products were analyzed by gas chromatography using a Silicone SE-30 column (3 m) and *n*-tridecane or *n*-hexadecane as an internal standard.

Figure 1 illustrates the change in catalytic activity of the $\text{Cs}_x\text{H}_{x-3}\text{PW}_{12}\text{O}_{40}$ system for the benzylation of benzene with the Cs content denoted by *x*, together with the change in surface area of the Cs salts. The catalytic activity once decreased with increasing *x* between 0 and 2 because of the decrease of acidity, but then jumped to attain the maximum at *x* = 2.5, which well corresponds to the sharp increase in the surface area at *x* = 2.5. Such a characteristic pattern of activity change with the Cs content was first reported by Misono *et al.* concerning the dehydration of 2-propanol and the conversion of dimethyl ether in the vapor phase.⁶⁾ The

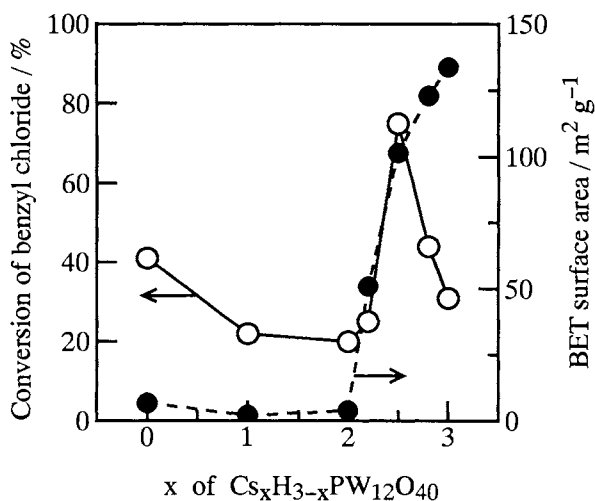


Fig. 1. Benzylolation of benzene over $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ catalyst. Benzene/ PhCH_2Cl /catalyst = 100/5/0.02 mmol, benzene reflux 2 h.

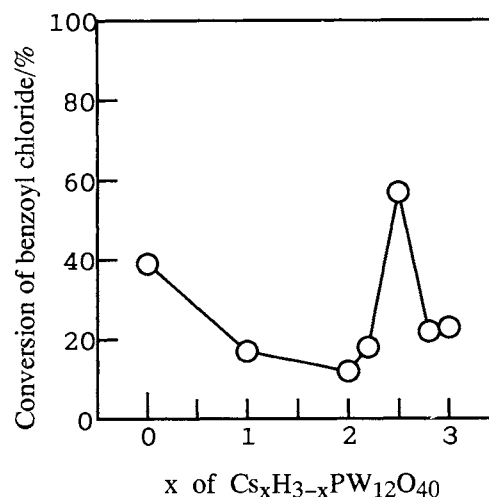


Fig. 2. Benzoylation of *p*-xylene over $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ catalyst. *p*-Xylene/ PhCOCl /catalyst = 100/5/0.01 mmol, *p*-xylene reflux 2 h.

turnover of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is 188 mol^{-1} , thus the catalytic activity is as high as that of the most active silica-supported heteropolyacid.⁴⁾ The selectivity for the major monoalkylated product of diphenylmethane was 63%. Dissolution of any active catalyst species from $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was not observed, since the alkylation did not proceed if the solid catalyst was removed from the reactor on the way of the reaction. It was confirmed through IR measurements that $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was stable during the reaction retaining its Keggin structure.

Quite a similar change in catalytic activity with the Cs content was also found for the acylation of *p*-xylene with benzoyl chloride (Fig. 2). The catalytic activity of the most active $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is much higher (turnover = 285 mol^{-1}) than those of silica-supported heteropolytungstic acids (turnover = ca. 100).⁴⁾ Y-type zeolite and clay montmorillonite exchanged with metal cations such as Al^{3+} , Fe^{3+} , and Zn^{2+} , which have been reported as effective catalysts for alkylation and acylation,^{1,2)} were inadequate to the acylation with acyl halide because considerable deactivations occurred due to the dissolution of active metal components. Acidic salts of heteropolymolybdic acid having large surface areas such as $\text{Cs}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ (surface area = $146 \text{ m}^2 \text{g}^{-1}$) were ineffectual as acylation catalysts because they readily decomposed during the reaction.

Table 1 summarizes the catalytic efficiency of various active acidic salts of heteropolytungstic acid for the benzylolation of benzene and the benzoylation of *p*-xylene. Acidic salts of heteropolytungstic acid generally worked as effective solid acid catalysts for alkylation and acylation in the liquid phase holding their Keggin structures, and no dissolution of the active species was observed with all of these salts catalysts. As for the salts of 12-tungstosilicic acid ($\text{M}_x\text{H}_{4-x}\text{SiW}_{12}\text{O}_{40}$), the maximum catalytic activity for the benzylolation of benzene was obtained at $x = 2$ for all of the alkali metal salts and the ammonium salt. It should be noted that the surface area of the active acidic salt increases with the ionic radii of the metal cation.

Other examples of acylation over the $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalyst were shown in Table 2, comparing with the results obtained for the parent free acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$. The free acid was usually much less effective for the acylation because of the dissolution into organic reaction media in addition to lower surface area.

Table 1. Friedel-Crafts Reactions over Alkali Metal Acidic Salts of Heteropolyacids

| Catalyst | Surface area /m ² g ⁻¹ | Benzylation of benzene ^{a)} Conversion of PhCH ₂ Cl/% | Benzoylation of <i>p</i> -xylene ^{b)} Conversion of PhCOCl/% |
|---|---|--|--|
| Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ | 102 | 75 | 57 |
| Rb _{2.5} H _{0.5} PW ₁₂ O ₄₀ | 91 | 49 | 64 |
| (NH ₄) _{2.5} H _{0.5} PW ₁₂ O ₄₀ | 90 | 53 | 46 |
| K _{2.5} H _{0.5} PW ₁₂ O ₄₀ | 41 | 75 | 18 |
| Cs ₂ H ₂ SiW ₁₂ O ₄₀ | 23 | 99 | 12 |
| Rb ₂ H ₂ SiW ₁₂ O ₄₀ | 35 | 43 | — |
| (NH ₄) ₂ H ₂ SiW ₁₂ O ₄₀ | 52 | 26 | — |
| K ₂ H ₂ SiW ₁₂ O ₄₀ | 4 | 72 | — |

a) Benzene/PhCH₂Cl/catalyst = 100/5/0.02 mmol, benzene reflux 2 h. b) *p*-Xylene/PhCOCl/catalyst = 100/5/0.01 mmol, *p*-xylene reflux 2 h.

Table 2. Friedel-Crafts Acylation over Cs_{2.5}H_{0.5}PW₁₂O₄₀^{a)}

| Substrates | | Product yield/% ^{b)} | |
|---|-------------------|---|---|
| Acylating agent | Aromatic compound | Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ | H ₃ PW ₁₂ O ₄₀ |
| (PhCO) ₂ O | <i>p</i> -xylene | 57 | 3 |
| (PhCO) ₂ O | anisole | 85 | 69 ^{c)} |
| (PhCO) ₂ O | chlorobenzene | 0 | 0 |
| PhCO ₂ H | <i>p</i> -xylene | 11 ^{d)} | 8 ^{e)} |
| PhCO ₂ H | anisole | 3 | 4 ^{f)} |
| Ac ₂ O | anisole | 89 | 50 ^{f)} |
| AcOH | anisole | 16 | 15 ^{f)} |
| <i>n</i> -C ₇ H ₁₅ COCl | mesitylene | 80 | 44 ^{f)} |

a) Yield is based on acylating agent. b) Acylating agent/aromatic compound/catalyst = 5/100/0.01 mmol, reflux 2 h. c) Catalyst was dissolved. d) Acylating agent/aromatic compound/catalyst = 5/100/0.05 mmol. The water liberated was continuously removed by means of Dean-Stark equipment. e) Acylating agent/aromatic compound/catalyst = 5/100/0.10 mmol. f) Catalyst was partly dissolved.

Reactive aromatic compounds such as anisole and *p*-xylene were acylated with benzoic anhydride and acetic anhydride effectively over $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ without the dissolution of the catalyst. Carboxylic acids were much less active as acylating agents than the corresponding anhydrides because of the liberation of water, but as shown in Fig. 3 the acylation became to proceed smoothly when the water produced was continuously removed, for example, by means of Dean-Stark equipment. Metal cation (Zn^{2+} , Fe^{3+})-exchanged montmorillonites were ineffectual for catalyzing the acylation of *p*-xylene with benzoic acid and anhydride.⁷⁾ Ce^{3+} -exchanged Y-type zeolite was reported to catalyze the acylation with long-chain aliphatic carboxylic acids, but ineffectual for the acylation using acetic acid.¹⁾ $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was also active for the acylation with aliphatic acyl halide such as *n*-octanoyl chloride. Insoluble acidic salts of heteropolytungstic acid thus behaved as preferable solid acid catalysts for liquid-phase Friedel-Crafts reactions using polar alkylating and acylating agents.

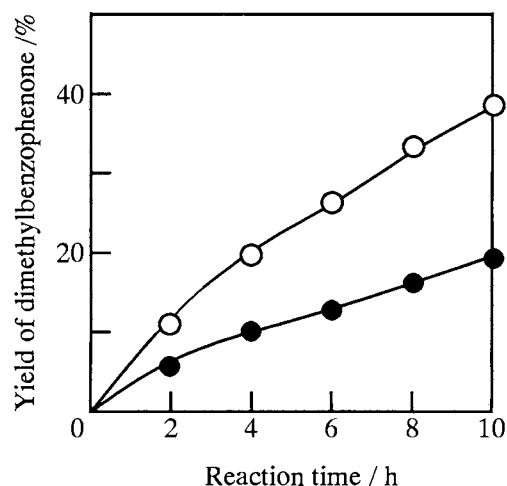


Fig. 3. Acylation of *p*-xylene with benzoic acid. Benzoic acid/*p*-xylene/catalyst = 5/100/0.05 mmol, ○: continuous removal of water, ●: without removal of water.

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