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CATALYSIS OF HETEROPOLY ACIDS ENTRAPPED IN ACTIVATED CARBON

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Activated carbon was found to be able to entrap a certain amount of heteropoly acids, resulting in solid acid catalysts. Heteropoly acids thus entrapped were hardly removed even by extraction with hot water or hot methanol. The entrapped catalysts offer convenient methods for liquid-phase etherification of alcohols and vapor-phase selective esterification.

Heteropoly acids (HPA) have been applied as catalysts to several acid-catalyzed reactions and oxidation reactions. We have recently reported that heteropoly anions play an important role in the efficient catalysis of HPA for the homogeneous liquid-phase reactions such as hydration of olefins[1,2], alcoholysis of epoxides[3] and oxidation of 1-butene[4]. HPA is usually employed in the liquid phase as soluble catalysts, as well as in the vapor phase as supported catalysts. But HPA often leaks out of catalyst supports even in vapor-phase reactions as previously reported on the hydration of ethylene[5], because HPA is extraordinarily soluble in water and is often very soluble in several organic solvents as well. It is, therefore, useful from the practical viewpoint to develop those supported HPA catalysts which can be applied to several reactions by fixed-bed catalysis with no leakage of HPA in the liquid phase or in the vapor phase.

We now report that activated carbon could tightly immobilize or entrap a certain amount of HPA and the HPA thus entrapped efficiently catalyzes the liquid-phase synthesis of butyl *tert*-butyl ether from the corresponding alcohols and the vapor-phase selective esterification of acetic acid with ethanol.

12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$) or 12-tungstosilicic acid ($H_4SiW_{12}O_{40}$) was first supported[6] on an activated carbon (Calgon F-300) and then washed with hot water or hot methanol by means of a Soxhlet extractor. The amount of HPA dissolved out of the carbon support varied with the initial HPA content, as well as with the kind of solvent used for extraction[7]. After a certain period of extraction, the removal of HPA from the carbon was no longer observed in any case (Fig. 1). Thus the entrapped catalysts with the maximum HPA content of 7.2-13.9 wt.% were obtained. The maximum HPA content varied little by the pretreatment of the carbon with 10% aqueous nitric acid, but moderately changed when different kinds of carbon were employed. On the other hand silica and diatomaceous earth, which are often used as supports for HPA in vapor-phase reactions, both proved to be incapable of immobilizing HPA, because the HPA supported on either of them was completely removed by solvent extraction. Moreover γ-alumina (JRC-ALO-5) was

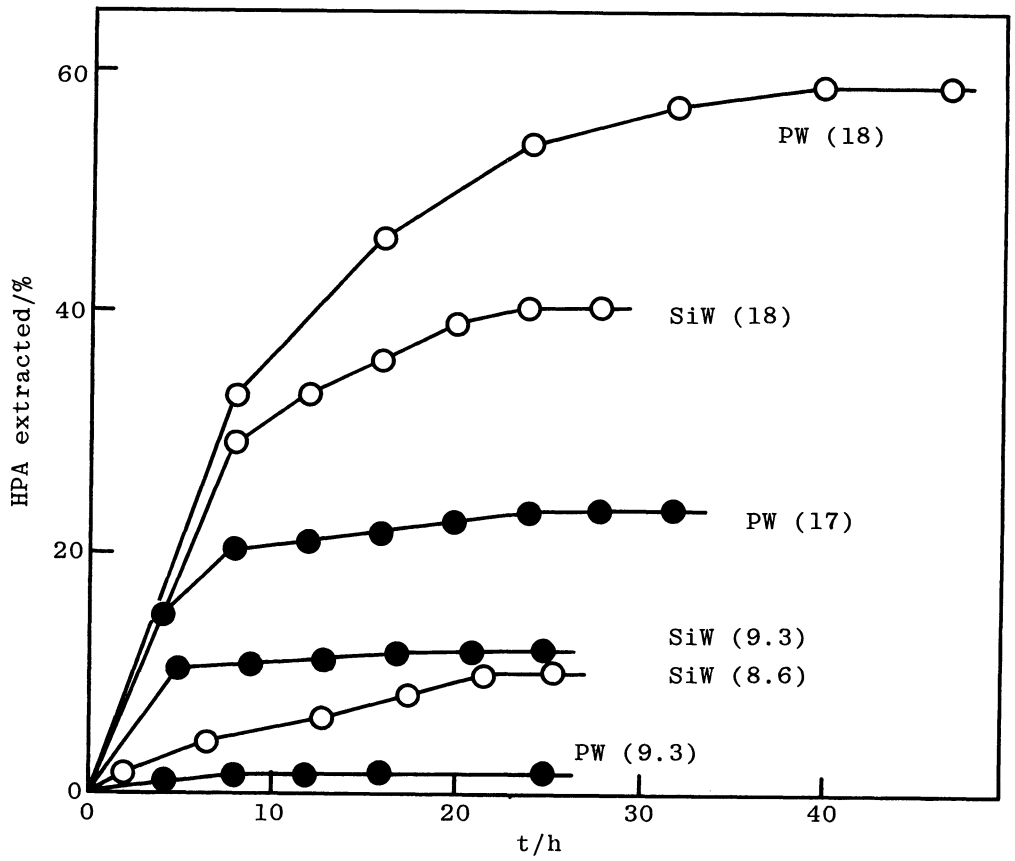

Fig. 1. Extraction of heteropoly acids supported on carbon with water(-○-) and methanol(-●-). PW:$H_3PW_{12}O_{40}$, SiW:$H_4SiW_{12}O_{40}$. The values in the parentheses denote the initial HPA contents (wt. %) before extraction.

also unsuitable owing to its surface basicity to cause the decomposition of HPA[8]. The unique property of activated carbon to entrap HPA appears to be due to its specific micro pore structure.

The 12-tungstophosphoric acid entrapped in carbon catalyzed the dehydration of butanol and *tert*-butyl alcohol to form butyl *tert*-butyl ether at 106°C in the liquid-phase suspension system (Table 1)[9]. Neither dibutyl ether nor isobutene was formed under this reaction condition. The reaction was repeated several times using the recovered catalyst by renewing the reactants. Through all the runs, no leakage of HPA from the carbon support was observed and the catalytic activity remained unchanged. The carbon itself had no activity for this reaction.

When a mixture of acetic acid and ethanol was allowed to flow over the 12-tungstosilicic acid entrapped in carbon at 120-150°C, a high yield of ethyl acetate was obtained (Table 2)[9]. The same catalytic activity held for a prolonged period of continuous operation (14 hours) at 105°C using the entrapped catalyst. No HPA was detected in the liquid product collected during the operation. The entrapped catalyst was nearly comparable in its efficiency for the esterification to Nafion-H catalyst which has recently been reported to be highly active for the

Table 1. Liquid-phase Dehydration of Butanol and *tert*-Butyl Alcohol into Butyl *tert*-Butyl Ether at 106°C using 12-Tungstophosphoric Acid entrapped in Carbon

Reaction repeated	*t*-BuOH conversion, %			
	30 min	60 min	90 min	120 min
1	12	22	29	35
2	14	24	31	36
3	13	23	30	36
4	14	22	29	36

a) An entrapped catalyst (0.58g) with an HPA content of 13.9 wt.%, which was obtained by methanol extraction, was added to butanol (5 ml) and *tert*-butyl alcohol (2 ml).

Table 2. Vapor-phase Esterification of Acetic Acid with Ethanol catalyzed by 12-Tungstosilicic Acid

Catalyst	Reaction temperature, °C	AcOH conversion, %[a)]	EtOH selectivity to AcOEt, %[a)]
Entrapped in carbon[b)]	150	95	99.5
Entrapped in carbon[b)]	120	83	99.7
Supported on silica[c)]	150	94	71.8
Carbon[d)]	150	22	100

a) Mean values during 4-7 hours later from the start of the reaction at a GHSV° of 347 h^{-1}.
b) The catalyst with an HPA content of 10.8 wt.% was prepared by water extraction.
c) The catalyst with an HPA content of 10.8 wt.% was prepared by impregnation method using a silica (Wakogel Q-22).
d) The same carbon as used for the entrapped catalyst.

same reaction in the vapor phase[10)]. It is noted that the formation of diethyl ether was remarkably suppressed when the entrapped catalyst was applied. On the other hand a silica-supported HPA catalyst having the same HPA content with the entrapped catalyst yielded a considerable amount of diethyl ether as a by-product.

The HPA entrapped in activated carbon will be conveniently applied as solid catalysts to several reactions not only in the liquid phase but also in the vapor phase.

References and Notes

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6) The activated carbon with the particle sizes of 0.4-0.7 mm was added to a methanol solution of HPA and the solvent methanol was removed under evacuation at 40°C.
7) The HPA extracted into solvents was determined by means of UV spectrometry using the wavelengths of 260 and 265 nm for aqueous and methanol solutions, respectively.
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9) The reaction products were analyzed by means of g.l.c. Butyl *tert*-butyl ether was identified by its ^{1}H-NMR spectrum and ethyl acetate by its IR spectrum.
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