One-pot Synthesis of Inorganic–Organic Hollow Microsphere Solid-Acid Catalysts in a W/O Microemulsion System

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Acid-supporting hollow microspheres were successfully prepared through a novel synthetic procedure on the introduction of a catalytic active species in the void space; one-pot synthesis was achieved by addition of 12-tungstophosphoric acid to the aqueous phase in a water-in-oil emulsion and simultaneous formation of a polyorganosiloxane shell (precursors are in oil phase) through sol–gel reactions. The resulting solid was porous and was active as solid-acid catalyst as shown by vapor-phase dehydration of ethanol.

Structural design of catalysts is an important aspect for the improvement of catalytic activity and selectivity. Carbon nanotubes,[1] mesoporous materials,[2] and zeolite membranes,[3] for example, possess characteristic shapes and are noted as highly designed catalysts. Hollow microspheres[4] are also interesting as highly designed catalysts with many advantages. We have reported the successful preparation of hollow microspheres from alkyltrichlorosilanes by using W/O emulsion and that the produced particles composed of polyorganosiloxane are microporous and hydrophobic.[5] The void space in the particle can be used as a catalyst container, and the shell of the particle can be regarded as a kind of membrane. It was recently reported that the shell of the hollow microspheres has played a role in molecular sieving[6] to reveal reaction selectivity and inhibition of supported metal agglomeration[7] to maintain catalyst lifetime.

Here we apply hollow microspheres as a catalyst container, namely, introduction of 12-tungstophosphoric acid (TPA) in the void space of hollow particles as a new supported acid catalyst. There are many reports on the preparation of heteropoly-acid-mounted catalysts[8] because heteropoly acids themselves act as strong acids without corrosion of equipment.[9] While most of the supported catalysts have been prepared by impregnation, one-pot synthesis can be achieved here by directly addition of TPA to W/O emulsion and simultaneous formation of a polyorganosiloxane shell through sol–gel reactions. In addition, hydrophobic characteristics of hollow particles derived from polyorganosiloxane is a merit when using for catalytic reactions such as oxidation of a hydrophobic reactant and dehydration to protect active sites from poisoning by water, improving catalytic activities. In the present study, vapor-phase dehydration of ethanol has been examined as a test reaction to elucidate the catalytic properties of the hollow microsphere supported acid catalysts.

A W/O microemulsion was formed by ultrasonic agitation of a mixture of octyltrichlorosilane (12 mmol) dissolved in toluene (50 mL) with aqueous TPA solution (50 mM, 0.79 mL). Then methyltrichlorosilane (9.0 mmol) dissolved in toluene (10 mL) was added to the emulsion to form hollow microsphere under magnetic stirring for 3 h with air flow (abbreviated as TPA-HMS). In the other case, a small amount of sorbitan monostearate (Span 60) was added in addition to octyltrichlorosilane (molar ratio of octyltrichlorosilane to Span 60 was 19) (abbreviated as S-TPA-HMS). The resulting solids were washed with toluene and subsequently dried at 393 K. The dehydration of ethanol was carried out under N_2 flow by using a fixed-bed flow reactor.[10] All of the sample catalysts were activated in air at 673 K for 3 h (Method of the sample preparation was summarized in Scheme[14]).

FE-SEM observation, as exemplified in Figure 1, revealed that all of the samples are microsphere with a cavity in each of the particles. In some cases, the shape of the particles is not a good sphere but deformed. The particle sizes are in a range of 1–4 µm (thickness of the shell: a few hundred nm) for TPA-HMS. When Span 60 was used as additive, the particle size has decreased to a range of 0.4–1 µm (thickness of the shell: below one hundred nm). It is thought that Span 60 acts as a strong emulsifier to give relatively stable microemulsion compared to that without Span 60. By crushing the particles by mortar and pestle, a cavity is observed in each particle, showing hollow particles. The supported quantities of TPA are $7–9 \times 10^{-2}$ and $2–3 \times 10^{-1}$ mmol/g for TPA-HMS and S-TPA-HMS, respectively.[11] In the XRD patterns (see Supporting Information, Figure S1),[14] TPA exists in both hollow particles as crystals with a particle size of ca. 20 nm (estimated from the Scherrer equation). From IR spectra of samples heat-treated at 673 K (see Supporting Information Figure S2),[14] absorption bands due to alkyl groups (νC–H) and Si–C bonds (δC–Si–C) are observed at around 2900 and 1400 cm^{-1}, respectively, showing that prepared microspheres are on organic–inorganic hybrid material showing hydrophobicity and are stable below 673 K.

Porosity has been shown only when the products are heat-treated at 673 K (N_2 adsorption/desorption isotherms are shown in Figure S3).[14] In our previous comnunication,[5] specific surface

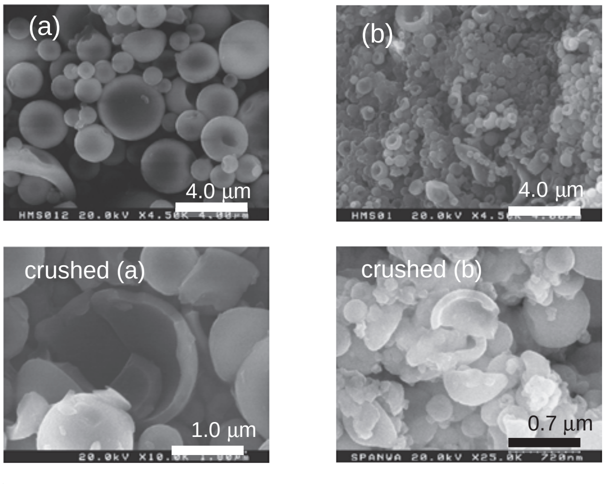

Figure 1. SEM images of (a) TPA-HMS and (b) S-TPA-HMS.

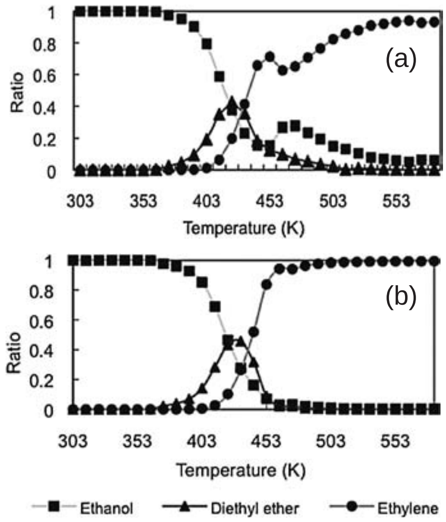

Figure 2. Reaction profiles of the ethanol conversion for (a) TPA-HMS and (b) S-TPA-HMS.

area of HMS (containing no TPA) without the heat-treatment was shown to be extremely small ($\approx 0\,m^2/g$). We have assumed that the sample (dried at 393 K) is composed of polyorganosiloxane including octyl and methyl groups and that the wall turns to polymethylsiloxane by treating at 673 K by losing octyl group, becoming microporous. When Span is used as the additive, the isotherm is type IV, indicating micro/mesoporous bimodal product. BET surface areas of TPA-HMS and S-TPA-HMS are 317 and $353\,m^2/g$, respectively.

As exemplified in Figure 2, both of the catalysts are active for dehydration of ethanol, suggesting that ethanol can access the catalytic sites through the shell of the microspheres and that the produced diethyl ether and ethylene can also pass through the shells. Notably, conversion to ethylene for S-TPA-HMS is almost 1 when the reaction temperature is 463 K, while diethyl ether forms for TPA-HMS even at 573 K. We assume that the difference in the reaction profile is derived mainly from the particle morphology; by being thin walled, relatively larger amounts of TPA can take part in the catalytic action.

The activity of ethanol conversion to diethyl ether for the hollow solid-acid catalyst (TPA-HMS) was compared with TPA supported on mesoporous silica (MCM-41).[12] It is shown that both TPA-HMS- and TPA-supporting MCM-41 are active as diethyl ether formation catalyst at 403 K but the activity of the former is about six times higher than that of the latter, even when the supported amount of TPA on the hollow microsphere ($7\text{–}9 \times 10^{-2}$ mmol/g) is close to that on MCM-41 (1.1×10^{-1} mmol/g) (Figure S4).[14] It was reported that the dehydration activity for alcohols (1-butanol) was improved by using organically modified silica (SBA-15 modified by ethane group) owing to the reduction of the acid-site deactivation associated with adsorption of water generated by the reactions.[13] The observed higher activity in the present system implies that the hydrophobicity of the TPA-HMS derived from methyl groups is effective for low-temperature dehydration reactions.

In conclusion, it has been demonstrated that TPA-supporting hollow microspheres are successfully prepared by using W/O emulsion and are active as solid-acid catalysts. The catalytic activity differs by changing the morphology (mainly the wall thickness) of the hollow sphere as well as imparting hydrophobicity to their surfaces. Efforts to improve various catalytic performance through morphosynthesis of a series of polyorganosiloxane hollow microsphere catalysts (control of shell thickness, particle size distribution, dispersion of catalytically active species and so on) are being made.

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10 The ethanol dehydration reaction was carried out in a temperature range of 303–573 K with a heating rate of 1 K/min under N_2 flow. Ethanol was supplied from a bubbler (273 K) to catalyst (0.05 g) with W/F of 36.6. Conversion of ethanol and yields of ethylene and of diethyl ether were determined by GC-FID.
11 The amounts of the supported TPA were based on the assumption that all of the added TPA deposited on the hollow microspheres. The amount of the hollow microsphere was estimated from subtracting the added TPA amount from yields of TPA-supporting catalysts. The ranges were obtained from duplicates.
12 Aqueous TPA (0.336 g) solution (4 mL) was impregnated in 1.0 g of MCM-41 and the product was dried at 323 K. Before the catalytic reactions, the catalyst was activated by heat-treatment at 393 K. The amount of supported TPA was 1.1×10^{-1} mmol/g.
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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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