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Encapsulation of a Polyoxometalate into an Organosilica Microcapsule for Highly Active Solid Acid Catalysis

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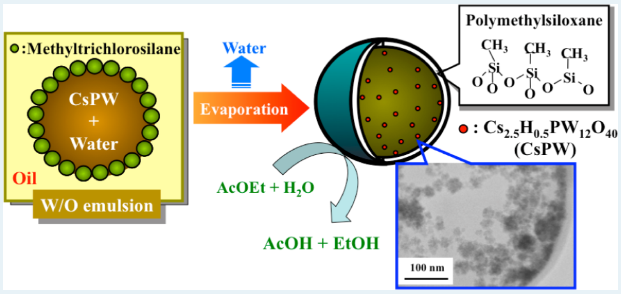
Supporting Information

ABSTRACT: We have developed a highly active and water-tolerant solid acid catalyst by encapsulating a polyoxometalate into hydrophobic hollow polymethylsiloxane microspherical particles. 12-Tungstophosphoric acid and a cesium salt of a heteropoly acid ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$, abbreviated as CsPW) were used for this purpose. The encapsulated catalysts were prepared by a sol−gel reaction of methyltrichlorosilane around water droplets containing heteropoly compounds in a water-in-oil emulsion. Both the catalysts were active in the hydrolysis of ethyl acetate in a large excess of water. While the 12-tungstophosphoric acid in the polymethylsiloxane microcapsules leached into the water during the repetition of the reaction, the activity of the CsPW encapsulated catalyst (0.86 $\text{mol}\cdot(\text{acid-mol})^{-1}\cdot\text{min}^{-1}$) was maintained. This activity was superior to that of bare cesium salt (0.34 $\text{mol}\cdot(\text{acid-mol})^{-1}\cdot\text{min}^{-1}$). To our knowledge, the CsPW encapsulated catalyst exhibits the highest activity among solid acid catalysts with respect to reaction rate per acidic proton. The polymethylsiloxane shell plays several roles including shielding of CsPW and allowing penetration of reactants (ethyl acetate and water) and products (ethanol and acetic acid) through the microporous membrane.



KEYWORDS: *tungstophosphoric heteropoly acid, cesium salt, encapsulation, silica, water-tolerant catalyst*

1. INTRODUCTION

The morphological design of catalysts is an important aspect for improving their catalytic activity and selectivity. Well-defined morphology, as exemplified by carbon fibers,[1] layered solid platelets,[2−4] nanoporous solid films,[5,6] and zeolite membranes,[7] has been recognized as being beneficial in the design of catalyst supports. Hollow microspheres[8,9] are also interesting as highly designed catalysts with numerous advantages; the void space in the particles can be used as a catalyst container, and the shell of the particle can be regarded as a type of membrane. The shell of the hollow microspheres has been reported to play a role in molecular sieving[10] to reveal reaction selectivity and to act as a retardant of supported metal agglomeration[11−14] for maintaining the lifetime of a catalyst.

Solid acid catalysts are well-known materials employed in a wide variety of industrial applications.[15] Although liquid acids such as H_2SO_4 and $AlCl_3$ are still utilized in the chemical industry, the replacement of the liquid catalysts with solid acids is desirable for the development of environmentally benign processes.[16,17] Water-tolerant solid acid catalysts have been developed to prevent the degradation of the catalytic activities of solid acids in aqueous solutions. The highly active solid acids in water, as reported in the literature, include H-ZSM-5 zeolite,[18,19] niobium oxide,[20] ion exchange resins (e.g., Nafion and Amberlyst-15), and sulfated amorphous carbons.[21]

Heteropoly acids (polyoxometalates) are water-soluble acid catalysts employed in various acid-catalyzed reactions,[17] and their supported heteropoly acid catalysts have been shown to function as solid acids in water.[22−24] An acidic cesium salt of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, HPW), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), is also highly active in acid-catalyzed reactions and is recognized as a water-tolerant catalyst.[25] However, leaching out and less sedimentation of the polyoxometalates during the reactions are problematic. Inumaru et al.[26] improved the catalytic activity of HPW molecules by immobilizing them in the nanospaces of organografted mesoporous silica. Horita et al.[27] reported that CsPW can be immobilized on organofunctionalized silica. A magnetically collectable solid acid has been produced via incorporation with a magnetic compound.[28] Acid−base interactions of heteropoly compounds with 3-aminopropyl groups in organosilicas have been adopted to prevent leaching of the heteropoly compounds into water. Encapsulation of heteropoly compounds into mesoporous molecular sieves,[29] a metal−organic framework (MOF),[30] and spherical silica microspheres[31,32] has been proposed as another approach.

Here, we report an alternative method to immobilize CsPW; we encapsulated the CsPW fine particles in a hollow polymethylsiloxane microsphere with a thin shell (Scheme 1). The synthetic approach was based on the deposition of an

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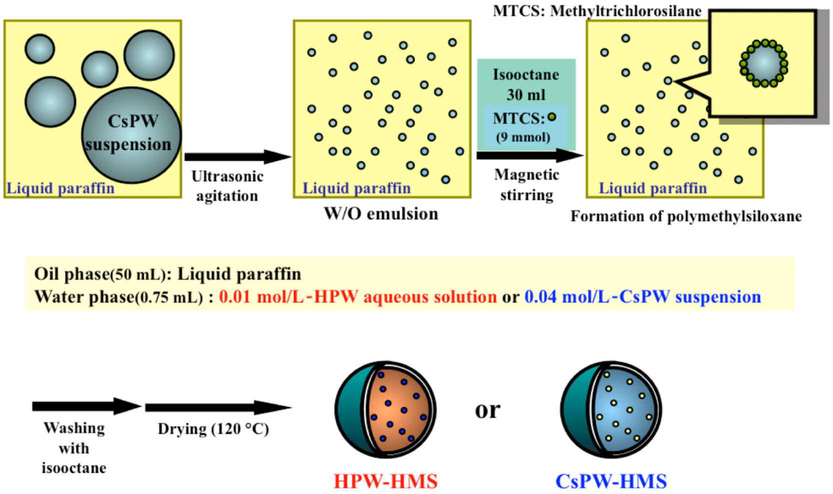
Scheme 1. Schematic Drawing of the Preparation of Polyoxometalate-Encapsulated HMS Catalysts



organosilica shell on water droplets in a water-in-oil (W/O) emulsion through a sol−gel reaction of alkylsilyl trichlorides.[33] When a specific compound (e.g., an acid catalyst[34] or precursors of magnetic compounds[35,36]) is included in the water droplets, vaporization of the water leads to encapsulation by the organosilica shell. In the present system, droplets of an aqueous CsPW suspension were dispersed in viscous liquid paraffin to create a W/O emulsion with good dispersion stability, and methyltrichlorosilane (MTCS) was subsequently hydrolyzed on the droplets to form CsPW−polymethylsilane microcapsules. As a result of water vaporization, CsPW fine particles were successfully immobilized into the capsules without the application of definite acid−base interactions. The polymethylsiloxane shell allowed the penetration of reactants (i.e., ethyl acetate and water) to promote the acid-catalyzed hydrolysis reactions in water and prevented the deactivation due to leaching of heteropoly compounds into the aqueous phase. Water-soluble HPW was also encapsulated to compare its reusability as a water-tolerant solid acid catalyst.

2. EXPERIMENTAL SECTION

2-1. Materials. Octyltrichlorosilane (OTCS) and MTCS were purchased from Aldrich Chemical Co., Ltd., and Shin-Etsu Chemical Co., Ltd., respectively. HPW, cesium carbonate, isooctane (2,2,4-trimethylpentane), and liquid paraffin were purchased from Wako Chemical Co., Ltd.. These chemicals were used without further purification.

2-2. Preparation of an Acidic Cs Salt of 12-Tungstophosphoric Acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW). CsPW was prepared by titration of an aqueous solution of HPW with an aqueous solution of Cs_2CO_3, according to the reported procedure.[37] The molar concentrations of the aqueous HPW and Cs_2CO_3 solutions were 0.08 and 0.10 M, respectively. We obtained an aqueous suspension of CsPW (0.04 M) by aging the resulting mixture for at least 1 day after the titration.

2-3. Preparation of Catalysts by Encapsulating CsPW and HPW into Hollow Polymethylsiloxane Microspherical (HMS) Particles. A W/O emulsion was created by mixing 0.01 M aqueous HPW solution (0.75 mL) and liquid paraffin (50 mL) by ultrasonic agitation. After 5 min of ultrasonic irradiation (19.5 kHz, 15 W/mm^2, ultrasonic homogenizer, US-600T produced by Nihon Seiki Seisakujo Co., Ltd.), the mixture was allowed to stand for 5 min at room temperature. The ultrasonic agitation was repeated five times. MTCS (1.35 g) in isooctane (30 mL) was poured into the W/O emulsion under magnetic stirring. The mixture was stirred at room temperature for more than 3 h to form a polymethylsiloxane shell around aqueous droplets. During the reaction, air with saturated water vapor (ca. 0.1 L/min) was continuously supplied. After centrifugation, the product was washed with isooctane and then dried at 323 K for 1 day. The dried product (abbreviated as HPW-HMS) was heated at 393 K in air for 1 day. Rather than using aqueous HPW solution as the water phase, a 0.04 M CsPW aqueous suspension (0.75 mL) was added to enclose CsPW in HMS (abbreviated as CsPW-HMS). HMS particles that did not contain these polyoxometalates were also prepared by the same procedure, except that deionized water was used as the water phase for the W/O emulsion. The amount of heteropoly compounds in the products was estimated from the tungsten contents in water by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after it was converted to aqueous form by alkali fusion.

2-4. Hydrolysis of Ethyl Acetate in Aqueous Solution. The hydrolysis of ethyl acetate was conducted in a two-neck Pyrex flask equipped with a refluxing condenser and a thermometer. The reaction was performed using an aqueous solution of ethyl acetate (30 mL, 18 mmol of ethyl acetate) at 343 K for 2 h with stirring. The amount of polyoxometalates used was 1.25×10^{-5} mol. A recycling reaction was performed with the CsPW and HPW-HMS catalysts. After the first run, the catalyst in the solution was recovered by filtration (Millipore, Omnipore PTFE membrane, 0.2 μm). After being dried at room temperature, the catalysts were used for the next run without any activation. This reaction was repeated three times. The reactant and product (ethanol and acetic acid) were commercially guaranteed grade reactants (Wako Pure Chemicals) and were used as received. All the solutions were prepared from Elix UV pure water (Millipore). The products were analyzed with a gas chromatograph using a DB-WAX capillary column (Agilent J&W).

2-5. Instrument. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku RINT 2200 V/PC diffractometer (monochromatic Cu Kα radiation), operated at 20 mA and 40 kV. Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR-4200 spectrophotometer by the KBr pellet method, and nitrogen adsorption−desorption isotherms were measured at 77 K on a Belsorp-mini (BEL Japan, Inc.). Before the adsorption experiments, the samples were heat-treated at 393 K under reduced pressure. Scanning electron microscopy (SEM) images were captured on a Hitachi S-4100 field-emission scanning electron microscope, operated at 15 kV. Scanning transmission electron microscopy (STEM) observations were conducted on a Hitachi High-Tech HD-2300A scanning transmission electron microscope and a JEOL JEM-2010 transmission electron microscope, operated at an acceleration voltage of 200 kV. ICP-AES was performed on a Shimadzu ICPS-7500 spectrometer. Elemental mapping images were obtained using a Shimadzu EPMA-1610 electron probe microanalyzer. Gas chromatography was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector.

3. RESULTS AND DISCUSSION

3-1. Preparation of Catalysts. When an HPW aqueous solution or a CsPW aqueous suspension (0.75 mL) was dispersed in liquid paraffin (50 mL) by ultrasonic agitation, a stable suspension was obtained as a W/O emulsion. The addition of MTCS induced precipitation in both cases where polyoxometalates were employed. SEM observations of the dried samples (CsPW-HMS and HPW-HMS), as exemplified in Figure 1, revealed that the samples contained spherical particles and that a certain portion of the samples exhibited a cup-shaped morphology. The sizes of the particles range from 0.1−3 and 0.1−2 μm for CsPW-HMS and HPW-HMS, respectively. The FTIR absorption bands of C−H (2960 and 1450 cm^{-1}), Si−C (1270 cm^{-1}), and Si−O−Si (1100−1000 cm^{-1}) bonds were observed (Supporting Information, Figure S1). Thus, hydrolyzed MTCS was polymerized around the droplets in liquid paraffin to produce polymethylsiloxane particles. The specific surface areas derived from Brunauer−Emmett−Teller (BET) plots of N_2 adsorption isotherms (Supporting Information, Figure S2) are listed in Table 1. Among the tested solids, CsPW-HMS exhibited a higher surface area (117 m^2/g), indicating the formation of a microporous polymethylsiloxane shell.

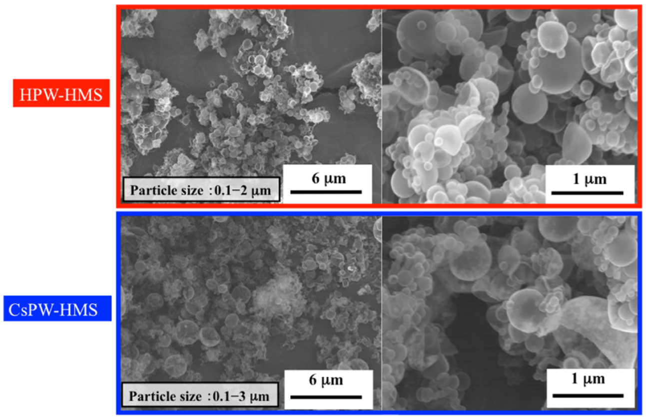


Figure 1. SEM images of HPW-HMS and CsPW-HMS catalysts.

Table 1. BET Surface Areas and Pore Volumes of the Samples

sample	BET surface area/m^2·g^{-1}	pore volume/10^{-2} cm^3·g^{-1} total	micropore[a]	mesopore[b]
CsPW-HMS	117	7.0	0.4	6.6
HPW-HMS	17	2.6	0.4	2.2
CsPW	157	16.9	10.3	6.6
HMS	28	0.057	0.3	5.4

[a] *t*-plot. [b] Barrett−Joyner−Halenda (BJH) method.

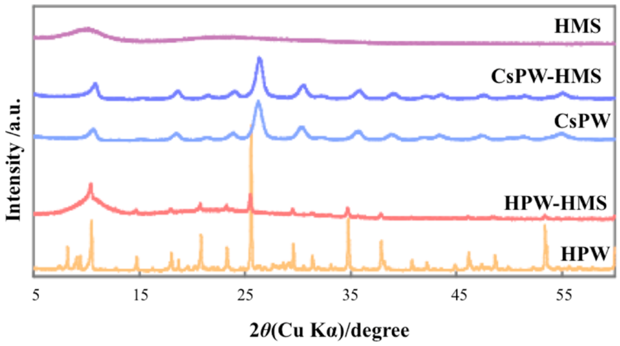


Figure 2. XRD patterns of the polyoxometalate-enclosed catalyst, HMS, and polyoxometalates.

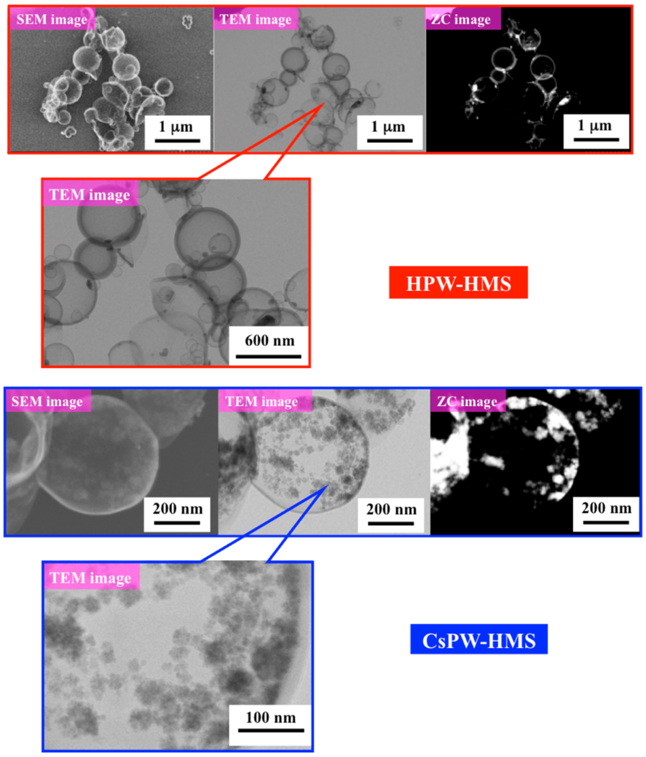


Figure 3. SEM images, bright-field TEM images, and dark-field STEM images of (top) HPW-HMS and (bottom) CsPW-HMS.

XRD patterns of the products are shown in Figure 2 together with those of CsPW, HPW, and HMS (without the polyoxometalates). HMS was shown to be amorphous. In the cases of CsPW-HMS and HPW-HMS, diffraction peaks due to the polyoxometalates were observed in their XRD patterns, and the positions of the peaks were identical to those of bare CsPW and HPW crystals, respectively; these results indicate that each heteropoly compound was included in HMS as a crystal. The amounts of HPW and CsPW included in the dried samples

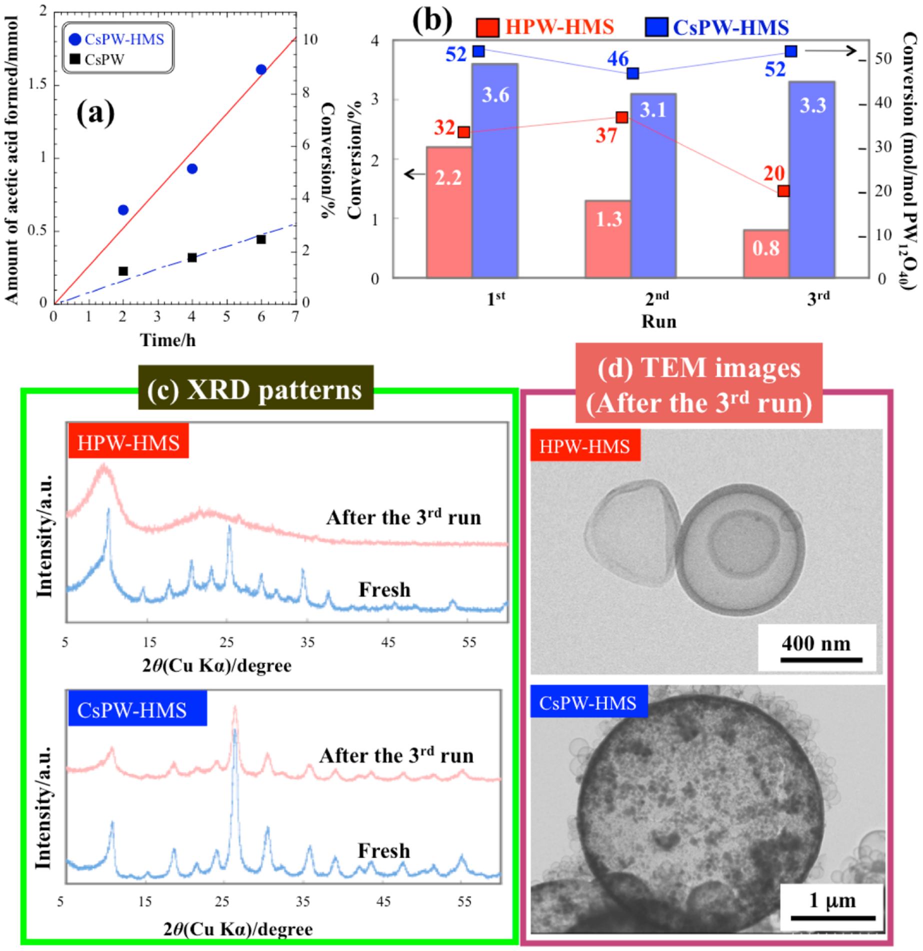


Figure 4. (a) Time courses of hydrolysis of ethyl acetate over CsPW-HMS and bare CsPW (amount of CsPW: 1.25 × 10^{-5} mol), (b) changes in conversion with repeated reactions (2 h for each run), (c) change in the XRD patterns of the polyoxometalate encapsulated by HMS after the third run of the hydrolysis reaction, and (d) TEM images captured after the third run.

Table 2. Catalytic Activity in the Hydrolysis of Ethyl Acetate in Water

			reaction rate		
catalyst	state of the catalyst	acid amount/mmol·g^{-1}	per catalyst weight/μmol·g^{-1}·min^{-1}	per acidic proton/mol·(acid-mol)$^{-1}$·min^{-1}	recovery[b] (%)
CsPW-HMS	solid	0.021	18	0.86	94
CsPW	solid	0.15	51	0.34	0
HPW-HMS	solid	0.010	0.92	0.092	97
HPW	liquid	1.0	84	0.084	0
H-ZSM-5[a]	solid	0.39	28	0.070	
γ-Al_2O_3[a]	solid	0.47	0	0	
H_2SO_4[a]	liquid	19.8	992	0.046	
HMS	solid		0	0	93

[a] Reference 25. [b] Ratio of the mass of catalyst collected by filtration (Millipore, Omnipore PTFE membrane, 0.2 μm) to the mass of catalyst added (*w*/*w*).

were 3 and 7 mass%, respectively. Figure 3 shows SEM, bright-field transmission electron microscopy (TEM), and dark-field STEM images of both samples. The dark-field STEM images confirmed that the core and shell were composed of polyoxometalates and organosilica, respectively, because the contrast of the core is greater than that of the shell. Notably, rattle-type core−shell structures were readily observed in the bright-field TEM images because of the thin polymethylsiloxane shell with a thickness of 20−30 nm. HPW existed as relatively large crystals within the hollow particles, whereas CsPW existed as minute particles (ca. 10 nm) on the internal surface of HMS. The crystal sizes of HPW and CsPW in the capsules were estimated, by Scherrer's equation from the XRD patterns, to be 44 and 11 nm, respectively. A majority of the CsPW was dispersed as nanoparticles inside HMS rather than being agglomerated. All the particles contained CsPW as confirmed by the elemental map of tungsten (Supporting Information, Figure S3).

3-2. Hydrolysis of Ethyl Acetate in Water. Figure 4a shows the time course of the hydrolysis of ethyl acetate over CsPW-HMS together with that of the hydrolysis over pristine CsPW. Both reactions proceeded in a catalytic manner under the present conditions, as shown in this figure. The products were only acetic acid and ethanol. Interestingly, the turnover frequency for CsPW-HMS per unit acid site was much higher (40 molecules h^{-1}), as indicated by the slope of the line in this figure; this turnover frequency was greater than that for the bare CsPW by 3-fold, even when the CsPW crystals were encapsulated by the polymethylsiloxane shell. The catalytic activities of various solid and liquid acids in the hydrolysis of ethyl acetate are summarized in Table 2. The activity was estimated from the amount of acetic acid produced after 2 h of the reaction and was normalized by unit time and amount of catalyst. Most inorganic solid acid catalysts (e.g., γ-Al_2O_3, HY zeolite, and SiO_2−Al_2O_3) have been reported to be inactive in water with the exception of H-ZSM-5 and Nb_2O_5.[25] HMS itself was also inactive in the hydrolysis reaction. The activity of the present CsPW-HMS catalyst exceeded those of other catalysts including H_2SO_4, HPW, and HPW-HMS with respect to reaction rate per acidic proton.

Figure 4b shows the changes in the catalytic activities of CsPW-HMS and HPW-HMS when the reaction was repeated three times. After the first run, the activity of HPW-HMS gradually decreased when it was filtered and reused during the reaction period. After the third run, HPW crystals were not observed in the XRD pattern (Figure 4c) and the TEM image (Figure 4d) of the catalyst. ICP analysis showed that HPW-HMS contained 40% of the total HPW. The deactivation is explained by leaching of HPW into the aqueous solution. However, the activity of CsPW-HMS was almost unchanged. In addition, the CsPW-HMS catalyst was readily recovered by filtration from aqueous media because of the occlusion of CsPW by hollow polymethylsiloxane microspherical particles, although CsPW passed through the filter paper (Table 2). XRD and TEM results (Figures 4c−d) reveal that CsPW crystals remained in the microcapsules of HMS after the third run. Although a half amount of HPW (5 μmol) was lost by leaching after the first run, as confirmed by the ICP analysis, 3% of the encapsulated heteropoly compounds in CsPW-HMS (5 μmol) was lost, probably due to leaching HPW in CsPW.[38−40] In the case where CsPW was mounted on the external surface of HMS by an impregnation method, no activity was observed after the first run due to the lack of CsPW on HMS (results of STEM observations are summarized in the Supporting Information, Figure S4). Thus, the polymethylsiloxane microcapsules serve as good reaction containers for solid acid catalysis by enclosing water-tolerant ultrafine CsPW particles.

To our knowledge, the catalytic activity in the CsPW-HMS system (0.86 mol·$(\text{acid-mol})^{-1}$·min^{-1}) is the highest among known solid acid catalysts. Because the polymethylsiloxane shell formed around the aqueous droplets of the CsPW suspension, the CsPW crystals may enfold around the aqueous droplets during the polymerization of the hydrolyzed MTCS. The larger surface area of CsPW-HMS (117 m^2/g of the sample containing 7 mass% of CsPW) compared with those of CsPW (157 m^2/g), HMS (28 m^2/g), and HPW-HMS (17 m^2/g) is probably due to the formation of nanospaces around the CsPW ultrafine particles, which results from the intertwining of polymethylsiloxane polymers with CsPW crystals. Inumaru et al. have reported that acidic protons of HPW in a hydrophobic environment of octyl groups in a mesopore exhibit extremely high catalytic activities in the hydrolysis of ester in water.[26] In the case of the present system, we deduce that the hydrophobic environment around CsPW in the polymethylsiloxane shell should lead to greater activity in the hydrolysis of ester in water. The enfolding of CsPW into the polymethylsiloxane shell during the MTCS polymerization may cause the production of leaching-free CsPW catalyst in the aqueous media.

4. CONCLUSIONS

CsPW nanocrystals were successfully incorporated into polymethylsiloxane hollow microspheres without the use of definite acid−base interactions to produce a highly active and readily collectable heterogeneous solid acid catalyst in water. This incorporation was achieved by the hydrolysis and polymerization of MTCS in a W/O emulsion system composed of liquid paraffin (oil phase) and an aqueous suspension of CsPW (water phase). The produced microcapsules hydrolyzed ethyl acetate in water, and the activity was superior to that over bare CsPW with respect to the reaction rate per acidic proton. The activity did not decrease when the reaction tests were repeated. The polymethylsiloxane thin shell shielded the CsPW nanoparticles against deactivation due to leaching heteropoly compounds and acted as a microporous membrane that allowed the penetration of the reactants (ethyl acetate and water) and products (ethanol and acetic acid).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

FTIR spectra (HMS and heteropoly compounds encapsulated by HMS, Figure S1), nitrogen adsorption−desorption isotherms of HMS and heteropoly compound-enclosed HMS and their pore size distributions (Figure S2), BEI and elemental mapping images of Si and W for CsPW-HMS particles (Figure S3), and SEM, bright-field TEM, and dark-field STEM images of CsPW-mounted HMS particles (prepared by an impregnation method) captured before the hydrolysis of ethyl acetate in water and after the first run (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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