$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ Nanoparticles Fixed on Silica Encapsulating Magnetic Iron Oxide as a Magnetically Separable Water-tolerant Solid Acid

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$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ fixed on silica encapsulating iron oxide nanoparticles through (3-aminopropyl)triethoxysilane could magnetically be separated from an aqueous solution. The catalyst showed activity for the hydrolysis of ethyl acetate in the presence of excess water and was reusable without significant loss of its inherent activity.

Although liquid acids, such as H_2SO_4 and $AlCl_3$, are utilized in large amounts as acid catalysts for the production of various chemicals, they should be replaced with solid acids, which are environmentally benign with respect to corrosiveness, safety, waste generation, ease of separation, and recovery. However, for reactions in which water participates as a reactant or product, such as hydration, hydrolysis, and esterification, only a few solid acids show acceptable performance.

An acidic Cs salt of 12-tungstophosphoric acid, $Cs_{2.5}H_{0.5}$-$PW_{12}O_{40}$ (Cs2.5), is highly active in acid-catalyzed reactions, even in the presence of a large excess of water,[1] and thus, it is a promising water-tolerant solid acid catalyst. However, Cs2.5 itself has drawbacks, including leaching of the heteropoly species into and difficulty in sedimentation from an aqueous solution,[2] which make recycling the catalyst difficult.

Magnetic separation is a convenient method for removing magnetizable particles by applying an appropriate magnetic field.[3] It has been demonstrated that a composite material with a mesoporous silica shell and an iron oxide core can easily be separated from an ethanolic suspension by using a magnet.[4] Mori et al. have synthesized catalytically-active magnetizable materials, including a single-site Ti-containing hexagonal mesoporous silica encapsulating iron oxide[5] and a ruthenium-loaded hydroxyapatite encapsulating iron oxide.[6] These results prompted us to fix Cs2.5 on iron oxide (Fe_xO_y) in order to easily separate it from an aqueous solution. However, fixing Cs2.5 on the untouched Fe_xO_y had no success. Thus, we have worked on a solution to the problem. Herein, we report the synthesis of a magnetically separable water-tolerant solid acid composed of Cs2.5 fixed on silica encapsulating Fe_xO_y (Fe_xO_y@SiO_2) using (3-aminopropyl)triethoxy silcane (APS).

Fe_xO_y was prepared according to the reported method.[5] $FeCl_2 \cdot 4H_2O$ (2.0 mmol) and $FeCl_3 \cdot 6H_2O$ (4.0 mmol) were dissolved in deoxygenated distilled water (200 cm^3) at room temperature. Then, aqueous ammonia (4 cm^3, 25% concentration) was added, and the solution was stirred for 3 h at room temperature to form Fe_xO_y nanoparticles.

2-Propanol (100 cm^3) was added to the resulting black suspension, and the suspension was heated to 313 K. After 30 min, tetraethyl orthosilicate (TEOS, 60.0 mmol) was added, and the suspension was stirred at 313 K for 21 h. After evaporating the solvent, the resulting solid was calcined at 523 K for 2 h (Fe_xO_y@SiO_2). As described later, the amount of TEOS was critical for fixing Cs2.5 on Fe_xO_y@SiO_2 using APS.

The XRD pattern of Fe_xO_y@SiO_2 showed a broad diffraction line at around 20° due to amorphous silica and lines attributed to Fe_3O_4 or γ-Fe_2O_3 (Figure 1S).[7] In the XPS spectra of Fe_xO_y@SiO_2 (Figure 2S),[7] there were only very weak peaks due to Fe 2p3/2 and Fe 2p1/2, whereas intense peaks were observed for bare iron oxide nanoparticles, indicating that the silica shell almost completely covered the iron oxide nanoparticles.

Then the modification of Fe_xO_y@SiO_2 with APS was conducted. Fe_xO_y@SiO_2 (1.3 g) pretreated at 523 K in a vacuum was added to a toluene solution (120 cm^3) of APS (85.6 mmol) at room temperature under N_2. After the suspension was stirred at 393 K for 4 h, the solid was separated by filtration with a membrane filter and dried under vacuum at 423 K for 12 h (denoted as APS/Fe_xO_y@SiO_2).

The surface area estimated from N_2-adsorption isotherm of APS/Fe_xO_y@SiO_2 was 260 $m^2\,g^{-1}$. From CN chemical analysis (2.43 and 0.69 wt % for C and N, respectively, and the C/N molar ratio was 4.11), it was determined that APS/Fe_xO_y@SiO_2 contained 0.49 mmol of APS per gram of Fe_xO_y@SiO_2, which corresponds to a surface density of amino groups of 1.1 molecules nm^{-2}. The presence of amino groups on APS/Fe_xO_y@SiO_2 was confirmed from its catalytic activity for a base-catalyzed reaction (Knoevenagel condensation, Figure 3S).[7]

To an aqueous suspension (10 cm^3) of APS/Fe_xO_y@SiO_2 (0.5 g), a colloidal solution of Cs2.5 (0.5 g) was added to obtain Cs2.5–APS/Fe_xO_y@SiO_2. The loading amount of Cs2.5 was 50 wt %. The colloidal suspension of Cs2.5 was prepared in advance according to a previously published method.[8] Finally, the solid Cs2.5–APS/Fe_xO_y@SiO_2 was collected by filtration and dried at room temperature. Figure 1 shows SEM images of APS/Fe_xO_y@SiO_2 and Cs2.5–APS/Fe_xO_y@SiO_2. APS/Fe_xO_y@SiO_2 showed an egg-shaped smooth surface of about 50 nm in diameter (Figure 1a). For Cs2.5–APS/Fe_xO_y@SiO_2 (Figure 1b), nanoparticles about 12 nm, which is the size of the primary crystallite of Cs2.5,[8] were attached on APS/Fe_xO_y@SiO_2, and no aggregation of the nanoparticles was observed.

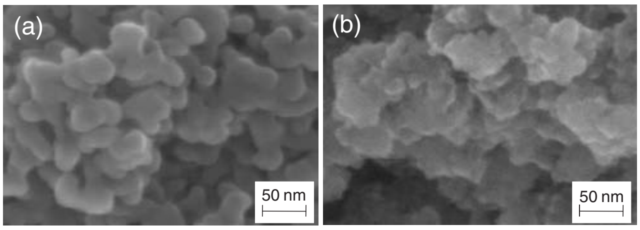

Figure 1. SEM images of (a) APS/Fe_xO_y@SiO_2 and (b) Cs2.5–APS/Fe_xO_y@SiO_2.

Figure 2. Separation of Cs2.5–APS/Fe_xO_y@SiO_2 from an aqueous solution containing ethyl acetate using an external magnet.

We showed that Cs2.5–APS/Fe_xO_y@SiO_2 could easily be separated in a few minutes from an aqueous solution containing 5 wt % ethyl acetate by placing a magnet near the glass tube. As shown in Figure 2, reddish-brown particles were attached to the wall, and a clear solution was obtained, indicating that Cs2.5–APS/Fe_xO_y@SiO_2 was magnetically separable. However, Cs2.5–APS/Fe_xO_y@SiO_2 containing a higher loading of Cs2.5 was not completely recovered (Figure 4S).[7] In other words, a clear solution was not obtained because the fixing of Cs2.5 was insufficient. In addition, when a smaller amount of TEOS (<60 mmol) was utilized, the fixing of Cs2.5 was also insufficient. In this case, the iron oxide surface was partially bare, which was confirmed by using XPS (Figure 2S) and functionalization of Fe_xO_y@SiO_2 surface was insufficient. In the case of the material that Cs2.5 was fixed on Fe_xO_y@SiO_2 without APS, Cs2.5 could not be recovered by a magnet, and the solution remained milky even when a magnet was placed near the glass tube (Figure 5S),[7] indicating that APS directly participates in the fixing Cs2.5 on APS/Fe_xO_y@SiO_2 with acid (Cs2.5)–base (APS) interaction.

The catalytic activity of Cs2.5–APS/Fe_xO_y@SiO_2 for the hydrolysis of ethyl acetate at 343 K for 2 h using 0.8 g of the catalyst in the presence of excess water was investigated. Fresh Cs2.5–APS/Fe_xO_y@SiO_2 gave 30% conversion (Figure 3). Upon completion of the reaction, the catalyst was attached to the wall of the glass reactor within a few minutes by placing a magnet outside the reactor. The recovered catalyst was collected for use in the next catalytic reaction after replacement of the reaction mixture with a fresh one. As Figure 3 demonstrates, Cs2.5–APS/Fe_xO_y@SiO_2 could be recycled without significant loss of its inherent activity at least four times. The amounts of leached heteropoly species and iron oxide were below the minimum limit of inductively coupled plasma (ICP) analysis. These results demonstrate that Cs2.5–APS/Fe_xO_y@SiO_2 is a magnetically separable and reusable water-tolerant solid acid.

In comparison, the reaction over Cs2.5 alone showed 45% conversion under similar reaction conditions using 0.4 g of the catalyst. The lower catalytic activity of Cs2.5–APS/Fe_xO_y@SiO_2 is due to the neutralization of the Cs2.5 protons with the amino groups on APS/Fe_xO_y@SiO_2 when it is fixed on APS/Fe_xO_y@SiO_2. This was confirmed because the Knoevenagel condensation did not progress (Figure 3S).[7] However, Cs2.5 alone could not be reused because the heteropoly species leached and because it is difficult to separate from an aqueous solution.[2] In other words, Cs2.5–APS/Fe_xO_y@SiO_2 is advantageous for practical applications.

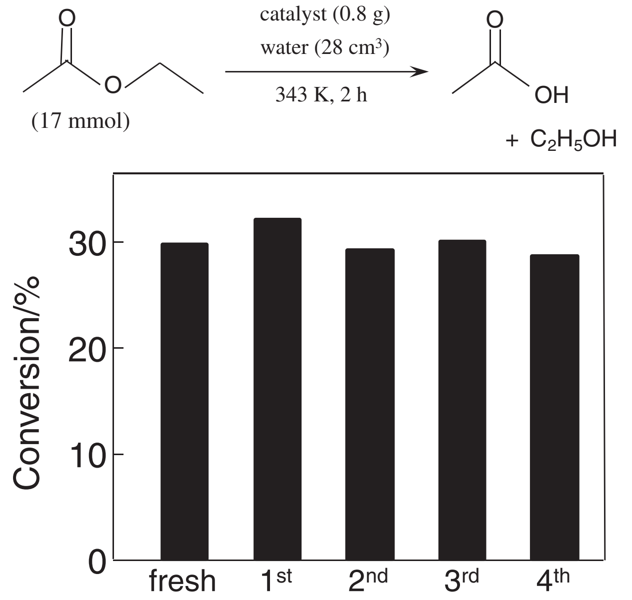

Figure 3. Hydrolysis of ethyl acetate in water over Cs2.5–APS/Fe_xO_y@SiO_2.

References and Notes

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