# $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ Bonded to an Amine Functionalized $SiO_2$ as an Excellent Water-tolerant Solid Acid

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Unlike $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$–$SiO_2$ composites combined using (3-aminopropyl)triethoxysilane are entirely insoluble and well sedimentable in reaction mixtures that contain a large excess of water. The catalytic activities for the hydration of olefin and hydrolysis of ester in the presence of excess water were comparable to those of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and were much higher than those of typical water-tolerant solid acids, such as H-ZSM-5 and $Nb_2O_5$.

Although liquid acids such as $H_2SO_4$ and $AlCl_3$ continue to be widely utilized in the chemical industry, these liquid acids should be replaced with solid acids, which are environmentally friendly with respect to corrosiveness, safety, waste generation, ease of separation, and recovery. However, in hydrolysis, hydration, and esterification, in which water participates as either a reactant or product, few solid acids exhibit acceptable activity.[1] High-silica H-ZSM-5 zeolite is the only commercial water-tolerant solid acid,[2] but it is limited to applications involving large-size reactants or products because of its small uniform pores.[3] Niobium oxide is reported to catalyze hydrolysis of phenyloxirane.[4] Some ion-exchange resins, such as Nafion and Amberlyst-15, exhibit high activity for water-related reactions. Recently, new classes of water-tolerant solid acid involving sulfuric acid-functionalized carbon material[5] and sulfated mesoporous silica[6] have been reported.

An acidic Cs salt of 12-tungstophosphoric acid, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (abbreviated as Cs2.5), is highly active for acid-catalyzed reactions, even if a large amount of excess water is present in the reaction mixture, being comparable to those of ion-exchange resins.[1,3] Thus, although recognized as a promising water-tolerant solid acid, Cs2.5 has drawbacks to be solved for its practical applications, that is, the leaching out of heteropoly species, and less-sedimentation in an aqueous phase under the reaction conditions. We herein report the synthesis of an entirely insoluble water-tolerant solid acid with high sedimentation consisting of Cs2.5 and amine-functionalized $SiO_2$ obtained from $SiO_2$ and (3-aminopropyl)triethoxysilane (abbreviated as APS), as well as the excellent water-tolerant catalysis properties thereof.

Cs2.5–$SiO_2$ composites were prepared using $SiO_2$ (Aerosil 50, $55\,m^2\,g^{-1}$), APS (Merck), and Cs2.5 as follows. $SiO_2$ (1.3 g) pretreated at 673 K in a vacuum was added to toluene solution ($200\,cm^3$) of APS (85.6 mmol) at room temperature in an atmosphere of $N_2$. After the suspension was mixed for 2 h at room temperature, the solid was separated by filtration with a membrane filter. The recovered solid was again dispersed in acidified water ($26\,cm^3$) including 6% aqueous HCl solution ($6\,cm^3$) and was separated and dried at 373 K (denote $SiO_2$–APS). CN elemental chemical analysis (0.28 and 1.10 wt % for N and C, respectively) confirmed that the $SiO_2$–APS contained 0.20 mmol of APS per gram of $SiO_2$, which corresponds to the surface density of $NH_2$, which is 2.3 molecules $nm^{-2}$. To the aqueous suspension of $SiO_2$–APS, a colloidal aqueous solution of Cs2.5 was added to obtain a composite consisting of $SiO_2$–APS and Cs2.5. The colloidal solution of Cs2.5 was prepared in advance using the method described in a previous paper.[7] Finally, the solid was again separated by filtration and then dried at room temperature (denoted $x$ wt % ($SiO_2$–APS)–Cs2.5, where $x$ wt % corresponds to the $SiO_2$–APS content).

The catalytic activities of 14 wt % ($SiO_2$–APS)–Cs2.5 for hydrolysis of ester and hydration of olefin are listed together with those of typical solid acids and Cs2.5 alone in Table 1. These reactions were performed in excess water using a glass reactor ($100\,cm^3$) under the reaction conditions described in the footnotes of Table 1. 14 wt % ($SiO_2$–APS)–Cs2.5 exhibited an activity (per unit weight of catalyst) comparable to those of Cs2.5, H-ZSM-5, and Amberlyst-15 for the hydrolysis of ethyl acetate, whereas $Nb_2O_5$ had a very low activity. Furthermore, 14 wt % ($SiO_2$–APS)–Cs2.5 was very highly active for the hydrolysis of bulky 2-methylphenyl acetate, while H-ZSM-5 was inactive. For the hydration of olefin, 14 wt % ($SiO_2$–APS)–Cs2.5 as well as Cs2.5 alone also showed a high activity comparable to Amberlyst-15 and superior in activity to H-ZSM-5 and $Nb_2O_5$. It should be noted that 14 wt % ($SiO_2$–APS)–Cs2.5 was more selective for hydration of α-pinene to α-terpineol than Cs2.5 and Amberlyst-15.

Figure 1 shows the effects of the content of $SiO_2$–APS in $x$ wt % ($SiO_2$–APS)–Cs2.5 on the conversion of ethyl acetate

**Table 1.** Catalytic data for water-related reactions for various water-tolerant solid acid

| Catalyst | Conversion/% | | | |
|---|---|---|---|---|
| | Hydrolysis | | Hydration | |
| | EA[a] | MPA[b] | DMB[c] | AP[d] |
| 14 wt % ($SiO_2$–APS)–Cs2.5[e] | 42 | 34 | 9 | 46(52) |
| Cs2.5[e] | 46 | 36 | 9 | 49(23) |
| H-ZSM-5 (Si/Al = 40)[f] | 44 | 0 | 5 | 0 |
| $Nb_2O_5$ | 2 | 1 | 0 | 0 |
| Amberlyst-15 | 43 | — | — | 56(27) |

[a]Hydrolysis of ethyl acetate (EA). Ethyl acetate 16.9 mmol, water $30\,cm^3$, catalyst weight 0.8 g, 343 K, and 2 h. [b]Hydrolysis of 2-methylphenyl acetate (MPA). 2-Methylphenyl acetate 4.03 mmol, water $60\,cm^3$, catalyst weight 0.5 g, 353 K, and 2 h. [c]Hydration of 2,3-dimethyl-2-butene (DMB). 2,3-Dimethyl-2-butene 32.8 mmol, water $36.6\,cm^3$, catalyst weight 0.5 g, 343 K, and 4 h. [d]Hydration of α-pinene (AP). α-Pinene 3.3 mmol, 80% aqueous solution of 1,4-dioxane 30 $cm^3$, catalyst weight 0.4 g, 343 K, and 4 h. Figures in parenthesis are selectivities to α-terpineol. [e]Cs2.5 = $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. [f]Si/Al = 36 only for hydration of AP.

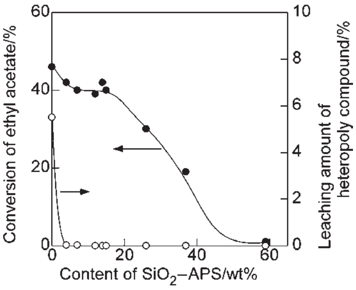

**Figure 1.** Effect of the content of $SiO_2$–APS in $SiO_2$–APS–Cs2.5 composite on (●) conversion of ethyl acetate and (○) leaching amount of heteropoly compound into the reaction mixture.

and the amount of released heteropoly compound into the reaction mixture. The released amounts of heteropoly compound were determined via UV spectroscopy, and for some cases ICP analysis was performed. The conversion for Cs2.5, that is 0 wt% of $SiO_2$–APS, was essentially retained until the content of $SiO_2$–APS increased up to 14 wt%. As the content of $SiO_2$–APS increased further, the conversion decreased and became zero when the content of $SiO_2$–APS was 59 wt%. Considering the total amounts of acid sites of Cs2.5 (number of $H^+$ in Cs2.5; 156 $\mu mol\,g^{-1}$) and basic sites of $SiO_2$–APS (number of $NH_2$ group; 200 $\mu mol\,g^{-1}$), all protons of Cs2.5 can be neutralized when the content of $SiO_2$–APS was 43 wt%. This is basically consistent with the catalytic results shown in Figure 1.

The leaching amount of heteropoly compound from Cs2.5 alone was 5.4% after the first run. In contrast, the release of heteropoly compound from $SiO_2$–APS–Cs2.5 composite was very small (less than 0.1% of the initial amount in $SiO_2$–APS–Cs2.5) for 4 and 7 wt% ($SiO_2$–APS)–Cs2.5 and was below the minimum limit of ICP analysis (<0.002%) for $SiO_2$–APS–Cs2.5 composites containing more than 14 wt% ($SiO_2$–APS). When the reaction was performed repeatedly, the conversions remained unchanged for the second and third runs over 14 wt% ($SiO_2$–APS)–Cs2.5. These results indicate that the $SiO_2$–APS–Cs2.5 composite was a reusable water-tolerant solid acid.

Figure 2 shows SEM micrographs of $SiO_2$ and 26 wt% ($SiO_2$–APS)–Cs2.5. The SEM micrograph of $SiO_2$–APS (Figure 2a) shows a smooth surface and a peanut shape of 50–100 nm in size, which was consistent with $SiO_2$. As demonstrated in Figure 2b, 26 wt% ($SiO_2$–APS)–Cs2.5 has rugged surfaces and consists of almost identically sized particles of $SiO_2$–APS, which are covered with fine grains. The size of the grains was estimated by SEM to be approximately 12 nm, which is the size of the primary crystallites of Cs2.5.[7] As reported previously,[7] an SEM image of Cs2.5 itself revealed lumps of much greater size, which can be distinguished from those shown in Figure 2b. These SEM micrographs revealed that the large aggregates (average size: 0.5 µm) of Cs2.5 in water become disconnected through the interaction with the surface of $SiO_2$–APS and primary Cs2.5 crystallites were attached on the surface. This is supported by the mesopore size distributions estimated by DH method based on the desorption isotherm of $N_2$. There are no mesopores in 26 wt% ($SiO_2$–APS)–Cs2.5, whereas Cs2.5 has mesopores of 4 nm in diameter attributed to the voids between the primary crystallites of Cs2.5.[7] Specific surface area (SSA) of 26 wt% ($SiO_2$–APS)–Cs2.5 was 130 $m^2\,g^{-1}$. This is larger than the sum of SSA of Cs2.5 alone (143 $m^2\,g^{-1}$) and $SiO_2$–APS, suggesting that the primary crystallites of Cs2.5 are highly dispersed on $SiO_2$–APS. From the surface area of $SiO_2$–APS (53 $m^2\,g^{-1}$) and the estimated area of one plane of a primary Cs2.5 crystallite (144 $nm^2$ per grain), assuming a cubic arrangement, 26 wt% ($SiO_2$–APS)–Cs2.5 probably has a structure with approximately 0.7 layers of the primary Cs2.5 crystallite on the surface of $SiO_2$–APS.

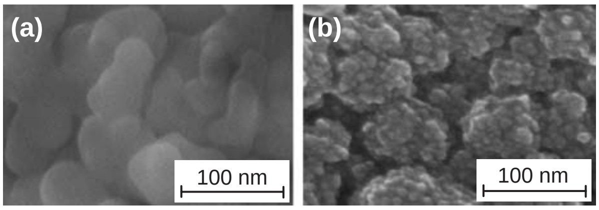

**Figure 2.** SEM images of (a) $SiO_2$–APS and (b) 26 wt% ($SiO_2$–APS)–Cs2.5.

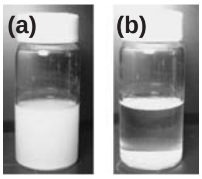

**Figure 3.** Photographs of the suspensions of (a) Cs2.5 and (b) 14 wt% ($SiO_2$–APS)–Cs2.5 in water.

Figure 3 shows photographs of the aqueous suspensions of Cs2.5 and 14 wt% ($SiO_2$–APS)–Cs2.5 after the sample powder was dispersed into water and the suspension was allowed to stand overnight at room temperature. These photographs clearly show that, whereas Cs2.5 remained a clouded colloid solution, 14 wt% ($SiO_2$–APS)–Cs2.5 was well sedimentable. This indicates that the bonding Cs2.5 to the surface of $SiO_2$–APS increases the sedimentation.

Since the leaching amount of heteropoly compound from a composite consisted of Cs2.5 and $SiO_2$ untreated with APS was almost the same as that of Cs2.5 alone, APS directly participates in the bonding Cs2.5 to $SiO_2$–APS. The surface density of the $NH_2$ group on the surface of $SiO_2$–APS (2.3 molecules $nm^{-2}$) is sufficient for the interaction with the $H^+$ over the surface of the primary crystallites of Cs2.5 (0.3 molecules $nm^{-2}$), which is estimated from the surface area of the primary crystallite of Cs2.5 and the amount of $H^+$. This results in the primary crystallite of Cs2.5 being tightly bonded to the surface of $SiO_2$–APS through acid–base interaction.

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