Solid Synthesis of $Cs_xH_{3-x}PW_{12}O_{40}$ Salts and Their Catalytic Activity for the Isomerization of *n*-Butane

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$Cs_xH_{3-x}PW_{12}O_{40}$ salts prepared by a simple solid-synthesis method show good catalytic activity in *n*-butane isomerization as those analogues prepared by traditional liquid-preparation method.

Heteropoly acids (HPA) have been extensively studied as acid and redox catalysts in both heterogeneous and homogeneous systems.[1–3] From the industrial application point of view, heterogenization by water-soluble HPA has attracted much attention.[4,5] The advent of water-tolerant $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ greatly improved the properties of HPA, such as surface area, porosity, acidity, shape selectivity, and hydrophobicity, and paved the way for the design of HPA catalysts which broke through their general limitations of low surface area and high solubility in polar solvents. The preparation of $Cs_xH_{3-x}PW_{12}O_{40}$ in liquid media was first proposed by Okuhara *et al.*[6] where an aqueous solution of Cs_2CO_3 was added dropwise to an aqueous solution of $H_3PW_{12}O_{40}$ under vigorous stirring,[7,8] then the resulting milky solution was aged overnight, and the product was obtained by evaporation of water at 323 K. The preparation conditions should be carefully controlled and the whole procedure is tedious, which is inconvenient for large scale preparation. Here, we report a simple solid-synthesis method for preparing $Cs_xH_{3-x}PW_{12}O_{40}$ ($x = 2.25$, 2.50, and 2.75). The products were characterized by XRD, IR, N_2 sorption, ^{31}P MAS NMR, and their catalytic activities were tested using *n*-butane isomerization as a model reaction. The results indicate that the $Cs_xH_{3-x}PW_{12}O_{40}$ samples prepared via the solid method are likely the same as those prepared via the liquid method.

The solid-synthesis method for the preparation of $Cs_xH_{3-x}PW_{12}O_{40}$ (denoted Cs-X-S, X = 2.25, 2.50, and 2.75) is as the follows: An appropriate amount of $H_3PW_{12}O_{40}$ and Cs_2CO_3 with $Cs^+/H_3PW_{12}O_{40}$ molar ratio of 2.25, 2.50, or 2.75 were ground in an agate mortar for 4 h or a ball mill for 0.5 h, then the solid powder was calcined at 573 K in flowing air for 2 h to assure the complete removal of CO_2 and H_2O. For comparison, the literature liquid method[7] was employed to prepare $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (denoted Cs-2.50-L) and the salt was calcined at 573 K in flowing air for 2 h before characterization and catalytic test.

IR spectra of the Cs-X-S samples (not shown) illustrate the typical vibration bands of Keggin structure. All Cs-X-S samples have the same XRD patterns as that obtained from the liquid method,[8] indicating that both solid and liquid samples have the identical crystalline phase (Figure 1). It is noticeable that the width of the peak at ca. 26.5° of the liquid sample is slightly larger than that of solid samples, suggesting the larger particle size of the solid samples. The specific surface area of Cs-2.25-S, Cs-2.50-S, and Cs-2.75-S are 71, 117, and 106 $m^2 g^{-1}$, respectively. The same trend has been observed for the salts prepared via the liquid method.[9] In addition, the surface area of Cs-2.50-S is somewhat smaller than that of Cs-2.50-L (123 $m^2 g^{-1}$), which is consistent with the difference of particle size observed from XRD.

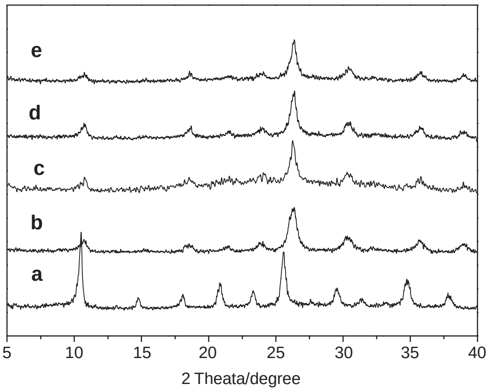

Figure 1. XRD patterns of (a) $H_3PW_{12}O_{40}$; (b) Cs-2.50-L; (c) Cs-2.25-S; (d) Cs-2.50-S; (e) Cs-2.75-S.

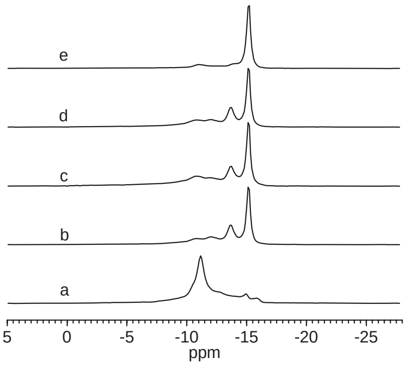

Figure 2. ^{31}P MAS NMR spectra of heteropoly compounds. (a) $H_3PW_{12}O_{40}$; (b) Cs-2.50-L; (c) Cs-2.25-S; (d) Cs-2.50-S; (e) Cs-2.75-S.

^{31}P MAS NMR spectrum of anhydrous $H_3PW_{12}O_{40}$ (Figure 2) exhibits a slightly broad peak at −11.1 ppm. The weak signals at the higher field may be assigned to the hydrated forms of $H_3PW_{12}O_{40}\cdot nH_2O$ because ^{31}P chemical shifts of $H_3PW_{12}O_{40}$ are very sensitive to its hydration levels.[10] Cs-2.75-S shows three peaks at −10.9, −13.4, and −15.1 ppm, corresponding to $H_3PW_{12}O_{40}$, $Cs_2HPW_{12}O_{40}$, and $Cs_3PW_{12}O_{40}$, respectively.[11] In the cases of Cs-2.25-S, Cs-2.50-S, and Cs-2.50-L, four peaks at −10.9, −12.0, −13.7, and −15.5 ppm appear, which are belong to $H_3PW_{12}O_{40}$ and $Cs_xH_{3-x}PW_{12}O_{40}$ ($x = 1$, 2, and 3) salts, respectively.[12] The NMR results above

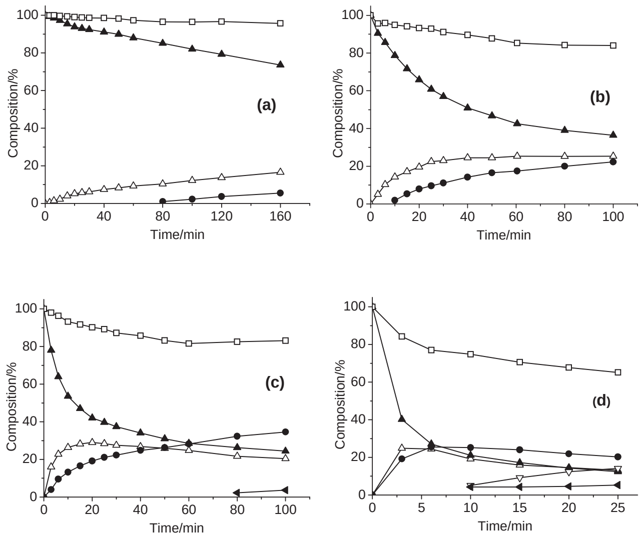

Figure 3. Isomerization of 1-^{13}C-*n*-butane over Cs-2.50-S at different temperatures. (a) 333 K; (b) 373 K; (c) 393; (d) 413 K. (▲) 1-^{13}C-*n*-butane; (△) 2-^{13}C-*n*-butane; (●) 1-^{13}C-*iso*-butane and 2-^{13}C-*iso*-butane; (▽) 1-^{13}C-propane and 2-^{13}C-propane; (◀) Pentane; (□) Total amount of ^{13}C-labeled species.

indicate that cesium salts prepared via solid method have the same structural features as that via liquid method. Moreover, the NH_3-TPD experiments also show no significant differences between Cs-2.50-S and Cs-2.50-L, except that the latter exhibits slightly lower acidic strength and amount. From the characterization results above, it is clear that the reaction of $H_3PW_{12}O_{40}$ and Cs_2CO_3 occurred stoichiometrically to form desired $Cs_xH_{3-x}PW_{12}O_{40}$ salts with similar properties as that prepared with the traditional liquid-preparation method.

1-^{13}C-*n*-butane isomerization was employed as a model reaction to verify the catalytic activity of these cesium salts.[13] Figure 3 illustrates the kinetic curves over Cs-2.50-S at 333, 373, 393, and 413 K derived from the ^{13}C MAS NMR spectra. 2-^{13}C-*n*-butane is detected at the initial stage and a small amount of ^{13}C-isobutane is found after 80 min of heating at 333 K. ^{13}C-isobutane appears earlier when increasing the temperature to 373 and 393 K. It is noticeable that the appearance of ^{13}C-isobutane is in concurrence with the decrease of total amount of ^{13}C-labels. This indicates that, although the isomerization mainly undergoes the monomolecular pathway at low temperature, bimolecular pathway becomes more significant at high temperature and even dominants at 413 K. The oligomers formed from alkenes through the bimolecular mechanism have broadened NMR peaks which are beyond the NMR detection limit. At 413 K, the appearance of ^{13}C-labeled propane and pentane further suggests the dominant bimolecular mechanism. The catalytic behavior of Cs-2.50-S is similar to its analogue prepared via the liquid-synthesis method.[13]

Table 1 shows the results of all catalysts in the isomerization of 1-^{13}C-*n*-butane at 393 K after 10 min. The catalytic activity of Cs-X-S samples follows the order of Cs-2.50-S > Cs-2.25-S > Cs-2.75-S, which is consistent with the result in the literature.[13,14] The conversion of 1-^{13}C-*n*-butane and the yield of ^{13}C-isobutane of Cs-2.50-S is even higher than that of Cs-2.50-L. The different catalytic activity of the solid and liquid samples is possibly caused by their slight differences in physicochemical properties, and the details are under further investigation.

Table 1. Conversion of 1-^{13}C-*n*-butane and product distribution over catalysts in the isomerization of 1-^{13}C-*n*-butane at 393 K after 10 min

Catalyst	Conv./%	Yield/%		
	1-^{13}C-*n*-C_4	2-^{13}C-*n*-C_4	^{13}C-*iso*-C_4	Other[a]
Cs-2.50-L	22.7	16.0	6.4	0.3
Cs-2.25-S	32.2	25.6	2.1	4.5
Cs-2.50-S	46.4	26.4	13.2	6.8
Cs-2.75-S	24.8	13.4	7.2	4.2

[a] The carbon species which is not NMR "visible."

In conclusion, $Cs_xH_{3-x}PW_{12}O_{40}$ salts ($x = 2.25$, 2.50, and 2.75) were successfully prepared using a solid-synthesis method. The Cs-2.50-S shows a good catalytic activity for the isomerization of *n*-butane as that of Cs-2.50-L. The present results indicate that the solid method is a feasible substitute for the liquid method, which may be used to prepare metal salts of HPA.

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