

# A pronounced catalytic activity of heteropoly compounds supported on dealuminated USY for liquid-phase esterification of acetic acid with *n*-butanol

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12-Phosphotungstic acid and its cesium salts supported on a dealuminated ultra-stable Y zeolite were prepared, and showed the high catalytic activity in the liquid-phase esterification of acetic acid with *n*-butanol. The supported  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  catalyst gave a high conversion of *n*-butanol of 94.6% and a selectivity for *n*-butyl acetate of 100%, accompanying the high water-tolerance and catalytic reusability without regeneration.

**KEY WORDS:** heteropoly acid; 12-phosphotungstic acid; Cs salts of PW; USY; esterification; *n*-butanol.

## 1. Introduction

Esterification is usually performed with various mineral acids as catalysts, such as  $\text{H}_2\text{SO}_4$ , HF,  $\text{H}_3\text{PO}_4$ , etc. The growing awareness of the unacceptability of these homogeneous catalysts gives a major impetus to the studies of the environmentally friendly solid acids; however, presently ion-exchange resin is the only solid acid commercially available for this purpose. Because these resins lack mechanical strength and thermal stability, and problems such as deactivation due to swelling occur, their usage is quite limited.

Heteropolyacids (HPAs) of Keggin type possess a strong Brønsted acidity and catalyze a wide variety of acid-catalyzed reactions [1–3]. The major disadvantages of HPAs as catalyst lie in their low surface area ( $< 10 \text{ m}^2/\text{g}$ ) as heterogeneous catalysts [4], and high solubility in a polar reaction system, which thus result in separation problems [5]. An immobilization of HPAs on a number of porous supports with high surface areas, such as silica [6], silica–alumina [7], active carbon [8], MCM-41 [9], SBA-15 [10], zeolite [5,11–14], etc., was therefore extensively studied. However, for polar reaction systems, the continuous leaching of HPAs from support into the reaction medium is the most severe problem for the supported samples [15]. Two research groups reported that Keggin structured HPAs could be encapsulated in the supercage of Y zeolite [13,14], and Mukai *et al.* [5] revealed that this encapsulated 12-molybdophosphoric acid showed water-tolerance and enhanced activity in the esterification of acetic acid with ethanol; however, the catalytic activities of all of the

obtained catalysts were still lower than homogeneous 12-molybdophosphoric acid.

Another alternative approach is to prepare HPA-salts by partially exchanging protons of the parent HPA with large cations, such as  $\text{Cs}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{NH}_4^+$ , which could be water-insoluble and present a surface area  $> 100 \text{ m}^2/\text{g}$  [16]. However, the small particles of HPA-salts cannot be used in packed- or slurry-bed reactors because of pressure-drop and filtration problems. Also, their insolubility makes conventional aqueous impregnation impossible to prepare supported HPA-salts catalysts. Izumi *et al.* [17] included HPA-salts in a silica matrix by means of a so-gel technique and Soled *et al.* [16] revealed an *in situ* deposition technique that impregnated HPA-salts onto silica, and they both evaluated the obtained insoluble solid acid catalysts in liquid-phase reactions. For liquid-phase esterification, only unsupported cesium salts of HPA has been tested [18].

We have recently prepared the 12-tungstophosphorous acid (PW) catalysts supported on dealuminated ultra-stable Y (USY) zeolite and SBA-15, and observed their high catalytic activities in the surface type reactions of the hydroisomerization of *n*-heptane and the alkylation of benzene with 1-dodecene, respectively [19–21]. In this work, we prepare PW and cesium salts of PW supported on dealuminated USY, and observe a very high catalytic conversion, selectivity and stability of the supported cesium salts of PW catalyst in the esterification of acetic acid with *n*-butanol.

## 2. Experimental

Dealuminated USY (DUSY) was prepared by the hydrothermal treatment of USY (Zhoucun Catalyst

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Factory, Si/Al = 6) with the calcinations of the sample in a confined 100% steam atmosphere at 650 °C for 3 h, followed by the acid treatment in 2 M HCl aqueous solution at 90 °C for 2 h. Supported PW ( $H_3PW_{12}O_{40} \cdot xH_2O$ , Shanghai Chem. Reagent Co., AR) samples, PW/SP, where SP stands for the support, namely, DUSY, USY or silica gel ( $SiO_2$ , Shanghai Silica Gel Factory,  $S_{BET} = 285 \text{ m}^2/\text{g}$ ), were prepared by the impregnation performed at room temperature with excess solution by contacting the corresponding support with the PW aqueous solution under constant stirring overnight, followed by evaporation at 70 °C and drying at 110 °C for 12 h. Supported Cs salts of PW,  $Cs_xH_{3-x}PW/DUSY$  ( $x = 1-3$ ), were obtained by sequential impregnation and *in situ* reaction on the support. Cesium carbonate was supported onto DUSY by the incipient wetness impregnation, dried at 110 °C for 12 h and calcined at 500 °C for 4 h. Following this, PW was introduced into the catalyst by the same procedure as that for PW/DUSY. The concentration of PW and  $Cs_xH_{3-x}PW$  in catalyst is 30% by weight for all samples. Before reaction, all the catalysts were activated in air at 200 °C for 3 h. A pure Cs-salt of PW ( $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ ) was prepared by adding the aqueous solution of  $Cs_2CO_3$  dropwise to the PW solution while stirring [22]. The resulting precipitate was dried at 110 °C overnight in vacuum and calcined at 200 °C for 3 h.

The catalytic activity of the obtained samples was tested in liquid-phase esterification of acetic acid with *n*-butanol in a 3-necked flask equipped with a magnetic stirrer and a condenser. The typical reaction conditions were as follows: 110 °C of reaction temperature, 1.5 ml/ml of the volume ratio of *n*-butanol to acetic acid, and 19 ml/g of the ratio of *n*-butanol to catalyst. The reaction mixture was sampled periodically and filtered to remove catalyst particles, followed by a GC analysis using a  $15 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$  FFAP capillary column with FID as the detector. For selected catalysts, the reusability was measured. After simply separating the used catalyst from the reaction medium by centrifuge, it was transferred and charged into the next reaction medium for a new reaction cycle without regeneration.

Water treatment for supported PW and PW-salts catalysts was carried out to examine the amount of heteropoly species released from the support in the liquid phase by the Perkin Elmer Lambda 35 UV-Visible spectrophotometer [23]. After stirred in water at room temperature for 1 h, the catalyst was recovered by filtering. This was repeated 5 times. The spectra from 200 to 400 nm were recorded for each filtrate with a built-in recorder, using quartz cells with 10 mm optical path. For the quantitative analysis, a calibration curve was created by using aqueous solution of PW, and the absorption band around 251 nm was used.

X-ray power diffraction (XRD) pattern was obtained on the Bruker D8 Advance diffractometer using the Ni-filtered  $CuK_{\alpha}$  radiation at 40 kV and 30 mA. BET surface area was achieved by  $N_2$  adsorption on the Coulter Omnisorp 100CX equipment. The acid strength of catalysts was measured with Hammett indicators, including anthraquinone ( $pK_a = -8.2$ ), *p*-nitrotoluene ( $pK_a = -11.35$ ), *p*-nitrochlorobenzene ( $pK_a = -12.70$ ), *m*-chloronitrobenzene ( $pK_a = -13.60$ ) and 2,4-dinitrofluorobenzene ( $pK_a = -14.52$ ).

### 3. Results and discussion

XRD patterns for various catalysts are illustrated in figure 1. The XRD curve of DUSY was very similar to that of USY, indicating the high comparative crystallinity of DUSY in spite of the combined treatment of steaming and HCl acid leaching. When PW was impregnated on USY or DUSY, peaks assigned to Y zeolite were comparable to those for the parent support, and no peak to PW crystal was detected, which implies the highly dispersion of PW anions on the support with the microporosity of support unaltered. For  $Cs_{2.5}H_{0.5}PW/DUSY$ , only peaks assigned to the Y zeolite were detected, however, the intensities decreased clearly. This demonstrates that the heteropoly species could highly disperse on DUSY support even with loading of Cs-salt of PW being as high as 30% whereas the structure of support could be retained.

The BET surface areas of various catalysts are listed in table 1. Pure PW exhibited a very low surface area of  $6 \text{ m}^2/\text{g}$ , and pure  $Cs_{2.5}H_{0.5}PW$  showed a considerable surface area of  $154 \text{ m}^2/\text{g}$ , which is in good agreement with the previous report [15]. On the other hand, the surface area of supported catalysts decreased remarkably compared with their parent supports, but still showed very high values. Table 1 also displays the acid strength ( $H_0$ ) for various catalysts. As expected, pure PW and  $Cs_{2.5}H_{0.5}PW$  showed superacidity with  $H_0$  being  $-13.6$ , which was lower than  $-11.93$  for 100%  $H_2SO_4$ . By contrast, USY and DUSY showed comparatively very weak acidity with  $H_0$  above  $-8.2$ . When PW were introduced on USY, a much weaker acid strength of  $-8.2$  was observed compared with pure PW. As known, when  $NH_4^+Y$  is subjected to hydrothermal treatment to produce USY, secondary mesopores are created with the removed Al species filling the insides of secondary pores. These retained Al species may be basicity, and accelerate the partial decomposition of PW on USY [14], which may accounts for the weak acidity of PW/USY. Further steaming and acid leaching for USY could not only create more secondary mesopores but also remove the extra-framework Al species from the zeolite crystal [24], as a result of which, PW/DUSY and  $Cs_xH_{3-x}PW/DUSY$  exhibited superacidity or near superacidity, as shown in table 1. On the other hand, it is

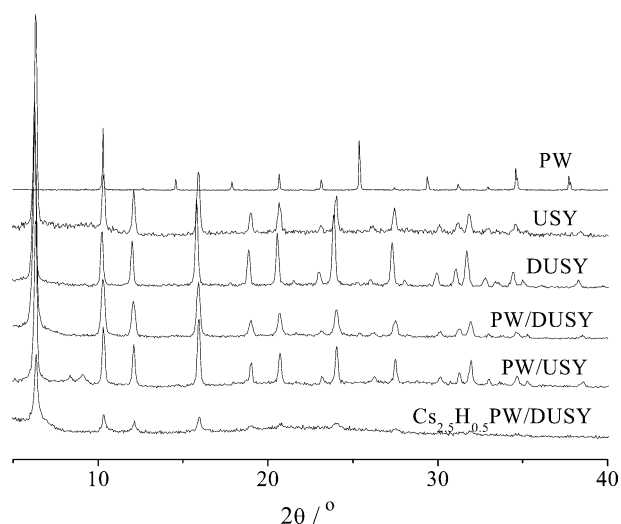


Figure 1. XRD patterns of various catalysts.

suggested that the mesopores of DUSY would be favorable to the dispersion of PW or  $Cs_xH_{3-x}PW$  on the support [12]. For all supported catalysts, the acidity was not as strong as that for the pure heteropoly compounds, which may ascribe to the weak interaction between heteropoly anions and the hydroxyl groups in the support [25]. As a control sample,  $PW/SiO_2$  also possessed superacidity with a  $H_0$  value of  $-12.7$ .

Under the employed conditions of reaction, the conversion of *n*-butanol reached the plateau value over all catalysts after 100 min of reaction time. Therefore catalytic activities of various catalysts in steady reaction state at 120 min of reaction time are compared in table 1. Over all catalysts, only the target product, *n*-butyl acetate, was detected, giving a selectivity of 100%. USY showed a very low conversion of 24.6%. After

dealumination, DUSY gave a higher conversion of 49.5%. This may relate with its more plenty of mesopores, which accelerates the reaction. Only a slight increase of conversion was obtained when PW was introduced onto USY. Over the pure PW and  $Cs_{2.5}H_{0.5}PW$  catalysts, conversions of 69.4 and 61.2% were obtained, respectively, which were higher than those over the USY and DUSY supports. Indeed, in 1993, Izumi *et al.* [18] measured the catalytic performance of pure  $Cs_{2.5}H_{0.5}PW$  in the esterification of acetic acid with ethanol in the liquid phase, and achieved very high catalytic activity, but they used different reaction conditions and did not mention the conversion and reaction time in their work. On the other hand, as shown in table 1, a drastic increase of conversion was achieved over  $PW/DUSY$  or  $Cs_xH_{3-x}PW/DUSY$  compared with DUSY, which was even much higher than that of the homogeneous PW catalyst or the water-tolerant pure Cs-salt of PW with the strongest acidity. In general, it can be proposed that the high activity of supported heteropoly compounds is associated with their high surface area, as well as their well dispersion on the support, and moreover, the activity corresponds with the acid strength for supported catalysts. The conversion found its maximum over  $Cs_{2.5}H_{0.5}PW/DUSY$ , which was 94.6% and evidently higher than those over  $PW/DUSY$  (86.4%) and  $PW/SiO_2$  (79.1%).

Figure 2 compares the catalytic activity between  $PW/DUSY$  and  $Cs_{2.5}H_{0.5}PW/DUSY$  after they were reused for 5 times. The conversion of *n*-butanol decreased dramatically for  $PW/DUSY$ , and only a very slow decrease of conversion was observed for  $Cs_{2.5}H_{0.5}PW/DUSY$ . At the fifth reaction cycle, only a low conversion of 47.6% was obtained for  $PW/DUSY$ , by contrast, a much high conversion of 81.6% could be achieved for  $Cs_{2.5}H_{0.5}PW/DUSY$ .

Table 2 compares the solubility of heteropoly compounds between the two DUSY supported catalysts during the water treatment. It was obvious that PW on DUSY was much easier to be released in water than  $Cs_{2.5}H_{0.5}PW$  on DUSY. As shown in table 2, during the first water treatment, a large amount of PW was leached into water with a very high concentration of heteropoly species in the filtrate (4657 ppm), which is more than ten times higher than that for  $Cs_{2.5}H_{0.5}PW/DUSY$ . Totally, after 5 times of water treatment, the leaching amount of PW was more than 6 times higher than that of the corresponding cesium salt. This observation well verifies that the very low catalytic stability of  $PW/DUSY$  in the esterification reaction is originated from its high leaching properties in polar medium, and the high reusability of  $Cs_{2.5}H_{0.5}PW/DUSY$  comes from its low leaching amount. It could be suggested that, the low leaching amount of heteropoly species for  $Cs_{2.5}H_{0.5}PW/DUSY$  is probably because of the existence of trace amount of free acid phases in the solid heteropoly acid salt [26]. On the other hand, the decrease of conversion in figure 2

Table 1

Physical chemical properties and catalytic activities of various catalysts in the esterification of acetic acid with *n*-butanol<sup>a</sup>

Catalyst	Surface area (m <sup>2</sup> /g)	Acid strength (H <sub>0</sub> )	Conversion (%)	Selectivity (%)
USY	645	> -8.2	24.6	100
DUSY	716	> -8.2	49.5	100
PW	6.0	-13.6	69.4	100
$Cs_{2.5}H_{0.5}PW$	154	-13.6	61.2	100
$PW/USY$	382	-8.2	31.7	100
$PW/DUSY$	466	-12.7	86.4	100
$Cs_1H_2PW/DUSY$	530	-12.7	89.4	100
$Cs_{1.5}H_{1.5}PW/DUSY$	527	-11.35	84.2	100
$Cs_2H_1PW/DUSY$	512	-11.35	81.3	100
$Cs_{2.5}H_{0.5}PW/DUSY$	496	-12.7	94.6	100
$Cs_3H_0PW/DUSY$	411	-8.2	78.7	100
$PW/SiO_2$	204	-12.7	79.1	100

<sup>a</sup> Reaction conditions: reaction temperature = 110 °C; reaction time = 120 min; *n*-butanol/acetic acid = 1.5 ml/ml; *n*-butanol/catalyst = 19 ml/g.

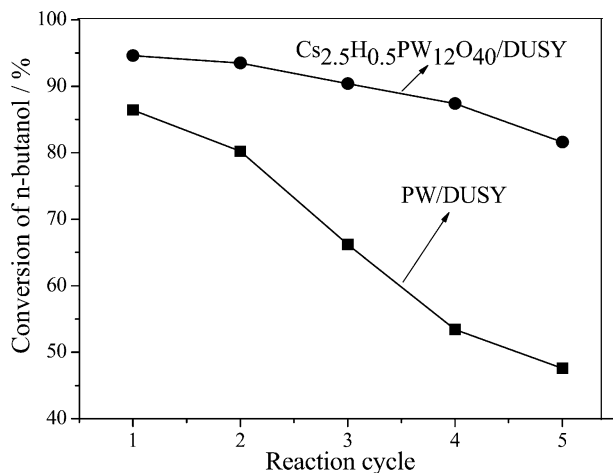


Figure 2. Comparison of the catalytic stability of PW/DUSY and  $Cs_{2.5}H_{0.5}PW/DUSY$  catalysts. (reaction temperature = 110 °C; reaction time = 120 min; *n*-butanol/acetic acid = 1.5 ml/ml; *n*-butanol/catalyst = 19 ml/g).

Table 2

Concentration of the heteropoly species in the filtrate after water treatment for PW/DUSY and  $Cs_{2.5}H_{0.5}PW/DUSY$  catalysts

Water treatment times	1	2	3	4	5	Total
Concentration for PW/DUSY (ppm)	4657	465	57	58	37	5274
Concentration for $Cs_{2.5}H_{0.5}PW/DUSY$ (ppm)	417	187	93	79	50	826

arising from the catalyst lost during the separation and transfer of the catalyst for the next reaction recycle cannot be excluded.

#### 4. Conclusions

We have prepared PW and cesium salts of PW catalysts supported on dealuminated USY zeolite, which showed very high conversion and 100% selectivity in liquid-phase esterification of acetic acid with *n*-butanol. Furthermore, the  $Cs_{2.5}H_{0.5}PW/DUSY$  catalyst was water-tolerant with high catalytic reusability. Thus this supported cesium salt catalyst can be industrially important as a solid acid catalyst in liquid-phase esterification.

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