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$H_3PW_{12}O_{40}/SiO_2$ for sorbitol dehydration to isosorbide: High efficient and reusable solid acid catalyst

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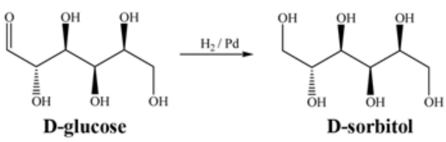
Abstract−Tungstophosphoric acids (PW) supported on various metal oxides (SiO_2, γ-Al_2O_3, TiO_2, ZrO_2 and CeO_2) were synthesized and used as catalysts for sorbitol dehydration to isosorbide for the first time. 30% PW/SiO_2 exhibited the best catalytic performance for sorbitol dehydration, over which 56% isosorbide selectivity could be gained at a 95% sorbitol conversion at 250 °C. The catalytic performance of regenerated 30% PW/SiO_2 catalysts by dichloromethane elution showed no loss after recycling five runs. Characterizations with UV-Vis, XRD, NH_3-TPD and thermal analysis techniques revealed that PW had a good dispersion, and the primary Keggin structure was preserved after supporting PW on different supports. The interaction between PW and oxides resulted in different acidity of catalysts, which affected conversion of sorbitol and selectivity for isosorbide. The final acidity order of supported PW catalysts was the following: $SiO_2>\gamma$-$Al_2O_3>TiO_2\approx ZrO_2>CeO_2$.

Key words: Tungstophosphoric Acid, Sorbitol, Isosorbide, Dehydration, Regeneration

INTRODUCTION

Anhydrous sugar alcohols, such as isosorbide, are known for their uses in therapeutics, food additives, surfactants and more recently in polyesters [1-3] and polyethers [4]. Incorporation of isosorbide into known polymers may be of interest for three reasons [2]. Firstly, isosorbide introduces chiral centers as an effect, which is particularly interesting for the preparation of cholesteric materials. Secondly, the thermal stability and stability against oxidation is higher than that of α, ω-dihydroxy- or diaminoalkanes. Thirdly, isosorbide units may raise the glass-transition temperature compared to polymers derived from α, ω-dihydroxyalkanes.

Isosorbide is the only sugar diol that is technically produced in large quantities [5]. Hence, it is the only relatively inexpensive diol which is based on renewable resources and is not based on oil or coal chemistry. The starting material for isosorbide production is starch, which is completely degraded by acidic or enzymatic hydrolysis. The hydrogenation of the resulting D-glucose yields D-sorbitol (Eq. (1)). Heating of D-sorbitol under vacuum and in the presence of an acidic catalyst results in a stepwise cyclization with elimination of water (Eq. (2)).



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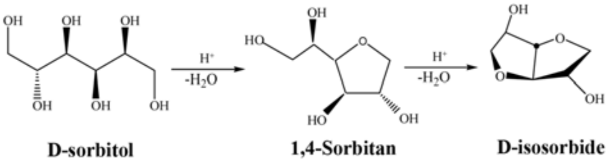

(2)

Examples of acid catalysts used commercially include mineral acids such as H_2SO_4 [6], HCl and H_3PO_4 [7], but the use of a homogeneous acidic catalyst introduces some processing issues such as a corrosion hazard for the reactors, and difficulties in product separation and recovery [8]. Environmental considerations and handling difficulties have led to sustained efforts in recent years to replace homogeneous acid catalysts with solid acid catalysts. Heteropoly acids (HPAs), particularly the Keggin-type ones, exhibit high acidic strengths and have performed admirably in a wide variety of acid-catalyzed reactions [9], as alcohol dehydration [10,11], alkylation [12,13] or esterification [14,15] reactions. The major disadvantages of HPAs as catalysts are their low thermal stability, low surface area (1-10 m^2 g^{-1}), separation problem from reaction mixtures and the solubility [16]. HPAs can be made insoluble solid acid with high thermal stability and high surface area by supporting them onto suitable supports having huge surface area, large pore diameter, pore volume, and well-ordered pore structure. The support provides an opportunity for HPAs to get dispersion over a large surface area, which increases catalytic activity. However, the acidity of supported HPAs strongly depends on the nature of the species present in the solid and the degree of interaction between the support and HPAs. The influence of support on both the acidity and catalytic performance of supported tungstophosphoric acid for dehydration of sor-

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bitol is rarely reported.

In this paper, supported tungstophosphoric acid catalysts were prepared and used as catalysts for sorbitol dehydration to isosorbide. The effect of support nature on the acidity and catalytic performance of supported tungstophosphoric acid was studied. Based on characterization results, a possible support-property relationship of supported tungstophosphoric acid was provided.

EXPERIMENTAL

1. Catalyst Preparation

Al_2O_3, SiO_2 and TiO_2 were purchased as commercial AR samples and calcined at 300 °C for 3 h in air before use. CeO_2 was prepared by air calcination of a commercial $Ce(NO_3)_3 \cdot 6H_2O$ (AR) at 500 °C for 4 h.

ZrO_2 was prepared by a method similar to that described by Chen and Coudurier [17]. 32.2 g of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 250 mL of water at room temperature; 28 wt% aqueous $NH_3 \cdot H_2O$ solution was added dropwise under vigorous stirring at room temperature up to a pH of 8.4. The gel was then filtered and washed with deionized water until there was no detectable chlorine in the washing water. The gel was dried at 120 °C for 24 h. The obtained solid was calcined under air condition at 450 °C for 3 h.

The HPAs solutions were prepared from tungstophosphoric acid (PW) and the solvent used was a mixture of deionized water and anhydrous ethanol, in a 1 : 1 volumetric ratio. The solutions were used to impregnate supports with different characteristics. The solids employed as supports were SiO_2, γ-Al_2O_3, TiO_2, ZrO_2 and CeO_2.

Silica-supported PW (PW/SiO_2) catalysts were prepared by impregnating SiO_2 with a solution of PW (with concentrations depending upon the loadings, wt%). The mixture was stirred overnight at room temperature, followed by drying in a vacuum at 70 °C for 24 h. A similar procedure was followed for the synthesis of PW/γ-Al_2O_3, PW/TiO_2, PW/ZrO_2, and PW/CeO_2.

All catalysts investigated in this work were calcined at 300 °C for 3 h in air and then pressed, crushed, and sieved to 30-50 mesh before use.

2. Characterization

UV-visible spectra were recorded in the wavelength range of 200-400 nm on a Perkin Elmer Lambda 25 spectrometer. The spectra of PW solution after contacting with different supports were obtained for contact times ranging from 0 to1,440 min.

Surface areas of catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2020 instrument. The samples were pretreated at 200 °C under vacuum.

Powder X-ray diffraction (XRD) patterns were obtained with a diffractometer (Philips X'Pro) using Cu$K\alpha$ radiation at 40 kV and 40 mA.

NH_3 temperature programmed desorption (NH_3-TPD) was carried out with a BEL-CAT-B-82 equipment connected with a thermal conductivity detector. Typically, the sample of 150 mg loaded in the quartz tube was first pretreated with high purity He of 50 mL min^{-1} at 250 °C for 1 h. The adsorption of NH_3 was performed at 100 °C in an NH_3-He (10 vol% NH_3) mixture for 0.5 h, and then the physically adsorbed NH_3 was purged by high purity He. TPD of ammonia was performed in the He flow by raising the temperature to 650 °C at a rate of 10 °C min^{-1} and the NH_3 liberated was detected by on line thermal conductivity detector. To avoid disturbing the Keggin's anion decomposition, a background was performed for every sample by using helium to replace of NH_3-He mixture with the same procedure as NH_3-TPD. The final NH_3-TPD curves were attained by subtracting the corresponding background curves.

The thermal analysis was carried out with a NETZSCH STA 409 PC thermal analyzer. The thermal analysis experiments were performed in air, using ca. 5 mg samples in a Al_2O_3 cell and a heating rate of 10 °C min^{-1}. The studied temperature range was 25-700 °C.

3. Typical Procedure for Dehydration of Sorbitol

The sorbitol dehydration measurements were performed at atmospheric pressure, in a fixed bed reactor packed with 0.5 g of the catalysts. The gas employed as carrier was nitrogen. The reaction feed, a sorbitol aqueous solution, was introduced into the reaction system by a syringe pump. The reaction products were quantified by HPLC (Dionex Ultimate 3000) equipped with an Aminex HPX-87 H column and differential refractive index detector.

Sorbitol conversion and product selectivity were calculated according to the following formula:

$$\text{Sorbitol conversion } (\%) = \frac{\text{Moles of sorbitol reacted}}{\text{Moles of sorbitol in the feed}} \times 100$$

$$\text{Product selectivity } (\%) = \frac{\text{Moles of carbon in a product defined}}{\text{Moles of carbon in sorbitol reacted}} \times 100$$

4. Catalyst Regeneration

After reaction for 6 h, the catalyst bed was cooled to 100 °C and dichloromethane was pumped into the bed (F=2.4 mL h^{-1}) for 24 h at this temperature. Then the catalyst was taken out and thoroughly washed with acetonitrile and dried at 120 °C for 2 h. After calcination at 300 °C, the catalyst was reused in the next run.

RESULTS AND DISCUSSION

1. Identification of Supported Species

The nature of the species present both in the impregnating solutions and on the supports has an essential influence on catalytic performance. To identify the existing state of PW species on supports, we have carried out detailed characterizations.

In the preparation of supported tungstophosphoric acid intended for acid catalyst, the identification of the species present in the impregnating solutions is particularly important due to the restricted stability in aqueous solution. The UV-visible spectra for different impregnation times of SiO_2, γ-Al_2O_3 with PW solution are shown in Fig. 1. The UV-visible spectrum of the initial PW solution before the contact with the supports showed a band at 267 nm, which was the characteristic band of the $[PW_{12}O_{40}]^{3-}$ heteropoly anion [18]. After contacting with supports, every spectrum presented the characteristic band of the $[PW_{12}O_{40}]^{3-}$. The intensity of that band decreased gradually with time, in parallel with the decrease in the PW concentration of the solution, as it was being adsorbed on the solid. Therefore, in the time range (0-1,440 min), the observed behavior indicated that, during the impregnation, the main species presented in the PW solution was the tungstophosphate anion which gradually disappeared from the solution as it was adsorbed on the different supports. The UV-visible spectra of TiO_2, ZrO_2, CeO_2 show the similar trend as that of SiO_2, γ-Al_2O_3.

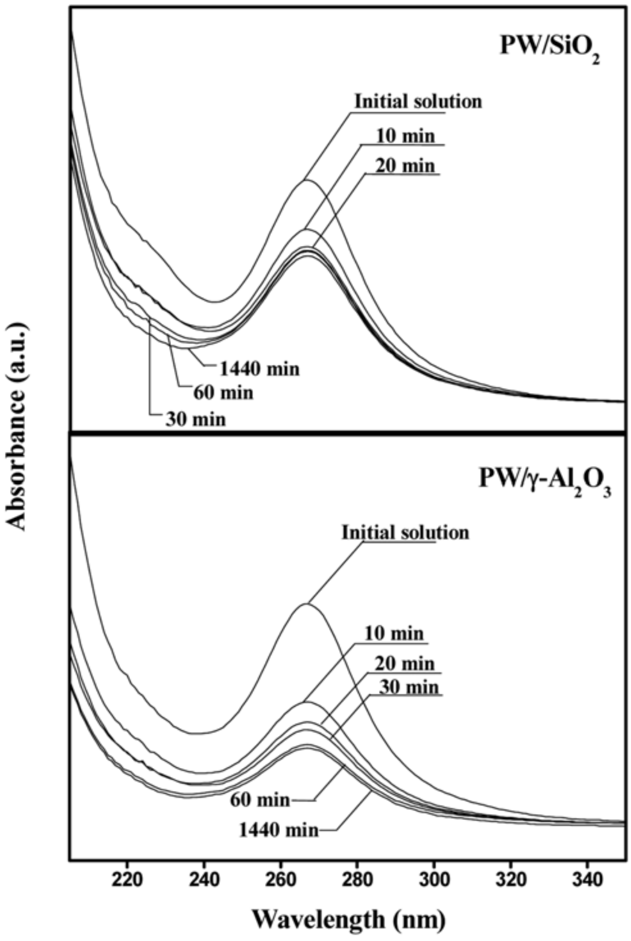

Fig. 1. UV-visible spectra for different impregnation times of SiO_2, γ-Al_2O_3 with the PW solution.

Table 1. Specific surface area of supports and supported PW

Catalyst	S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)
SiO_2	105.7	0.46
γ-Al_2O_3	263.7	0.43
ZrO_2	62.6	0.08
TiO_2	6.5	0.04
CeO_2	86.9	0.17
30% PW/SiO_2	94.6	0.50
30% PW/γ-Al_2O_3	207.2	0.26
30% PW/TiO_2	10.4	0.024
30% PW/ZrO_2	41.1	0.04
30% PW/CeO_2	63.5	0.16

The results obtained from the textural analysis of the samples based on nitrogen adsorption are presented in Table 1. The surface area of supported catalysts decreased remarkably compared to their parent supports except for TiO_2, but still showed high values. The reduction in the surface area of supported catalysts might be due to the blockage of pores by PW species. TiO_2 exhibited a low surface area of 6.5 $m^2\ g^{-1}$ which was increased up to 10.4 $m^2\ g^{-1}$ after supporting PW. This could be caused by aggregation of PW species on TiO_2 surface due to the low surface area of TiO_2.

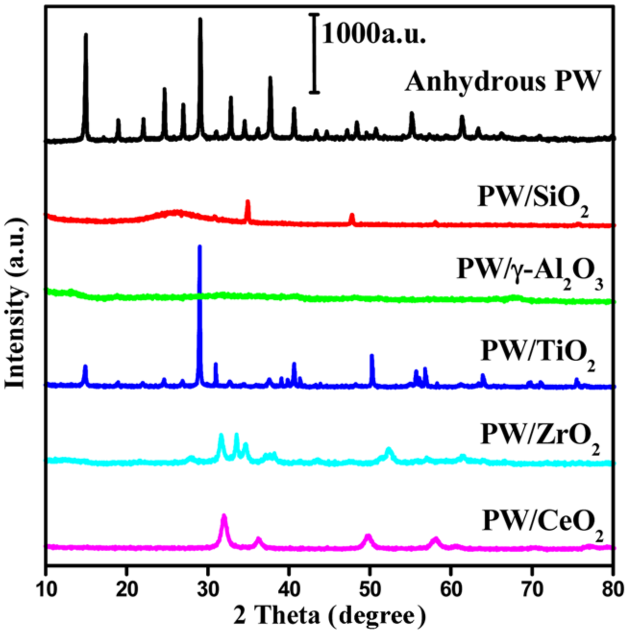

Fig. 2. XRD patterns of anhydrous PW; 30 wt% PW supported on SiO_2, γ-Al_2O_3, TiO_2, ZrO_2, CeO_2 samples.

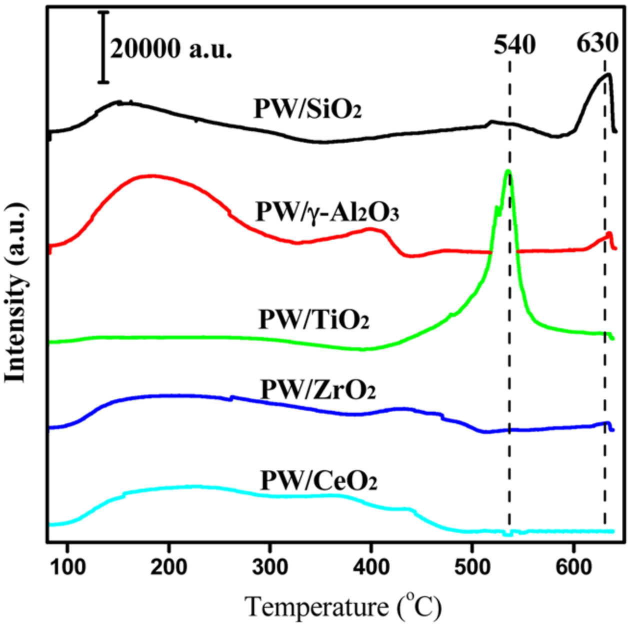

Fig. 3. NH_3-TPD profiles of supported PW catalysts.

XRD patterns of pure-PW reference sample in anhydrous forms (after heating at 200 °C for 2 h in air) and PW deposited on supports are shown in Fig. 2. After deposition of PW on supports by impregnation, the patterns of PW on SiO_2, γ-Al_2O_3, ZrO_2, CeO_2 were the same as the ones of the supports' counterpart and displayed none of the characteristic peaks of dehydrated PW, indicating PW had a good dispersion on these supports. Conversely, the characteristic peaks of dehydrated PW appeared on the diffractogram of PW/TiO_2 due to the low surface area of TiO_2. This was consistent with the results of surface area.

2. Characterization of Acidity

The acidity of supported PW had an important influence on sorbitol conversion and product distribution. The acidity of the metal oxides-supported PW catalysts was characterized by NH_3 temperature-programmed desorption. To avoid the disturbance of the Keggin's anion decomposition, a background was performed for every sample using pure helium to replace of NH_3-He mixture with the same procedure as NH_3-TPD. The NH_3-TPD curves depicted in Fig. 3 were attained by subtracting the corresponding background curves. All the NH_3-TPD curves displayed one or two wide peaks from 110 to approximately 450 °C. Thus, it seemed that there was a broad distribution of weak and moderate acidity in these supported PW catalysts. The NH_3-TPD curve of PW/TiO_2 showed a sharp peak around at 540 °C. Combined with the results of XRD and surface area, this peak could be ascribed to the intrinsic acidity of aggregated PW species on TiO_2 surface. Ammonium desorption from 600 to 640 °C was observed in all the curves except for PW/CeO_2, indicating the strong acidity presented in supported PW catalysts. The strong acidity decreased as the following order: $SiO_2>\gamma\text{-}Al_2O_3>TiO_2\approx ZrO_2>CeO_2$.

It is reported that the acidity of supported PW catalysts depends on the nature of the species present and on the interaction degree with the support [19]. The systems showing lower interaction degree result in more acidic catalysts. Differential thermal analysis (DTA) could reflect the interaction degree of PW with the supports. Fig. 4 depicts the derivative DTA diagram of bulk PW and supported catalysts. The derivative DTA of bulk PW showed two endothermic peaks at 65 and 189 °C associated with the loss of water, and an exothermic peak at 590 °C. The second endothermic peak was ascribed to the dehydration of $H_3PW_{12}O_{40}\cdot 6H_2O$ phase and the exothermic one was assigned to the Keggin's anion decomposition. After supporting on oxides, the two endothermic peaks disappeared as a consequence of PW dispersion on the supports. Meanwhile, the exothermic peak moved to low temperature (505-562 °C) with the following order: $SiO_2<\gamma\text{-}Al_2O_3<TiO_2\approx ZrO_2$, except for CeO_2 which shifted to high temperature at 625 °C. The temperature of Keggin's anion decomposition could reflect the interaction between PW and supports, which determined the final acidity of supported PW catalysts. Supported PW showing lower decomposition temperature possessed weaker interaction with supports. The catalysts with lower interaction degree resulted in the stronger acidity. Therefore, the resulting acidity order obtained by impregnation of different supports was the following: $SiO_2>\gamma\text{-}Al_2O_3>TiO_2\approx ZrO_2>CeO_2$. This was consistent with the result of NH_3-TPD.

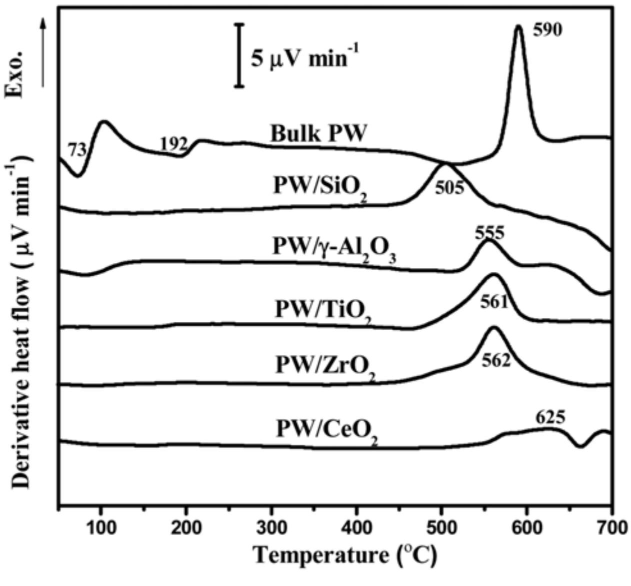

Fig. 4. Derivative DTA profiles of bulk PW and supported catalysts.

Table 2. Effects of various catalysts in dehydration of sorbitol

Catalyst	Conversion (%)	Selectivity (%)		
		1,4-Sorbitan	Isosorbide	Others^a
SiO_2	27.91	-	-	100
$\gamma\text{-}Al_2O_3$	7.13	-	-	100
ZrO_2	32.12	88.67	4.75	6.58
TiO_2	37.66	91.25	5.46	3.29
CeO_2	35.17	-	6.37	93.63
30% PW/SiO_2	95.78	18.9	45.75	35.35
30% $PW/\gamma\text{-}Al_2O_3$	77.05	51.99	42.53	5.48
30% PW/TiO_2	60.13	67.69	21.99	10.32
30% PW/ZrO_2	58.38	74.72	22.02	3.26
30% PW/CeO_2	52.05	18.64	26.25	55.11

^{a}Selectivity for others=100-total selectivity for all identified products; Other products mainly include coke and unknowns

Reaction condition: Sorbitol feedstock, 10 wt%; F=2.4 mL h^{-1}; N_2 flow rate, 30 mL min^{-1}; Catalyst, 0.5 g; TOS, 6 h; Temperature, 220 °C

3. The Effect of Support Nature on Catalytic Performance

The catalytic results of tungstophosphoric acid supported on different oxides are listed in Table 2. To disclose the catalytic performance of supported tungstophosphoric acid, the catalytic results of blank supports are also given in Table 2. It should be noted that no reaction occurred in the absence of catalyst under the conditions of Table 2. Among all the tested catalysts, PW/SiO_2 was the most selective catalyst for isosorbide. The difference of catalytic performances could be attributed to the surface acid/base properties of supports and the interaction degree between PW and oxide supports. These catalytic performance data were used for the correlation with the acidity of supported PW catalysts. The conversion of sorbitol and selectivity for isosorbide decreased as the following order: $SiO_2>\gamma\text{-}Al_2O_3>TiO_2\approx ZrO_2>CeO_2$ and $SiO_2>\gamma\text{-}Al_2O_3>TiO_2\approx ZrO_2\approx CeO_2$, respectively. This trend was well in agreement with the trend of acidity of supported PW catalysts. PW supported on SiO_2 possessed the strongest acidity among all the tested supports. The stronger acidity of PW/SiO_2 contributed to the higher sorbitol conversion and selectivity for isosorbide.

Considering the possibility of PW leaching, the reaction mixture after 6 h was diluted five fold and tested by UV-visible spectrum. As depicted in Fig. 5(a), only PW/TiO_2 catalyzed reaction mixture exhibited an adsorption band at around 267 nm assigned to Keggin type $PW_{12}O_{40}^{3-}$ anions, whereas in other cases no such band was visible. Combined with the results of nitrogen adsorption and XRD, the PW leaching of PW/TiO_2 catalyst could be caused by the aggregation of PW species on TiO_2 surface. In view of the strong acidity and no PW leaching during reaction, PW/SiO_2 was chosen as a model

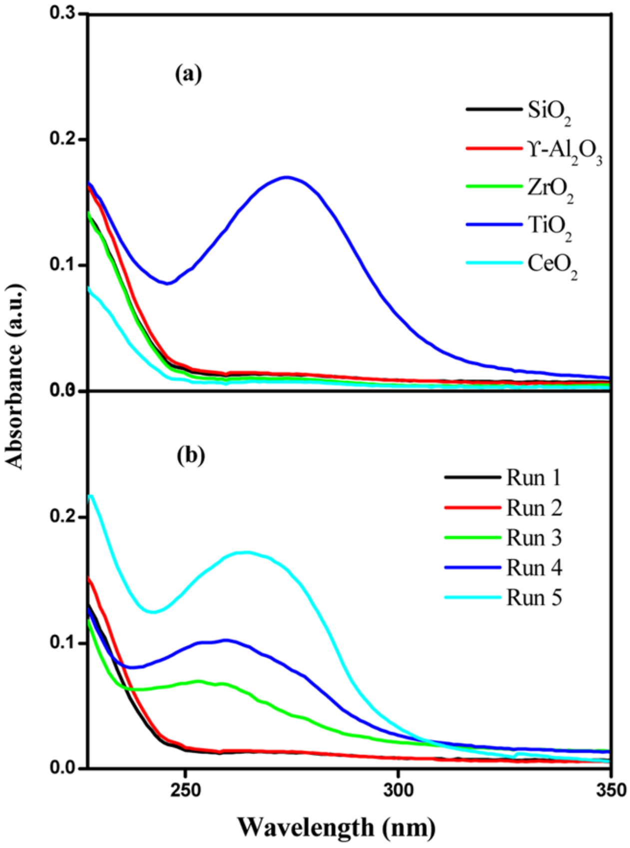

Fig. 5. UV-visible spectra of (a) reaction mixture of PW supported on SiO_2, γ-Al_2O_3, TiO_2, ZrO_2, CeO_2, (b) dichloromethane after going through reacted 30% PW/SiO_2 catalyst for each run.

Table 3. Effects of percent of PW on SiO_2 in dehydration of sorbitol

Catalyst	Conversion (%)	Selectivity (%)		
		1,4-Sorbitan	Isosorbide	Others[a]
5% PW /SiO_2	90.12	6.78	29.30	63.92
10% PW /SiO_2	95.85	8.84	36.28	54.88
20% PW /SiO_2	95.74	9.08	35.09	55.83
30% PW /SiO_2	95.78	18.9	45.75	35.35
40% PW /SiO_2	94.70	11.43	41.08	47.49
50% PW /SiO_2	94.84	12.27	41.27	46.46

[a] Selectivity for others=100-total selectivity for all identified products; Other products mainly include coke and unknowns

Reaction condition: Sorbitol feedstock, 10 wt%; F=2.4 mL h^{-1}; N_2 flow rate, 30 mL min^{-1}; Catalyst, 0.5 g; TOS, 6 h; Temperature, 220 °C

system to perform the successive research.

4. The Effect of Loading Amount on Catalytic Performance of PW/SiO_2

Table 3 shows the catalytic results of sorbitol dehydration over PW/SiO_2 with different loading amount. The amount of PW had a very slight effect on the catalytic activity. All samples showed a high conversion >90%. Sorbitol molecule had a high reactivity in the presence of an acidic catalyst at high temperature. Sorbitol converted to more dehydrated products over strong acidic catalyst. However, it tended to convert to coke more than dehydrated products over weak acidic catalyst. Hence, the conversion of sorbitol remained almost the same in Table 3. The results showed that 30% PW/SiO_2 had the highest selectivity to isosorbide of 45.75%. Therefore, 30% PW/SiO_2 was selected as a model catalyst for the following studies which were focused on sorbitol dehydration reaction paths.

5. Effect of Contact Time and Temperature on Dehydration of Sorbitol

To clarify the reaction routes over 30% PW/SiO_2 catalyst, we have investigated the effect of the contact time, expressed W/F, on the conversion of sorbitol to products at 250 °C, where W and F denote the catalyst weight and the total flow rate, respectively. The sorbitol conversion increased almost proportionally to the contact time. Fig. 6 shows that the selectivity to 1,4-sorbitan increased significantly as the contact time decreased, suggesting that 1,4-sorbitan was the primary product and the consecutive dehydration of

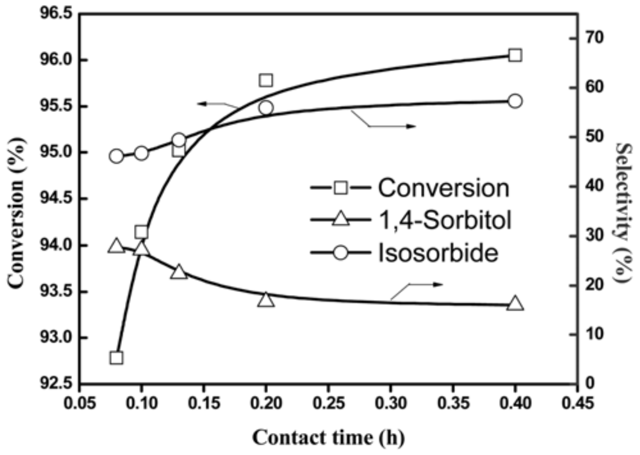

Fig. 6. Effect of contact time on 30% PW/SiO_2 catalyzed dehydration of sorbitol. Reaction condition: Sorbitol feedstock, 10 wt%; N_2 flow rate, 30 mL min^{-1}; Catalyst, 0.5 g; TOS, 6 h; Temperature, 250 °C.

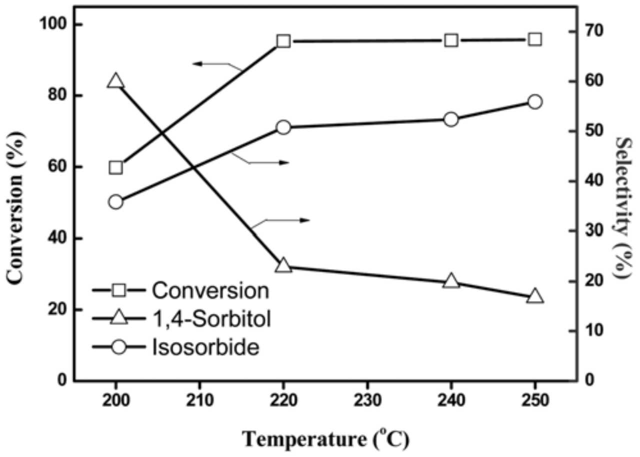

Fig. 7. Effect of temperature on 30% PW/SiO_2 catalyzed dehydration of sorbitol. Reaction condition: Sorbitol feedstock, 10 wt%; F=2.4 mL h^{-1}; N_2 flow rate, 30 mL min^{-1}; Catalyst, 0.5 g; TOS, 6 h.

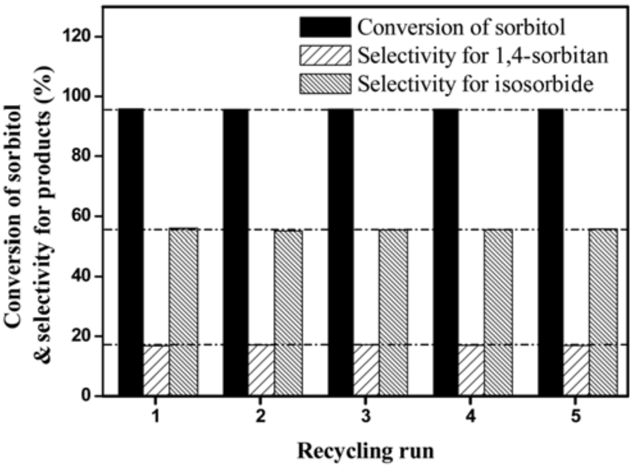

Fig. 8. Conversion of sorbitol and selectivity for 1,4-sorbitan and isosorbide over fresh PW/SiO$_2$ catalyst (Run 1) and regenerated PW/SiO$_2$ catalyst by dichloromethane elution (Run 2-Run 5). Reaction condition: Sorbitol feedstock, 10 wt%; F=2.4 mL h^{-1}; N$_2$ flow rate, 30 mL min^{-1}; Catalyst, 0.5 g; TOS, 6 h; Temperature, 250 °C.

1,4-sorbitan gave isosorbide.

The effect of reaction temperature on the conversion of sorbitol and the product selectivity over 30% PW/SiO$_2$ was studied in the temperature range 200-250 °C and the results shown in Fig. 7. It can be seen that the conversion of sorbitol increased up to 95.78% with increasing the reaction temperature to 250 °C, whereas the selectivity for 1,4-sorbitan decreased from 59.79 to 16.75% and the selectivity for isosorbide increased from 35.78 to 55.89%. It should be noted that the conversion of sorbitol was sensitive to temperature below 220 °C. However, almost no improvement of conversion was obtained with further increasing temperature to 250 °C, indicating that 220 °C was adequate for sorbitol activation on 30% PW/SiO$_2$. Besides, the selectivity for isosorbide was significantly increased with temperature enhancement, indicating that the formation of isosorbide needed higher temperature than that of 1,4-sorbitan.

6. Catalytic Performance of Regenerated 30% PW/SiO$_2$ Catalyst

Fig. 8 shows the conversion of sorbitol and selectivity for 1,4-sorbitan and isosorbide over fresh 30% PW/SiO$_2$ catalyst and regenerated one with respect to recycling run. Both fresh and regenerated catalysts exhibited *ca.* 95% conversion of sorbitol. 30% PW/SiO$_2$ catalyst regenerated by dichloromethane elution exhibited the same selectivity for 1,4-sorbitan and isosorbide as fresh catalyst without any catalyst deactivation with respect to recycling run. This indicated that dichloromethane elution was an efficient method for the regeneration of 30% PW/SiO$_2$ catalyst. In view of the possibility of PW leaching during dichloromethane elution, the dichloromethane of each cycle was diluted five fold and confirmed with UV spectrum to check the leached PW. As shown in Fig. 5(b), for runs 1 and 2, no band of Keggin $PW_{12}O_{40}^{3-}$ anions was observed. However, this band emerged and gradually increased from run 3 to run 5, demonstrating that dichloromethane elution resulted in PW leaching to some extent. It should be noted that the amount of leached PW could be neglected compared with 30 wt% loading.

The concentration of initial PW solution was 0.075 g mL^{-1} in Fig. 1. This solution was diluted two-thousand fold to perform the UV spectrum, due to the high sensitivity of UV spectrometer. In Fig. 5(b), dichloromethane of each cycle was diluted only five fold and confirmed with UV spectrum. The band of Keggin anion could be well observed at this diluted concentration. However, it was invisible if dilution was more than 50 fold. Hence, we concluded that the amount of leached PW could be neglected compared with 30 wt% loading. This very tiny leach of PW could be hard to affect the catalytic performance of 30%PW/SiO$_2$. Therefore, the same activity was kept after five cycles.

CONCLUSIONS

Dehydration of sorbitol is studied with PW supported on various oxides. 30% PW/SiO$_2$ gives the highest conversion of sorbitol and selectivity for isosorbide compared to the other catalysts. The regeneration with dichloromethane elution of the catalyst is found to be efficient. The final acidity of supported PW catalyst is determined by PW species presenting on the supports and the interaction with supports. PW/SiO$_2$ catalyst showing the weaker interaction possesses stronger acidity than other tested catalysts. Therefore, the better catalytic performance is obtained over PW/SiO$_2$ catalyst.

In summary, supported PW is found to be efficient, reusable, inexpensive and ecofriendly solid acid catalyst for dehydration of sorbitol to isosorbide. High yields of the products, mild reaction conditions and simple experimental procedure and product isolation make this an important complement to the existing methods.

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