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Catalytic Efficiency of Cesium and Potassium Salts of Dodecatungstophosphoric Acid Supported on Silica and Comparison with $H_3PW_{12}O_{40}/SiO_2$[1]

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Abstract—Pure tungstophosphoric acid, potassium tungstophosphate, and cesium tungstophosphate with varying extent of substitution of protons by Cs or K ions x (x = 1, 2, 2.5, and 3) have been prepared and are supported on silica by the wet impregnation method. The extent of loading was fixed at 20 wt %. For the sake of comparison, unloaded Cs_x and K_x (x = 1) salts of tungstophosphoric acid were prepared by the precipitation method. The supported catalysts were characterized by FT-IR, XRD, specific surface area measurements, and catalytic conversion of *tert*-butanol. The results revealed that the catalytic conversion of *tert*-butanol proceeds mainly via dehydration yielding isobutene. The Cs_1PW/SiO_2, HPW/SiO_2, and K_1PW/SiO_2 catalysts were more active than their unsupported samples. The previous solids showed greater catalytic activity and stability. Unexpectedly, substitution of one proton of tungstophosphoric acid by a cesium or potassium ion exerted no measurable effect on the catalytic activity of the treated solids, in spite of decreasing the Brønsted acidity of Cs_1PW/SiO_2 and K_1PW/SiO_2 indicating that the acidity of HPW/SiO_2 decrease may be due to the interaction between HPW and the SiO_2 surface. On the other hand, significant decrease in the catalytic activity took place upon increasing the cation content (x) to x = 2, 2.5, and 3.

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1. INTRODUCTION

The development of high performance catalysts is very important for chemical technologies. 12-heteropolyacids with Keggin structures have been an object of research for a long time [1–10]. Heteropolyacids (HPA) have proved to be the alternative of traditional acid catalysts, such as sulfuric acid and aluminium chloride, due to their strong acidity, environmental benignity, and ability to be used repeatedly. But pure HPA used as heterogeneous catalysts are hindered by their low specific area, rapid deactivation, and relatively poor stability. However, dodecatungstophosphoric acid is the most extensively studied [4, 11–16], since it possesses super acidity [17]. Partially exchanging protons of heteropolyacid with large cations typically demonstrate different physicochemical properties than those of their precursor acids. For example, partially exchanging protons of the parent HPA with large cations, such as Cs^+, K^+, Rb^+, and NH_4^+, could be water-insoluble and present a rather high surface area [18]. In addition, these heteropolyacid salts improved thermal stability more than their parent acids [5, 18]. These catalysts were also tested as catalysts for several reactions with the final objective of industrial use [6, 7, 19] as alcohol dehydration [8, 12], alkylation [9, 20], or esterification reactions [21]. The biggest activities were achieved upon partially substitution of HPA protons with Cs stoichiometry, for example, equal to 2.5. The performance of this catalyst is attributed to its high surface area and its micro- and mesoporous structures [22, 23]. On the other hand, the BET surface area of cesium dodecatungstophosphate was shown to decrease with increasing the cesium content to 2 [24], leading to a decrease in the activities of these catalysts.

Another method to improve the efficiency of the heteropolyacid catalysts is achieved by supporting on various carriers such as mesoporous silica [25], aluminosilicates [26], zirconia [11, 27], alumina and active carbons [28, 29]. Because of the basic nature of alumina and zirconia, they led to decompose HPA, resulting in a deformation of the parent Keggin structure, thereby reducing the overall activity [11, 27]. For supported heteropolyacids, solid state NMR has shown that strong interactions exist between heteropolyacids and their supports, depending on the nature of the support and the degree of dispersion of the heteropolyacid [14, 30]. When tungstophosphoric acid (HPW) is supported on silica, two distinct forms of heteropolyacid are deposited on the surface of silica, namely, the bulk crystalline phase and the interacting form [31].

[1] This article was submitted by the authors in English.

The use of high surface area support materials such as silica in this paper can accommodate cesium and potassium tungstophosphate due to its intrinsic inertness [8, 32, 33]. Also, Kim et al. [14] have reported that the silica matrix was a suitable support to prevent the leakage of heteropolyacid in aqueous media. This method may allow us to increase the effective surface area of Cs_x or K_x ($x < 2.5$) salts of tungstophosphoric acid, thereby transforming them into more effective catalysts.

Preparation of supported alkaline metal heteropolyacid salts was the object of investigation of several authors [13, 16, 34, 35]. The prepared supported alkaline Cs_x and K_x tungstophosphates on SiO_2 (20 wt %) with nominal compositions x = 1, 2, 2.5, and 3 were characterized by different physicochemical techniques.

The aim of this work is to improve the catalytic efficiency of $Cs_1H_2PW_{12}O_{40}$, $H_3PW_{12}O_{40}$, and $K_1H_2PW_{12}O_{40}$ via supporting on a suitable support material such as SiO_2. Furthermore, a comparative study has been carried out on the catalytic activity expressed by the total conversion of *tert*-butanol between the supported tungstophosphoric acid on silica and supported alkaline Cs_x and K_x (x = 1, 2, 2.5, 3.0) tungstophosphates on SiO_2 with the same loading 20 wt %.

2. EXPERIMENTAL

2.1. Materials

Cesium (Cs_x) and potassium (K_x) (x = 1) dodecatungstophosphates were prepared by adding dropwise an appropriate volume of aqueous $CsNO_3$ (Aldrich) or KNO_3 (Koch-light) to an aqueous solution of dodecatungstophosphoric acid (BDH) over a water bath at 343 K with constant stirring for 4 h. The resulting precipitates were evaporated, dried at 383 K for 4 h, and calcined at 573 K for 2 h. Tert-butyl alcohol (Carlo ERBA) that is chromatographically pure was used.

The silica support material was used for different catalysts having a BET surface area of about 645 m^2/g. It was crushed, sieved into grains of 0.2–0.4 mm, and then calcined in a hot-air oven at 773 K for 4 h. Pure $H_3PW_{12}O_{40}$ was supported on silica (20 wt %) by impregnation using a butanolic solution, dried at 383 K overnight, and then calcined at 573 K for 2 h.

For sake of comparison, the silica-supported cesium and potassium salts of tungstophosphoric acid were prepared by impregnation adopting the method suggested by Choi et al. [13]. First $CsNO_3$ or KNO_3 was impregnated onto silica powder (20 wt %) and dried at 383 K overnight. Then, it was calcined at 573 K for 2 h. Following this, the butanolic solution of tungstophosphoric acid was impregnated followed by drying at 383 K overnight and calcination at 573 K for 2 h. The quantity of $CsNO_3$ or KNO_3 used had the nominal compositions $Cs_x(K_x)H_{3-x}PW_{12}O_{40}$ (where x = 1, 2, 2.5, and 3). The catalyst symbols was submitted as Cs_xPW/SiO_2, HPW/SiO_2, and K_xPW/SiO_2.

2.2. Techniques

FT-IR spectra of various solids were recorded on a BRUKER Vector 22-Germany spectrometer in KBr pellets in the range of 4000–400 cm^{-1} under atmospheric conditions. The samples were heated at 573 K before each measurement.

XRD investigation of various prepared solids was carried out using a Philips diffractometer type (PW–1390). The patterns were run with Ni-filter and Cu radiation (λ = 1.5405 Å) at 40 kV and 30 mA. The scanning rate was fixed at 5° in 2θ/min.

The surface area measurements of the selected samples were performed by the BET method from nitrogen adsorption–desorption isotherms obtained at 77 K.

The catalytic activity of various solids was studied by using the catalytic conversion of *tert*-butanol in a conventional flow-type reactor under atmospheric pressure. The reactor tube is a Pyrex glass of 20 cm long and 1 cm internal diameter packed with glass beads except in the zone where the catalyst bed is located. The catalyst bed is placed in the middle of the reactor tube. The weight of the catalyst used was 200 mg, and a digital thermometer was used to measure the temperature of the catalyst. Both reactor and furnace are placed inside a Pyrex glass jacket of 5 cm diameter.

The catalysts investigated were activated in situ prior to exposure to the alcohol vapor by heating at 573 K for 1 h in a current of argon flowing at a rate of 20 ml min^{-1}. The reaction was carried out in the temperature range from 323 to 423 K. In the case of studying the effect of repeated use of the selected catalysts on their activities, the samples were reheated at 573 K for 2 h under flow of argon gas.

The reaction mixture was analyzed using a gas chromatograph (PerkinElmer Autosystem XL with flame ionization detector) equipped with capillary column (fused silica) of 15 m length, 0.25 mm internal diameter, with film thickness 1.0 μm; the capillary column was packed with Carbowax 20M, and the oven temperature was set at 333 K. The detector was kept at 493 K.

Preliminary experiments showed that the conversion of alcohol in the absence of a catalyst did not take place even for the reaction carried out at 423 K.

3. RESULTS AND DISCUSSION

3.1. FT-IR Investigation of Various Catalyst Samples

The primary structure of the supported catalysts was identified by comparing their FT-IR absorbance bands to those of bulk tungstophosphoric acid with the wave number range 4000–400 cm^{-1}.

Rocchiccioli-Deltcheff et al. [36] assigned the four main Keggin anion vibration bands of tungstophospho-

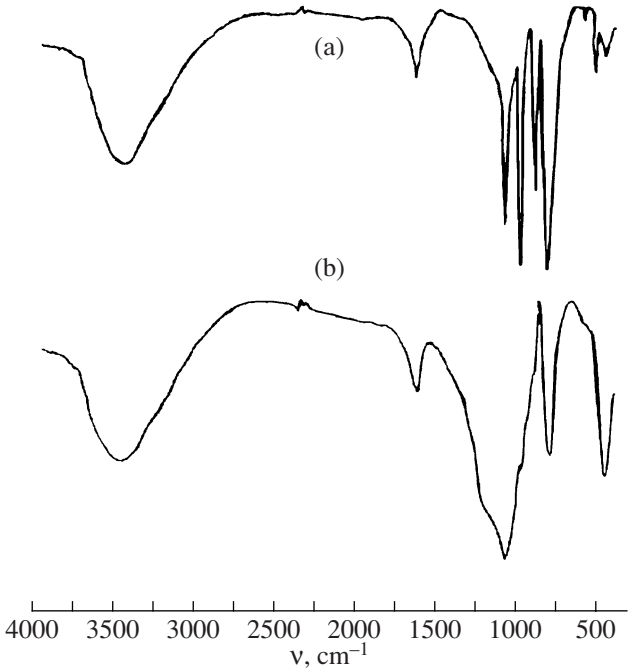

Fig. 1. FT-IR spectra of (a) HPW, (b) HPW/SiO_2.

ric acid as follows: the one that appeared at 1080 cm^{-1} to the $\nu_{as}(PO_a)$ vibration, that at 982 cm^{-1} to the terminal $\nu_{as}(W = O_d)$ vibration, and those at 890 and 810 cm^{-1} to $\nu_{as}(W–O_b–W)$ and $\nu_{as}(W–O_c–W)$, respectively. The spectra of tungstophosphoric acid (Fig. 1a) shows bands at 1080, 982, 882, and 806 cm^{-1}. These bands can be assigned to the stretching vibrations of $\nu_{as}(PO_a)$, $\nu_{as}(W = O_d)$, $\nu_{as}(W–O_b–W)$, and $\nu_{as}(W–O_c–W)$, respectively.

Figures 1b, 2, and 3 show the FT-IR spectra of HPW/SiO_2, K_xPW/SiO_2, and Cs_xPW/SiO_2 (x = 1, 2, 2.5, 3). It is notable that the bands at 1080–806 cm^{-1}, characteristic of the Keggin structure, are almost the same for cesium and potassium salts of tungstophosphoric acid. Examination of Figs. 1–3 showed that supporting HPW, K_xPW, and Cs_xPW on SiO_2 resulted in some structure modification as evidenced from the change in sharpness and area of bands at 1080–806 cm^{-1}.

The characteristic peak at 1080–1081 cm^{-1} (PO_a) for the HPW/SiO_2 (20 wt %) and silica-supported acid salts with a small amount of Cs_x (x = 1 and 2) or K_x (x = 1) broadened compared with that of tungstophosphoric acid (Figs. 1–3) owing to the overlapping of PO_a and Si–O–Si vibrations. Therefore, it is believed that a strong chemical interaction, not a simple physical adsorption, exists between tungstophosphoric acid and the silica surface. Similarly, the same result has been postulated by Peng et al. [37] in studying IR-spectra of $Cs_{1.5}H_{1.5}PMo_{12}O_{40}/SiO_2$. However, the spectra of the previous supported catalysts showed a measurable decrease in the intensities of $\nu(W = O_d)$, $\nu(W–O_b–W)$, and $\nu(W–O_c–W)$ vibration bands. On the other hand, the spectra of supported acid salt catalysts with a high extent of Cs_x (x = 2.5 and 3) or K_x (x = 2, 2.5, and 3) show all the characteristic peaks of Keggin structure with high area and sharpness suggesting the existence of weak interaction between these salts and the silica surface.

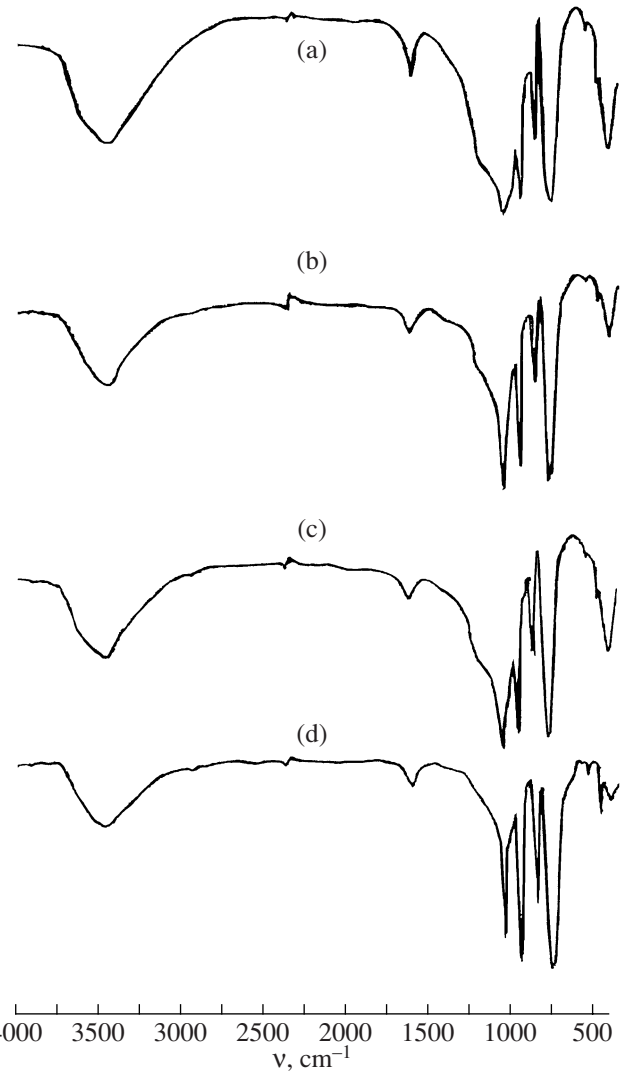

Fig. 2. FT-IR spectra of (a) K_1PW/SiO_2, (b) K_2PW/SiO_2, (c) $K_{2.5}PW/SiO_2$, (d) K_3PW/SiO_2.

The comparison between Figs. 1–3 revealed the following: (i) Loading of HPW, K_xPW, and Cs_xPW (x = 1, 2, 2.5, and 3) on SiO_2 led to a small decrease in the intensity of the band at 3450 cm^{-1}. (ii) The increase in potassium or cesium content on silica-supported catalysts resulted in a progressive decrease in the area of the bands at 3450 cm^{-1}. These findings might suggest that both SiO_2 used as a catalyst support and incorporation of K or Cs in the supported system brought about a measurable decrease in the acidity of the treated solid as evidenced from the decrease in the area of the band

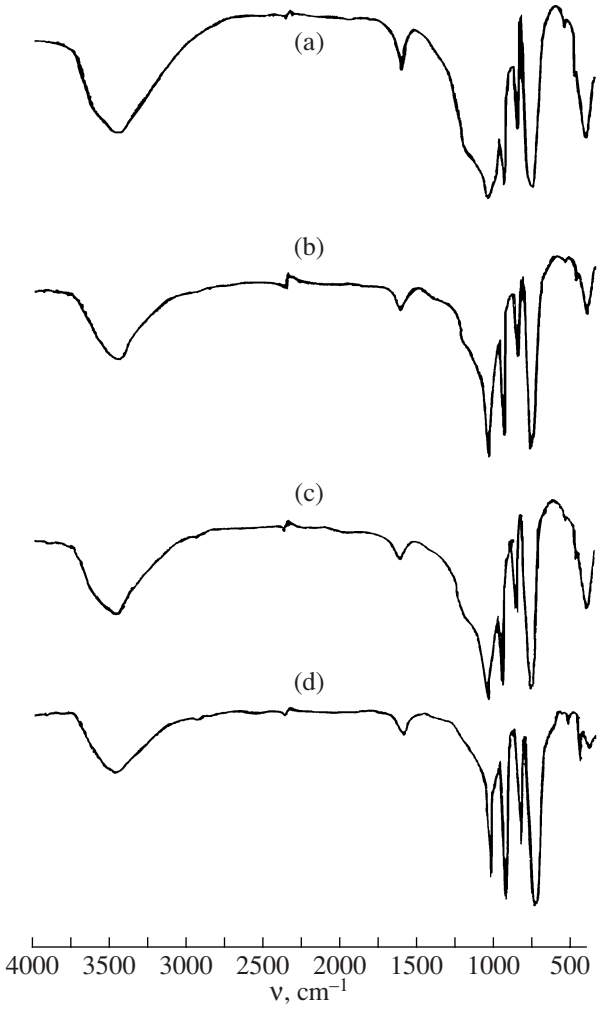

Fig. 3. FT-IR spectra of (a) Cs_1PW/SiO_2, (b) Cs_2PW/SiO_2, (c) $Cs_{2.5}PW/SiO_2$, (d) Cs_3PW/SiO_2.

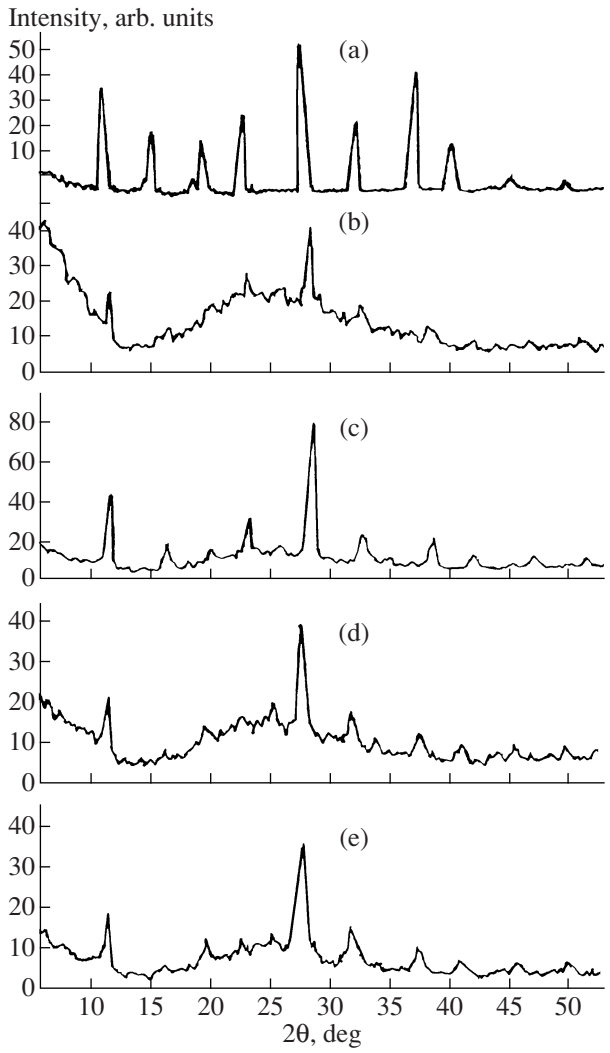

Fig. 4. XRD spectra of HPW, K_1PW/SiO_2, $K_{2.5}PW/SiO_2$, Cs_1PW/SiO_2, and $Cs_{2.5}PW/SiO_2$ from top to bottom.

at 3450 cm^{-1}. (iii) Incorporation of K_x or Cs_x led to some kind of structure modification, especially for the supported K or Cs dodecatungstophosphate samples. This conclusion has been deduced from the observed change in sharpness and area of the bands at 1080–806 cm^{-1}, but Keggin anions are still present on the silica surface in all catalyst samples.

3.2. XRD Analysis of Different Solids

XRD investigation of silica support material and the HPW/SiO_2 catalyst was carried out. The diffractogram, not given, showed that the investigated solids were amorphous. The XRD of tungstophosphoric acid and its cesium or potassium salts supported on silica are illustrated in (Fig. 4). Figure 4 shows that supporting HPW on silica (20 wt %) led to a complete disappearance of all characteristic diffraction peaks of HPW. The amorphous nature of acid-supported silica suggested that its crystallite size is very small, beyond the detection limit of the X-ray diffractometer (1–2 nm) and/or its presence in a very small amount. So, HPW should be present on the silica surface and may form a two-dimensional layer showing a strong interaction occurs between HPW and OH groups on silica according to the following Eq. (1):

$$H_3PW_{12}O_{40} + mOH/Si \longrightarrow H_{3-m}PW_{12}O_{40}/Si + mH_2O. \quad (1)$$

This finding is in agreement with that reported by Izumi et al. [8] and Kozhevnikov et al. [25]. These authors claimed the absence of all characteristic diffraction peaks of HPW until an extent of loading of 20 wt %. However, these finding are not consistent with the results reported by Kuang et al. [4] and López–Salinas et al. [11]. This difference may be attributed to changes in the preparation and pretreatment conditions.

On the other hand, the diffraction lines of the cubic HPW phase (c.f. Fig. 4) were observed for supported cesium and potassium salts of tungstophosphoric acid as evidenced from the results. However, the X-ray dif-

Table 1. The specific surface area (S_{BET}) of the prepared catalysts

Catalyst	Surface area (S_{BET}), $m^2\ g^{-1}$
SiO_2	645
HPW	7
HPW/SiO_2	542
K_1PW	11.6
K_1PW/SiO_2	268
$K_{2.5}PW/SiO_2$	250
Cs_1PW	9.9
Cs_1PW/SiO_2	291
$Cs_{2.5}PW/SiO_2$	255

fractogram shows the presence of HPW crystalline phase in the supported Cs_x or K_x tungstophosphate catalysts. The degree of crystallinity of acid increases upon increasing the amount of Cs or K ions.

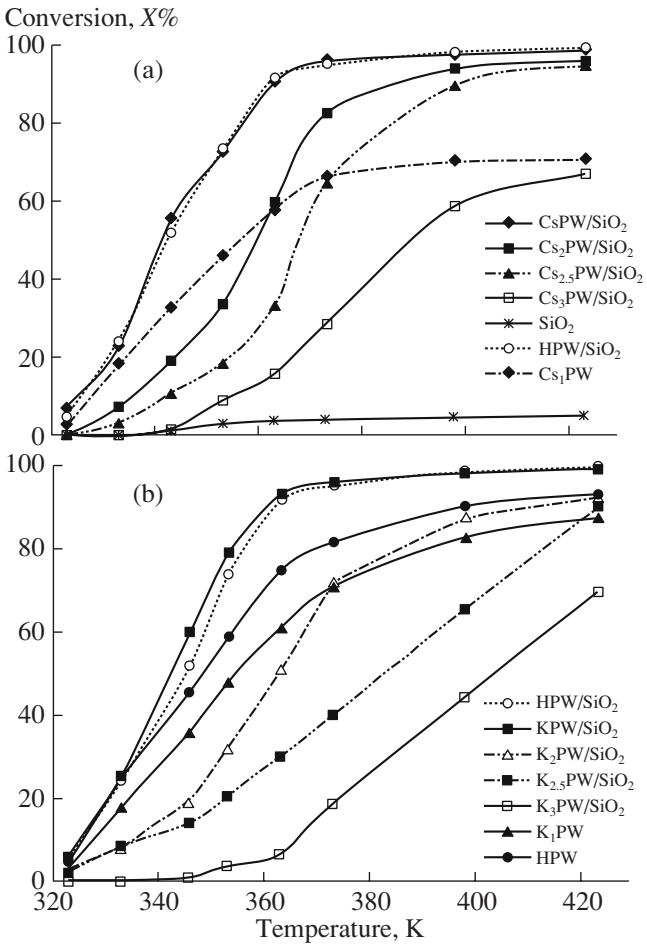

Fig. 5. Total conversion *X*, %, of *tert*-butanol as a function of reaction temperature over supported catalysts.

3.3. Specifics Surface Area Measurements

The specific surface area measurements of the selected samples were performed by the BET method from nitrogen adsorption–desorption isotherms obtained at 77 K. Table 1 shows the specific surface area (S_{BET}) of the prepared catalysts. It is clear from this table that the specific surface area (S_{BET}) of pure silica calcined at 773 K measured 645 m^2/g and decreases to 542 m^2/g upon impregnation of HPW with 20 wt %. This decrease, which attained 16%, is very small as compared with that reported in the literature (31%) [12]. The limited decrease in the S_{BET} of the silica support material treated with 20 wt % HPW could be attributed to the location of acid molecules in the pores of silica.

However, alkali treatment of the supported system investigated with different amounts of Cs_x or K_x brought about a significant decrease in the S_{BET} to an extent proportional to the amount of potassium or cesium added as shown in Table 1. The maximum decrease in the S_{BET} of acid-supported silica due to treating with Cs_x or K_x ($x = 2.5$) fell to 60.5 and 61.2%, respectively. This significant decrease in the S_{BET} of acid-supported silica could be discussed in terms of the effective crystallization of silica support material upon substitution of protonic acid with K or Cs ions. In fact, the employed silica support material and the sample treated with 20 wt % HPW are amorphous in nature and underwent an effective crystallization upon treatment with K or Cs ions (c.f., Fig. 4).

On the other hand, unsupported HPW, Cs_1PW, and K_1PW catalysts measure very small specific surface areas (c.f., Table 1).

3.4. Catalytic Properties of Different Solids

The catalytic conversion of *tert*-butanol was carried out over various catalysts at temperatures ranging between 323 and 423 K under a constant partial pressure of alcohol (100 Torr). Figure 5 shows the variation of % of conversion of *tert*-butanol as a function of the reaction temperature for various catalysts. It is clear from this figure that the total conversion increases upon increasing the reaction temperature reaching a constant value at 373 K for most of the samples investigated.

The reaction products consist mainly of isobutene together with a small amount of isooctene that may be produced via dimerization of isobutene. However, this reaction took place over various catalysts at a temperature of >373 K. This finding readily suggested that the catalytic conversion of *tert*-butanol over various catalysts proceeds mainly via dehydration and having selectivity bigger than 92% at 373 K. Tables 2 and 3 include variation selectivity towards dehydration and dimerization processes during the conversion of *tert*-butanol, which was carried out at different temperatures for various solids.

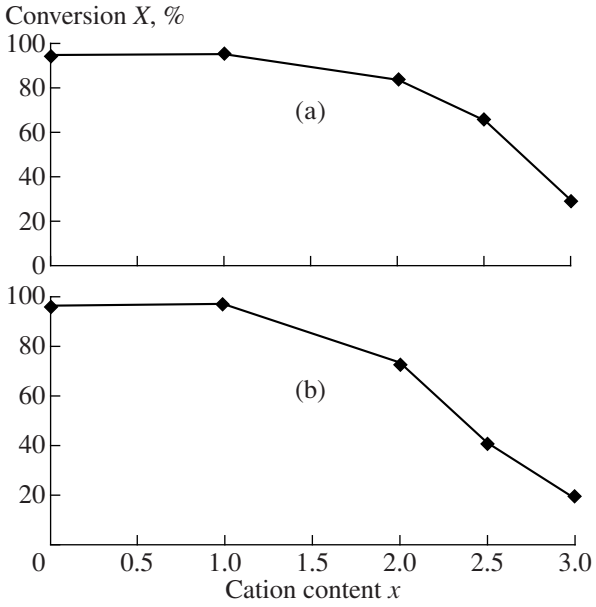

Fig. 6. Total conversion X, %, of *tert*-butanol at 373 K as a function of cation content, x, over (a) Cs_xPW/SiO_2 and (b) K_xPW/SiO_2.

It is interesting to note that the selectivity towards isooctene formation decreases upon increasing substituted protons of tungstophosphoric acid by Cs_x or K_x ($x > 2$) ions (Tables 2, 3). This finding may suggest that these catalysts exhibit very small dimerization selectivity and have a small amount of acidic sites on the surface. In a previous study, Corma et al. [38] reported that the propene oligomerization and *n*-butane isomerization were correlated with the concentration of protons on the surface.

However, examination of Fig. 5 shows that HPW, Cs_1PW, and K_1PW catalysts have smaller catalytic activity than their silica-supported samples due to the very small specific surface area (7, 9.9, and 11.6 $m^2\ g^{-1}$, respectively). It has been reported by several authors [38–40] that the surface acidity of cesium salts of tungstophosphoric acid decreases in the presence of small amount of Cs_x ($x < 2$). This decrease has been related to the formation of ultrafine precipitate of particles (probably $Cs_3PW_{12}O_{40}$, 8–10 nm) which are thickly covered by $H_3PW_{12}O_{40}$, being deposited upon evaporation of water, and form large aggregates, whereby the hydrogen form is possibly acting as a cement substrate. After heat treatment they are converted to particles having a size similar to before heat treatment and nearly uniform composition, but with a small specific surface area [39, 40].

The disadvantage of HPW, Cs_1PW, and K_1PW catalysts can be overcome by supporting on a suitable support material having a big specific surface area such as SiO_2. Therefore, supporting these samples on silica results in an increasing number of the catalytically active sites and the growth of the surface area to 542, 291, and 268 $m^2\ g^{-1}$, respectively, for HPW/SiO_2, Cs_1PW/SiO_2, and K_1PW/SiO_2. This significant increase in the specific surface area is expected to be accompanied by a corresponding increase in the catalytic activity as shown in Fig. 5.

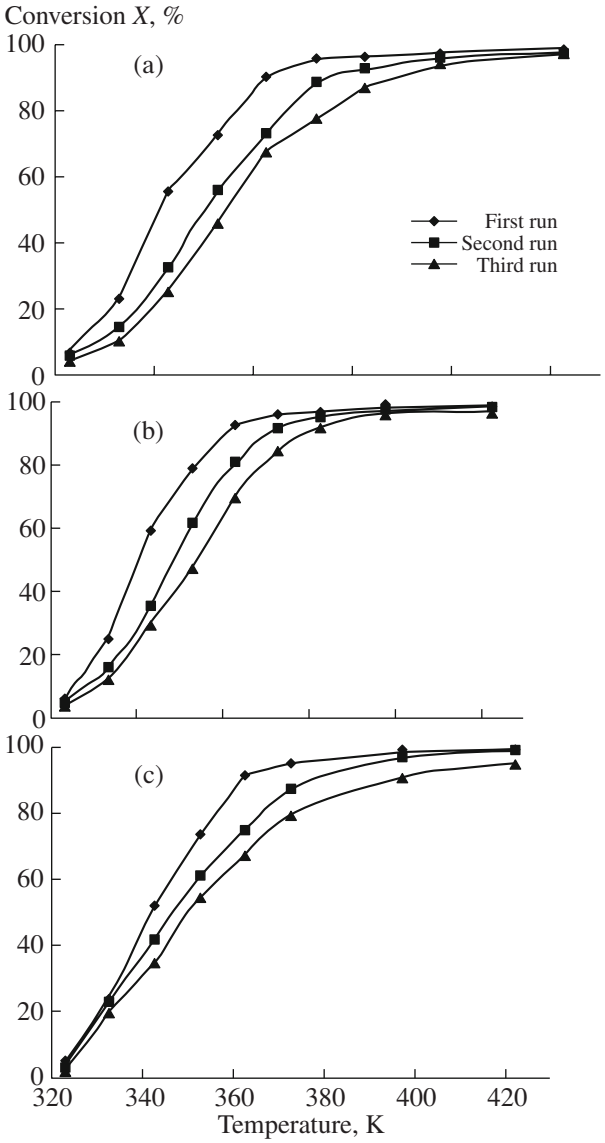

Fig. 7. Changes in the catalytic activity by reusing of (a) Cs_1PW/SiO_2, (b) K_1PW/SiO_2, and (c) HPW/SiO_2 vs. temperature for the conversion of *tert*-butanol.

Figure 5a shows that the silica support material has very small catalytic activity suggesting its inertness as reported in the literature [8, 12, 32, 33].

The conversion of *tert*-butanol carried out at 373 K by HPW/SiO_2, Cs_xPW/SiO_2, and K_xPW/SiO_2 is given in Fig. 6 as a function of cation content per Keggin unit (x). It can be observed that the overall conversion over HPW/SiO_2 reached ~96% at 373 K. The high activity of this particular catalyst sample can express an effective increase in the surface concentration of active sites taking part in the catalytic process. It is clearly shown from

Table 2. Selectivity in the conversion of *tert*-butanol over supported cesium tungstophosphate

Catalyst sample	Temp., K	Selectivity, %	
		isobutene, %	isooctene, %
Cs_1PW/SiO_2	323	100.0	0.0
	333	99.3	0.7
	343	99.2	0.8
	353	99.0	1.0
	363	97.8	2.2
	373	95.3	4.7
	398	86.1	13.9
	423	80.8	19.2
Cs_2PW/SiO_2	323	100.0	0.0
	333	100.0	0.0
	343	100.0	0.0
	353	100.0	0.0
	363	99.7	0.3
	373	99.3	0.7
	398	95.7	4.3
	423	91.6	8.4
$Cs_{2.5}PW/SiO_2$	323	100.0	0.0
	333	100.0	0.0
	343	100.0	0.0
	353	100.0	0.0
	363	100.0	0.0
	373	99.7	0.3
	398	97.8	2.2
	423	92.6	7.4
Cs_3PW/SiO_2	323–423	100	0

Table 3. Selectivity in the conversion of *tert*-butanol over supported HPW and potassium tungstophosphate

Catalyst sample	Temp., K	Selectivity, %	
		isobutene, %	isooctene, %
HPW/SiO_2	323	100.0	0.0
	333	99.2	0.8
	343	98.0	2.0
	353	98.1	1.9
	363	96.4	3.6
	373	92.7	7.3
	398	83.7	16.3
	423	80.9	19.1
K_1PW/SiO_2	323	100.0	0.0
	333	100.0	0.0
	343	100.0	0.0
	353	99.5	0.5
	363	97.8	2.2
	373	93.7	6.3
	398	88.8	11.2
	423	87.0	13.0
K_2PW/SiO_2	323	100.0	0.0
	333	100.0	0.0
	343	100.0	0.0
	353	100.0	0.0
	363	100.0	0.0
	373	99.4	0.6
	398	94.6	5.4
	423	88.8	11.2
$K_{2.5}PW/SiO_2$	323	100.0	0.0
	333	100.0	0.0
	343	100.0	0.0
	353	100.0	0.0
	363	100.0	0.0
	373	99.8	0.2
	398	95.8	4.2
	423	91.6	8.4
K_3PW/SiO_2	323–423	100	0

Fig. 6 that substitution of one proton of tungstophosphoric acid with a cesium or potassium ion exerted no effect on the catalytic activity of the treated solids, in spite of decreasing the Brønsted acidity of Cs_1PW/SiO_2 and K_1PW/SiO_2 (as evidenced by FT-IR results). This finding may be due to a strong interaction between free protons of HPW and OH of the surface of silica. However, in the supporting of HPW over silica with a small loading 20 wt %, HPW forms finely dispersed species on the silica surface (c.f., XRD results) and "interacting species" such as $(SiOH_2)^+(H_2PW_{12}O_{40})^-$ may be formed. It is clear that this interaction of HPW and the OH surface of silica led to proton transformation to the silica surface which results in a decrease of acidity (the strong interaction is confirmed by FTIR results). So, fewer protons are available for the catalytic reaction. These results are consistent with a previous study published by Kozhevnikov et al [25]. These authors claimed the interaction of HPW with the surface of silica takes place more easily on samples having an extent of loading smaller than 30 wt %. However, in another study [14] the authors reported that this interaction includes the trapping of some acidic proton of heteropolyacid in the basic OH groups of silica support and results in a decrease in the acid strength of the heteropolyacid.

Figure 6 shows that the catalytic activity of Cs_xPW/SiO_2 and K_xPW/SiO_2 decreases progressively by increasing the number of proton molecules substituted by cesium or potassium ions. This decrease was,

however, more pronounced at the degree of substitution of 2.5 protons. This finding could be discussed in terms of both SiO_2 being used as a catalyst support and incorporation of K_x or Cs_x ($x > 2$) in the supported system, which brought about a measurable decrease in the acidity of the treated solid as evidenced in the FTIR results. This decrease in the acidity may lead to a decrease in the catalytic activity.

Surprisingly, the Cs_3PW/SiO_2 and K_3PW/SiO_2 catalysts have limited catalytic activity in this reaction (conversion = 28.3 and 18.6%, respectively at 373 K) in spite of the absence of acidic protons. So, their catalytic activity may be due to the presence of residual protons in the solid lattice.

Stability of the catalyst is a very important factor before using any catalyst for an industrial application.

In the present study, the mass of the catalyst sample used (200 mg) was too small to examine the efficiency of the catalyst. The reusability of 20 wt % of HPW/SiO_2, Cs_1PW/SiO_2, and K_1PW/SiO_2 was studied three times and is shown in Fig. 7. After the first use and before every reuse, the catalysts were recalcined at 573 K for 2 h in a current of argon as an inert gas to remove the adsorbed reactant and products.

When HPW/SiO_2, Cs_1PW/SiO_2, and K_1PW/SiO_2 were used repeatedly, a minor decrease in the conversion was observed, although no significant effect was observed in the final conversion at high temperature. This result may indicate that the previous catalysts may have a suitable catalytic stability. The stability of HPW/SiO_2, Cs_1PW/SiO_2, and K_1PW/SiO_2 was also confirmed by FTIR spectra of fresh and reused samples (not shown). No change in the primary Keggin anion was observed for the catalysts used. The same behavior was obtained on $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on K-10 (20%) in the presence of benzoyl chloride for benzoylation of anisole [41].

CONCLUSIONS

The following are the main conclusions that may be drawn from the results:

(1) FT-IR investigation of HPW/SiO_2, Cs_xPW/SiO_2, and K_xPW/SiO_2 (where x = 1, 2, 2.5, and 3) suggested a decrease in the acidity of the treated solid. This decrease was found to be a result of both SiO_2 being used as a catalyst support and incorporation of K or Cs in the supported system.

(2) Loading HPW on silica 20 wt % led to the complete disappearance of all diffraction lines of the HPW phase indicating the role of SiO_2 in much increasing the degree of dispersion of the acid.

(3) Supporting cesium or potassium salts of dodecatungstophosphoric acid on silica 20 wt % hinders the role of silica in increasing the dispersion of the acid. This hindrance ran parallel to the cation content of Cs_x or K_x per Keggin unit (x).

(4) The S_{BET} of SiO_2 decreases upon treatment with 20 wt % of HPW and also upon treatment with cesium or potassium salts of HPW with the same extent of loading, 20 wt %.

(5) All investigated catalyst samples solids are highly selective toward dehydration of *tert*-butanol yielding isobutene. A small amount of isooctene was formed at a temperature above 373 K on the catalyst surface.

(6) Silica support material showed no measurable catalytic activity. However, unsupported HPW and its cesium and potassium salts showed a measurable activity, which was found to increase by loading on SiO_2 20 wt %.

(7) Cesium and potassium salts of HPW supported on SiO_2 exhibited a noticeable catalytic activity which decreased progressively by increasing the degree of substitution of protons of the acid.

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