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Research paper

A Novel Brønsted-Lewis acidic catalyst based on heteropoly phosphotungstates: Synthesis and catalysis in benzylation of *p*-xylene with benzyl alcohol

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ABSTRACT

A novel Brønsted-Lewis acidic catalyst, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, has been prepared by the replacement of protons in neat phosphotungstic acid with both organic and metal cations and characterized by FT-IR, Py-IR, XRD, TG-DTG, ICP-AES, BET, elemental analysis and *n*-butylamine potentiometeric titration techniques. This hybrid heterogeneous catalyst with both Brønsted and Lewis acidity can efficiently promote the conversion of dibenzyl ether, the self-condensation product of benzyl alcohol, to the benzylation products, as well restrain the polybenzylation of aromatics. As a result, it exhibits excellent catalytic activity and selectivity in the benzylation of *p*-xylene with clean benzylation reagent benzyl alcohol. Thus, an environmentally friendly route for the benzylation reaction of *p*-xylene with high atomic economy has been developed by this reusable $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ catalyst.

1. Introduction

Friedel-Crafts benzylation of aromatic is a key direct carbon–carbon bond forming reaction in organic synthesis to produce diarylmethanes and their derivatives, commercial significance pharmaceutical intermediates [1,2]. This industrial process suffers from many problems like pollution, corrosion and difficulty in the separation and recovery of catalysts due to the employment of benzyl chloride as the reagent or homogeneous acid such as $AlCl_3$, $FeCl_3$, and H_2SO_4 as catalysts [3,4]. Benzyl alcohol (BA) is a friendly benzylation reagent to substitute benzyl chloride in view of atom economy and environment factor. Many environmentally friendly catalysts have been studied in benzylation reactions with BA to overcome the problems of mineral acids [5–11]. However, it has been found that the self-condensation of BA is more favorable than benzylation of aromatics with less reactivity over the catalyst without enough catalytic activities [12]. Moreover, the monobenzylated aromatics would further react with BA to produce bulky polybenzylated aromatics at high reaction temperature or strong acidity [10,13]. Some heteropoly compounds (HPCs) catalysts with specific heteropoly anions have exhibited good catalytic activities and selectivities for desired monobenzylated aromatics in the reaction with BA being the benzylation reagent. However, in most cases, these HPCs need to be impregnated onto or encapsulated into porous carriers to overcome the high solubility in polar substance (especially for instance, water generating during benzylation) or the low surface areas [14–17].

Recently, a new modification for heteropolyacid (HPA) catalysts has been developed *via* organic cations bonding ionically to heteropolyanion, just like ionic liquids (ILs) [18–27]. Leng [19] has found that the acid strength of heteropoly ionic liquids could be improved effectively by employing propane sulfonate (PS) functionalized organic cations. However, the PS group in organic cations could only provide enough acid strength for some reactions which were easy to realize, such as esterification [23–25]. In our previous work, heteropoly acidic salts with higher acid strength have been developed *via* the partial replacement of protons by the organic cation with acidic PS groups, and have exhibited good activity, selectivity and stability in the benzylation of anisole with BA [28]. Unfortunately, as to the case of *p*-xylene (PX) with less activation degree, it was difficult to achieve an excellent selectivity for monobenzylation *via* single Brønsted acid sites provided by the heteropoly organic acidic salts, due to the forming of dibenzyl ether (DBE) [29]. On the other hand, Hafnium-exchanged het-

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eropoly acid has been found a favorable catalytic and recycling performance due to the high Lewis acidity [30]. Herein, based on the high charge numbers of heteropoly anions, sulfated organic cations $[TEAPS]^+$ (TEAPS: 3-(triethylammonio) propane sulfonate) with Brønsted acidity and metal cations Hf^{4+} with Lewis acidity were introduced together as counter ions for heteropoly anions $PW_{12}O_{40}{}^{3-}$, establishing a novel heteropoly organic-inorganic salt catalyst, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, with both Brønsted and Lewis acidity. As a solid catalyst, this heteropoly organic-inorganic salt which has the similar structure of ionic liquids and enough water resistance has exhibited excellent activity, selectivity and reusability in the benzylation of PX with BA.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical grade and phosphotungstic acid hydrate was dried at 120 °C. The spectra of Fourier transform infrared spectroscopy (FT-IR) for catalyst samples (for Py-IR test, samples (0.50 g) were put in a vacuum drier together with pyridine (3.0 mL) at 2 Kpa for 12 h prior to measurement) in KBr disks was recorded on a Nicolet iS10 FT-IR instrument in the 400–4000 cm^{-1} range. The measurement of X-ray diffraction (XRD) was performed by used a Rigaku DMAX 2500 PC diffractometer equipped with Cu K_α radiation in the 2θ range of 5−90°. The thermal analysis (TG-DTG) was performed with Netzsch TG209F1 instrument in dry N_2 at a heating rate of 20 °C/min from 30 to 800 °C. The content of the elements in the catalyst was determined by Elementar Vario ELIII system and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) with a Prodigy XP ICP spectroscope. The acidity of prepared catalysts was determined by potentiometric titration [31,32]. The Brunauer Emmett Teller (BET) specific surface areas were determined with a Micromeritics ASAP 2010 apparatus.

2.2. Preparation of organic-inorganic heteropoly salts

Contrastive catalysts, $[TEAPS]_3PW_{12}O_{40}$ and $Hf_{0.5}HPW_{12}O_{40}$, were prepared according to the literatures [19,33]. Analogously, equimolar triethylamine and 1,3-propanesultone were dissolved in ethyl acetate and stirred at 50 °C for 24 h under nitrogen atmosphere. The obtained white precipitate, 3-(triethylammonio) propane sulfonate (TEAPS), was filtered, washed with ethyl acetate and dried at 100 °C for 6 h. Next, a solution of intermediate TEAPS and $HfCl_4$ in water was dropped into another aqueous solution of the calculated amount of $H_3PW_{12}O_{40}$. The solution was stirred at room temperature for 24 h, distilled to remove water, and washed with ethyl acetate. Finally, the obtained solid was dried in a vacuum at 80 °C for 6 h to give organic-inorganic heteropoly salts $Hf_x[TEAPS]_yH_zPW_{12}O_{40}(4x + y + z = 3)$.

2.3. General procedure for the benzylation of p-xylene with benzyl alcohol

The typical procedure for benzylation reactions was as follows: PX, BA, and catalyst $Hf_x[TEAPS]_yH_zPW_{12}O_{40}$ were added proportionally to a round-bottomed flask with a thermometer, a magnetic stirrer and a reflux condenser. The resulting mixture was stirred vigorously at 140 °C for 2 h then was cooled to room temperature. The reaction solution, from which the generated water and precipitated catalyst had been removed, was analyzed by a gas chromatography (GC-9790) equipped with an FID detector and a capillary column (OV-1701, 50 m × 0.25 mm × 0.25 μm) to determine the conversion of BA and the selectivity of benzylation products.

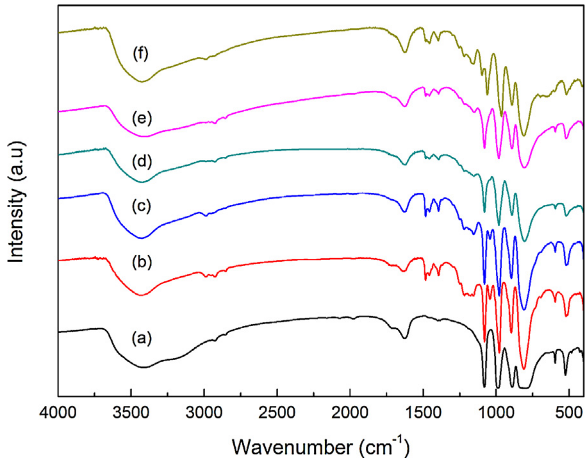


Fig. 1. FT-IR spectra of organic-inorganic heteropoly salts. (a) $H_3PW_{12}O_{40}$, (b) $[TEAPS]_3PW_{12}O_{40}$, (c) $Hf_{0.25}[TEAPS]HPW_{12}O_{40}$, (d) $Hf_{0.25}[TEAPS]_2PW_{12}O_{40}$, (e) $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, (f) Reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$.

The products were identified by GC–MS (HP6980/5973) analysis after the separation of products on a DB-35 column with He as carrier gas.

3. Results and discussion

3.1. Characterization of the organic-inorganic heteropoly salts

The FT-IR spectra (Fig. 1) of prepared organic-inorganic heteropoly salts, comparing with that of the neat $H_3PW_{12}O_{40}$, show that the catalysts $Hf_x[TEAPS]_yH_zPW_{12}O_{40}$, $[TEAPS]_3PW_{12}O_{40}$, and reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ have four featured peaks similar to those of $H_3PW_{12}O_{40}$ [1080 (P-O), 984 (W = O), 891 (W-O_{b1}-W) and 802 cm^{-1} (W-O_{b2}-W)], which are assigned to the Keggin structure. On the other hand, feature peaks at 2989, 1483, 1394 and 1150 cm^{-1} are detected to verify the presence of $[TEAPS]^+$ in these catalysts [20,24]. Obviously, for the organic-inorganic heteropoly salts, the still observed four peaks of Keggin structure together with the simultaneous occurrence of characteristic peaks of organic groups indicate that the structures of both organic cations and heteropoly anions are well preserved. Moreover, the FT-IR spectrum of the used $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ shows no obvious structural change in the catalyst during benzylation (Fig. 1).

Besides, the Py-IR results of prepared organic-inorganic heteropoly salts (Fig. 2) show the existence of featured peaks 1536 cm^{-1} (referred to Brønsted acid) and 1447 cm^{-1} (referred to Lewis acid), which proves the Brønsted-Lewis double acidity of these hybrids and also reveals that both metal ions and sulfated organic cations have been introduced into the structure of $H_3PW_{12}O_{40}$ successfully.

N-butylamine potentiometric titration results of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ and contrastive catalysts are shown in Table 1. Generally, in terms of *n*-butylamine potentiometric, the initial electrode potential indicates the acid strength of catalyst, and the titration jump indicates the total acid amount. It can be seen that introducing organic cations, even with highly acidic sulfonic acid groups (TEAPS), into $H_3PW_{12}O_{40}$ leads to a significant reduction in acid strength. However, there is no distinct influence on acid strength to introduce Hf^{4+} into phosphotungstic acid. Moreover, the total acid amount of these catalysts prevailingly depends on the volume of cations and anions, as well as their bonding. Therefore, the prepared organic-inorganic heteropoly salt, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, demonstrates higher acid strength and total acid amount than highly acidic heteropoly ionic liquid $[TEAPS]_3PW_{12}O_{40}$ because of the existing of Hf cations in struc-

Table 1
The acidity of organic-inorganic heteropoly salts.

No.	Catalyst	Solubility (25 °C)		Acid strength (mV)	Total acid amount (mmol/g)
		In water	In *p*-xylene		
1	$H_3PW_{12}O_{40}$	Yes	Not	814	0.89
2	$Hf_{0.5}HPW_{12}O_{40}$	Not	Not	811	0.94
3	$[TEAPS]_3PW_{12}O_{40}$	Almost not	Not	657	0.82
4	$Hf_{0.25}[TEAPS]HPW_{12}O_{40}$	Not	Not	673	0.80
5	$Hf_{0.5}[TEAPS]PW_{12}O_{40}$	Not	Not	685	0.84
6	Reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$	Not	Not	683	0.83

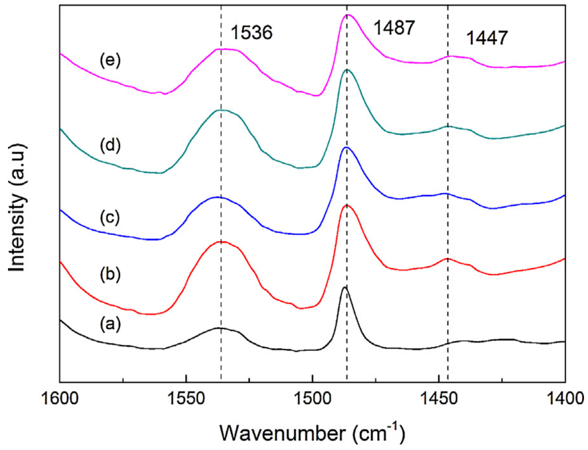


Fig. 2. Py-IR spectra of organic-inorganic heteropoly salts. (a) $H_3PW_{12}O_{40}$, (b) $Hf_{0.25}[TEAPS]HPW_{12}O_{40}$, (c) $Hf_{0.25}[TEAPS]_2PW_{12}O_{40}$, d) $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, e) Reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$.

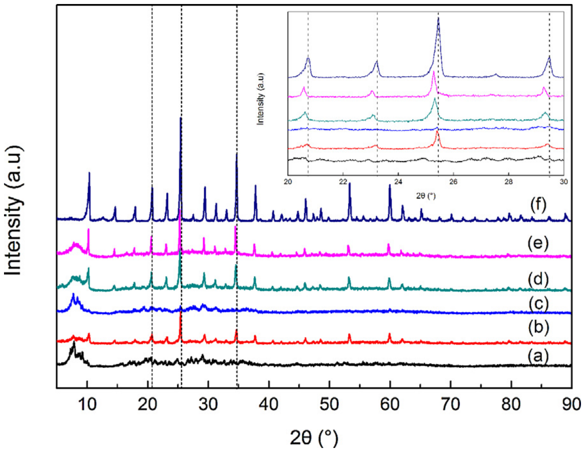


Fig. 3. XRD patterns of organic-inorganic heteropoly salts. (a) $[TEAPS]_3PW_{12}O_{40}$, (b) $Hf_{0.25}[TEAPS]HPW_{12}O_{40}$, (c) $Hf_{0.25}[TEAPS]_2PW_{12}O_{40}$, (d) $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, (e) Reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, (f) Raw materials mixture.

ture. In addition, it is found that the reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ has no obvious change in acid properties. In order to obtain the specific surface areas of these catalysts, BET investigations were also conducted. The results show that the introducing of Hf^{4+} into $H_3PW_{12}O_{40}$ structure ($H_3PW_{12}O_{40}$: 1.199 m^2/g) leads to a slightly increased specific surface area ($Hf_{0.5}HPW_{12}O_{40}$: 1.627 m^2/g). However, the introducing of TEAPS leads to a reduced one ($[TEAPS]_3PW_{12}O_{40}$: 0.738 m^2/g). Meanwhile, the catalyst $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ with both Hf^{4+} and TEAPS has a specific surface area which is lower than that of $Hf_{0.5}HPW_{12}O_{40}$ but higher than that of $H_3PW_{12}O_{40}$ ($Hf_{0.5}[TEAPS]PW_{12}O_{40}$: 1.520 m^2/g). Furthermore, the specific surface area of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ has no obvious reduction after reused (1.457 m^2/g).

Powder XRD patterns of prepared organic-inorganic heteropoly salt, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, and contrastive catalysts are shown in Fig. 3, comparing with that of the raw materials mixture including $H_3PW_{12}O_{40}$, $HfCl_4$ and the intermediate TEAPS. The broad diffraction peaks at 2θ of 15–38° indicate smectic-state appearances of the prepared heteropoly salt samples with organic group, differing from those of $H_3PW_{12}O_{40}$ with high crystallinity [26,27]. The phase change of the hybrid compounds has been due to replacement of protons in $H_3PW_{12}O_{40}$ with $[TEAPS]^+$ [27]. On the other hand, according to literature [33], lower angles shifts of the XRD peaks would be observed when the protons of $H_3PW_{12}O_{40}$ were exchanged by metal ions such as Cs^+, $Sm^{3+}$and Hf^{4+} due to the expansion of unit cell volume. Thus, shifts clearly observed in Fig. 3 also indicate exchanges of protons of $H_3PW_{12}O_{40}$ by Hf^{4+}. In addition, the XRD spectrum of the reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ shows no obvious structural change (Fig. 3). These XRD results are in keeping with the observations made from FT-IR (Figs. 1 and 3).

The TG curve of the prepared organic-inorganic heteropoly salt, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ (Fig. 4) shows that about 8 unbound or crystal water molecules were lost during 30–275 °C (calculated weight loss: 4.85%). Moreover, decomposition peaks of sulfonic group and organic framework in $[TEAPS]^+$ (calculated weight loss: 6.63%) are observed at 302.1 °C and 407.6 °C respectively. The decomposition peak at 595.8 °C (calculated weight loss: 3.61%) is explained by the decomposition of $PW_{12}O_{40}{}^{3-}$. The TG profile also indicates that the prepared organic-inorganic heteropoly salt, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, is quite stable below 302.1 °C.

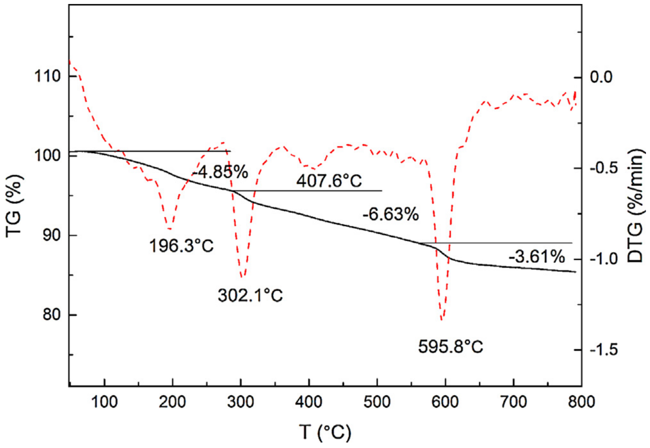


Fig. 4. TG-DTG profile of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$.

The contents of Hf, P and W elements in $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ were characterized by ICP-AES to demonstrate the molecular organization of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ (Table 2). The results show that all of the three experimental values are in line with, but slightly lower than the theoretical ones. It can be attributed to about 8 molecules unbound or crystal water in the prepared catalyst which has been proved by TG- DTG (Fig. 4).

The contents of C, H and S elements in fresh $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ were characterized by elemental analy-

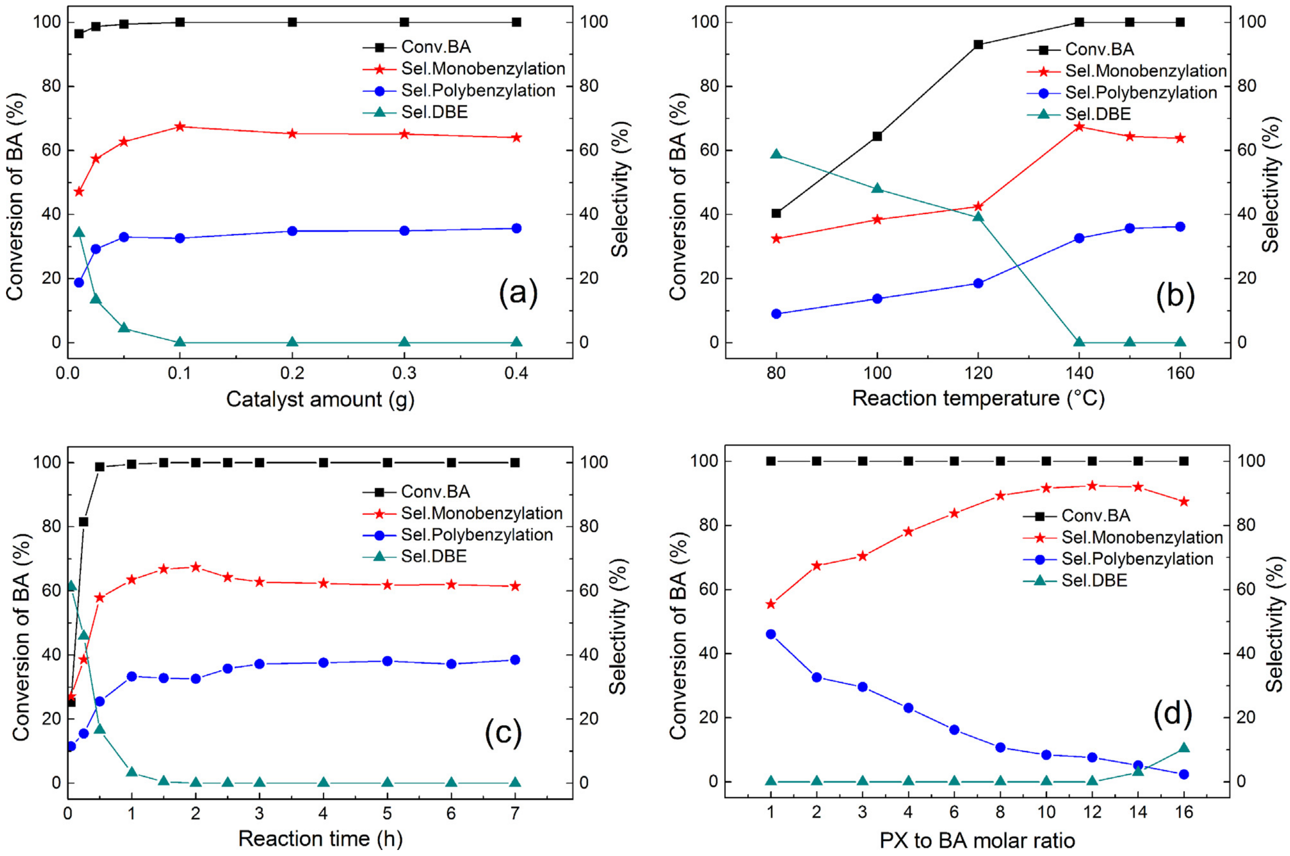


Fig. 5. Influences of catalyst amount (a), reaction temperature (b), reaction time (c), and molar ratio of PX to BA (d) on the conversion and selectivity over $Hf_{0.5}[TEAPS]PW_{12}O_{40}$. Reaction conditions: BA (0.05 mol), $n_{PX}:n_{BA} = 2$, 140 °C, 2 h (a); catalyst (0.1 g), BA (0.05 mol), $n_{PX}:n_{BA} = 2$, 2 h (b); catalyst (0.1 g), BA (0.05 mol), $n_{PX}:n_{BA} = 2$, 140 °C (c); catalyst (0.1 g), BA (0.05 mol), 140 °C, 2 h (d).

Table 2
The Hf, P and W elements contents of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ by ICP-AES.

No.	Element	Expected content/%	Experimental content/%
1	Hf	2.80	2.74
2	P	0.97	0.92
3	W	69.12	66.14

Table 3
The C, H and S elements contents of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ by elemental analysis.

No.	Element	Expected content/%	Experimental content/%	
			Fresh	Reused
1	C	3.39	3.23	3.20
2	H	0.66	1.25	1.26
3	S	1.01	0.97	0.95

sis and shown in Table 3. It can be seen that the experimental values of C and S elements are also in line with, but slightly lower than the theoretical ones. In contrast, the experimental value of H is higher than the theoretical one. These results can be attributed to the unbound or crystal water and can confirm the above results of TG-DTG and ICP-AES. Moreover, the $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ catalyst after used in the benzylation reaction shows similar elemental content as the fresh one.

3.2. Catalytic performances of organic-inorganic heteropoly salts in benzylation of PX with BA

Catalytic performances of the prepared hybrid, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, and contrastive catalysts in benzylation of PX with BA were investigated under the same conditions. The conversion and product distribution was analyzed by GC and GC–MS (Table 4). It can be seen that PX cannot react with BA at all in the conditions of no catalyst or the TEAPS being used, even pure Lewis acid anhydrous $HfCl_4$ was used, the catalytic activity is still very low. As expected, due to the electron-donating effect of methyl groups in PX, dibenzylation and even multiple benzylation would occur over the catalysts with enough acid strength. Furthermore, another main by-product coming from the intermolecular dehydration process of BA, DBE, would be generated easily over the catalysts with only Brønsted acid sites, even the super acid $H_3PW_{12}O_{40}$. Meanwhile, the Lewis acidity from enough Hf^{4+} can effectively avoid the intermolecular dehydration of BA to produce DBE, but intensify the polybenzylation of PX. When both Hf^{4+} with Lewis acidity and $[TEAPS]^+$ with Brønsted acidity were introduced together into the structure of ${PW_{12}O_{40}}^{3+}$ in a suitable ratio to form $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ with Brønsted-Lewis double acidity, no DBE and less polybenzylation products were found than $Hf_{0.5}HPW_{12}O_{40}$ did. Kumar.et al. [30] reported a series of hafnium salts of heteropoly phosphotungstic acid(Hf_xTPA) with both Brønsted and Lewis acidity and their catalytic performance of benzylation of anisole with DBE. It was found that $Hf_{0.5}HPW_{12}O_{40}$, the one with appropriate ratio of Brønsted acid and Lewis acid was the most efficient catalyst in the above reaction. This result can indicate the synergistic effect of Brønsted and Lewis acid sites [34] and account for the excellent performance of the prepared organic-inorganic heteropoly salt, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, compared to $H_3PW_{12}O_{40}$ and $HfCl_4$ in benzylation of PX with BA. (Table 4).

Fig. 5 shows the effects of catalyst dosage, reaction temperature, reaction time and the molar ratio of reactants on the catalytic per-

Table 4
Catalytic benzylation performances of organic-inorganic heteropoly salts [a].

No.	Catalyst	Conv. of BA/%	Product distribution/%		
			Monobenzylation[b]	Polybenzylation	DBE
1	–	0	0	0	0
2	$H_3PW_{12}O_{40}$	99.1	61.3	28.2	10.5
3	$HfCl_4$	4.1	25.6	0.4	74.0
4	TEAPS	0	0	0	0
5	$Hf_{0.5}HPW_{12}O_{40}$	100	62.4	37.6	0
6	$[TEAPS]_3PW_{12}O_{40}$	98.6	47.6	28.9	23.5
7	$Hf_{0.25}[TEAPS]HPW_{12}O_{40}$	98.4	56.8	30.9	12.3
8	$Hf_{0.25}[TEAPS]_2PW_{12}O_{40}$	98.7	52.4	28.2	19.4
9	$Hf_{0.5}[TEAPS]PW_{12}O_{40}$	100	67.4	32.6	0

[a] Reaction conditions: catalyst (0.1 g), BA (0.05 mol), $n_{PX}:n_{BA} = 2$, 140 °C, 2 h.
[b] 2,5-dimethylbenzylbenzene.

formance when $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ was utilized to catalyze the benzylation of PX with BA. It can be seen that more DBE will generate in the case of low catalyst dosage being employed (Fig. 5a). While, all the 0.05 mol of reactant BA could be transformed as well as the formation of DBE could be inhibited under the condition of using 0.1 g of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ which has provided enough catalytic active sites. However, the more catalyst dosage was used, the more polybenzylated products would be observed. Hence, it indicates 0.1 g of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ is the suitable catalyst dosage in view of 0.05 mol of reactant BA (Fig. 5a).

The catalytic activity of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, as well as the selectivities for monobenzylation and polybenzylation, will enhance with the increasing of reaction temperature (Fig. 5b). A considerable amount of BA would undergo self-condensation process with lower activation energy to produce DBE at lower reaction temperature. It has been observed that all the BA would turn into monobenzylated or polybenzylated products at an optimal temperature of 140 °C, without DBE detected. However, higher temperature than 140 °C would result in decreasing of selectivity for monobenzylation due to further polybenzylation.

Under the above optimal catalyst dosage and reaction temperature, the excellent catalytic activity of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ has been demonstrated (Fig. 5c). The conversion of BA can reach 100% within 1 h. Furthermore, with the increasing of reaction time, the selectivity for monobenzylated products enhances remarkably and achieves a maximum within 2 h. At the same time, the content of by-product DBE declines from 60% to zero Together with the results of Fig. 5a and b, an opinion that the self-condensation of BA with lower energy barrier competes with benzylation process of which products have higher thermodynamic stability can be held [12,29,35]. Moreover, DBE, the self-condensation product of BA, can also attack the benzene ring of PX as a benzylated reagent to proceed monobenzylation, even polybenzylation process [36]. In order to confirm this point, the reaction of PX with DBE being the benzylated reagent was carried out under the same reaction conditions (Fig. 6). As can be seen from Fig. 6, DBE could be consumed completely and converted into benzylated products within 2 h under the above conditions. Meanwhile, the monobenzylated product was liable to undergo consecutive reaction to produce polybenzylated products. Furthermore, either Brønsted or Lewis acid sites can realize a catalytic effect in this reaction. To sum up the above results and discussion, a plausible mechanism of PX benzylation with BA over the $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ catalyst with Brønsted and Lewis acidity is proposed (Scheme 1).

Besides, the influence of PX to BA molar ratio on the catalytic performance of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ in benzylation was investigated to restrain the polybenzylation process and improve the selectivity for monobenzylation. The molar ratio has almost no effect on the catalytic activity of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ (Fig. 5d). Consistent with the expected, the more PX served, the lower probability of polybenzylation had been found. However, once the molar ratio of PX to BA was over 12, the content of DBE tended to increase due to the excessive attenuation of catalytic active sites by PX. From what has been discussed above, an excellent catalytic benzylation result with 100% of BA conversion and 92.4% of 2,5-dimethylbenzylbenzene selectivity has been achieved under the optimal reaction conditions: $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ (0.1 g), BA (0.05 mol), $n_{PX}:n_{BA} = 12$, 140 °C, 2 h.

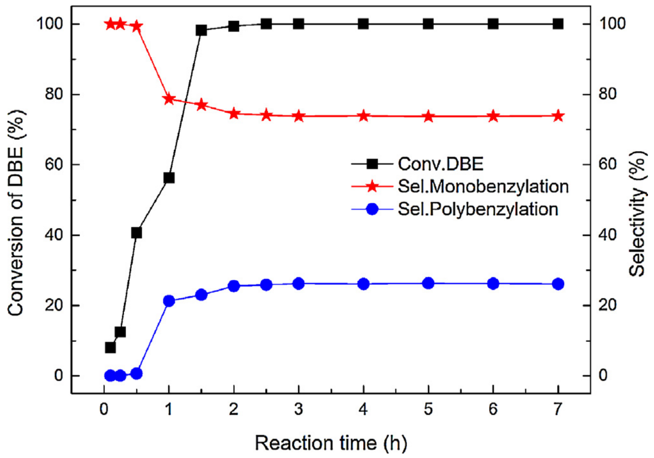


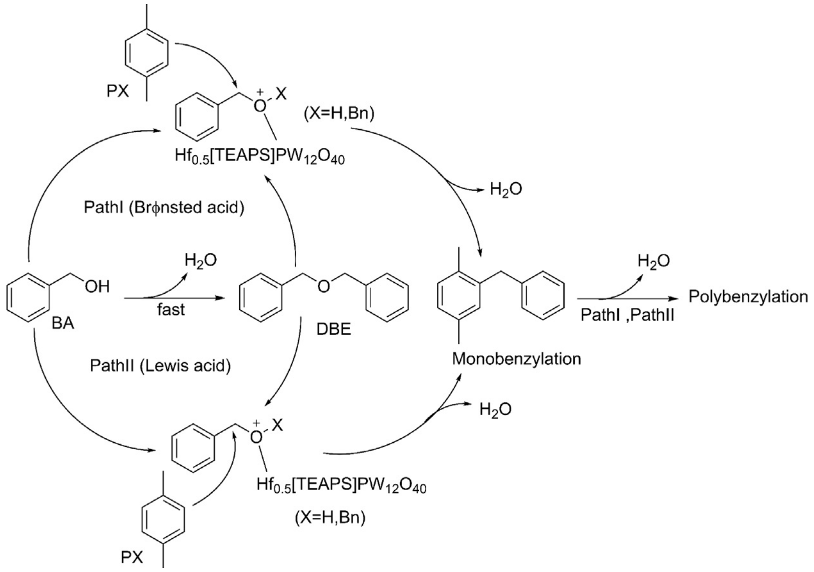
Fig. 6. Benzylation of PX with DBE being the benzylation reagent over $Hf_{0.5}[TEAPS]PW_{12}O_{40}$. Reaction conditions: catalyst (0.1 g), DBE (0.05 mol), $n_{PX}:n_{DBE} = 2$, 140 °C, 2 h.

3.3. Substrate extension

The benzylations of several benzene compounds which have different groups with BA over $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ were also investigated (Table 5). As can be seen, similar excellent conversion and selectivity for monobenzylation with PX could be obtained within 2 h in the case of activated benzene compounds. However, as to the benzylation of chlorobenzene and benzene itself, the formation of DBE was still hard to be avoided under the conditions of this paper.

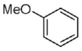
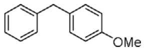
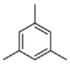
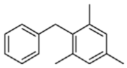
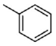
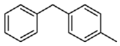
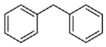
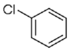
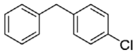
3.4. Reusability of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ catalyst

The reusability of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ in benzylation of PX under the above optimal reaction conditions was investigated using a seven-run recycling test. The solid catalyst, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, precipitated to the bottom of the reactor after the reaction, allowing separation from the solution *via* simple centrifugation. The separated catalyst was washed with ethyl acetate, dried in a hot air oven at 120 °C for 1 h and reused for the next run. $Hf_{0.5}[TEAPS]PW_{12}O_{40}$



Scheme1. Benzylation reaction mechanism of PX with BA over $Hf_{0.5}[TEAPS]PW_{12}O_{40}$.

Table 5
Benzylation of different aromatic substrates over $Hf_{0.5}[TEAPS]PW_{12}O_{40}$[a].

No.	Substrate	Benzylation product (major)	Conv.of BA/%	Product distribution/%		
				Monobenzylation (*o*-:*p*-)	polybenzylation	DBE
1			100	97.1 (48:52)	2.9	0
2			100	96.8	3.2	0
3			100	91.7 (47:53)	8.3	0
4			97.9	46.2	7.0	46.8
5			98.4	41.8 (6.3:93.7)	4.1	54.1

[a] Reaction conditions: $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ (0.1 g), BA (0.05 mol), $n_{substrate}:n_{BA} = 12$, 140 °C, 2 h.

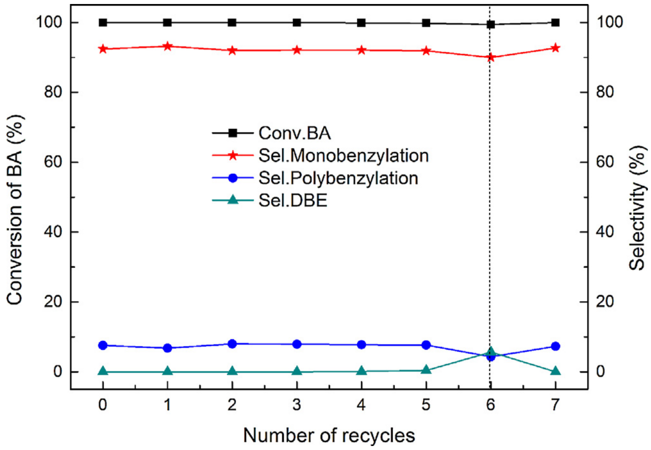


Fig. 7. The performance of the reused catalyst. Reaction conditions: $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ (0.1 g), BA (0.05 mol), $n_{PX}:n_{BA} = 12$, 140 °C, 2 h.

catalyst could maintain excellent activity and selectivity after 5 cycles (Fig. 7). ICP-AES was employed to test the dissolved residue of catalyst in the reaction product phase. It has been found that no P element was detected. In addition, the FT-IR, XRD spectra, acidity, BET and elemental analysis of fresh and reused $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ (Fig. 1) reveal that no obvious change of the catalyst has occurred after benzylation. However, only 0.0803 g of the recycled catalyst after 6 runs was found due to operational loss, which can account for the lower catalytic performance of catalyst after 6 runs. As respected, when 0.0200 g of fresh catalyst was added into the recycled catalyst in the 7th run, the catalytic performance recovered to the initial level. The above results exhibit the favorable reusability of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ in benzylation of PX with BA.

4. Conclusions

Introducing sulfated organic cation $[TEAPS]^+$, and metal cation Hf^{4+}, together as counter ions for $PW_{12}O_{40}{}^{3-}$ to form heteropoly organic-inorganic salt can obtain a novel efficient catalyst, $Hf_{0.5}[TEAPS]PW_{12}O_{40}$, for benzylation of PX with BA. The suitable Brønsted-Lewis double acidity both from the positive ions part of $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ catalyst can effectively restrain the formation of DBE and polybenzylation products, and has led to excellent catalytic activity as well as selectivity for monobenzylation. Besides, the prepared solid $Hf_{0.5}[TEAPS]PW_{12}O_{40}$ catalyst, dissolving neither in organic phase nor in the water formed during the reaction, has exhibited quite steady reusability demonstrated by a seven-run recycling test. Under the optimum conditions, 100% of BA conversion and as high as 92.4% of selectivity for monobenzylation have been achieved.

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