

Comparative studies on alkylation of phenol with *tert*-butyl alcohol in the presence of liquid or solid acid catalysts in ionic liquids

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Abstract

Alkylation of phenol with *tert*-butyl alcohol (TBA) was carried out in ionic liquids [bmim]PF₆, [omim]BF₄, and [hmim]BF₄. Comparative studies on the catalytic properties of ionic liquids, H₃PO₄ and some solid acidic catalysts, such as HZSM-5, H-β, HPW, and HPW/MCM-41, were carried out under identical reaction conditions. Solvent effect has been as well studied. The use of ionic liquids was found to enhance the catalytic properties of the catalysts used.

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1. Introduction

The alkylation reaction of phenol with *tert*-butyl alcohol (TBA) is of both industrial importance and academic relevance. The alkylated phenol products are used as raw materials for the manufacture of a variety of resins, durable surface coatings, varnishes, wire enamels, printing inks, surface-active agents, rubber chemicals, antioxidants, fungicides, petroleum additives, ultraviolet absorbers, and heat stabilizers for polymeric materials [1–5]. Investigation of both homogeneous and heterogeneous catalysts for this typical Friedel–Crafts alkylation reaction resulted in different selectivities and activities based mainly on the acidity of the catalysts used. Catalysts used for this reaction include Lewis acids, such as AlCl₃ and BF₃ [6], Brønsted acids, such as H₃PO₄, H₂SO₄, HF, HClO₄ [7], cation-exchange resin [8], mesoporous materials [1], zeolites [2,3], molecular sieves [5], and also supercritical and near-supercritical water [4]. Room-temperature ionic liquids [9] are finding growing applications as alternative reaction media for separations [10] and organic transformations [11–19]. Recent examples of such organic transformations include hydrogenations [11],

Friedel–Crafts reactions [12], Diels–Alder reactions [13], Heck reactions [14], Bischler–Napieralsky reactions [15], olefin dimerizations [16], cross-couplings [17], hydroformylations [18], and oxidations [19]. The desirable advantages of ionic liquids such as lack of vapor pressure, wide liquid range, and thermal stability have made them exceptional reaction media. Accordingly, they are emerging as novel replacements for volatile organic compounds, mainly used as solvents in organic transformations. Ionic liquids have already been used as catalysts for Friedel–Crafts alkylation of benzene with dodecene in order to produce linear alkyl benzene compounds [20].

Friedel–Crafts alkylation reaction is very valuable for the synthesis of many compounds especially those important for industries. This reaction is catalysed by acids. The acid used for the catalysis has a profound effect on the selectivity and conversion. It was found the 12-tungstophosphoric acid H₃PW₁₂O₄₀ (HPW) is the most acidic of the Keggin series [21]. When this acid was supported on a carrier with large surface area, its catalytic performance was improved [22,23]. Recently, HPW/MCM-41 systems were used to catalyze several reactions such as the alkylation of isobutene using butene [23] and alkylation of 4-*tert*-butylphenol using isobutene and styrene [24], the conversion of 1,3,5-triisopropylbenzene [25], and the gas-phase synthesis of methyl *tert*-butyl ether (MTBT) [26]. However, HPW/MCM-41 catalysts have not yet been used for the alkylation reaction of phenol with TBA.

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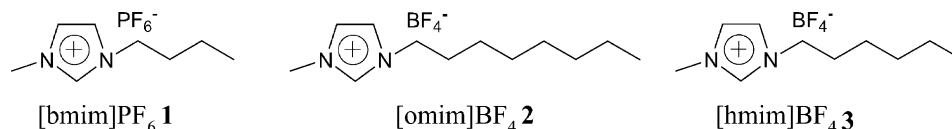


Fig. 1. Structure of ionic liquids 1–3.

In this paper, we report the alkylation of phenol with *tert*-butyl alcohol with an enhanced activity in the presence of ionic liquids, such as [bmim]PF₆ (**1**), [omim]BF₄ (**2**), and [hmim]BF₄ (**3**) (Fig. 1). For comparison, some solid acid catalysts, such as HZSM-5, H-β, HPW, and HPW/MCM-41 were also used to catalyze the occurrence of the reaction.

2. Experimental

2.1. Materials

Ionic liquids **1–3** were purchased from solvent-innovation GmbH and were used as received. Prior to use, phenol was purified by sublimation, *tert*-butyl alcohol, light petroleum, dichloromethane, and hexane were redistilled.

The preparation of three HPW (*x*%) / MCM-41 catalysts (where *x*% is the respective HPW content of 15, 30, and 50 wt.%) were reported elsewhere [26]. HZSM-5 (Si/Al = 27.5, 0.5–1.2 μm) and H-β (Si/Al = 30.6, 0.3–1.0 μm) were prepared from NaZSM-5 and Naβ by using ion-exchange procedure.

2.2. Catalytic reaction

The alkylation experiments were carried out in sealed tubes in 60 °C for 4 h, with a constant initial molar ratio of 1:2 of phenol:TBA. After the completion of the reactions, the tubes were cooled, the products were extracted from the reaction mixture by using light petroleum and quantified (mol%) by a gas chromatograph (GC, HP-6890) equipped with a flame ionization detector and an HP-5 capillary column containing crossed linked 5%-phenyl and 95%-dimethylsiloxane copolymer.

3. Results and discussion

The alkylation reaction of phenol with *tert*-butyl alcohol is a typical acid-catalyzed reaction. The distribution

of products is largely dependent on the acidity and the temperature of the reaction system as shown in Scheme 1. Weak acid catalysts mainly lead to an etherified product (phenyl alkyl ether, *t*-BPE). The presence of phenolic (–OH) group kinetically favors *o*-alkylation (*o*-isomer, e.g. *o*-TBP); however, due to steric hindrance thermodynamically unfavoured *o*-isomer (*o*-TBP) is readily isomerized into less hindered *p*-isomer (*p*-TBP), especially in moderately acidic media. When strongly acidic catalysts are used, 2,4-di-*tert*-butylphenol (2,4-DTBP) is a dominant product; *o*- and *p*-isomers formed initially are isomerized to *m*-TBP at high temperatures or in strongly acid media.

3.1. Effect of different ionic liquids

The acidity and coordination properties of an ionic liquid are essentially determined by the nature of its anion [9b]. Ionic liquids with BF₄[–] and PF₆[–] are known to be neutral. Our previous research has showed that [bmim]PF₆ (**1**) can catalyze the alkylation of phenol with TBA with high conversion and selectivity towards 2,4-DTBP [27]. It was found that 2,4-DTBP was dominant in the mixture of *ortho-tert*-butylphenol (*o*-TBP), *para-tert*-butylphenol (*p*-TBP), and 2,4-di-*tert*-butylphenol (2,4-DTBP) produced. However, when this reaction was carried out in [omim]BF₄ (**2**) and [hmim]BF₄ (**3**), only phenyl ethers (*o*-ether) were produced under the similar reaction conditions with a medium conversion of phenol (see Table 1 and Fig. 2). The acidity of [bmim]PF₆ ionic liquid for its pronounced effect on the selectivity may be attributed to HF produced as a result of [PF₆][–] decomposition. In this case, issues like safety and corrosion should be taken into account [27,28]. Also, additional efforts and costs should be considered to avoid the liberation of toxic and corrosive HF into the environment.

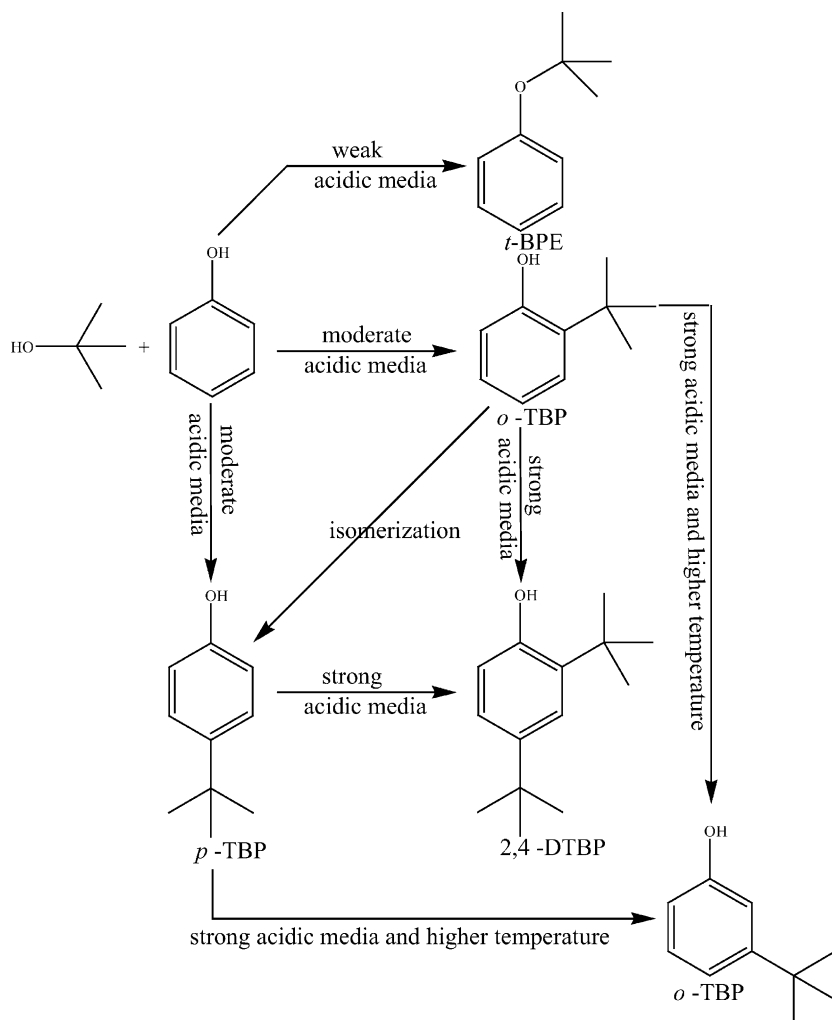
3.2. Effect of ionic liquids on the catalytic activity of H₃PO₄

The alkylation of phenol with TBA can be catalyzed by H₃PO₄ [7]. In order to investigate the effect of ionic liquids

Table 1
Alkylation of phenol with TBA in different ionic liquids

Entry	Ionic liquid	Conversion of phenol (%)	Selectivity of <i>o</i> -TBP (%)	Selectivity of <i>p</i> -TBP (%)	Selectivity of 2,4-DTBP (%)	<i>O</i> -ether (%)
1	[bmim]PF ₆	90.3	13.8	10.9	75.3	–
2	[omim]BF ₄	42.3	–	–	–	99.2
3	[hmim]BF ₄	43.6	–	–	–	99.5

*Conditions: 60 °C, phenol/TBA 1:2 mol/mol, 20 mol% ionic liquid, 4 h.

Scheme 1. Effect of acid media on the alkylation of phenol with *t*-butyl alcohol.

on the catalytic activity of H_3PO_4 for the alkylation of phenol with TBA, a mixture of ionic liquid/ H_3PO_4 (1:1 v/v) was prepared and the reaction was carried out in the usual manner. The results were striking (see Table 2 and Fig. 3). A modest conversion of phenol was obtained (44.5%, entry 4) when H_3PO_4 was used alone without ionic liquids. The results (entry 5) showed that when a $[\text{bmim}]\text{PF}_6/\text{H}_3\text{PO}_4$ mixture (1:1 v/v) was used, both the conversion of phenol

and the selectivity of 2,4-DTBP decreased in comparison to those obtained when $[\text{bmim}]\text{PF}_6$ was used solely (Table 1, entry 1). This may be due to the dilution of the catalyst concentration when 50 vol.% H_3PO_4 was used in the catalytic system. However, H_3PO_4 helped the other two ionic liquids, $[\text{omim}]\text{BF}_4$ (Table 2, entry 6) and $[\text{hmim}]\text{BF}_4$ (entry 7), to improve their catalytic activity. Not only the conversion of phenol increased more than 25%, but also the selectivity of the products shifted from *o*-phenol ether to *o*, *p*-TBP and 2,4-DTBP. It was observed that the conversion of phenol

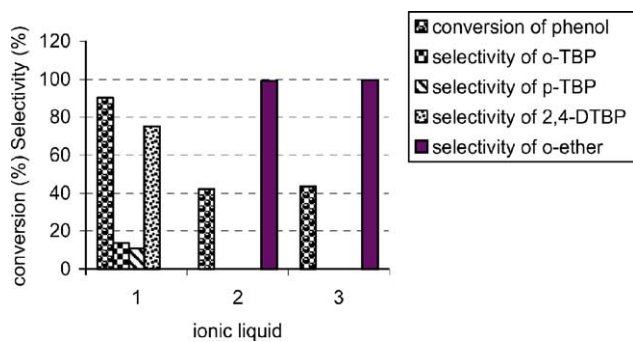


Fig. 2. Effect of different ionic liquids.

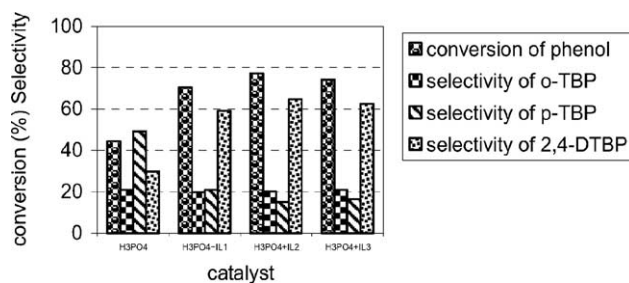
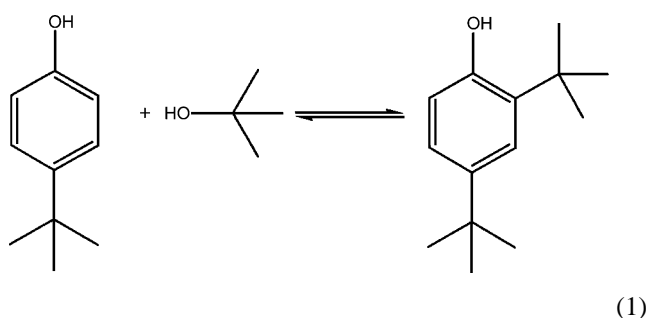
Fig. 3. Effects of ionic liquids on the catalytic activity of H_3PO_4 .

Table 2
Alkylation of phenol with TBA by H₃PO₄ in different ionic liquids

Entry	Catalyst	Conversion of phenol (%)	Selectivity of <i>o</i> -TBP (%)	Selectivity of <i>p</i> -TBP (%)	Selectivity of 2,4-DTBP (%)
4	H ₃ PO ₄	44.5	21.0	49.2	29.7
5	[bmim]PF ₆ + H ₃ PO ₄ (1:1 v/v)	70.3	19.8	20.9	59.3
6	[omim]BF ₄ + H ₃ PO ₄ (1:1 v/v)	77.3	20.1	15.0	64.9
7	[hmim]BF ₄ + H ₃ PO ₄ (1:1 v/v)	74.3	21.0	16.4	62.5

*Conditions: 60 °C, phenol/TBA 1:2 mol/mol, H₃PO₄/ionic liquid (1:1 v/v); total amount: ~3 wt.% of phenol, 4 h.

in ILs/H₃PO₄ (1:1 v/v) mixtures was much higher than that when H₃PO₄ was used alone as well (Table 2, entry 4). Another important feature to be noted is that selectivity to 2,4-DTBP was high when a mixture of IL/H₃PO₄ was used compared to that when H₃PO₄ was used alone. These results suggested that ionic liquids ameliorate the catalytic activity of H₃PO₄. That may be because 2,4-DTBP is more soluble in ionic liquids than in H₃PO₄. Therefore, the shift in Eq. (1) may occur more easily in ionic liquids.



3.3. Comparative studies with some solid acids

To compare the activity and catalytic properties of the above ionic liquid based homogenous catalytic systems with heterogenous catalysts, we synthesized HZSM, zeolite H-β, HPW, and HPW (x%)/MCM-41 catalysts, where x% is the respective HPW content of 15, 30, and 50 wt.%. Their properties have been listed in Table 3. They were used to study the alkylation of phenol with TBA under similar reaction conditions (60 °C with phenol:TBA molar ratio of 1:2 for 4 h) in hexane. The results are shown in Table 4 and Fig. 4. It is clear that the performance of the solid catalysts is governed by the acidity and pore structure of the zeolites. As shown

in Table 3, The low activity of zeolite HZSM-5 (Table 4, entry 8) can be easily explained by small channel structures, which did not allow a proper diffusion of the starting material and the products in the pores of HZSM-5. Larger pore zeolite H-β was beneficial especially for the selectivity of *p*-TBP (Table 4, entry 9). The catalytic properties of the HPW and HPW (x%)/MCM-41 catalysts were almost the same. An increase in the loading of HPW on the MCM-41 resulted in a higher acidity of the catalysts where both the conversion of phenol and the selectivity of *p*-TBP were not much affected. This might be because of a partial blockage of the monodimensional channels of MCM-41 by small aggregates of HPW, thus, decreasing the accessibility of the acid sites to the reactants, which is in agreement with the findings of Blasco et al. [23]. The aggregation of HPW may be also the reason that the surface of HPW/MCM-41 decreased with the increase in the HPW loading as we found before (see Table 3) [26].

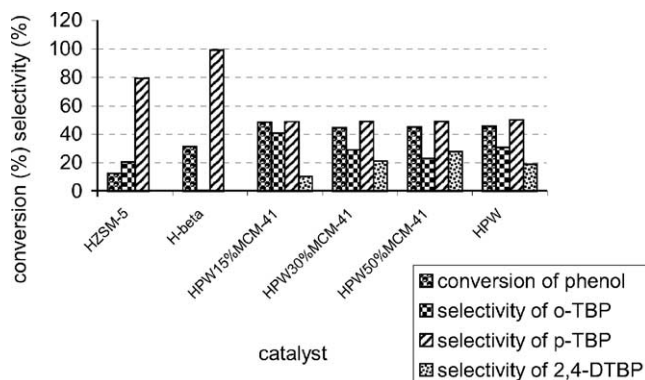


Fig. 4. Comparison studies with solid acids.

Table 3
Structural data of HZSM-5, H-β, and HPW/MCM-41 catalysts

Samples	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (Å)	HPW phase
HZSM-5	441	0.24	~5.4	–
H-β	650	0.35	~7.0	–
HPW	<10			Crystalline
HPW(15%)/MCM-41	1128	0.98	30.0	Amorphous
HPW(30%)/MCM-41	632	0.53	29.7	Amorphous
HPW(50%)/MCM-41	499	0.40	29.5	Amorphous

Table 4
Alkylation of phenol with TBA in different solid acid catalysts

Entry	Catalyst	Conversion of phenol (%)	Selectivity of <i>o</i> -TBP (%)	Selectivity of <i>p</i> -TBP (%)	Selectivity of 2,4-DTBP (%)
8	HZSM-5	12.6	20.5	79.5	–
9	H- β	31.5	0.7	99.3	–
10	HPW(15%)/MCM-41	48.5	40.7	48.9	10.4
11	HPW(30%)/MCM-41	44.8	29.0	49.0	21.2
12	HPW(50%)/MCM-41	45.3	23.3	49.0	27.7
13	HPW	45.8	30.8	50.2	19.0

*Conditions: 60 °C, phenol/TBA 1:2 mol/mol, catalysts amount: ~3 wt.% of phenol, in hexane, 4 h.

3.4. Solvent effect investigation on some solid acids catalysts system

In order to investigate solvent effects on the catalytic properties of some solid catalysts, we chose [hmim]BF₄ **3** (IL3) as solvent to study this reaction catalyzed by above solid acids. Results are summarized in Table 5. In the case of HZSM-5 and H- β zeolites, when the reaction was conducted in IL3, the conversions of phenol have been improved (shown in Table 5 rows (a) and (b)), which is presumably due to IL3 attached to the surface of the zeolites. When IL3 dispersed to the surface of zeolites, the cation part attacked the partial negative oxygen atom of –OH group, while the anion BF₄[–] attacked the partial positive acidic center as a result of dipolar interaction. The dispersion and electronic interaction between IL3 and zeolite might increase local acidity of these solid acids, which consequently improved the catalytic properties of these two solid acids. However, the products distribution was not greatly affected (Fig. 5a and b), which indicated that the structure of the channel of HZSM-5 and H- β remained during the reaction of phenol with TBA under present reaction conditions while interaction occurred between IL3 and the surface of these two zeolites.

The conversion of phenol increased by more than 5% when the reaction was carried out in IL3 instead of hexane and catalyzed by HPW (Table 5 row (f)). Moreover, the selectivity to 2,4-DTBP has been almost doubled. This indicates that the catalytic activity of HPW has been improved in IL3. It may be presumably due to the interaction of IL3 with HPW. The presumed process is shown in Scheme 2a. The fast exchange of ions between HPW and IL3 may give [hmim]₃[PW₁₂O₄₀] and small amount of HBF₄ in situ, which improved the Brønsted acidity of the catalytic system and consequently accelerated the alkylation of phenol with TBA. As was the case of H₃PO₄, 2,4-DTBP has higher solubility in IL3, which resulted in higher conversion of phenol and better selectivity of 2,4-DTBP.

The reaction was conducted in IL3 using HPW/MCM-41 as catalysts. The results varied with the loading of HPW on MCM-41 (Table 5 rows (c), (d), and (e) and Fig. 5c–e). When the loading of HPW was 15 or 30%, the conversion of phenol decreased; however, the selectivity to *p*-TBP increased. Especially when the loading of HPW was 15%, the effect of IL3 was more significant: the conversion of phenol dropped by more than 16%, while the selectivity to 2,4-DTBP increased by more than 12%. In contrast, when the loading of HPW was 50%, the conversion of phenol increased by around 5%;

Table 5
Solvent effects on Alkylation of phenol with TBA in different solid acid catalysts

Number	Catalyst	Conversion of phenol (%)	Selectivity of <i>o</i> -TBP (%)	Selectivity of <i>p</i> -TBP (%)	Selectivity of 2,4-DTBP (%)
(a)	HZSM-5/hexane	12.6	20.5	79.5	–
	HZSM-5/IL3	15.2	21.2	78.8	–
(b)	H- β /hexane	31.5	0.7	99.3	–
	H- β /IL3	42.2	0.5	99.5	–
(c)	HPW(15%)/MCM-41/hexane	48.5	40.7	48.9	10.4
	HPW(15%)/MCM-41/IL3	32.4	32.6	61.2	6.2
(d)	HPW(30%)/MCM-41/hexane	44.8	29.0	49.0	21.2
	HPW(30%)/MCM-41/IL3	40.3	25.2	54.6	20.2
(e)	HPW(50%)/MCM-41/hexane	45.3	23.3	49.0	27.7
	HPW(50%)/MCM-41/IL3	60.2	15.2	32.2	52.6
(f)	HPW/hexane	45.8	30.8	50.2	19.0
	HPW/IL3	50.9	22.3	40.3	37.5

Comparison between hexane and ionic liquid **3** [hmim]BF₄ (IL3). *Conditions: 60 °C, phenol/TBA 1:2 mol/mol, catalysts total amount: ~3 wt.% of phenol, IL3: 1 ml, 4 h.

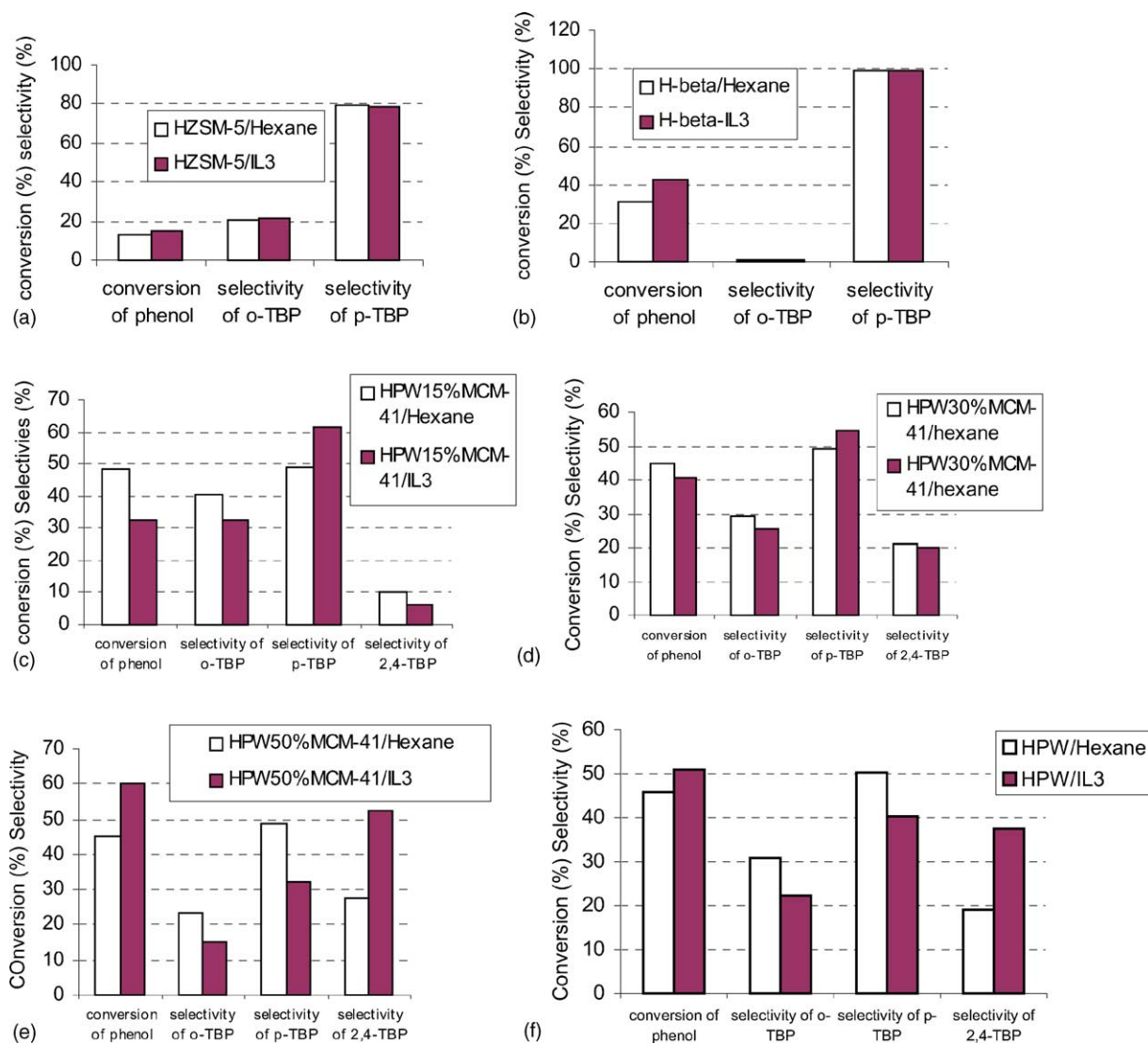


Fig. 5. Effects of ionic liquids on the catalytic activity of solid acid catalyst (a) HZSM-5; (b) H- β ; (c) HPW(15%)/MCM-41; (d) HPW(30%)/MCM-41; (e) HPW(50%)/MCM-41; and (f) HPW.

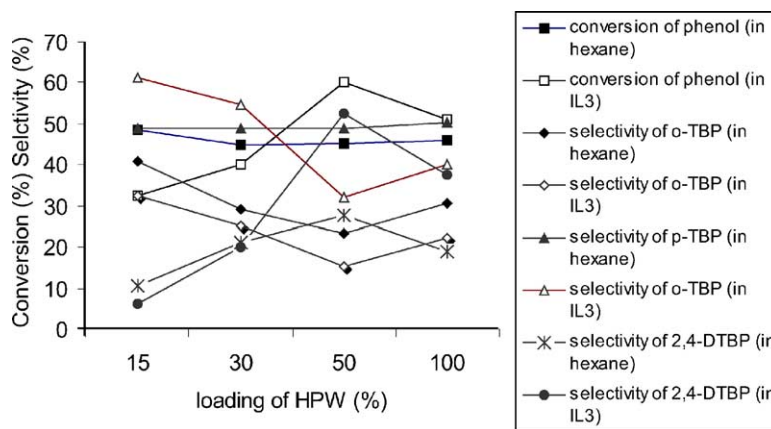
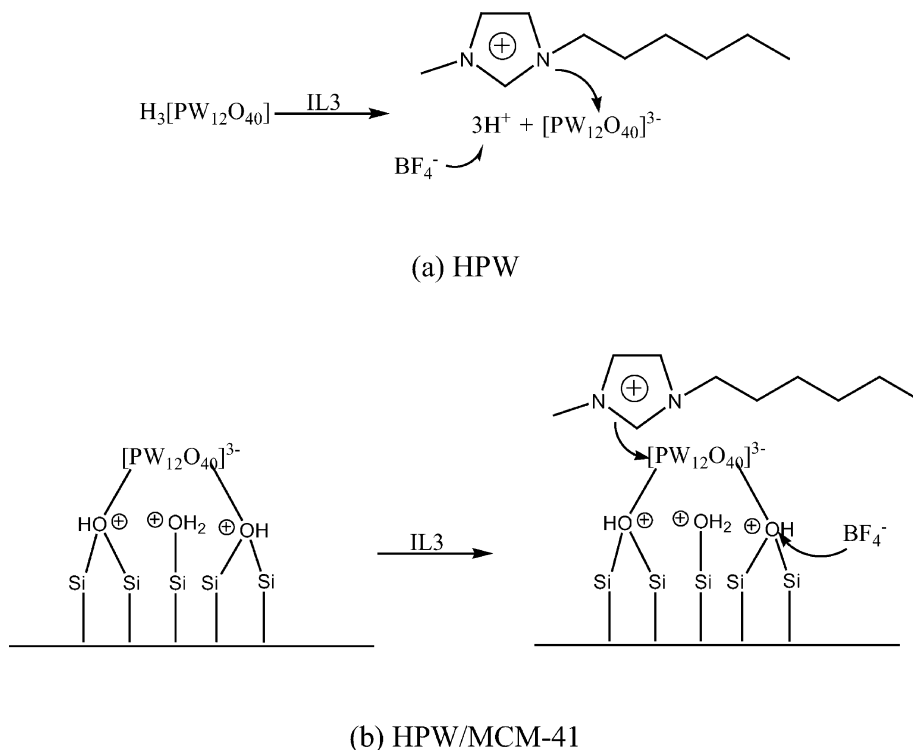


Fig. 6. Performance of HPW/MCM-41 in IL3: the effects of the loading of HPW on MCM-41.



Scheme 2. Presumed process of the interaction between IL3 and solid acids.

however, the selectivity to *p*-TBP decreased by 10%, and that to 2,4-DTBP almost doubled. Their different performances were easily observed from Fig. 6. These results may be caused by the interaction between IL3 and HPW/MCM-41. As shown in the presumed process (Scheme 2b), due to the ionic reactions, the IL3 cation attacked the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion, while the anion BF_4^- attacked the positive OH group of HPW/MCM-41. As a result, part of HPW/MCM-41 lost its acidic activity when the loading of HPW was relatively low. When the loading of HPW was high, IL3 may react with the small aggregates of HPW more easily and freely, which may not only help the HPW distribute on the surface of MCM-41 more homogeneously but also improve the catalytic properties through the reaction between IL3 and the free HPW.

4. Conclusion

The alkylation of phenol with *tert*-butyl alcohol was carried out in a batch mode with various catalysts. Solvent effects have been investigated both in liquid (H_3PO_4) and solid acids. ILs can help H_3PO_4 increase its catalytic activity, resulting in better conversion and selectivity. When reaction was conducted in hexane, the activity of small pore zeolite HZSM-5 was low while the activity of large pore zeolite H- β was high with excellent selectivity to *p*-TBP. The activities of the HPW and HPW (*x*%)/MCM-41 catalysts were almost the same. The effects of IL3 on the solid acids varied with the properties of solid acids. Conversion of phenol was improved without much effect on products

distribution when HZSM-5 or H- β was used as catalysts. IL3 improved the catalytic activity of HPW giving higher conversion and better selectivity to 2,4-DTBP. The performance of HPW/MCM-41 varied with the loading of HPW on MCM-41. The selectivity to *p*-TBP increased at the expense of conversion of phenol when 15 or 30% of HPW was loaded on MCM-41, and the selectivity to 2,4-DTBP doubled as well as the conversion of phenol increased when the loading HPW was 50%. Presumable reasons and interaction process between IL3 and solid acids have been addressed. Further investigation is under going.

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References

- [1] A. Sakthivel, S.K. Badamali, P. Selvam, *Microporous Mesoporous Mater.* 39 (2000) 457.
- [2] A.V. Krishnan, K. Ojha, N.C. Pradhan, *Org. Process Res. Dev.* 6 (2002) 132.
- [3] K. Zhang, H. Zhang, G. Xua, S. Xiang, D. Xu, S. Liu, H. Li, *Appl. Catal. A: Gen.* 207 (2001) 183.
- [4] (a) K. Chandler, F. Deng, A.K. Dillow, C.L. Liotta, C.A. Eckert, *Ind. Eng. Chem. Res.* 36 (1997) 5175;
(b) T. Sato, G. Sekiguchi, T. Adschiri, K. Arai, *Chem. Commun.* 17 (2001) 1566.

- [5] S. Sumbramanian, A. Mitra, C.V.V. Satyanarayana, D.K. Chakrabarty, *Appl. Catal. A: Gen.* 159 (1997) 229.
- [6] G. Sartori, F. Bigi, G. Casiraghi, G. Carnati, L. Chiesi, A. Arduini, *Chem. Ind.* 22 (1985) 762.
- [7] A.A. Carlton, *J. Org. Chem.* 13 (1948) 120.
- [8] K.G. Chandra, M.M. Sharma, *Catal. Lett.* 19 (1993) 309.
- [9] (a) T. Welton, *Chem. Rev.* 99 (1999) 2071;
(b) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 3772;
(c) R. Seddon, *Chem. Commun.* 23 (2001) 2399.
- [10] (a) L.A. Blanchard, J.F. Brennecke, *Ind. Eng. Chem. Res.* 40 (2001) 287;
(b) J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, *Chem. Commun.* 16 (1998) 1765;
(c) S. Dai, Y.H. Ju, C.E. Barnes, *J. Chem. Soc. Dalton Trans.* 8 (1999) 1201;
(d) A.E. Visser, R.P. Swatloski, W.M. Reichert, S.T. Griffin, R.D. Rogers, *Ind. Eng. Chem. Res.* 39 (2000) 3596.
- [11] P.J. Dyson, D.J. Ellis, D.G. Parker, T. Welton, *Chem. Commun.* 1 (1999) 25.
- [12] A. Stark, B.L. MacLean, R.D. Singer, *J. Chem. Soc. Dalton Trans.* 1 (1999) 63.
- [13] T. Fisher, A. Sethi, T. Welton, J. Woolf, *Tetrahedron Lett.* 40 (1999) 793.
- [14] (a) V.P.W. Böhm, W.A. Herrmann, *Chem. Eur. J.* 6 (2000) 1017;
(b) A.J. Carmichael, M.J. Earle, J.D. Holbrey, P.B. McCormac, K.R. Seddon, *Org. Lett.* 1 (1999) 997;
(c) L. Xu, W. Chen, J. Xiao, *Organometallics* 19 (2000) 1123;
(d) W.A. Herrmann, V.P.W. Böhm, *J. Organomet. Chem.* 572 (1999) 141.
- [15] (a) Z.M.A. Judeh, C.B. Ching, J. Bu, A. McCluskey, *Tetrahedron Lett.* 43 (2002) 5089;
(b) Z.M.A. Judeh, H.Y. Shen, C.B. Ching, L.C. Feng, S. Selvasothi, *Tetrahedron Lett.* 43 (2002) 9381.
- [16] B. Ellis, W. Keim, P. Wasserscheid, *Chem. Commun.* 4 (1999) 336.
- [17] N. Miyaura, A. Suzuki, *Chem. Rev.* 95 (1995) 2457, and references cited therein.
- [18] Y. Chauvin, H. Olivier, L. Mubmann, *FR 95 (14)* (1995) 147.
- [19] C.E. Song, E.J. Roh, *Chem. Commun.* 10 (2000) 837.
- [20] C. DeCastro, E. Sauvage, M.H. Valkenberg, W.F. Holderich, *J. Catal.* 196 (2000) 86.
- [21] M. Misono, N. Mizuno, K. Katamura, A. Kasei, Y. Konishi, K. Sakata, T. Okuhara, Y. Yoneda, *Bull. Chem. Soc. Jpn.* 55 (1982) 400.
- [22] I.V. Kozhevnikov, *Cat. Rev. -Sci. Eng.* 37 (1995) 311.
- [23] T. Blasco, A. Corma, A. Martinez, P. Martinez-Escolano, *J. Catal.* 177 (1998) 306.
- [24] I.V. Kozhevnikov, A. Sinnema, R.J.J. Jansen, K. Pamin, H. van Bekkum, *Catal. Lett.* 30 (1995) 241.
- [25] A. Ghanbari-Siahkali, A. Philippou, J. Dwyer, M.W. Anderson, *Appl. Catal., A* 192 (2000) 57.
- [26] Q.-H. Xia, K. Hidajat, S. Kawi, *J. Catal.* 209 (2002) 433.
- [27] H.-Y. Shen, Z.M.A. Judeh, C.B. Ching, *Tetrahedron Lett.* 44 (2003) 981.
- [28] P. Wasserscheid, R. Van Hal, A. Bösmann, *Green Chem.* 4 (2002) 400.