

Selective alkylation of phenol with *tert*-butyl alcohol catalyzed by Brønsted acidic imidazolium salts

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Abstract

Alkylation reaction of phenol with *tert*-butyl alcohol (TBA) catalyzed by SO₃H-functionalized ionic liquids has been investigated. The influences of different ionic liquids, reaction time, reaction temperature, reactant ratio (mole ratio of phenol to that of TBA), the amount and the recycle of ionic liquid were studied. The conversion of phenol and the selectivity of 2,4-DTBP were 80.4 and 60.2%, respectively, under optimum reaction condition. At the same time, the reaction mechanism was discussed based on the distribution of products.
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Keywords: Alkylation; Phenol; *tert*-Butyl alcohol; Acid catalysis; Ionic liquid

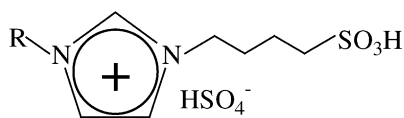
1. Introduction

Alkylation reaction of phenol with *tert*-butyl alcohol (TBA) is an important reaction both in organic synthesis and chemical manufacturing. 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 results in different selectivity and activities based mainly on the acidity of the catalysts used. 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. At the same time, small amounts of 2,6-di-*tert*-butylphenol (2,6-DTBP), 2,4,6-tri-*tert*-butylphenol (2,4,6-TTBP) and 4-(2,2,4-trimethylpentyl)-phenol are also formed. 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]. Liquid acid catalysts cause equipment corrosion and environmental pollution while solid acids deactivate rapidly due to the build-up of coke. Although cation-exchange resins show a good performance, thermal stability and fouling of the resins are also major problems.

Ionic liquid is a new class of solvent entirely composed of ions. Their use as an environmentally benign alternative for conventional solvents has received much attention [9–15]. Recently, advancement in the field of ionic liquids research provides another route for achieving task-specific ionic liq-

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- I: R=CH₃
 II: R=CH₂CH₃
 III: R=CH₂CH₂CH₂CH₃
 IV: R=CH₂CH₂CH₂CH₂CH₂CH₃

Fig. 1. The Brønsted acidic ionic liquids used in this study.

uids in which a functional group is covalently tethered to the cation or anion of the ionic liquid, especially to the two N atoms in the imidazole ring [16–18]. When an alkane sulfonic acid group is covalently tethered to the IL cation, the IL would be a strong Brønsted acid [19]. These SO₃H-functionalized ionic liquids have exhibited great potential in replacement of conventional homogenous and heterogeneous acidic catalysts because they are fluxible, nonvolatile, noncorrosive and immiscible with many organic solvents [20–22].

Shen et al. have reported that 1-butyl-3-methylimidazoliumhexafluorophosphate ([bmim]PF₆) can catalyze alkylation of phenol with TBA with high conversion and selectivity towards 2,4-DTBP [23]. However, the acidity of [bmim]PF₆ for its pronounced effect on the selectivity may be attributed to HF produced as a result of PF₆[−] decomposition [24]. In this case, issues like safety and corrosion should be taken into account and additional efforts and costs should also be considered to avoid the liberation of toxic and corrosive HF into the environment. Meanwhile, the recycle of the ionic liquid is not discussed. Therefore, further investigation is necessary to elucidate the merits of using ionic liquid as catalyst for this alkylation.

In this paper, we first report an efficient and environmentally benign alkylation reaction of phenol with TBA using SO₃H-functionalized ionic liquids (Fig. 1) as a substitute for conventional homogenous and heterogeneous acidic catalysts. The influences of different ionic liquids, reaction time, reaction temperature, reactant ratio (mole ratio of phenol to that of TBA), the amount and the recycle of ionic liquid were investigated. The present work revealed that alkylation reaction of phenol with TBA could be accomplished with high yield and good selectivity via the use of those ionic liquids as catalysts.

2. Experimental

2.1. Materials and reagents

All solvents and chemicals in the experiment were commercially available and used without further purification unless otherwise stated. *N*-Methylimidazole and 1,4-butane sulfone were purchased from Aldrich.

2.2. Preparation of ionic liquids

The SO₃H-functionalized ionic liquids I–IV were synthesized according to literature [19,22]. 1-Ethylimidazole, 1-butylimidazole and 1-hexylimidazole were prepared from imidazole and halogenated hydrocarbon in ethanol using slightly excess of sodium as a sacrificial reagent according to literature [25].

2.2.1. Preparation of 1-alkyl-3-(butyl-4-sulfonate) imidazolium betaines [19,22]

N-Alkylimidazole (10 mmol) is stirred solvent free with 1,4-butanediol (10 mmol) at room temperature for 4 days. After solidification of the mass, it was washed three times with ethyl ether and dried under high vacuum (yield of 1-methyl-3-(butyl-4-sulfonate) imidazolium betaine: 2.1 g, 96.2%).

2.2.2. Preparation of SO₃H-functionalized ionic liquids [19,22]

A stoichiometric amount of concentrated sulphuric acid was added dropwise to 1-alkyl-3-(butyl-4-sulfonate) imidazolium obtained and stirred for 4 h at 353 K to form the ionic liquid. The IL phase was then washed repeatedly with toluene and ethyl ether to remove nonionic residues, and dried in vacuum (393 K, 0.01 Torr). The product was formed quantitatively and in high purity as assessed by NMR spectroscopy (Varian Mercury-plus 300BB instruments). Spectroscopic data for ionic liquid I: ¹H NMR (300 MHz, DMSO-d₆, TMS); δ 1.526 (m, 2H), 1.828 (m, 2H), 2.554 (t, 2H, *J*=7.8 Hz), 3.820 (s, 3H), 4.125 (t, 2H, *J*=6.9 Hz), 7.697 (s, 1H), 7.753 (s, 1H), 9.157 (s, 1H), 11.543 (bs, 2H). ¹³C NMR (75 MHz, DMSO-d₆, TMS); δ 22.14, 29.14, 36.36, 49.06, 51.08, 122.97, 124.28, 137.33. Positive-ion FABMS (*m/z*, ZAB-HS instrument): 57.0, 137.1, 184.9, 218.9, 437.0. The thermal decomposition point of ionic liquid I was determined by TGA (Perkin-Elmer TGA Pyris1 instrument, 10 K min^{−1} heating rate under nitrogen) to be 600.2 K.

Ionic liquid II: ¹H NMR (300 MHz, DMSO-d₆, TMS); δ 1.379 (t, 3H, *J*=7.5 Hz), 1.530 (m, 2H), 1.860 (m, 2H), 2.564 (t, 2H, *J*=7.5 Hz), 4.168 (m, 4H), 7.764 (s, 1H), 7.790 (s, 1H), 8.616 (bs, 2H), 9.229 (s, 1H). ¹³C NMR (75 MHz, DMSO-d₆, TMS); δ 15.71, 22.15, 29.10, 44.86, 49.12, 51.06, 122.81, 123.10, 136.49.

Ionic liquid III: ¹H NMR (300 MHz, DMSO-d₆, TMS); δ 0.852 (t, 3H, *J*=7.2 Hz), 1.211 (m, 2H), 1.528 (m, 2H), 1.738 (m, 2H), 1.864 (m, 2H), 2.577 (t, 2H, *J*=7.5 Hz), 4.155 (m, 4H), 7.782 (s, 2H), 7.950 (bs, 2H), 9.239 (s, 1H). ¹³C NMR (75 MHz, DMSO-d₆, TMS); δ 13.94, 19.45, 22.15, 29.10, 31.95, 49.15, 51.06, 123.13, 136.73.

Ionic liquid IV: ¹H NMR (300 MHz, DMSO-d₆, TMS); δ 0.808 (t, 3H, *J*=6.6 Hz), 1.216 (m, 6H), 1.530 (m, 2H), 1.748 (m, 2H), 1.863 (m, 2H), 2.561 (t, 2H, *J*=7.5 Hz), 4.150 (m, 4H), 7.782 (s, 2H), 8.140 (bs, 2H), 9.239 (s, 1H). ¹³C NMR (75 MHz, DMSO-d₆, TMS); δ 14.49, 22.12, 22.52, 25.80, 29.13, 29.94, 31.17, 49.15, 49.49, 51.04, 123.15, 136.76.

2.3. Catalytic experiment

The catalytic experiments were carried out in a 20 ml autoclave with a glass tube inside equipped with magnetic stirring at autogeneous pressure. A typical batch consisted of 10 mmol of phenol, 6 mmol of TBA, and 3 mmol of ionic liquid. The temperature was maintained at 343 K and the speed of stirring was 600 rpm. Qualitative and quantitative analyses were conducted with a PE Q-Mass 910 GC/MS and a SP-3400 GC-FID detector equipped with a capillary column. The concentration of reactant and product was directly given by the system of GC chemstation according to the area of chromatograph peak.

3. Results and discussion

3.1. Effect of different ionic liquids

The experiments were carried out at a molar ratio of phenol/TBA = 1/0.6 for two reasons: (i) to avoid the formation of large amounts of secondary products, such as the oligomers of isobutene, and (ii) to diminish the influence of the water formed by the dehydration of *tert*-butanol in situ. At the same time, the excess of phenol is small enough to have a crucial influence on the alkylation reaction [26]. The influence of different ionic liquids on the catalytic activity in alkylation of phenol with TBA as observed was illustrated in Table 1. It could be seen that alkylation of phenol with TBA in these ionic liquids gave a mixture of *o*-TBP, *p*-TBP, 2,6-DTBP and 2,4-DTBP. No *t*-BPE or *m*-TBP were produced even at high phenol conversion. At the same time, no products of isobutene oligomerization were detected by GC-MS, which might be ascribed to the lower reaction temperature in this kind of ionic liquids [27]. The conversion from ionic liquid IV as catalyst (entry 4) was slight better than that from other ionic liquids (entries 1–3), which indicated that the length of the side chain of the cation had little impact on the catalytic performance [28].

3.2. Effect of reaction time

Fig. 2 shows the activity and product selectivity of ionic liquid IV as a function of reaction time for alkylation of phenol with TBA at 343 K with a molar ratio of phenol to TBA of 10:6 (based on phenol). In the early stages of the reaction (<5 min), the products were *o*-TBP and *p*-TBP. As the con-

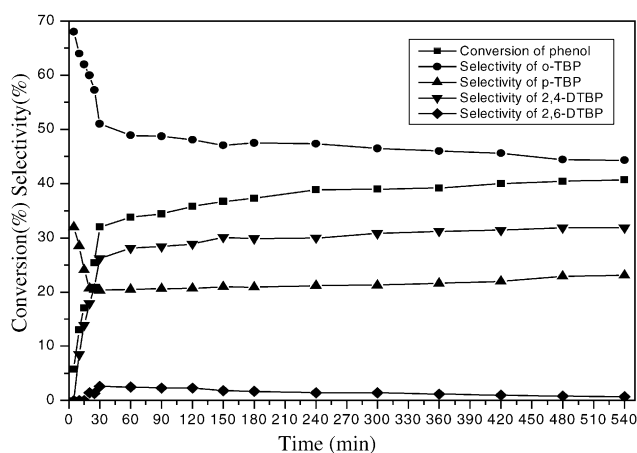


Fig. 2. Phenol conversion and product selectivity vs. reaction time. Condition: phenol:TBA:ionic liquid IV (10:6:3) mole ratio; 343 K.

version of phenol increased (<15 min), a large decrease in the yield of *o*-TBP and *p*-TBP was observed, and 2,4-DTBP and 2,6-DTBP were produced in order. In the all stages of the reaction no *t*-BPE was produced; indicating C-alkylated products were not formed through the *t*-BPE rearrangement reaction or hydrolysis [26]. *t*-BPE was produced when CCl₄ was used as a solvent for this reaction and the O-alkylation was simply suppressed by a slight increase in the reaction temperature from 30 to 45 °C [23,29]. Fig. 2 also shows clearly that the catalyst activity and the selectivity of 2,4-DTBP reach an equilibrium level after 8 h. Therefore, all the experimental data were obtained within the initial 8 h of the reaction. Ionic liquid can be entirely miscible with reactants and the reaction is in a homogeneous phase. The total mole of the reaction system and the concentration of catalyst do not change (1 mol of water needs 1 mol of TBA). So the equilibrium can be seen, in agreement with the observations of Shen et al. [23].

3.3. Effect of reaction temperature

The effect of temperature change on the conversion of phenol was studied in the range of 313–353 K. As could be seen from Fig. 3, the conversion of phenol increased with an increase in temperature from 313 to 343 K. In contrast, at reaction temperatures above 343 K, little increase in phenol conversion was observed. Therefore, the suitable reaction temperature range was inferred to be from 313 to 343 K. As the temperature was raised from 313 to 343 K, a decrease in the selectivity for the *o*-TBP and 2,6-DTBP was observed. Interestingly, an increase in the selectivity for 2,4-DTBP and

Table 1
Alkylation of phenol with TBA in different ionic liquids^a

Entry	ILs	Conversion of phenol	Selectivity of <i>o</i> -TBP	Selectivity of <i>p</i> -TBP	Selectivity of 2,4-DTBP	Selectivity of 2,6-DTBP
1	I	36.5	40.2	28.1	29.5	2.2
2	II	37.7	41.4	25.0	31.9	1.4
3	III	37.9	42.6	24.3	31.6	1.4
4	IV	39.2	44.2	21.8	32.5	1.5

^a Reaction condition: 343 K, phenol/TBA/ILs 10:6:3 mol/mol/mol, 6 h.

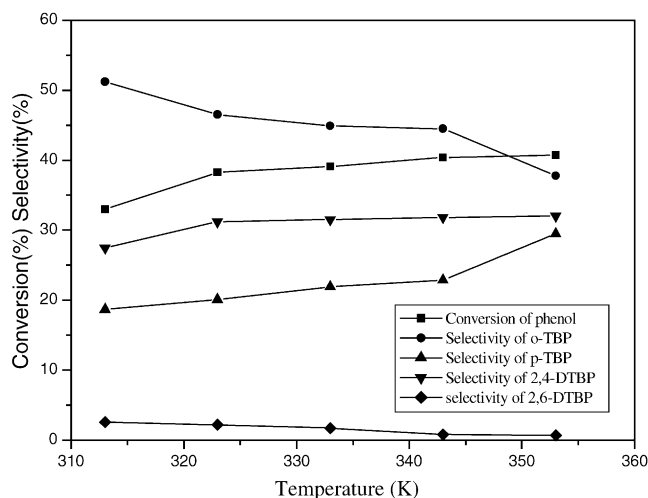


Fig. 3. Phenol conversion and product selectivity vs. reaction temperature. Condition: phenol:TBA:ionic liquid IV (10:6:3) mole ratio; 8 h.

p-TBP was observed. This result could be attributed to the transformation of *o*-TBP into *p*-TBP under relative high temperature [24]. Considering the phenol conversion and product distribution, the optimum reaction temperature was inferred to be 343 K. At this temperature, the selectivity for 2,4-DTBP was the highest at high phenol conversions.

3.4. Effect of the reactant ratio

A series of reactions were carried out to establish the effect of reactant ratio on the conversion and selectivity under exactly the same conditions (at 343 K for 8 h using 3 mmol of ionic liquid per 10 mmol phenol) except using variable amounts of TBA (6, 10, 20, 30 and 40 mmol) while keeping the amount of phenol constant at 10 mmol. The results are shown in Fig. 4. It was observed that as the amount of TBA increases, the conversion of phenol and selectivity for 2,4-

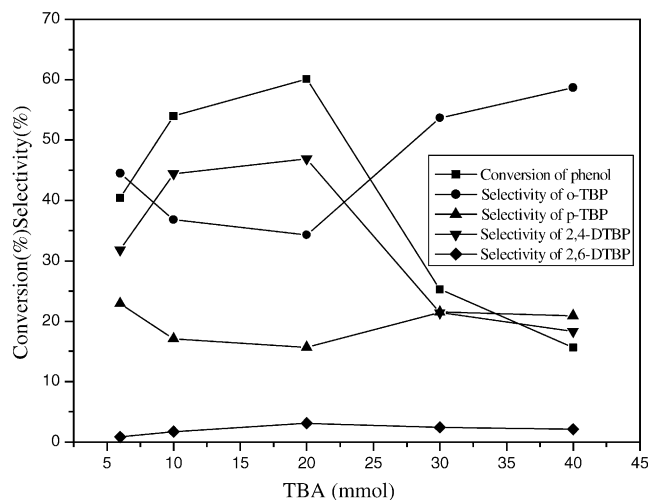


Fig. 4. Phenol conversion and product selectivity vs. amount of TBA added. Condition: 343 K; 8 h, 3 mmol ionic liquid IV (10 mmol phenol).

DTBP passed through a maximum, while the selectivity for *o*-TBP and *p*-TBP passed through a minimum. This might be due to the dilution of the catalyst concentration by TBA. The *o*-TBP and *p*-TBP were formed especially in moderately acidic media, while 2,4-DTBP was formed when strongly acidic catalyst was used [24]. The maximum phenol conversion and the highest selectivity for 2,4-DTBP were observed when the mole ratio of phenol:TBA was 1:2. Therefore, all further experiments were carried out with the mole ratio of phenol to TBA being 1:2, i.e. 20 mmol TBA per 10 mmol phenol.

3.5. Effect of the amount of ionic liquid

The effect of the amount of ionic liquid on the reaction was studied by varying the quantity of ionic liquid (3, 5, 10, 15 and 20 mmol/10 mmol phenol). The reactions were carried out under similar reaction conditions as described previously. As shown in Fig. 5, it was observed that with an increase in the proportion of ionic liquid, the conversion of phenol increase and the selectivity for 2,4-DTBP passed through a maximum and then decreased as the dosage of ionic liquid was increased. At the same time, the selectivity for *o*-TBP and *p*-TBP was decreased. When the amount of ionic liquid was 20 mmol, 2,4,6-TTBP (ca. 10%) was produced. This was attributed to the increase of acidity in reaction system, which could change the distribution of products. The highest conversion of phenol and the best selectivity for 2,4-DTBP were obtained when the amount of ionic liquid used was 15 mmol/10 mmol phenol.

3.6. Recycle of ionic liquid

In order to examine the regenerability of the ionic liquid, the ionic liquid was extracted by *n*-hexane (2 × 3 ml) and vacuumized for 4 h at 393 K for another cycle. The ionic liquid was assessed by ¹H NMR spectroscopy and no traces of

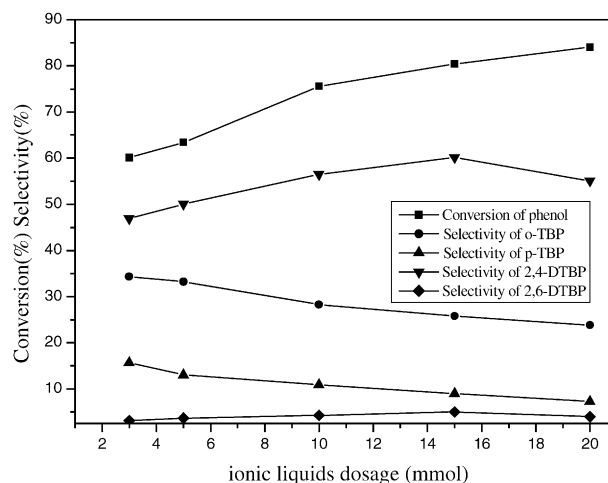


Fig. 5. Phenol conversion and product selectivity vs. amount of ionic liquid. Condition: 343 K, 8 h, 10 mmol phenol, phenol:TBA mole ratio, 1:2.

Table 2
Recycling of ionic liquid IV in the alkylation of phenol with TBA^a

Run	Conversion of phenol	Selectivity of <i>o</i> -TBP	Selectivity of <i>p</i> -TBP	Selectivity of 2,4-DTBP	Selectivity of 2,6-DTBP
1	80.3	25.8	9.0	60.2	5.1
2	79.9	24.7	8.9	60.8	5.5
3	79.0	25.1	9.4	59.9	5.7
4	79.5	25.4	9.7	59.1	5.8

^a Reaction condition: 343 K, phenol/TBA/ILs 10:20:15 mol/mol/mol, 8 h.

products and reactant were detected. The results of the catalyst recycling experiment are shown in Table 2. It could be seen that ionic liquid IV was utilized repeatedly over three times without any apparent loss of the conversion and selectivity.

3.7. Mechanism

From the product distribution and with good probability the following mechanism can be postulated. The first step is the protonation of TBA generating a carbocation, which reacts with the nucleophilic sites of the phenol. Alternatively, the carbocation dehydrates to reactive isobutylene, which can also be an alkylating agent under the reaction condition. Isobutylene or carbocation reacts with phenol through a C-alkylation to give rise to the desired alkylphenol. Further investigation about the mechanism is now undergoing.

4. Conclusion

In conclusion, the alkylation of phenol with TBA catalyzed by Brønsted acidic ionic liquid was successful. The optimum reaction conditions for this reaction were a molar ratio of 1:2 of phenol to TBA, 15 mmol ionic liquid per 10 mmol phenol, 343 K for 8 h. At this time, the conversion of phenol and the selectivity of 2,4-DTBP were 80.4 and 60.2%, respectively. The ionic liquid was utilized repeatedly over three times without any apparent loss of the conversion and selectivity. The present study shows that Brønsted acidic ionic liquid has a potential application in the production of 2,4-DTBP with good activity and selectivity.

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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] 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] W.A. Herrmann, V.P.W. Böhm, *J. Organomet. Chem.* 572 (1999) 141.
- [9] P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* 39 (2000) 3772.
- [10] J. Dupont, R.F. de Souza, P.A.Z. Suarez, *Chem. Rev.* 102 (2002) 3667.
- [11] C.M. Gordon, *Appl. Catal. A: Gen.* 222 (2002) 101.
- [12] H. Olivier, *J. Mol. Catal.* 146 (1999) 285.
- [13] T. Welton, *Chem. Rev.* 99 (1999) 2071.
- [14] H. Olivier, L. Magna, *J. Mol. Catal. A* 182–183 (2002) 419.
- [15] J.D. Holbrey, K.R. Seddon, *Clean Prod. Processes* 1 (1999) 223.
- [16] K.W. Kottsieper, O. Stelzer, P. Wasserscheid, *J. Mol. Catal. A* 175 (2001) 285.
- [17] E.D. Bates, R.D. Mayton, I. Ntai, J.H. Davis Jr., *J. Am. Chem. Soc.* 124 (2002) 926.
- [18] J. Gui, Y. Deng, Z. Hu, Z. Sun, *Tetrahedron Lett.* 45 (2004) 2681.
- [19] A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weaver, D.C. Forbes, J.H. Davis, *J. Am. Chem. Soc.* 124 (2002) 5962.
- [20] D.C. Forbes, K.J. Weaver, *J. Mol. Catal. A* 214 (2004) 129.
- [21] Y. Gu, F. Shi, Y. Deng, *J. Mol. Catal. A* 212 (2004) 71.
- [22] J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu, Z. Sun, *Catal. Commun.* 5 (2004) 473.
- [23] H.-Y. Shen, Z.M.A. Judeh, C.B. Ching, *Tetrahedron Lett.* 44 (2003) 981.
- [24] H.-Y. Shen, Z.M.A. Judeh, C.B. Ching, Q.-H. Xia, *J. Mol. Catal. A* 212 (2004) 301.
- [25] P. Bonhote, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* 35 (1996) 1168.
- [26] E. Dumitriu, V. Hulea, *J. Catal.* 218 (2003) 249.
- [27] Y. Gu, F. Shi, Y. Deng, *Catal. Commun.* 4 (2003) 597.
- [28] J. Fraga-Dubreuil, K. Bourahla, M. Rahmouni, J.P. Bazureau, J. Hamelin, *Catal. Commun.* 3 (2002) 185.
- [29] A. Corma, H. Garcia, J. Primo, *J. Chem. Res.* 1 (1988) 40.