

Synthesis of SO₃H functionalized ionic liquids and their catalytic performance in the butylation of phenols with *tert*-butanol

Xinwen Guo*, Lei Gao, Xiaowa Nie, Min Liu, Xin Liu, Xiumei Liu, JinXia Zhou

^a State Key Lab of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116012, Chin, *Xinwen Guo: guoxw@dlut.edu.cn

Introduction

SO₃H functionalized ionic liquids have been synthesized in 2002 by Forbes [1]. They offered a new possibility for developing environmental friendly acid catalysts because it combined the advantages of both liquid acids and solid acids, for example, uniform acid sites, water and air stable, easy separation and reusable [2]. In this paper, three series of SO₃H functionalized ionic liquids were synthesized and used for butylation of phenols. The results show that the SO₃H-functionalized ionic liquids are efficient and reusable catalysts for the butylation of phenols. The reaction mechanism was investigated by using theoretical calculation method.

Experimental

Three series of ionic liquids were synthesized by using nitrogen-containing compounds and 1,4-butane- or 1,3-propane sultone according to the literature [1,3]. The obtained ionic liquids were identified by NMR and ESI-MS analysis. The data of thermal stability for the ionic liquids were obtained by TGA (SDT851e) at a heating rate of 10K/min under nitrogen. UV-Vis spectra were obtained by UV (HP8453).

The alkylation of phenols with TBA was carried out in a glass reactor. The qualitative analysis of the products was conducted on a HP6890/5973 GC/MS with a HP-5MS column; the quantitative analysis was carried out on a 7890 GC (Shanghai Tianmei Co.) equipped with a SE-30 column (30m×0.25mm).

Results and discussion

Alkylation of phenol, p-cresol, m-cresol, o-cresol, catechol and hydroquinone with TBA was investigated respectively. The results are listed in Table 1. It can be seen that the catalytic performance of the ionic liquids was controlled dominantly by the anion which can improve the selectivity; Catalytic activity of ionic liquids are more than that of solid acids (H-β) and similar to that of traditional acids for

alkylation of m-cresol under mild reaction conditions and Ionic liquids can be recycled over four times without any loss of conversion and selectivity for alkylation of hydroquinone. Only in the butylation of catechol, there is no ether product and the reason was explained by calculation result.

Table 1 Alkylation of phenols with *tert*-butanol in different ionic liquids

Entry	Catalysts	Reactant	Main product	Conv / %	Sel / %
1	H ₂ SO ₄	phenol	4- <i>tert</i> -butyl phenol	80	59
2	IL9	phenol	2- <i>tert</i> -butyl phenol	82	51
3	IL10	phenol	2- <i>tert</i> -butyl phenol	79	52
4	IL13	phenol	2- <i>tert</i> -butyl phenol	42	41
5	IL5	o-cresol	2- <i>tert</i> -butyl-6-methylphenol	70	41
6	IL5	p-cresol	2- <i>tert</i> -butyl-p-cresol	79	92
7	IL10	m-cresol	2- <i>tert</i> -butyl-5-methylphenol	81	97
8	H-β	m-cresol	2- <i>tert</i> -butyl-5-methylphenol	30	79
9	H ₂ SO ₄	m-cresol	2- <i>tert</i> -butyl-5-methylphenol	82	95
10	IL14 ¹	hydroquinone	2- <i>tert</i> -butyl hydroquinone	67	74
11	IL14 ²	hydroquinone	2- <i>tert</i> -butyl hydroquinone	65	71
12	IL14 ³	hydroquinone	2- <i>tert</i> -butyl hydroquinone	65	75
13	IL14 ⁴	hydroquinone	2- <i>tert</i> -butyl hydroquinone	65	74
14	IL9	catechol	4- <i>tert</i> -butyl catechol	42	97

Reaction conditions: Entry 1-4: 343k, phenol /TBA/cat molar ratio: 1/1/1, 7h ; Entry 5: 343k, o-cresol/TBA/IL molar ratio:1/1/1, 6h ; Entry 6: 343k, p-cresol TBA/IL molar ratio:1/1/1, 7h ; Entry 7-9: 363K, m-cresol/TBA/ cat molar ratio :1/1/0.75, 8h, dosage of catalysts=10% weight of reactants; Entry10-13: 343k, hydroquinone/TBA/IL molar ratio:1/1.5/0.5, 1.5h. 1,2,3,4 were recycling times of IL14; Entry 14: 423k, catechol/TBA/IL molar ratio : 2/1/0.1, 3h.

Conclusion

A series of SO₃H functionalized ionic liquids were successfully synthesized by using industrial materials, and they exhibited high selectivity in the alkylation of phenols with *tert*-butanol. Hence, it can be used as a substitute of traditional acids in the butylation of phenols under mild reaction conditions.

Acknowledgements

This project was sponsored by Program for New Century Excellent Talents in University (NCET -04-0268) and by the 111 Project.

References

- 1 A.C. Cole, J.L. Jensen, I. Ntai, K.L.T. Tran, K.J. Weave, D.C. Forbes, J.H. Davis, J. Am. Chem. Soc. 124 (2002) 5962.
- 2 Y. Gu, F. Shi, Y. Deng, Catal. Commun 4 (2003) 597–601.
- 3 J. Gui, X. Cong, D. Liu, X. Zhang, Z. Hu, Z. Sun, Catal. Commun.5 (2004) 473.