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Articles

Jacob M. Crosthwaite, Victoria A. Farmer, Jason P. Hallett, Tom Welton

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Epoxidation of alkenes by OxoneTM using 2-alkyl-3,4-dihydroisoquinolinium salts as catalysts in ionic liquids

The use of 2-alkyl-3,4-dihyroisoquinoliunium salts as catalysts for the epoxidation of alkenes by OxoneTM was investigated in a variety of ionic liquids.

Jian-Ying Wang, Feng-Yun Zhao, Run-Jing Liu, Yong-Qi Hu

Journal of Molecular Catalysis A: Chemical 279 (2008) 153

Oxidation of cyclohexane catalyzed by metal-containing ZSM-5 in ionic liquid

A convenient and efficient application of *tert*-butyl hydroperoxide/metal-containing ZSM-5 in ionic liquids [emim]BF₄ for the oxidation of cyclohexane to cyclohexanone and cyclohexanol is described. As shown in the below table, good yields and higher selectivity of products were obtained in ionic liquid compared with in molecular solvent. The catalytic activity of FeZSM-5 was superior to that of other MZSM-5 and the as-received HZSM-5 in ionic liquid. For cyclohexane oxidation catalyzed by FeZSM-5, 20.9% conversion of cyclohexane and 98.2% selectivity of desired products were obtained in ionic liquid. The catalyst/ionic liquid system could be successfully recycled by a simple decantation procedure without significant loss of activity.

Catalyst	Solvent	Conversion (mol%)	Product distribution (mol%) ⁰				Selectivity of
			-one	-ol	СННР	-one/-ol	-one+-ol+CHHP (%)
HZSM-5	no solvent	0.98	0.3	0.68	0	0.44	100
HZSM-5	acetone	3.29	0	1.29	1.17	0	74.7
FeZSM-5	acetone	3.81	0.6	1.35	1.03	0.44	78.2
HZSM-5	[emim]BF4	15.8	6.98	2.70	5.64	2.59	97.0
NiZSM-5	[emim]BF4	15.9	8.2	2.84	4.39	2.89	97.1
CoZSM-5	[emim]BF4	14.2	9.82	3.53	0.71	2.78	99.0
MnZSM-5	[emim]BF4	15.5	10.3	3.06	1.77	3.39	97.6
FeZSM-5	[emim]BF ₄	20.9	12.1	3.27	5.15	3.70	98.2
CuZSM-5	[emim]BF4	9.5	6.15	3.31	0	1.86	100

Reaction conditions: 0.15 g catalyst, 27.8 mmol cyclohexane, 55.6 mmol TBHP (85% in H₂O). ml (6.25 g) ionic liquid, 12h and 90 °C; -one, cyclohexanone; -ol, cyclohexanol; CHHl cyclohexyl hydroperoxide.

Xinzhong Li, Wumanjiang Eli

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A green approach for the synthesis of long chain aliphatic acid esters at room temperature

Two novel Brønsted acidic ionic liquids (2a and 2b) served as efficient and reusable catalysts, which could promoted Fischer esterification of long chain aliphatic acids with methanol and ethanol, the reactions carried out smoothly at room temperature with excellent yields.

$$R^{1}COOH + R^{2}OH \xrightarrow{10mol\%} R^{1} C OR^{2} + H_{2}O$$

$$3--4.5h Yield: 85-99\%$$

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Pedro Montes-Navajas, Avelino Corma, Hermenegildo Garcia

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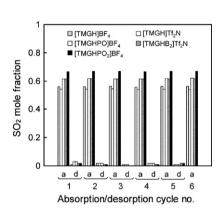
Supramolecular ionic liquids based on host-guest cucurbituril imidazolium complexes

Jun Huang, Anders Riisager, Rolf W. Berg, Rasmus Fehrmann

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Tuning ionic liquids for high gas solubility and reversible gas sorption

Novel 1,1,3,3-tetramethylguanidinium ionic liquids are highly efficient, reversible absorbents for gaseous sulfur dioxide and ammonia, providing unprecedented gas absorption capability of up to two moles at ambient conditions. Gas absorption enthalpies, Raman and UV-vis spectra of the gas-saturated ionic liquids reveal moderate solvent-solute interaction facilitating their applications for gas-storage, -separation and reaction media for, e.g. catalytic processes involving gaseous reactants.



Shi-Wei Liu, Shi-Tao Yu, Fu-Sheng Liu, Cong-Xia Xie, Lu Li, Kai-Hui Ji

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Reactions of α -pinene using acidic ionic liquids as catalysts

Hydration of $\alpha\text{-pinene}$ and esterification of $\alpha\text{-terpineol}$ have been investigated in the presence of various acidic ionic liquids. It was found that the cations of ionic liquids determined catalytic performance of acidic ionic liquids, and the anions had obvious effect on the selectivity of desired products. It was also found that ionic liquid 1-methyl-3-(3-sulfo-propyl)-imidazolium dihydrogen phosphate ([HSO_3-pmim]H_2PO_4) exhibited outstanding catalytic properties in both reactions. Furthermore, the effective product isolation combined with the recyclable catalyst is expected to contribute to the development of clean and environmentally friendly strategy for the synthesis of $\alpha\text{-terpineol}$ and $\alpha\text{-terpinyl}$ acetate.

Pralhad A. Ganeshpure, Gigi George, Jagannath Das

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Brønsted acidic ionic liquids derived from alkylamines as catalysts and mediums for Fischer esterification: Study of structure–activity relationship A series of ionic liquids based on alkylammonium salts were synthesized. The ionic liquids were used as catalysts and mediums for the esterification of acetic acid with 1-octanol as a probe to understand their structure—activity relationship in the Fisher esterification.

CH₃-COO-CH₂-(CH₂)₆-CH₃ + H₂O

Ionic liquids:

$$\begin{split} &[Et_9NH][HSO_4], \ [Et_9NH][H_2PO_4], \ [Et_9NH][BF_4], \ [Et_9NH][p-CH_3C_6H_4SO_3], \\ &[Et_2(PhCH_2)NH][HSO_4], \ [p_-Bu_9NH][HSO_4], \ [p_-Oct_9NH][HSO_4], \\ &[Et_2NH_2][[HSO_4], \ [Et_9NH_2][[H_2PO_4], \ [Et_9NH_2][[BF_4], \ [i-Pr_2NH_2][HSO_4], \\ &[EtNH_3][[HSO_4], \ [EtNH_3][[H_2PO_4], \ [EtNH_3][[BF_4]] \end{split}$$

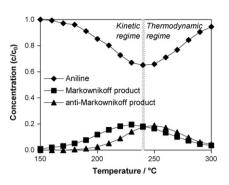
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Carsten Sievers, Oriol Jiménez, Richard Knapp, Xilei Lin, Thomas E. Müller, Andreas Türler, Birgit Wierczinski, Johannes A. Lercher

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Palladium catalysts immobilized in thin films of ionic liquid for the direct addition of aniline to styrene

The addition of aniline to styrene was catalyzed with a novel type of bi-functional catalyst, where a palladium complex and Brønsted acid were immobilized in a thin film of supported ionic liquid. While the reaction was selective for the Markownikoff product at low temperatures, formation of the *anti*-Markownikoff product was also observed at higher temperatures.



Takehiko Sasaki, Mizuki Tada, Chongmin Zhong, Takao Kume, Yasuhiro Iwasawa

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Immobilized metal ion-containing ionic liquids: Preparation, structure and catalytic performances in Kharasch addition reaction and Suzuki cross-coupling reactions

Shifang Liu, Nick Thomson, Alan Pettman, Zeynab Hyder, Jun Mo, Jianliang Xiao

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Ionic liquids as solvent for regioselective arylation of α -substituted allylic alcohols by aryl bromides

Ionic liquid is shown to promote the Pd-DPPP catalyzed regioselective Heck arylation of α -substituted allylic alcohols by aryl bromides, affording β/γ ratios of up to 78/22.

Heather E. Lanman, Rene-Viet Nguyen, Xiaoquan Yao, Tak-Hang Chan, Chao-Jun Li

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Evaluating Lewis acid catalyzed hydroalkylation of alkenes in neat and in ionic liquids

Addition of 1,3-dicarbonyls to alkenes is catalyzed by 10% SnBr $_4$ in ionic liquid or by 10% Cu(OTf) $_2$ in solventless conditions. The method is more environmentally benign and avoids the use of volatile organic solvents.

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L. Mantarosie, S. Coman, V.I. Parvulescu

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Comparative behavior of various lipases in benign water and ionic liquids solvents

Lin-Fei Xiao, Qun-Feng Yue, Chun-Gu Xia, Li-Wen Xu

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Supported basic ionic liquid: Highly effective catalyst for the synthesis of 1,2-propylene glycol from hydrolysis of propylene carbonate

Hydrolysis of propylene carbonate to 1,2-propylene glycol was performed by using a SBIL catalyst. It was found that more than 99% yield and selectivity were obtained in the presence of SBIL at the optimum conditions. Additionally, the catalyst could be reused at least up five times with slight loss of catalytic activity.

O +
$$H_2O$$
 SBIL HO OH

Selectivity: >99%
Yield: >99%

Jinliang Song, Zhaofu Zhang, Tao Jiang, Suqin Hu, Wenjing Li, Ye Xie, Buxing Han

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Epoxidation of styrene to styrene oxide using carbon dioxide and hydrogen peroxide in ionic liquids.

Epoxidation of styrene to styrene oxide using carbon dioxide and hydrogen peroxide in ionic liquids was studied. The various reaction parameters in the epoxidation of styrene were investigated. The pressure of CO_2 , equivalents of KOH and H_2O_2 , reaction time and different ionic liquids had influence on the conversion of styrene and the yield of styrene oxide.

Kam Loon Fow, Stephan Jaenicke, Thomas E. Müller, Carsten Sievers

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Enhanced enantioselectivity of chiral hydrogenation catalysts after immobilisation in thin films of ionic liquid

Chiral complexes immobilized in silica supported thin films of ionic liquid provided considerable enantioselectivity in the hydrogenation of acetophenone. In contrast, no enantioselectivity was observed in the corresponding homogeneous catalysis. As explanation for this phenomenon, the formation of solvent cages of ionic liquid molecules around the organometallic complexes is proposed, which leads to enhanced substrate—catalyst interactions.

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C. Paun, J. Barklie, P. Goodrich, H.Q.N. Gunaratne, A. McKeown, V.I. Pârvulescu, C. Hardacre

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Supported and liquid phase task specific ionic liquids for base catalysed Knoevenagel reactions