Electronic Supplementary Information (ESI)

Highly effective tandem hydroformylation-acetalization of olefins using a long-life Brønsted acid-Rh bifunctional catalyst in ionic liquid/alcohol systems

Xin Jin,* [a, b] Kun Zhao, [a] Feifei Cui, [a] Fangfang Kong [a] and Qiangqiang Liu [a]

[a] Department of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China. Fax: (+86)-532-84022719; Tel: (+86)-532-84022719; E-mail: jinx1971@163.com
[b] Key Laboratory of Oil & Gas Fine Chemicals (Ministry of Education), Xinjiang University, Wulumuqi 830046, China

Characterization of the phase behavior and miscibility of IL/alcohol/1-alkene systems

All miscibility determinations were carried out by cloud titration method according to literature report.[1] IL, 1-alkene and the internal standard were added in 15 mL glass Schlenk tube and heated with a super thermostatic cistern under stirring. Upon reaching the set temperature, alcohol was added dropwise using a syringe until the cloudy mixture turned homogeneous. The volume of the added alcohol was recorded.

Table 1 The phase behavior and miscibility of [bmim][BF_4]/MeOH/1-octene system.

T (℃)	$m_{[bmim][BF4]}$ (g)	$V_{1\text{-octene}}$ (mL)	$V_{cyclohexane\ (internal\ standard)}$ (mL)	V_{MeOH} (mL)	Miscibility
60	1	0.6	0.1	2.30	miscible
65	1	0.6	0.1	2.15	miscible

Table 2 The phase behavior and miscibility of [bmim][PF_6]/MeOH/1-octene system.

T (℃)	$m_{[bmim][PF6]}$ (g)	$V_{1\text{-octene}}$ (mL)	$V_{cyclohexane\ (internal\ standard)}$ (mL)	V_{MeOH} (mL)	Miscibility
60	1	0.6	0.1	2.30	miscible
65	1	0.6	0.1	2.05	miscible

Table 3 The phase behavior and miscibility of [bmim][Tf_2N]/MeOH/1-octene system.

T (℃)	$m_{[bmim][Tf2N]}$ (g)	$V_{1\text{-octene}}$ (mL)	$V_{cyclohexane\ (internal\ standard)}$ (mL)	V_{MeOH} (mL)	Miscibility
60	1	0.6	0.1	1.75	miscible
65	1	0.6	0.1	1.50	miscible

Table 4 The phase behavior and miscibility of [bmim][BF_4]/EtOH/1-octene system.

T (℃)	$m_{[bmim][BF4]}$ (g)	$V_{1\text{-octene}}$ (mL)	$V_{cyclohexane\ (internal\ standard)}$ (mL)	V_{EtOH} (mL)	Miscibility
70	1	0.6	0.1	1.70	miscible
75	1	0.6	0.1	1.60	miscible

Table 5 The phase behavior and miscibility of [bmim][BF_4]/MeOH/1-decene system.

T (℃)	$m_{[bmim][BF4]}$ (g)	$V_{1\text{-decene}}$ (mL)	$V_{n\text{-octane (internal standard)}}$ (mL)	V_{MeOH} (mL)	Miscibility
60	1	0.72	0.1	5.00	miscible
65	1	0.72	0.1	4.80	miscible

Table 6 The phase behavior and miscibility of [bmim][BF_4]/MeOH/1-dodecene system.

T (ºC)	$m_{[bmim][BF4]}$ (g)	$V_{1\text{-dodecene}}$ (mL)	$V_{n\text{-decane (internal standard)}}$ (mL)	V_{MeOH} (mL)	Miscibility
60	1	0.85	0.1	9.00	miscible
65	1	0.85	0.1	8.85	miscible

Table 7 The phase behavior and miscibility of [bmim][BF_4]/1,2-propanediol/1-octene system.

T (ºC)	$m_{[bmim][BF4]}$ (g)	$V_{1\text{-octene}}$ (mL)	$V_{cyclohexane\ (internal\ standard)}$ (mL)	$V_{1,2\text{-propanediol}}$ (mL)	Miscibility	
					Bottom layer	Top layer
20	1	0.6	0.1	0.3	[bmim][BF_4]/1,2-propanediol	1-octene/cyclohexane
80	1	0.6	0.1	0.3	[bmim][BF_4]/1,2-propanediol	1-octene/cyclohexane
80	1	0.6	0.1	0.5	[bmim][BF_4]/1,2-propanediol	1-octene/cyclohexane
80	1	0.6	0.1	1.0	[bmim][BF_4]/1,2-propanediol	1-octene/cyclohexane
80	1	0.6	0.1	2.0	[bmim][BF_4]/1,2-propanediol	1-octene/cyclohexane

Table 8 The phase behavior and miscibility of [bmim][BF_4]/ethylene glycol/1-octene system.

T (ºC)	$m_{[bmim][BF4]}$ (g)	$V_{1\text{-octene}}$ (mL)	$V_{cyclohexane\ (internal\ standard)}$ (mL)	$V_{ethylene\ glycol}$ (mL)	Miscibility	
					Bottom layer	Top layer
20	1	0.6	0.1	0.2	[bmim][BF_4]/ethylene glycol	1-octene/cyclohexane
80	1	0.6	0.1	0.2	[bmim][BF_4]/ethylene glycol	1-octene/cyclohexane
80	1	0.6	0.1	0.5	[bmim][BF_4]/ethylene glycol	1-octene/cyclohexane
80	1	0.6	0.1	1.0	[bmim][BF_4]/ethylene glycol	1-octene/cyclohexane
80	1	0.6	0.1	2.0	[bmim][BF_4]/ethylene glycol	1-octene/cyclohexane

Determination of rhodium loss

The sample was transferred into 25 mL Teflon liner of the steel hydrothermal synthesis reactor, heated on a hotplate to evaporate the volatile materials, then cooled to room temperature and 15 mL concentrated HNO_3 (65%, guaranteed reagent grade) was added. The hydrothermal synthesis reactor was sealed, allowed to stand overnight, then heated in an oven at 180 °C for 24 h. The mixture was cooled to room temperature, heated on a hotplate to remove HNO_3 (<0.5 mL residue), then double distilled water was added and the volume was set to 10 mL using a volumetric flask. The Rh loss was then measured by ICP-AES.

The photo of the homemade autoclave

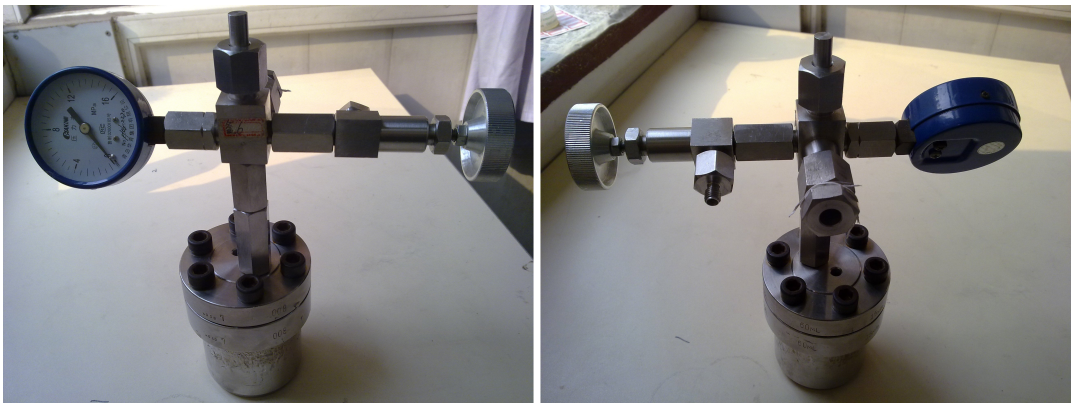

Fig. 1 The photo of 60 ml homemade stainless steel autoclave

References

1 A. Behr, G. Henze, D. Obst and B. Turkowski, *Green Chem.*, 2005, **7**, 645.