

1-butene/isobutane alkylation catalyzed by binary mixtures of ionic liquid and mineral acid

Shengwei Tang^{1,2}, Aaron Scurto¹, Christopher Lyon¹, Bala Subramaniam^{1*}

¹Center for Environmentally Beneficial Catalysis, University of Kansas, Lawrence, KS 66047, USA

² College of Chemical Engineering, Sichuan University, Chengdu 610065, P. R. China

* bsubramaniam@ku.edu

Introduction

Alkylation of isobutane with various olefins is a major process for the production of environmentally friendly gasoline. Current commercial alkylation processes are catalyzed by either concentrated sulfuric acid or hydrofluoric acid. The sulfuric acid process produces large amounts of spent acid and acid soluble oils. Anhydrous HF is highly toxic and its leakage results in dangerous stable aerosols at the ground level. Hence, efforts continue to develop alternative processes that are relatively safe. Solid acids have shown promise as environmentally benign alternatives to the mineral acids; however, deactivate rapidly, resulting in low product yield and loss of reaction selectivity. Recently, room temperature ionic liquids (RTILs) such as chloroaluminate ILs have been investigated as catalysts for isobutane/butene alkylation.^[1-2] These investigations show that a good quality alkylate can be realized; however, chloroaluminate ILs are extremely oxophilic forming adducts with C=O functionalities and reacting irreversibly with traces of water to form HCl. The present work investigates binary mixtures of acidic ionic liquid with either HSO₄⁻ or CF₃SO₃⁻ as anion and sulfuric acid or trifluoromethanesulfonic acid as catalysts for isobutane/1-butene alkylation.

Materials and Methods

Acidic ionic liquid, [OMIm]HSO₄ (1-octyl-3-methylimidazolium hydrogen sulphate)^[3], [HMIm][Tf₂N] (1-Hexyl-3-methylimidazolium bis(trifluoromethanesulfonato) amide),^[3] [MBSIm]HSO₄ (1-methyl-3-(butyl-4-sulfonate) imidazolium hydrogen sulphate),^[4] [MBSIm]OTf (1-butyl-3-(butyl-3-sulfonyl) imidazolium trifluoromethanesulfonate)^[5] were prepared as described in the cited literature. All the ionic liquids were analyzed by ¹H-NMR. The alkylation experiments were performed in a 50 mL Hastelloy autoclave reactor. The experimental unit and analytical procedures are described elsewhere.^[6] Batch experiments, each lasting 10-30 minutes, were performed by pumping 20 ml pre-mixed isobutane/butene mixture into the reactor containing a certain amount of the binary IL/acid mixture. Following each reaction cycle, the hydrocarbon layer was collected in a dry-ice acetone bath and analyzed.

Results and Discussion

As shown in Table 1, ILs such as [HMIm][Tf₂N], [MBSIm]OTf, [BMIm]HSO₄ and [MBSIm]HSO₄ do not provide good alkylation activity (Entries 2-5). In contrast, a binary mixture of IL + H₂SO₄ with a IL weight fraction of roughly 20 - 30 % showed much better activity and C₈ alkylate product selectivity (Entries 6-10 in Table 1). Among the ILs used for creating the binary mixtures, the [OMIm]HSO₄ IL (Entry 10) showed the best combination of activity and C₈ alkylate selectivity presumably because of improved isobutane solubility in the binary mixture compared to other IL/acid mixtures. For a given IL, the use of trifluoromethanesulfonic acid, which has a stronger acidity than sulfuric acid, displayed better activity and C₈ alkylate selectivity compared to mixtures of IL + H₂SO₄ (Entries 7, 8, 11, 12). The binary mixture of [OMIm]HSO₄ and trifluoromethanesulfonic acid was investigated with a

feed I/O ratio of 7.5. As illustrated in Fig 1, stable activity and C₈ alkylate selectivity were obtained over 25 cycles, when the IL/acid mixture was reused. In contrast, the lifetime of the H₂SO₄ was only 3-6 cycles. Further, the C₈ selectivity and the TMP/DMH ratio obtained with the binary IL/acid mixture were higher than those obtained with H₂SO₄.

Table 1. Isobutane /1-butene alkylation results (Feed: 20 ml; I/O in feed=10; P=2bar)

Run	IL	Acid	Catal (g)	Acid (%)	IL(%)	Temp (°C)	Time (min)	Conv %	C ₈ Selec %	TMP/DMH
1		H ₂ SO ₄	0	100	0	11	20	97.25	61.73	6.07
2	[HMIm][Tf ₂ N]		25.84	0	100	11	30	16.23	6.83	0.01
3	[MBSIm]OTf		28.86	0	100	8.5	20	4.90	3.97	0.00
4	[BMIm]HSO ₄		24.47	0	100	11	20	33.34	6.09	0.12
5	[MBSIm]HSO ₄		27.10	0	100	12	20	5.75	59.63	7.19
6	[HMIm][Tf ₂ N]	H ₂ SO ₄	39.01	91.26	8.74	11	20	92.77	60.11	5.09
7	[MBSIm]OTf	H ₂ SO ₄	37.39	71.82	28.12	11	20	93.71	56.67	4.82
8	[BMIm]HSO ₄	H ₂ SO ₄	30.93	58.32	41.67	11.3	20	94.40	57.62	4.91
9	[MBSIm]HSO ₄	H ₂ SO ₄	36.14	74.02	25.98	9.5	20	96.19	67.12	6.42
10	[OMIm]HSO ₄	H ₂ SO ₄	25.07	76.33	23.67	10	10	96.34	75.82	6.84
11	[MBSIm]OTf	CF ₃ SO ₃ H	31.79	66.7	33.3	10	10	95.42	71.21	5.66
12	[BMIm]HSO ₄	CF ₃ SO ₃ H	29.32	76.79	23.21	8	10	98.13	72.36	8.05

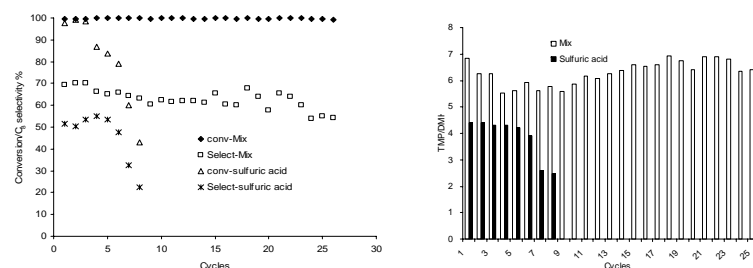


Figure 1. Effect of catalyst reuse on butene conversion, C₈ selectivity and TMP/DMH ratio. Feed I/O ratio: 7.5, Temperature: ~10°C, Cycle time: 10 minutes, Pressure: ~2 bar.

Significance

Binary mixtures of ionic liquids and mineral acids are better alternatives to mineral acids by providing tunable acidity and solubility (such that the feed components are soluble in the catalyst mixture while the C₈ alkylate products are not) along with reduced vapor pressures of the acid mixture, enhancing inherent safety of the process.

References

- Liu, Z., Zhang, R., Xu, C. and Xia, R. *Oil Gas J.* **104**(40),52 (2006)
- Liu, Y., Hu, R. and Xu, C. *Appl Catal A-Gen.* **346**, 189 (2008)
- Wasserscheid, P., Sessing, M. and Korth W. *Green Chem.* **4**, 134 (2002)
- Gui, J., Ban, H., Cong, X. and Zhang, X. *J Mol Catal A-Chem* **225**, 27 (2005)
- Gu, Y., Shi, F., Deng, Y. *J Mol Catal A-Chem* **212**, 71 (2004)
- Lyon, C., Subramaniam, B. and Pereira, C. *Catalyst Deactivation 2001. Stud Surf Sci Catal.* **139**, 221 (2001).