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Silica-Supported Sodium Sulfonate with Ionic Liquid: A Neutral Catalyst System for Michael Reactions of Indoles in Water

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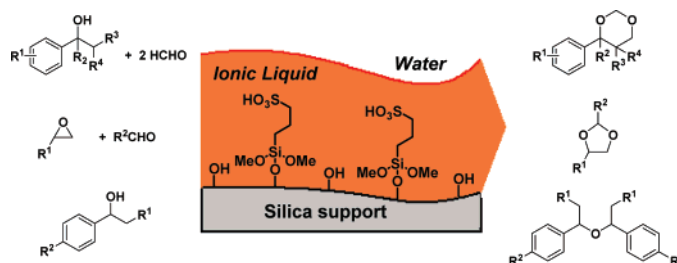
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ABSTRACT



Coating of silica-supported sulfonic acid catalysts with hydrophobic ionic liquid leads to a significant improvement of catalyst selectivity. Many organic reactions, including Prins cyclization, cycloaddition of epoxide to aldehyde, and dehydrative etherification of secondary benzyl alcohols, proceed well in formalin or pure water. In particular, tandem dehydration/Prins cyclization reactions of tertiary and secondary alcohols with formaldehyde were developed for the first time.

Immobilization of molecular catalysts onto a solid support is a promising strategy to facilitate the separation of the catalyst from the products. However, this approach generally decreases the catalytic performance, including the activity and/or selectivity. To solve this problem, researchers deliberately modified the surface of catalysts to be hydrophobic, hydrophilic, or amphiphilic with the hope of accelerating approach of substrate to the active centers.¹ Even if such approaches were efficient to improve the catalytic activity, these strategies were far less efficient to improve the selectivity of solid catalysts, which still remains a huge challenge for heterogeneous catalysis. For the moment, one

of the most common methods to improve the selectivity of heterogeneous catalysts is to use a shape-selective material as solid support or directly as catalyst.² Unfortunately, most of these shape-selective systems are difficult to design and prepare. Furthermore, the substrate scope of shape-selective catalysts was rather limited because their selectivities are strictly dependent on the substrate hindrance.

Recently, Kobayashi and co-workers have developed silica-supported metal catalysts with hydrophobic ionic liquids for organic reactions in water.³ It was observed that activities of silica-supported catalysts were significantly improved by coating of ionic liquids. The authors suggested that the ionic liquid creates a hydrophobic environment on the siliceous surface resulting in better diffusion of organic substrates to the catalytic sites. However, if it is now well-

(1) See some recent examples for hydrophobic derivatization: (a) Liu, P. N.; Gu, P. M.; Wang, F.; Tu, Y. Q. *Org. Lett.* **2004**, *6*, 169. (b) Zhang, H.; Zhang, Y.; Li, C. *J. Catal.* **2006**, *238*, 369. (c) Yang, Q.; Ma, S.; Li, J.; Xiao, F.; Xiong, H. *Chem. Commun.* **2006**, 2495. (d) Ahu, B. Y.; Seok, S. I.; Baek, I. C.; Hong, S.-I. *Chem. Commun.* **2006**, 189. For hydrophilic derivatization: (e) Bass, J. D.; Anderson, S. L.; Katz, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 5219. (f) Notestein, J. M.; Katz, A. *Chem. Eur. J.* **2006**, *12*, 3954. (g) Bass, J. D.; Solovoyov, A.; Pascall, A. J.; Katz, A. *J. Am. Chem. Soc.* **2006**, *128*, 3737. For amphiphilic derivatization: (h) Otani, W.; Kinbara, K.; Zhang, Q.; Ariga, K.; Aida, T. *Chem. Eur. J.* **2007**, 1731.

(2) (a) Tada, M.; Iwasawa, Y. *Chem. Commun.* **2006**, 2833. (b) Roeflaers, M. B. J.; Sels, B. F.; Uji-i, H.; De Schryver, F. C.; Jacobs, P. A.; De Vos, D. E.; Hofkens, J. *Nature* **2006**, *439*, 572.

(3) (a) Gu, Y.; Ogawa, C.; Kobayashi, J.; Mori, C.; Kobayashi, S. *Angew. Chem., Eng. Ed.* **2006**, *45*, 7217. (b) Gu, Y.; Ogawa, C.; Kobayashi, S. *Org. Lett.* **2007**, *9*, 175.

established that there exists a clear synergistic effect between ionic liquids and organomodified silica, *no example of selectivity improvement resulting from this strategy was reported yet*. Herein, we show that the coating of silica-supported sulfonic acids with hydrophobic ionic liquid not only increases the catalyst activity in water but also considerably improves the process selectivity in many Brønsted acid-catalyzed reactions. This association between ionic liquid and organomodified silica offers new routes for selectivity improvement of heterogeneous catalysts (Figure 1).

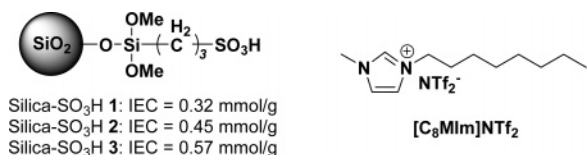


Figure 1. Silica materials and ionic liquid.

Preparation of silica-supported sulfonic acids (SiO₂–SO₃H) was performed according to the reported method (see the Supporting Information).⁴ The obtained functionalized silica was then added to an acetonitrile solution of [C₈MIm]–NTf₂. After 5 min of stirring at room temperature, volatile components were removed under reduced pressure affording a powdery and free-flowing solid here named SiO₂–SO₃H–IL.

The performance, activity, and selectivity of SiO₂–SO₃H–IL were first investigated in the Prins cyclization, which is an important carbon–carbon bond-forming reaction and widely used for organic synthesis.^{5,6} Previously, Prins cyclization reaction of styrene has been carried out in organic solvents such as acetonitrile and 1,2-dichloroethane⁷ using paraformaldehyde as the HCHO source. Quite recently, Gu et al. have reported a novel hydrophobic Brønsted acidic ionic liquid (HBAIL)-catalyzed Prins cyclization of styrene derivatives using formalin as the HCHO source instead of relatively expensive paraformaldehyde.⁸ However, the catalytic activity of HBAIL was far from satisfactory, and the substrate scope was rather limited. Reddy et al.⁹ reported a Prins cyclization using well-organized mesoporous silica (SBA-15) functionalized with sulfonic acid groups as catalyst. However, this acidic mesoporous silica was unable to catalyze the reaction in formalin.

We set out to examine SiO₂–SO₃H 1-catalyzed Prins cyclization of α -methylstyrene in formalin, and as observed

by Reddy et al., a very messy mixture composed of oligomers of α -methylstyrene and their corresponding Prins adducts was produced (Table 1, entry 1). To our great delight, when

Table 1. Prins Cyclization of α -Methylstyrene in Water Using Formalin as Formaldehyde Source^a

entry	catalyst	yield (%)
1	SiO ₂ –SO ₃ H 1	23 ^c
2 ^b	SiO ₂ –SO ₃ H 1–[C ₈ MIm]NTf ₂	94
3	no catalyst	0
4	H ₂ SO ₄	42 ^d
5	HCl	30 ^d
6	CF ₃ SO ₃ H	<5 ^c
7	HBAIL ^e	<5 ^c

^a Mole ratio of formaldehyde to α -methylstyrene is 4:1. ^b 25 wt % IL (respect to weight of silica catalyst) was deposited. ^c Yield determined at total conversion, in this case oligomerization mainly occurs. ^d GC yield. ^e HBAIL = [(*n*-C₈H₁₇)₃N(CH₂)₄SO₃H]NTf₂.

25 wt % of [C₈MIm]NTf₂ was loaded on SiO₂–SO₃H 1, a significant yield improvement was observed affording **2a** in 94% yield (Table 1, entry 2). This clearly indicates the efficiency of ionic liquid for this transformation. As a comparison, Brønsted mineral or organic acids, such as H₂SO₄, HCl, and triflic acid were also examined, and no yield over 50% was obtained under the same conditions (Table 1, entries 4–6). Similarly, with HBAIL,⁸ an extensive polymerization of α -methylstyrene was observed highlighting the high selectivity of SiO₂–SO₃H 1–[C₈MIm]NTf₂ system (Table 1, entry 7).

Table 2 shows the substrate scope of SiO₂–SO₃H 1–[C₈MIm]NTf₂ catalyst for Prins cyclization in formalin. Many styrene derivatives were smoothly converted to the corresponding 1,3-dioxanes in high to excellent yields. Interestingly, SiO₂–SO₃H 1–[C₈MIm]NTf₂ can be reused at least four times without appreciable loss of activity and selectivity (Supporting Information).

Taking into account that, under acidic conditions, alcohols can be dehydrated to the corresponding olefins, we then investigated the feasibility of using SiO₂–SO₃H–IL to catalyze the tandem dehydration/Prins cyclization of alcohols in formalin. As shown in Table 3, with SiO₂–SO₃H 1–[C₈MIm]NTf₂ as catalyst, 2-phenyl-2-propanol was successfully converted to the desired 1,3-dioxane in 92% yield (Table 3, entry 1). Two tertiary alcohols such as 1-phenyl-1-cyclohexanol and 2-(4-chlorophenyl)propanol were also successfully converted to the desired 1,3-dioxane products in 94% and 92% yields, respectively (Table 3, entries 2 and 3).

Unfortunately, all attempts to use secondary alcohols, for example 1-(*p*-tolyl)ethanol, in this tandem reaction failed due to formation of ether and dimerization products (Table 3, entry 4). Interestingly, when 25 wt % of [C₈MIm]NTf₂ was

- (4) Li, P. H.; Wang, L. *Adv. Synth. Catal.* **2006**, *348*, 681.
 (5) (a) Prins, H. J. *Chem. Week* **1919**, *16*, 1072. (b) Arundale, E.; Mikeska, L. A. *Chem. Rev.* **1952**, *51*, 505.
 (6) Bach, T.; Löbel, J. *Synthesis* **2002**, 2521.
 (7) (a) Yadav, J. S.; Reddy, B. V.; Bhaishya, G. *Green Chem.* **2003**, *5*, 264. (b) Li, G.; Gu, Y.; Ding, Y.; Zhang, H.; Wang, J.; Gao, Q.; Yan, L.; Suo, J. J. *Mol. Catal. Chem.* **2004**, *218*, 147. (c) Swapna, B. S. V.; Sridhar, C.; Saileela, D.; Sunacha, A. *Synth. Commun.* **2005**, *35*, 1177. (d) Delmas, M.; Gaset, A. *Tetrahedron Lett.* **1981**, *22*, 723.
 (8) Gu, Y.; Ogawa, C.; Kobayashi, S. *Chem. Lett.* **2006**, *35*, 1176.
 (9) Reddy, S. S.; Raju, B. D.; Kumar, V. S.; Padmasri, A. H.; Narayanan, S.; Rao, K. S. R. *Catal. Commun.* **2007**, *8*, 261.

Table 2. Prins Cyclization of Styrenes Using $\text{SiO}_2\text{--SO}_3\text{H}\text{--}[\text{C}_8\text{MIm}]\text{NTf}_2$ as Catalyst in Formalin^a

$\text{R}^1\text{---}\text{C}_6\text{H}_4\text{---}\text{CH}=\text{CH}\text{---}\text{R}^2\text{---}\text{R}^3\text{---}\text{R}^4 + 2 \text{HCHO} \xrightarrow[\text{Water, 90 }^\circ\text{C, 4.5 h}]{\text{SiO}_2\text{--SO}_3\text{H } \mathbf{1} \text{ (5 mol\%)} \text{ [C}_8\text{MIm}]\text{NTf}_2 \text{ (25 wt\%)}} \text{R}^1\text{---}\text{C}_6\text{H}_4\text{---}\text{CH}(\text{OCH}_2\text{CH}_2\text{O})\text{---}\text{R}^2\text{---}\text{R}^3\text{---}\text{R}^4$			
Entry	Olefin	Product	Yield (%)
1			95
2 ^b			92
3			94
4 ^c			96
5 ^c			92
6 ^d			89
7			90
8 ^e			94

^a Mole ratio of formaldehyde to α -methylstyrene is 4:1. ^b 6 h. ^c 80 $^\circ\text{C}$. ^d 12 h. ^e Reused four times.

loaded over mesoporous silica $\text{HMS}\text{--SO}_3\text{H}$ ¹⁰ instead of $\text{SiO}_2\text{--SO}_3\text{H } \mathbf{1}$, a remarkable selectivity improvement was observed and 1-(*p*-tolyl)ethanol was converted to 4-*p*-tolyl-1,3-dioxane in 74% yield (Table 3, entry 5). It is interesting to note that without coating of $\text{HMS}\text{--SO}_3\text{H}$ with $[\text{C}_8\text{MIm}]\text{NTf}_2$ only a trace amount of product was detected by GC (Table 3, entry 6). It is difficult to offer an explanation for these results, which suggest the existence of a complex synergistic effect between ionic liquid and the siliceous mesoporous structure. This point deserves further investigation.

In order to show the versatility of the $\text{SiO}_2\text{--SO}_3\text{H}\text{--IL}$ system, we then moved on to the selective transformation of epoxides. It is well-known that epoxides are unstable under aqueous acidic conditions and tend to form the corresponding diols or oligomers. Remarkably, in formalin, a cycloaddition of formaldehyde to 1,2-dodecane oxide exclusively occurred in the presence of $\text{SiO}_2\text{--SO}_3\text{H } \mathbf{2}\text{--}[\text{C}_8\text{MIm}]\text{NTf}_2$, and the corresponding 1,3-dioxolane derivative was obtained in 90% yield (Table 4, entry 1). Substrate scope of $\text{SiO}_2\text{--SO}_3\text{H } \mathbf{2}\text{--}[\text{C}_8\text{MIm}]\text{NTf}_2$ was then investigated. Under our condi-

(10) Karam, A.; Gu, Y.; Jérôme, F.; Douliez, J.-P.; Barrault, J. *Chem. Commun.* **2007**, 2222.

Table 3. Tandem Dehydration/Prins Cyclization Reactions of Tertiary and Secondary Alcohols Catalyzed by $\text{SiO}_2\text{--SO}_3\text{H}$ with or without Ionic Liquid in Formalin^a

$\text{R}^1\text{---}\text{C}_6\text{H}_4\text{---}\text{CH}(\text{OH})\text{---}\text{R}^2 + 2 \text{HCHO} \xrightarrow[\text{Water, 90 }^\circ\text{C, 4.5 h}]{\text{SiO}_2\text{--SO}_3\text{H } \mathbf{1} \text{ (5 mol\%)} \text{ [C}_8\text{MIm}]\text{NTf}_2 \text{ (25 wt\%)}} \text{R}^1\text{---}\text{C}_6\text{H}_4\text{---}\text{CH}(\text{OCH}_2\text{CH}_2\text{O})\text{---}\text{R}^2$				
Entry	Substrate	Catalyst	Product	Yield (%)
1		$\text{SiO}_2\text{--SO}_3\text{H } \mathbf{1}\text{--}[\text{C}_8\text{MIm}]\text{NTf}_2$		92
2		$\text{SiO}_2\text{--SO}_3\text{H } \mathbf{1}\text{--}[\text{C}_8\text{MIm}]\text{NTf}_2$		94
3		$\text{SiO}_2\text{--SO}_3\text{H } \mathbf{1}\text{--}[\text{C}_8\text{MIm}]\text{NTf}_2$		92
4		$\text{SiO}_2\text{--SO}_3\text{H } \mathbf{1}\text{--}[\text{C}_8\text{MIm}]\text{NTf}_2$		< 5 ^b
5		$\text{HMS}\text{--SO}_3\text{H}\text{--}[\text{C}_8\text{MIm}]\text{NTf}_3$		74
6		$\text{HMS}\text{--SO}_3\text{H}$		< 5 ^b

^a Mole ratio of formaldehyde to alcohol is 4:1. ^b Yield determined by GC at total conversion of reactants, ether, and dimerization products were mainly produced in this case.

tions, an aqueous solution of chloroacetaldehyde (45%, w/w) readily reacted with 1,2-dodecane oxide to give the corresponding 1,3-dioxolane adduct in 92% yield (Table 4, entry 2). In pure water, analogous cycloaddition of 3-phenylpropionaldehyde to 1,2-dodecane oxide also proceeded well (93% yield) (Table 4, entry 3). Other epoxides, such as 1,2-epoxy-9-decene and epichlorohydrin, were also applicable in this system (Table 4, entries 4–7). Interestingly, the double bond of 1,2-epoxy-9-decene, known to be unstable under acidic conditions, was not affected during the catalytic process.

Finally, the dehydrative etherifications of secondary benzyl alcohols were investigated in water using our catalytic system. These reactions are generally catalyzed by transition metals such as palladium chloride,^{11a} zinc chloride,^{11b} bis-(dithiobenzyl)nickel(II),^{11c} and $\text{MeAl}(\text{NTf}_2)_2$ ^{11d,e} or iodine.^{11f} Brønsted acid catalysts are rarely used in this reaction due to the easy dehydration of benzyl alcohols to the corresponding styrene derivatives.^{11g,h} As a perfect illustration, when Brønsted acid $\text{SiO}_2\text{--SO}_3\text{H } \mathbf{3}$ was used as catalyst for

(11) (a) Miller, K. J.; Abu-Omar, M. M. *Eur. J. Org. Chem.* **2003**, 7, 1294. (b) Kim, S.; Chung, K. N.; Yang, S. *J. Org. Chem.* **1987**, 52, 3917. (c) Kesling, H. S., Jr. US 4518806, 1985. (d) Ooi, T.; Ichikawa, H.; Itagaki, Y.; Maruoka, K. *Heterocycles* **2000**, 52, 575. (e) Wang, C.-H. *J. Org. Chem.* **1963**, 28, 2914. (f) Castro, B. A. *J. Am. Chem. Soc.* **1950**, 72, 5311. (g) Kalendkowska, M.; Kalendkowski, B.; Nowakowski, L.; Olkowsky, H. *Neftekhimiya* **1980**, 20, 436. (h) Luzader, G. B. Hall, M. E. US 2927064, 1960.

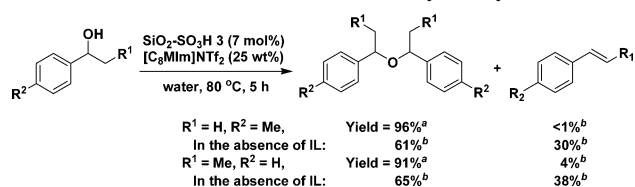
Table 4. Cycloaddition of Epoxides to Aldehydes in Water Using $\text{SiO}_2\text{--SO}_3\text{H}$ –IL as Catalyst

$\text{R}^1\text{--}\text{epoxide} + \text{R}^2\text{CHO} \xrightarrow[\text{water, 90 } ^\circ\text{C, 4 h}]{\text{SiO}_2\text{--SO}_3\text{H } \mathbf{2} \text{ (5 mol\%)} \text{ [C}_8\text{MIm]NTf}_2 \text{ (25 wt\%)}} \text{R}^1\text{--}\text{acetal}$				
Entry	Epoxide	Aldehyde	Product	Yield (%)
1		HCHO		90
2				92
3				93
4		HCHO		94
5 ^a				95
6				93
7 ^b				89

^a 80 °C, 3.5 h. ^b Epichlorohydrin was used in excess (1.5 equiv relative to aldehyde), 5 h.

etherification of 1-tolyl-1-ethanol, 30% of 4-methylstyrene was produced to the detriment of the desired ether, which was formed in only 61% yield. The coating of $\text{SiO}_2\text{--SO}_3\text{H}$ **3** with 25 wt % of $[\text{C}_8\text{MIm}]\text{NTf}_2$ led again to a significant selectivity improvement, and the ether was obtained in 96%

Scheme 1. Etherification of Secondary Benzyl Alcohols



^a Isolated yield. ^b GC yield.

yield. The same tendency was also observed in the case of 1-phenyl-1-propanol (Scheme 1). These results thus show the versatility of this strategy and clearly illustrate that the coating of siliceous materials with hydrophobic ionic liquid can advantageously increase their catalytic performances leading to highly active and selective catalysts in water.

In conclusion, we show here that the coating of Brønsted acid silica materials with hydrophobic ionic liquid $[\text{C}_8\text{MIm}]\text{NTf}_2$ affords heterogeneous catalysts which are able to perform highly selective organic transformations in formalin or pure water. This synergistic effect between organomodified silica and ionic liquids is key to render the catalytic system selective. In particular, tandem dehydration/Prins cyclization reactions of tertiary and secondary alcohols in formalin were developed for the first time. This association between ionic liquid and organomodified silica offers new routes for selectivity improvement of heterogeneous catalysts.

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Supporting Information Available: Preparation of catalyst, experimental details, and characterization of products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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