

# One-step C=N, C=O bonds cleavage and C=O, C=N bonds formation over supported ionic liquid in water<sup>☆</sup>

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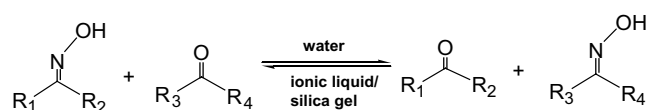
**Abstract**—At ambient reaction temperature, the silica gel confined ionic liquid catalysts were perfectly combined with water as an effective catalytic system for simultaneous C=N and C=O bonds transformation with a TONs exceeding 300 mol mol<sup>-1</sup>.  
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Recently, interest has been growing in studying organic reactions in water due to its natural abundance, the inherent advantages as well as the increasing environmental consciousness of the chemical community, which led to the search for more efficient and environmentally friendly methods for chemical synthesis.<sup>1</sup> Many reactions traditionally carried out in organic solvents, especially in which old bonds cleavage or new bonds formation occurred, can be carried out in water now with additional interesting features,<sup>2</sup> while the need of water-soluble catalysts usually inhibited its extensive application. At the same time, on the basis of the highly charged nature, ionic liquids, which combine good and tunable solubility properties with the absence of measurable vapor pressure and excellent thermal and chemical stabilities, have attracted significant attentions in recent years<sup>3</sup> and were widely recognized and accepted. Its feasibility for replacing volatile organic solvents and toxic catalysts in alkylation,<sup>4</sup> polymerization,<sup>5</sup> hydrogenation,<sup>6</sup> carbonylation,<sup>7</sup> etherization,<sup>8</sup> Heck reactions,<sup>9</sup> carbon dioxide activation<sup>10</sup> and Beckmann rearrangement,<sup>11</sup> etc., was successfully conducted. Unfortunately, large amounts of organic solvents were usually used both in the separation of product from the ionic liquid and in the washing of the ionic liquid catalyst system for reuse, which caused unamiable chemical processes. Therefore, to develop a new process using supported ionic liquid catalyst<sup>12</sup> and water solvent together should

be highly desired because the application of organic solvents can be avoided and the separation of ionic liquid catalysts from the product can also be simplified.

Herein, we report a novel reaction, oxime transformation, in which the silica gel supported ionic liquid catalysts and water media together were used. In this process, remarkable features different from those deoxygenation<sup>13</sup> (only one C=N bond cleavage) or oximation<sup>14</sup> (only one C=O bond formation) reactions reported previously are that the C=N, C=O bonds (two chemical bonds) cleavage and new C=O, C=N bonds (two chemical bonds) formation occurred simultaneously (Fig. 1). The same amounts of new ketone and oxime could be obtained as the amounts of oxime and ketone consumed, for example, the hydroxylamine from the oxime was transferred into the given ketone stoichiometrically with the formation of a new ketone.

The reaction between cyclohexanone oxime and acetone was firstly conducted to investigate the possibility of C=N and C=O bonds transformation using ionic liquid catalysts, for example, DMImBF<sub>4</sub>, in water. Only 22.5% of conversion was achieved when bulk ionic liquid DMImBF<sub>4</sub> was used as catalyst directly and similar results were obtained if pure silica gel was used together



**Figure 1.** C=N and C=O bonds transformation over ionic liquid/silica gel in water.

**Keywords:** Ionic liquid; Water; Supported.

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**Table 1.** Results of C=N and C=O bonds transformation between cyclohexanone oxime and acetone over ionic liquid/silica gel in water

Entry	Ionic liquid <sup>a</sup>	Con. (%) <sup>b</sup>	Sel. (%) <sup>c</sup>	TON <sup>d</sup>
1	DMImBF <sub>4</sub>	22.5	>99	12
2	DMImPF <sub>6</sub> /silica gel	93.8	>99	240
3	EMImPF <sub>6</sub> /silica gel	93.1	>99	170
4	BPyBF <sub>4</sub> /silica gel	92.8	>99	140
5	BMImBF <sub>4</sub> /silica gel	94.0	>99	150
6	DMImBF <sub>4</sub> /silica gel	92.1	>99	200
7 <sup>e</sup>	DMImBF <sub>4</sub> /silica gel	~2	>99	1.2
8 <sup>f</sup>	DMImBF <sub>4</sub> + silica gel	22	>99	12

<sup>a</sup> CMIm = 1-cetyl-3-methyl imidazolium; DMIm = 1-decyl-3-methyl imidazolium; BMIm = 1-butyl-3-methyl imidazolium; EMIm = 1-ethyl-3-methyl imidazolium; BPy = N-butyl pyridinium.

<sup>b</sup> Conversions of cyclohexanone oxime.

<sup>c</sup> Selectivities to acetone oxime.

<sup>d</sup> TON = mole of oxime converted per mole of ionic liquid.

<sup>e</sup> Without addition of water as solvent.

<sup>f</sup> The silica gel was synthesized through same procedure as other catalysts without addition of ionic liquid.

with the ionic liquid DMImBF<sub>4</sub> (Table 1, entry 1). The catalytic activities of other ionic liquids such as BMImBF<sub>4</sub>, CMImBF<sub>4</sub>, BMImPF<sub>6</sub>, DMImPF<sub>6</sub>, CMImPF<sub>6</sub>, etc. were also investigated in this reaction, and 10–30% of conversion and >99% of selectivity were also achieved. In order to further improve the conversion of the reaction, a series of silica gel confined ionic liquid catalysts were synthesized and used in this reaction, and >90% of conversions and nearly 100% selectivities were obtained (entries 2–6). The application of water as solvent was also a key factor for the high catalytic efficiency because the reaction could not proceed effectively without addition of water (entry 7). It is worthwhile to note that the TONs of the silica gel confined ionic liquid catalysts were 10–20 times higher than that using bulk ionic liquids as catalysts (entry 8). These results suggested that some synergism occurred between the silica gel and ionic liquids after confinement.

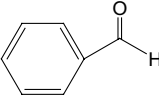
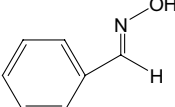
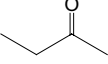
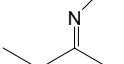
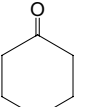
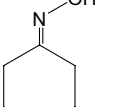
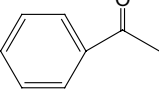
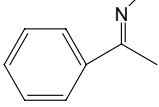


In order to investigate the universality of the catalyst, DMImBF<sub>4</sub>/silica gel was further used in C=N and C=O bonds transformation reactions between several other oximes and acetone. As it was shown in Table 2, longer reaction time was needed to get good results when using aromatic oximes, for example, *p*-methoxyl benzaldoxime and *p*-nitro benzaldoxime, as reactants, which conversions and selectivities were all nearly 100% (entries 1–2). At the same time, poor result was obtained when using acetophenone oxime as reactant. The conversion was only 31.0% after reacted for 96 h (entry 3), which may be attributed to the steric hindrance of acetophenone oxime. The results of C=N and C=O bonds transformation reactions between aliphatic oximes and acetone were not so good as that using aromatic oximes as reactants and the conversions were only 74.8% and 92.1% when using acetaldehyde oxime and butanone oxime, respectively (entries 4–5).

**Table 2.** Results of C=N and C=O bonds transformation between different kinds of oximes and acetone over catalyst DMImBF<sub>4</sub>/silica gel in water<sup>a</sup>

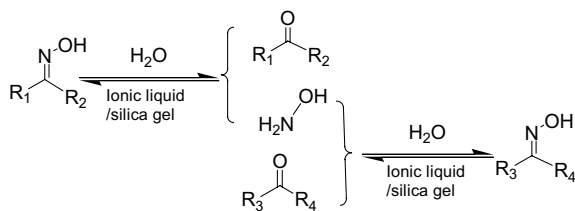
Entry	Oxime	Product	<i>t</i> (h)	Con. (%)	Sel. (%)	TON
1			96	>99	>99	160
2			96	>99	>99	150
3			96	31.0	>99	60
4			96	74.8	>99	310
5			24	92.1	>99	310

<sup>a</sup> Same reaction condition as in Table 1 was used.

**Table 3.** Results of C=N and C=O bonds transformation between different ketones (aldehydes) and acetone oxime over catalyst DMI<sub>2</sub>BF<sub>4</sub>/silica gel in water<sup>a</sup>

Entry	Ketone (aldehyde)	Oxime	t (h)	Con. (%)	Sel. (%)	TON
1			10	95.1	>99	320
2			18	94.6	>99	320
3			6	95.2	>99	320
4			48	16.0	>99	50
5			3	93.6	>99	320

<sup>a</sup> Same reaction condition as in Table 1 was used.

**Figure 2.** A possible procedure for C=N and C=O bond transformation.

A series of oximes and acetone could also be obtained efficiently through this method if using the corresponding ketones and acetone oxime as reactants. The conversion of acetone oxime was about 94–95% and selectivities of acetone and corresponding oximes, for example, benzaldoxime, butanone oxime and cyclohexanone oxime, were all >99% except that using acetophenone as reactant (Table 3, entries 1–4). An unexpected result was obtained when using acetaldehyde as reactant, which conversion reached to 93.6% if reacted for 3 h (entry 5) while the conversion of acetaldehyde oxime was only 74.8% between the C=N and C=O bonds transformation of acetaldehyde oxime and acetone under same reaction conditions.

In consideration of all the results discussed above, it could be conjectured that there was an equilibrium point between the added and newly formed oximes and ketones. A possible procedure for this process was given in Figure 2. The deoximation of oximes in the presence of water should be the first step, then the hydroxylamine simultaneously reacted with the ketone/aldehyde presented, which behaves as hydroxylamine acceptors, and the reaction stopped at the equilibrium point.

In summary, a novel reaction for stoichiometrical transformation of C=N and C=O bonds was effectively developed over silica gel confined ionic liquid catalysts using water as solvent with a TONs exceeded 300 mol mol<sup>-1</sup>. The supported ionic liquids were perfectly combined with water, which simplified the separation of ionic liquid catalysts from the products and completely avoided the using of organic solvents.

*Ionic liquid/silica gel catalysts were synthesized as following procedure:* Ten millilitre of tetraethyl silicate (TEOS), 1 mL of ionic liquid and 7 mL of ethanol were added into a 100 mL of conical flask, respectively. After the formation of clean and homogeneous liquid mixture, 5 mL of hydrochloric acid (5 M) was added and the mixture became coagulated gradually. After aged at 60 °C for 12 h, the resulted solid mixture was dried in vacuum for 3 h with ca. 1–5 mmHg vacuum at 150 °C and 4–5 g solid catalyst samples were obtained, the contents of ionic liquids in silica gel were 20–25 wt %.

*Reaction conditions:* Oxime (0.2 g), catalyst (0.01 g), ketone or aldehyde (2 mL) and water (6 mL) were respectively, added into a 25 mL round bottom and stirred at room temperature (ca. 20 °C) for 2–96 h. Qualitative analyses were conducted with a HP 6890/5793 GC–MS. Quantitative analyses were conducted with a HP 1790 GC. The results were given by the chemstation.

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