

One-pot synthesis of silica gel confined functional ionic liquids: effective catalysts for deoximation under mild conditions

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Abstract—Several acid-functional ionic liquids were physically confined into the silica gel through a sol–gel process and used as effective catalysts for deoximation reactions, which proceeded under ambient temperatures without addition of any co-catalysts or oxidizing and reducing agents.

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Recovery of ketone and aldehyde from oximes is an important reaction because oxime serves as an efficient protective group for carbonyls, which are extensively used for the purification of carbonyl compounds.¹ At the same time, oximes could be prepared from non-carbonyl compounds, and the regeneration of carbonyl compounds from oximes represents a potential route for syntheses of ketones and aldehydes.² Various methods, including acid-catalytic hydrolysis, reductive deoximation, and oxidative deoximation, have been developed for these processes.³ Unfortunately, stoichiometric acid, oxidizing or reducing agents were generally needed to neutralize, oxidize or reduce the hydroxylamine formed during the reactions as mentioned above. In addition, the using of large amounts of Ni, Cr, Mn, and Zn, etc. usually causes environmental pollution seriously. Therefore, the development of clean, highly efficient catalytic process for deoximation reactions should be highly desired.

As a new kind of catalytic media with very low vapor pressure and high dissolvabilities towards many organic and inorganic substances, room temperature ionic liquids have been attracted growing interests and many catalytic reactions proceeded in ionic liquids as reaction media were reported with excellent performance.⁴ More

recently, it was found that the ionic liquids could be efficient dehydrating agents, in which methyl *tert*-butyl ether could be produced from the dehydration between *tert*-butyl alcohol and methanol, and disubstituted ureas could be obtained from the reactions between amines and carbon dioxide,⁵ and therefore, ionic liquids may also be effective catalysts for cleavage of hydroxylamine from the oximes especially with the ionic liquids in which an acid group was incorporated. Herein, a series of acid-functional ionic liquids were synthesized (Fig. 1) for the deoximation reactions and high conversion and selectivity were achieved. Then, immobilization of these ionic liquids with silica gel by a sol–gel method⁶ was further conducted for easy separation of catalyst and increase of the catalytic efficiency for the deoximation reactions.

Firstly, the cyclohexanone oxime was used as a probe substrate to investigate the possibility of the pure functional ionic liquids as the deoximation catalysts. As it is shown in Table 1, all the pure functional ionic liquids exhibited high catalytic activities on the deoximation of cyclohexanone oxime. The conversions of cyclohexanone oxime could reach to 80–90% with ca. 100% selectivities. The presence of the substituted alkyls on the imidazolium cation was found to have strong impact on the conversion and selectivity. With the increasing of the carbon number of the side chain, the conversion of cyclohexanone oxime decreased remarkably while the selectivity was maintained ca. 99%.

Based on the results achieved, the silica gel confined these acid-functional ionic liquids as catalysts were then

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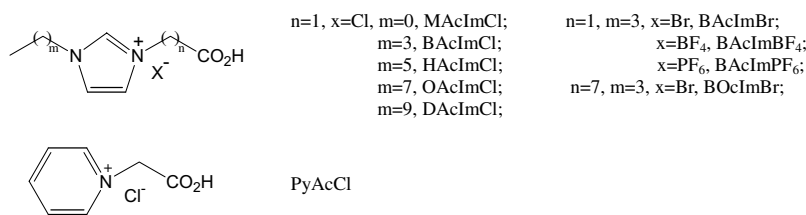


Figure 1. Ionic liquid in which an acid group was incorporated upon the side chain of imidazolium cation.

Table 1. Results of deoximation of cyclohexanone oxime over silica gel confined ionic liquids and pure ionic liquid catalysts^a

Entry	Catalysts	Conversion (%)	Selectivity (%)	TON ^b
1	MAcImCl/silica gel	94.3 (94.4) ^c	>99	118 (30)
2	BAcImCl/silica gel	92.5 (94.8)	>99	143 (37)
3	HAcImCl/silica gel	90.3 (92.1)	>99	158 (40)
4	OAcImCl/silica gel	76.9 (93.7)	>99	150 (46)
5	DAcImCl/silica gel	72.4 (83.7)	>99	155 (45)
6	BAcImBF ₄ /silica gel	93.8 (93.2)	>99	180 (45)
7	BAcImPF ₆ /silica gel	94.1 (94.2)	>99	219 (55)
8	BAcImBr/silica gel	88.2 (94.6)	>99	164 (49)
9	BOcImBr/silica gel	26.6 (84.6)	>99	65 (52)
10	PyAcCl/silica gel	92.2 (96.8)	>99	114 (30)
11 ^d	BAcImBF ₄ /silica gel	90.1	>99	173

^a Reacted for 2 h.

^b Turn over number of ionic liquid = mole of oxime converted per mole of ionic liquid.

^c The data in brackets were results of the deoximation over pure ionic liquid catalysts.

^d The immobilized catalyst was reused for the second time.

tested so as to obtain a highly efficient and easily separable deoximation catalyst system. It can be seen from Table 1 that exceeded 90% of conversions and ca. 100% of selectivities were achieved over most of the immobilized catalysts investigated. It is worth noting that almost the same conversions and selectivities as the pure ionic liquid catalysts were obtained, although the amount of ionic liquid contained in the silica gel, which was only ca. 25% of the amount of ionic liquid needed as pure ionic liquid catalysts under same reaction conditions, indicating that the immobilization of ionic liquids in the silica gel would not only reduce the amount of ionic liquid greatly but also result in an effective catalyst for deoximation. It could be observed more clearly, if comparing the TON of cyclohexanone oxime over the pure and immobilized ionic liquid catalysts, that the TONs of immobilized ionic liquids as catalysts were almost four times as higher as that of using pure ionic liquids as catalysts. The reusability of the immobilized ionic liquid catalyst was also examined. It can be seen that 90.1% of conversion and 99% of selectivity were maintained when BAcImBF₄/silica gel catalyst was reused for the second time, which suggested that the reusability of such catalysts was possible although only 8 mg of immobilized ionic liquid catalyst was left, this may be mainly attributed to the catalyst losing during separation of the catalyst from the resulted reaction mixture, after the first reaction.

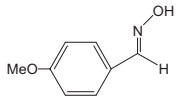
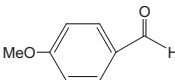
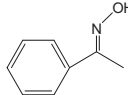
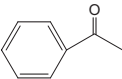
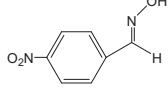
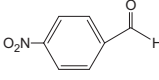
As one of the most effective catalysts for the deoximation reactions, BAcImBF₄/silica gel was further used for the deoximation reactions of several other oximes so as to investigate the universality of such novel catalyst

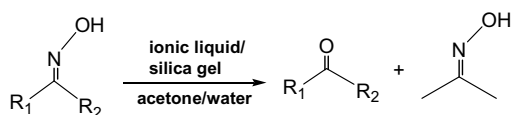
system (Table 2). It can be seen that longer reaction time was needed for deoximation of aromatic oximes. For example, ca. 100% of conversions and selectivities could be achieved when *p*-methoxyl benzaldehyde and *p*-nitro benzaldehyde were used as substrates after the deoximation reaction proceeded for 72 h. The isolated yields of *p*-methoxyl benzaldehyde and *p*-nitro benzaldehyde were also obtained (89% and 96%). At the same time, poor result was given when using acetophenone oxime as substrate, and the conversion was only 19% after the reaction proceeded for 72 h. This may be attributed to the steric hindrance of acetophenone oxime. 73% and 93% of conversions and 99% of selectivities were also achieved, respectively when using acetaldehyde oxime and butanone oxime as substrates.

An interesting result was that no reaction occurred when using acetone oxime as reactant, and nearly the same amounts of acetone oxime was produced when using other oximes as substrates (Fig. 2). These experimental results suggested that the formation of acetone oxime may be an important step for the deoximation reactions proceeding, and the presence of water was also indispensable because the reaction could not occur without addition of water.

In conclusion, a new method for deoximation reactions with a series of immobilized acid-functional ionic liquids with silica gel was developed under mild reaction conditions. The excellent conversions and selectivities were achieved with higher catalytic efficiency, easy separation and reusability. The uses of stoichiometric reducing or oxidizing agents were also avoided.

Table 2. Deoxygenation of different oxime substrates over BACImBF₄/silica gel catalyst

Entry	Oximes	Products	<i>t</i> (h)	Conversion (%)	Selectivity (%)	TON	Yields (%)
1			72	>99	>99	142	89
2			72	19	>99	34	—
3			72	73	>99	268	—
4			72	>99	>99	129	96
5			24	93	>99	276	—
6			48	—	—	—	—

**Figure 2.** A possible route for the deoxygenation of oximes over silica gel confined ionic liquids.

Preparation of the ionic liquids and ionic liquids confined in silica gel: Following ionic liquids containing acid groups were synthesized and used here: MAcImCl (M=methyl, Ac=acetoxy), BAclmBr (B=*n*-butyl), BAclmCl, BAclmBF₄, HAclmCl (H=*n*-hexyl), BAclmPF₆, OAclmCl (O=octyl), BOclmBr (Oc=octylic acid), DAclmCl (D=decyl) and PyAcCl (Py=pyridinium).

Ionic liquids containing acid groups, in which the anion were Cl[−] or Br[−], were synthesized by reacting of alkyl imidazole with the corresponding halide substituted carboxylic acid in toluene under reflux for about 24 h and the acid functional ionic liquids containing BF₄[−] or PF₆[−] were further obtained by double decomposition of these halide containing ionic liquids with corresponding salts.

The silica gel confined ionic liquid was obtained as following procedure: After 10 mL of TEOS (tetraethyl silicate) was heated to 60 °C in a conical flask with stirring, the mixture of ionic liquid (1 g)+ethanol (5 mL) was transferred into the conical flask quickly. Then, 2 mL of HCl (35 wt%) and 3.5 mL of H₂O were added and the resulted mixture became gradually coagulated.

After ageing at 60 °C for 12 h, the mixture was then dried in vacuum at 100 °C for 3 h.

General procedure for deoxygenation reaction: For each reaction, oxime (0.2 g), silica gel confined functional ionic liquids or pure functional ionic liquid catalysts (0.01 g), acetone (2 mL) and water (6 mL) were successively added into a 25 mL round bottom, and then the reaction proceeded at room temperature with vigorous stirring for 2–72 h. Qualitative analyses were conducted with a HP 6890/5793 GC–MS with a 30 m×0.25 mm×0.33 μm capillary column and with chemstation containing a NIST Mass Spectral Database. Quantitative analyses were conducted with a HP 1790 GC equipped with a FID detector, 30 m×0.25 mm×0.33 μm capillary column. Conversion and selectivity were calculated according to the chromatograph peak areas given by the chemstation. After reaction, the catalyst was obtained by filtration, washed with acetone twice and then reused for the second time.

As to the isolated yields of corresponding aldehydes, only deoxygenation of *p*-methoxyl benzaldoxime and *p*-nitro benzaldoxime were conducted due to the great difference between the boiling point of acetone oxime and corresponding aldehydes. The separation was conducted as follows: after reaction, the resulted liquid mixture containing solid catalyst was filtrated to separate the catalyst, and a solution of acetone, water, acetone oxime, and desired aldehyde was left. Then this solution was distilled at 120 °C with ca. 1–5 mmHg vacuum to remove acetone, water, and acetone oxime. The desired product, that is aldehyde, was given and weighted to obtain the isolated yield.

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