Application of an immobilized ionic liquid for the preparation of hydroxylamine via hydrolysis of cyclohexanone oxime

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Preparation of hydroxylamine via hydrolysis of cyclohexanone oxime was studied over porous SiO₂ supported acid ionic liquid catalyst. The catalyst [SPIPTES]CF₃SO₃@SiO₂ was prepared through sol-gel method and characterized by elemental analysis, IR and TG, etc. Various parameters such as reaction temperature and time, catalyst amount were investigated systematically. The optimized reaction conditions investigated were catalyst:cyclohexanone oxime (mass ratio) 4:1, conducted at 60°C for 1 h. Since the present hydrolysis reaction is

Introduction

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Hydroxylamine (NH₂OH) is an important intermediate for the production of ε -caprolactam. It has aroused extensive attention in virtue of their applications such as pharmaceutical,^[1] pesticide,^[2] rubber,^[3] dye,^[4] military^[5] and nuclear industries.^[6] Nowadays much effort has been devoted to preparing NH₂OH. The common way is neutralization method. Inorganic base reacts with hydroxylamine salt to make hydroxylamine.^[7] Another approach is an alcohol reaction. This process needs alkali metal oxide reacting with alcohol to form an alkoxide, and then the alkoxide reacting with the hydroxylamine salt to give hydroxylamine.^[8] However, these methods suffer from some drawbacks like complicated reaction process, the corrosive material handling, producing by-products and using inorganic bases. Recently, Mantegazza^[9] used ammonia, hydrogen peroxide as raw materials to synthesize NH₂OH directly over titanium silicalite catalyst. However, the amount of ammonia employed in this process is much larger than that of hydrogen peroxide, and the yield of hydroxylamine is too low (< 1%) to apply to industry.

In addition, hydroxylamine can also be produced from hydrolysis of oximes (cyclohexanone oxime, 2-butanone oxime, etc).^[10] Actually, synthesis of oximes is conducted using

[a] S. Wang, J. Liu, P. Cheng, Z. Li, Prof. D. Zhang, Prof. Q. Yang, Prof. X. Zhao, Prof. Y. Wang Hebei Provincial Key Lab of Green Chemical Technology and High Efficient Energy Saving Hebei Province Technology Institute of Green Chemical Industry School of Chemical Engineering and Technology Hebei University of Technology Tianjin (China), 300130 E-mail: zds1301@hebut.edu.cn yqiusheng@hebut.edu.cn controlled by thermodynamics, the conversion of cyclohexanone oxime could not be very high. However, reasonable result was achieved under the optimized reaction conditions. Cyclohexanone oxime conversion was 38.41% and NH₂OH yield was 37.65%. Additionally, combining experiments with density functional theory calculations, a possible catalyst structure and reaction pathway involved protonated cyclohexanone oxime mechanism was proposed for the present hydrolysis in this study.

hydroxylamine salt and ketones as raw materials in the industrial process. Thus, it was taken for granted that the reverse reaction as hydrolysis of oximes to form hydroxylamine is not practicable. Fortunately, with the development of titanium silicalite catalyst and its application to direct synthesis of oximes from ketones,^[11] the oximes can be produced easily without using hydroxylamine salt. From this point of view, the process of synthesizing NH₂OH from the hydrolysis of oximes (Reaction (1)) is proposed to overcome above-mentioned drawbacks.^[12]

$$\begin{array}{c} \text{NOH} & \text{O} \\ H^+ \\ H_2 \text{O} \end{array} + \text{NH}_2 \text{OH} \end{array}$$
 (1)

Up till now, there are several types of catalysts approaching for the hydrolysis reaction. Firstly, inorganic acids like sulfuric acid and hydrochloric acid are used as catalyst, although the hydrolysis reaction rate of oximes in the acidic solution is very high, the conversion of oximeis still unsatisfied. Thus the reaction tended to be controlled by thermodynamics rather than dynamics.^[10] However, the process suffers from some drawbacks, such as corrosion of the equipment and discharge pollution. Second route involves a subcritical water catalytic system carried out under severe reaction condition.^[13] And the third approach involves a new catalytic system to hydrolysis of cyclohexanone oxime, which includes a liquid mixture of ionic liquids (ILs) 1-butyl-3-methylimidazole and CuCl₂, FeCl₃ or other metal chlorides.^[14] The homogeneous ionic liquid catalytic system overcomes the above-mentioned difficulties such as corrosion and severe condition. But it has several drawbacks in terms of separation and recycling of ILs.^[15]

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> In recent years, acid ILs have drawn considerable attentions as an environmentally benign catalyst owing to their unique characteristics such as low melting point, negligible volatility, high solubility, high thermal stability and tunable acidity.^[16] However, several drawbacks of the traditional ionic liquids including difficulty of product separation and catalyst recovery, largely restricted their widespread practical applications.^[17] For these reasons, many works have been focused on supported ILs over different materials, such as silica,^[18] polymers,^[19] and magnetic materials.^[20] The produced mesoporous silica using TEOS as silica source possessed the excellent characteristics such as stable mesoporous structure, high surface area, controllable pore size and a large amount of silanol group. These advantageous characteristics made mesoporous silica an attractive solid support in the field of catalysis and functional materials.^[21] These excellent characteristics made the mesoporous silica an attractive solid support for the preparation of ionic liquid catalyst. Hassan^[22] immobilized loaded trifluoromethylsulfonyl ionic liquids onto silicon dioxide by physical impregnation to prepare the supported catalyst, which was used for the adsorption of lead ions and obtained good results (\geq 99%). Seyed^[23] reported that methyl imidazole chloride ionic liquid was loaded onto SiO₂ by chemical bond method, being as catalyst for dehydrogenation of formic acid. Robabeh^[24] studied that SiO₂-supported N-methylimidazolium chloride ILs was used for oxidation of olefins into their corresponding epoxides. Wang^[25] pointed out that 1-methyl-3-(triethoxylsililyl propyl) imidazole chloride was directly fixed in silica gel by covalent bond for removing sulfur compounds from fuel. Han^[26] successfully synthesized sulfonated ionic liquid supported by silica gel, which showed excellent activity in synthesis of glycerol monolaurate. However, there were few studies about the preparation of immobilized Brønsted acidi ILs catalyst using TEOS as silica source, and its application for hydrolysis of cyclohexanone-oxime.

> Therefore, the objective of this study was to investigate the possibility of using supported acid ionic liquids as catalyst in the hydrolysis reaction of cyclohexanone oxime. Various parameters including different catalyst, catalyst amount, reaction temperature and time, were investigated for optimization of the hydrolysis process. In the course of this investigation, we achieved a novel route for synthesis of NH₂OH from cyclo-

hexanone oxime over porous ${\rm SiO}_2$ supported acid ionic liquid catalyst.

Results and Discussion

Reaction optimization

Effect of different supported ILs catalysts

Since the hydrolysis of cyclohexanone oxime to NH₂OH is controlled by thermodynamics,^[10] and the conversion of cyclohexanone oxime could not be very high. The activity of different supported ILs catalysts prepared by impregnation or sol-gel method is listed in Table 1. From which it can be found that, the main products are cyclohexanone and hydroxylamine. All the supported ILs catalysts have some activity toward the hydrolysis. The supported ionic liquid 1-butylsulfonate-3-methvlimidazolium trifluoromethanesulfonate catalyst gives 18.67% cyclohexanone oxime conversion (X_{Cyo-O}) with 11.19% hydroxylamine yield (Y_{NH2OH}). While for [SPIPTES]CF₃SO₃/SiO₂ catalyst, the conversion of cyclohexanone oxime increases to 37.13% (the NH₂OH yield is 36.69%). So the [SPIPTES]CF₃SO₃/SiO₂ catalyst seem to be a better choice for the reaction. However, when the [SPIPTES]CF₃SO₃/SiO₂ was recycled and used for the second time, the cyclohexanone oxime conversion was decreased to 24.49%. A similar trend was found over the other supported ILs catalysts prepared by the impregnation method. The catalytic activity is greatly decreased, and almost half of the activity is lost on these recycled catalysts (No. 1~6). The reusability of the prepared catalyst is not satisfactory and the activity loss of the catalyst is great.

As for [SPIPTES]CF₃SO₃@SiO₂-5 catalyst (No. 8), it was prepared by sol-gel method. The cyclohexanone oxime conversion is 38.41% on fresh catalyst. For the recycled catalyst, the conversion is still relatively high (35.52%). It means that ionic liquids grafted by chemical bonding (proved by IR, BET and SEM in supporting information) have better stability than that of catalysts prepared by impregnation. For this reason, the [SPIPTES]CF₃SO₃@SiO₂ catalyst was selected for further optimization.

No.	Catalyst sample	Fresh catalyst		Recycled catalyst	
		X_{Cyo-O} (%)	Υ _{NH2OH} (%)	Х _{суо-О} (%)	Y _{NH2OH} (%)
1	1-butylsulfonate-3-methylimidazolium trifluoromethanesulfonate/SiO ₂	18.67	11.19	14.52	10.34
2	N-butylsulfonate pyridinium tosylate/SiO ₂	23.39	12.99	15.91	10.61
3	N-propylsulfonate pyridinium hydrogensulfate/SiO ₂	26.89	17.28	16.19	13.83
4	1-propylsulfonic-3-methylimidazolium trifluoroacetate/SiO ₂	27.59	19.88	17.56	15.04
5	1-butyl-3-methyl-imidazolium-tosylate/SiO ₂	34.39	28.71	20.63	18.75
6	1-propylsulfonate-3-methylimidazolium trifluoromethanesulfonae/SiO ₂	34.87	29.32	20.86	19.34
7	[SPIPTES]CF ₃ SO ₃ /SiO ₂	37.13	36.69	24.49	23.34
8	[SPIPTES]CF ₃ SO ₃ @SiO ₂ -5	38.41	37.65	35.52	34.86

Effect of different sol-gel conditions for [SPIPTES] CF₃SO₃@SiO₂

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A series of [SPIPTES]CF₃SO₃@SiO₂ catalysts were prepared using different sol-gel process. The activity of the fresh and recycled catalysts was measured. The results are shown in Table 2. The addition of H₂O and sol-gel time has important impacts on the activity of [SPIPTES]CF₃SO₃@SiO₂ catalysts. With the addition of H₂O from 15 mL to 45 mL, cyclohexanone oxime conversion increases from 31.32% to 36.37% over the fresh catalysts. When the catalysts were used for second time, the conversion decreased obviously (see Table 2). As the addition amount of H₂O increases to 55 mL, the conversion of cyclohexanone oxime decreases slightly to 36.01%. The reason may be that with the increase of water added, the solution mixture is gradually uniform and the dispersion of each material becomes better, which is conducive to the grafting of ionic liquid. However, excessive water will reduce the concentration of each substance, leading to the relative dilution of system concentration and the decrease of solution viscosity, which makes it difficult to form glue.

The effect of sol-gel time on catalyst activity was also examined. With the increase of sol-gel time from 1 h to 4 h, the activity loss (Δ) over these catalysts decreases gradually from 3.32% to 2.62%. With further increasing of sol-gel time to 6 h, the activity loss increases to 3.62%. Thus 4 h was a better choice for the present sol-gel process.

Moreover, the loss of catalyst activity was also increased from 2.62% to 4.06% with the decreasing of prehydrolysis time from 7 h to 2 h. It maybe that the uniform mixing of reaction liquid need more time, which is favorable for the bonding between ionic liquid and silica. A suitable sol-gel time is 7 h.

In addition, when [SPIPTES]CF₃SO₃@SiO₂-16 catalyst was prepared without adding templating agent (PEO-PPO-PEO). It gives only 25.31% cyclohexanone oxime conversion. For the

other catalysts with using templating agent, the activity was improved greatly. It indicates that adding templating agent is beneficial to improve the activity of the catalyst. PEO-PPO-PEO addition amount also can affect the catalytic activity. With the increasing of template agent from 1 g to 4.95 g ([SPIPTES] CF₃SO₃@SiO₂-6), the loss of catalytic activity decreases from 5.32% to 2.62%, when PEO-PPO-PEO amount increased to 6 g, catalytic activity loss increases slightly. It means that the addition of template agent is needed to reach a certain amount. Otherwise, it would hinder the grafting process^[27] as well as its catalytic activity. Based on these results, the [SPIPTES] CF₃SO₃@SiO₂-6 catalyst was taken as a preferred catalyst and used for further optimization.

Effect of reaction temperature

The effect of reaction temperature was explored. The results are shown in Figure 1. It can be seen that the conversion of cyclohexanone oxime (X_{Cyo-O}), as well as the yield of NH₂OH (Y_{NH2OH}), increases as the reaction temperature is raised from 40 °C to 60 °C. Since the hydrolysis reaction of cyclohexanone oxime is an endothermic reaction, the increase in temperature favors the hydrolysis process.^[10] However when the temperature exceed 60 °C, the conversion tends to be flat (38.26 % ~ 39.08 %). Meanwhile, the NH₂OH product would be decomposed at high temperature. Hence 60 °C was chosen as a suitable reaction temperature.

Table 2. Effect of different preparation conditions on the hydrolysis reaction.							
Catalyst	H ₂ O (mL)	Sol-gel time (h)	Prehydrolysis time (h)	Template agent (g) ^a	X _{Cvo-O} (%)		
	-	-			1st ^b	2nd ^c	Δ^{d}
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -1	15	1	7	4.95	31.32	26.85	-4.47
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -2	25	1	7	4.95	33.27	28.02	-5.25
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -3	45	1	7	4.95	36.37	31.94	-4.43
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -4	55	1	7	4.95	36.01	30.73	-5.28
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -5	45	1	7	4.95	33.61	30.29	-3.32
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -6	45	4	7	4.95	38.41	35.79	-2.62
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -7	45	6	7	4.95	37.88	34.26	-3.62
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -8	45	4	5	4.95	35.21	32.23	-2.98
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -9	45	4	3	4.95	34.68	30.86	-3.82
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -10	45	4	2	4.95	34.31	30.25	-4.06
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -11	45	4	7	6	33.25	29.85	-3.40
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -12	45	4	7	4	32.56	28.01	-4.55
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -13	45	4	7	3	31.24	26.98	-4.26
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -14	45	4	7	2	30.55	26.92	-4.63
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -15	45	4	7	1	29.34	24.02	-5.32
[SPIPTES]CF ₃ SO ₃ @SiO ₂ -16	45	4	7	0	25.31	19.63	-5.68

^a Template agent is polyethylene oxide-polypropylene oxide-polyethylene oxide (PEO-PPO-PEO). ^b 1st is the conversion of cyclohexanone oxime over the fresh catalyst. ^c 2nd is the conversion of cyclohexanone oxime over the recycled catalyst. ^d the activity loss ($\Delta =$ 2nd-1st)



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Figure 1. Effect of temperature on the hydrolysis of cyclohexanoneoxime.

Reaction conditions: cyclohexanone oxime = 0.5 g, catalyst: cyclohexanone oxime = 4, $H_2O = 30$ mL, 1 h

Effect of reaction time

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The influence of reaction time was also studied. The results are shown in Figure 2. It can be found that the overall trend of X_{Cyo-O} and Y_{NH2OH} is increasing gradually with the time prolonging. When the initial reaction time is 0.5 h, cyclohexanone oxime conversion is low(20.88%). After that, the conversion generally increases to 37.68% at 1 h and then remains steady as the time increasing from 1 h to 2.5 h. These results show that the hydrolysis reaction rate is relatively fast and the reversible reaction rapidly reached balance during the reaction period. Although the present reaction rate is relatively high, cyclohexanone oxime conversion is still not satisfactory. Thus the reaction tended to be controlled by thermodynamics rather than dynamics.^[10] Therefore, one hour is enough for the hydrolysis.



Figure 2. Effect of time on the hydrolysis of cyclohexanone-oxime.

Reaction conditions:cyclohexanone oxime = 0.5 g, catalyst: cyclohexanone oxime = 4, H_2O = 30 mL, 60 °C

Effect of catalyst/cyclohexanone oxime ratio

The influence of catalyst ([SPIPTES]CF₃SO₃@SiO₂-6)/cyclohexanone oxime mass ratio was investigated. The results are shown in Figure 3. It showed that the ratio has a significant effect on the hydrolysis. Increasing catalyst:cyclohexanone oxime mass ratio (1:1-4:1) would gradually increase the conversion of cyclohexanone oxime from 13.6% to 37.36%. An increase of catalyst amount leads to acidic sites increase, which is beneficial to the reaction. However, when the ratio is increased from 4:1 to 5:1, the conversion tends to be gentle. And further increasing the ratio does not meet economic requirements. Therefore, a suitable mass ratio of catalyst:cyclohexanone oxime is 4:1.

Reaction conditions:(c) cyclohexanone oxime = 0.5 g, $H_2O = 30$ mL, 60 °C, 1 h

Reproducibility test of catalyst

After completion of the hydrolysis reaction, the catalyst was filtered and washed several times with ethanol, and then dried in vacuum for further use. In the next round of reaction, the recycled catalyst and new reactant were added to carry out the reaction. Catalyst activity was evaluated by comparing X_{Cyo-O} and Y_{NH2OH} . The results are showed in Figure 4. It was found that the conversion of cyclohexanone oxime and the yield of NH₂OH decrease gradually after using five times. The decrease of the catalyst activity may be due to the loss of ionic liquid during the recovery process. The chemical composition of fresh and reused [SPIPTES]CF₃SO₃@SiO₂-6 catalysts (after five times) was characterized by elemental analysis. As shown in Table 3, the S element is 1.74%. So the fresh ionic liquid has a loading of 14.79% (based on the data of S element). After five cycles, the catalyst loading is 11.43%. According to the results of elemental



Figure 3. Effect of catalyst/cyclohexanone oxime ratio on the hydrolysis of cyclohexanone-oxime.



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Figure 4. Catalytic performance of re-used [SPIPTES]CF₃SO₃@SiO₂-6

Table 3. Elemental analysis of [SPIPTES]CF3SO3@SiO2-6 catalyst.									
Catalyst	Elemen N%	t C%	H%	S%					
Fresh [SPIPTES]CF ₃ SO ₃ @SiO ₂ 5th [SPIPTES]CF ₃ SO ₃ @SiO ₂	0.87 0.86	5.84 5.10	0.84 0.78	1.74 1.46					

analysis, it seems a little release of [SPIPTES]CF $_3$ SO $_3$. The release amount of ionic liquid is about 3.36%. This is one of the reasons for the decrease of catalytic activity.

In addition, the acidic ionic liquid may combine with a small amount of alkaline hydroxylamine (considering that hydroxylamine is usually existed in the form of inorganic acidic hydroxylamine salts) during the reaction process. Thus degradated the catalytic activity. To further investigate that the decrease in catalytic activity of the recovered catalyst is due to the chemical action between the acidic center and hydroxylamine, acid-base titration was used to determine the acid amount between fresh and recovered catalyst. The results showed that acid content of the fresh catalyst was 0.78 mmol/g. While the recovered one decreased to 0.12 mmol/g. It is verified that the deactivation of the recovered catalyst is due to the decrease of the amount of effective acid in the catalyst.

Reaction conditions: Cyclohexanone oxime = 0.5 g, catalyst amount = 2 g, H_2O = 30 mL, temperature = 60 °C, time = 1 h

Preliminary study on the structure of supported [SPIPTES] $CF_3SO_3@SiO_2-6$ catalyst

The catalyst [SPIPTES]CF₃SO₃@SiO₂ was characterized by BET, IR and TG, etc (see supporting information). The results showed that ionic liquid has been immobilized on silica-gel by chemical covalent bond.

To further clarify the structure for [SPIPTES]CF $_3$ SO $_3$ @SiO $_2$ -6, quantitative calculation methods were used as follows.

Structure analysis for the [SPIPTES]CF₃SO₃@SiO₂-6 by computational method

A model of amorphous silica containing 4 tetrahedral silicon atoms (T4) was obtained from the crystal structure of the zeolite H-MOR, with all silicon atoms terminated in oxygen. To create the dual-site model containing the grafted ILs adjacent to a silanol group, two terminal Si–O fragments are substituted for Si-OH and Si-IL respectively.

Density functional theory (DFT) calculations were performed using a M062X hybrid function with the Gaussian 09 program package. This M062X method with dispersion correction is preferred to be a general purpose for describing nonbonded interactions.^[28] It has been verified to be appropriate for silica cluster and ionic liquids system in a number of previous studies.^[29] Molclus program was used to study the possible structure of cations by conformation search, and then the most stable five structures were chosen. With placing anions on different positions around cations, the structure for [SPIPTES] CF₃SO₃@SiO₂-6 with the lowest energy can be obtained by optimizing at the level of 6-31+g(d,p) in the gas phase.^[30] Frequency analyses were conducted with the same basis set to confirm that the optimized structures were ground states without imaginary frequency. In addition, geometry parameters and electrostatic potentials were determined, and Natural bond orbital (NBO) analysis was performed for the optimized structures of the grafted ionic liquids.

Structure analysis for the [SPIPTES]CF₃SO₃@SiO₂-6 by DFT calculations

Density functional theory calculations were further carried out to verify the structure. The typical five structures and the distance between each atom are depicted in Figure 5 and Figure 6. The cation part grafted on the surface of silicon cluster has three active hydrogens, such as H25, H26 and H27. There are strong interactions between the active hydrogen and oxygen involved trifluoroalfonic acid and sulfonic acid group. The two structures (a and b in Figure 6) both have lower energy than the latter three structures (c, d, e in Figure 6) by more than 3 kcal/mol. The structure a is the most stable structure of the five, and which energy is only 0.22 kcal/mol lower than that of structure b.

We further studied the optimal structure a and b on the structural parameters, NBO charge and stabilization energy of E(2). According to the van der Waals radius of the H and O atoms, the shorter the distance between 2.7 Å and 1.0 Å (between hydrogen to the oxygen atom), the stronger the H bond. In structures a, there are two strong H bonds in the structure: O51... H26-O13, O52...H17-O27, the bond length is 1.4470 Å, 1.8008 Å, corresponding to 82.86 kcal/mol and 19.36 kcal/mol respectively for the stabilization energy of E(2), the former E(2) maybe comes mainly from the electrostatic interactions. Secondly, there are also three moderate H bonds between O50, O17 and neighbouring H with the distance of 2.1-2.3 Å, resulting in the total E(2) of more than 19.00 kcal/mol.





Figure 5. Optimized geometry (distance unit: Å, blue) of the [SPIPTES]CF₃SO₃@SiO₂.



Figure 6. Optimized geometry (distance unit: Å, blue) of the [SPIPTES]CF₃SO₃@SiO₂.



Figure 7. Catalyst preparation process of [SPIPTES]CF₃SO₃@SiO₂

Thirdly, weak H bonds come into being around O14 within the cation moiety. Apparently, two strong and two moderate H bonds take place between CF_3SO_3 and the cation moiety. These E(2) originate from the lone pair electron orbital of the O atom, and which provides electrons to the neighboring antibonding orbital. In summary, the stability of structure a emerges from the strong interaction between the CF_3SO_3 and the cation moiety.

In structures b, two strong and two moderate H bonds appear, but the strongest H bond occurs in the cation itself, i.e. The distance is 1.4813 Å of O13-H26...O17 along with the E(2) of 64.02 kcal/mol. Additional weak H bonds grow near O50, O51, O52. Compared with the structure a, the structure b arises from the stability of the cation moiety. Form the analysis of NBO charge, the overall NBO charge transferred from the cation moiety to CF_3SO_3 is 0.188e for the structure a, while the NBO charge is 0.120e in the structure b, thus indicating stronger interaction between two parts for the structure a than the structure b.

To sum up, two typical structures (structure a and b) both exist on the surface of silica cluster. The NBO charge of H25, H26 and H27 on the grafted ionic liquid cations is hold from 0.30 to 0.58, especially more than 0.55 of NBO charge of the latter two. And thus the acidity is $H25 < H26 \approx H27$. H26 and H27 with strong acidity play an important role, while H25 with weak acidity plays a synergistic role during the catalytic reaction.

The Gibbs free energy value in the parenthesis is the gap to the structure **a** (unit: kcal/mol)

Additionally, combining the DFT calculations with experiment results, a possible reaction pathway involved protonated cyclohexanone oxime mechanism for the present hydrolysis was proposed as shown in supporting information.



Conclusion

In this work, preparation of NH₂OH via hydrolysis of cyclohexanone oxime was studied over porous SiO₂ supported acid ionic liquid catalyst. The catalyst [SPIPTES]CF₃SO₃@SiO₂ was prepared through sol-gel method and characterized by BET, IR and TG, etc (shown in supporting information). Various parameters such as reaction temperature and time, catalyst amount were investigated systematically.

Preliminary study on the structure of supported ILs was studies by quantitative computation, and a reaction mechanism was also proposed. The optimized reaction conditions investigated were catalyst:cyclohexanone oxime (mass ratio) 4:1, conducted at 60 °C for 1 h. Since the present hydrolysis is controlled by thermodynamics, cyclohexanone oxime conversion was 38.41% and NH₂OH yield was 37.85% under the optimizedreaction conditions. The catalyst [SPIPTES] CF₃SO₃@SiO₂ still has acceptable results after using five times.

Additionally, combining experiments with density functional theory(DFT) calculations, a possible catalyst structure and reaction pathway involved protonated cyclohexanone oxime mechanism for the present hydrolysis was proposed in this study (shown in supporting information). Thus, the immobilized ionic liquid catalyst [SPIPTES]CF₃SO₃@SiO₂ prepared in this study was proved to be a high efficient heterogeneous catalyst for the hydrolysis of cyclohexanone.

Experimental Section

Materials and reagents

Cyclohexanoneoxime (\geq 99.0%), imidazole (\geq 99.0%), 1,3-propanesultone (\geq 99.0%), trifluoromethanesulfonic acid (\geq 99.0%), anhydrous ethanol (\geq 99.7%), tetraethyl orthosilicate (\geq 99.0%) and 3chloropropyltriethoxysilane were supplied by Aladdin Company of Shanghai, China. Toluene (>99.0%) and hydrochloric acid (36 wt%) were obtained by Haotian Company of Tianjin, China. Ionic liquids 1-butylsulfonate-3-methylimidazolium trifluoromethanesulfonate $(\geq 99.0\%)$,N-propylsulfonate pyridinium hydrogensulfate $(\geq 99.0\%)$, N-propylsulfonate (≥99.0%),1-propylsulfonic-3-Methylimidazoliumtrifluoroacetate (>99.0%),1-butyl-3-methyl-imidazolium-tosylate (299.0%),1-propylsulfonate-3-methylimidazolium trifluoromethanesulfonate (>99.0%), were supplied by Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China. All other chemicals were of commercial reagent grade and were used without further purification.

Catalyst preparation

Method I: catalysts (ILs/SiO₂) were prepared by impregnation method

Typically, 2 g of carrier SiO_2 was weighed, and then 0.5 g of ILs was accurately weighed and dissolved in ultra-pure water (9 mL) to prepare the impregnation solution. Then the prepared impregnating solution was slowly and evenly dripped onto the carrier silica. After being impregnated for 36 h at room temperature, it was put into a vacuum drying chamber and dried at 80 °C to obtain the

supported ILs catalyst (ILs/SiO₂). Several ILs/SiO₂ catalysts were prepared by impregnation method as shown in Table 1.

Method II: several [SPIPTES]CF₃SO₃@SiO₂ catalysts were prepared by sol-gel method

A series of supported ILs catalysts [SPIPTES]CF₃SO₃@SiO₂ were prepared by sol-gel method, giving rise to porous silica materials^[31] and ionic liquid gel-type silica where ILs is confined within the silica particle.

Firstly, The appropriate amount of imidazole, 0.1 mol of 3chloropropyltriethoxysilane and 10 mL of anhydrous toluene were added into a 100 mL three-necked flask. Then the reaction mixture was reacted under nitrogen atmosphere and toluene reflux for 24 h. After that, the mixture was distilled under reduced press to obtain 3-(1-imidazolium) propyl triethoxysilane (IPTES).

Secondly, the obtained IPTES, 10 mL of anhydrous toluene and 0.1 mol of 1,3-propanesultone were added to a 100 mL threenecked flask, the mixture was reacted under nitrogen atmosphere and toluene reflux for 24 h as well, which can obtain 3-(3-sulfonic acid propyl-1-imidazole) propyl triethoxysilane (SPIPTES).

Thirdly, equimolar CF_3SO_3H was added dropwise to the prepared SPIPTES. After that, the mixture was reacted at 80 °C to obtain ionic liquid [SPIPTES] CF_3SO_{3} , which was washed three times by Diethyl ether.

Finally, [SPIPTES]CF₃SO₃ was added in a 100 mL three-necked flask of ethanol solution of tetraethyl orthosilicate (TEOS:EtOH = 1: 0.7), which to cause hydrolysis and condensation reaction, and then hydrochloric acid was added to form a gel, which was aged at 60 °C for 12 h and dried at 100 °C for 2.5 h to obtain a porous SiO₂ supported ILs catalyst (denoted as [SPIPTES]CF₃SO₃@SiO₂).

Catalytic activity measurements

The hydrolysis reaction was carried out in a 100 mL three-necked flask. Typically, 0.5 g of cyclohexanone oxime, 2 g of [SPIPTES] CF₃SO₃@SiO₂ catalyst and 30 mL of deionized water were loaded into the flask. Then the mixture was stirred for about 1 h at 60 °C. After completion of the reaction, extraction with toluene was conducted at the reaction temperature. Then the solid ILs catalyst was separated from the reaction solution by centrifugal separation, cyclohexanone and unreacted cyclohexanone oxime were obtained from the organic phase, and hydroxylamine was obtained from the aqueous phase. The separated ILs catalyst was washed three times with ethanol, and then dried in vacuum (-0.1 MPa, 80 °C) for further use.

The organic phase was identified by comparison of their retention time with those of authentic samples, and by a Thermo Trace DSQ gas chromatography-mass spectrometry. The concentrations of organic components were analyzed by a 7890B gas chromatography. A capillary column of DB-WAX was used for most analyses. Figure 8 shows a typical gas chromatogram. From which it can be found that besides the organic product cyclohexanone, no other byproduct was observed. Cyclohexanone oxime conversion (X_{Cyo-0}) was calculated by the following (Equation (1)). The hydroxylamine in the aqueous phase was analyzed by oxidation-reduction titration with potassium permanganate,^[30] and the yield of hydroxylamine (Y_{NH2OH}) was calculated by (Equation (2)).





Figure 8. Gas chromatography of reaction product for the hydrolysis of cyclohexanone oxime: 1.Toluene; 2. Cyclohexanone; 3. Cyclohexanone oxime.

$$XCyo - O = \left[1 - \frac{\frac{WCyo - O}{MCyo - O}}{\sum \frac{WI}{MI}}\right] \cdot 100\%$$
(1)

$$YNH2OH = \frac{(V1 - V2) \cdot 10^{-3} \cdot C1 \cdot \frac{5}{2}}{nCyo - O} \cdot 100\%$$
(2)

Where:

V₁ is the amount of potassium permanganate standard solution,

 V_2 is the amount of potassium permanganate standard solution in the blank test,

 C_1 is the concentration of potassium permanganate standard solution,

Wi is the weight percentage of i component in the products,

Mi is the molar mass of i component,

 $W_{\text{Cyo}-\text{O}}$ is the weight percentage of cyclohexanone oxime component,

 n_{Cyo-O} is the molar of cyclohexanone oxime component,

M_{Cyo-O} is the molar mass of cyclohexanone oxime component.

Catalyst characterization

Elemental analysis was performed on the Virio EL C/H/N elemental analyzer produced by elementar element analysis system, Germany. The sample was 0.02800 mg, the decomposition temperature was $950 \sim 1200 \,^{\circ}$ C, and $2 \sim 3 \,\text{L}$ He was consumed for each analysis. Determination range: C (0.0330 mg abs), H (0.033 mg abs), N (0.0310 mg abs).

The surface area, pore volume and pore diameter of ILs catalysts were measured by nitrogen adsorption-desorption at -196 °C using a Micromeritics ASAP 2020 instrument. The pore volume and pore diameter were estimated from the desorption branch of the N₂ is other by using the Barrett-Joyner-Halenda (BJH) method, and the surface area was calculated by Brunauer-Emmett-Teller (BET) method.

Infrared (IR) spectra of the samples were recorded with a Nicolet Nexus 470 FT-IR spectrometer using the potassium bromide pellet technique.

The TA2000 differential thermal analyzer of DuPont was used for thermogravimetric (TG) analysis of the samples, and the temperature rose from room temperature to 800 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

Additionally, structure analysis for the [SPIPTES]CF₃SO₃@SiO₂ by density functional theory (DFT) of quantitative computation calculations were performed, using M062X hybrid function with the Gaussian 09 program package.

Acknowledgements

This work supported by the National Natural Science Foundation of China (21878069, 21646015) and Natural Science Foundation of Hebei Province (B2016202335).

Keywords: Acidity · Density functional calculations · Heterogeneous catalysis · Hydrolysis · Ionic liquids · Supported catalysts

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Manuscript received: October 8, 2020 Revised manuscript received: January 11, 2021 Accepted manuscript online: January 12, 2021