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Article

One-pot conversion of cyclohexanol to ϵ -caprolactam using a multifunctional Na_2WO_4 -acidic ionic liquid catalytic system

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ABSTRACT

Na_2WO_4 -acidic ionic liquid was used as a simple, ecofriendly, recyclable and efficient catalytic system for the one-pot conversion of cyclohexanol to ϵ -caprolactam. The effect of the structure of the ionic liquid on the catalytic activity of this system was investigated, and the results revealed that sulfonic acid-functionalized ionic liquids with HSO_4^- as an anion gave the best results. The highly efficient performance of this catalyst system was attributed to the phase-transfer behavior of the cation of the ionic liquid, the improved coordination of the substrate to bisperoxotungstate during the oxidation reaction, and the stabilization of the intermediate formed during the Beckmann rearrangement.

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1. Introduction

ϵ -Caprolactam (CL) is an important precursor of nylon-6 and several other plastics, and the global market for this material reached 5 million metric tons per annum in 2015 [1]. CL is currently manufactured from cyclohexanone, which is converted to cyclohexanone oxime (CHO) before undergoing a rearrangement process to give CL via a three step process. The yield for the Beckmann rearrangement of CHO to CL is high when fuming sulfuric acid is used as catalyst and solvent. However, there are several disadvantages associated with this process, including (1) the formation of a large amount of ammonium sulfate, which is generated as a by-product during the neutralization of the hazardous sulfuric acid waste with ammonia, (2) the corrosion of the reactors because of the strongly acidic conditions, and (3) the environmental pollution caused by the use of fuming sulfuric acid. Although cyclohexanone can

be obtained by the hydrogenation of phenol [2], the preferred route for the industrial manufacture of this material involves the direct oxidation of cyclohexane. However, the aerobic oxidation of cyclohexane to cyclohexanone has limited the overall efficiency of this three-step process because of the low yields achieved with each pass, which are usually in the range of 3%–8% with a selectivity of around 80% for cyclohexanone over cyclohexanol [3]. Based on the increasing demand for environmentally friendly processes, the development of an ecofriendly and economically viable procedure for the one-pot synthesis of CL is highly desirable. Several groups have investigated the direct synthesis of CL from cyclohexane using various strategies, including conducting the reaction in the presence of nitrosyl sulfuric acid [4–9] or using nitrocyclohexane as a substrate [10]. One group even investigated the possibility of using cyclohexanone in combination with ammoximation and Beckmann rearrangement reactions over Nb-MCM-41 catalysts

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[11], which resulted in a CL yield of about 10%. Ishii's group [12] reported the synthesis of CL from cyclohexane and *t*-butyl nitrite, using *N*-hydroxyphthalimide (NHPI) as a catalyst, which gave a CL yield of 43%. However, the conditions used in this reaction resulted in the decomposition of NHPI to give phthalic acid and several other related impurities, thereby limiting the utility of this approach. Raja et al. [13] developed a one-step process for the conversion of cyclohexanone to CL using bimetallic Mn(III)Mg(II)AlPO-5 as a bifunctional catalyst. The maximum conversion of cyclohexanone achieved under these conditions was 68.3%, with selectivity of 5.7% and 77.9% for CHO and CL, respectively. More recently, Shin et al. [14] reported a multifunctional Pd/Sc(OTf)₃/ionic liquid catalyst for the tandem one-pot conversion of phenol to CL in 67% yield using a large excess (300 mol%) of 1-butyl-methylimidazolium hexafluorophosphate ([bmim]PF₆) as an additive. Although this reaction gave a high phenol conversion and good selectivity for CL, it was difficult to separate the IL from the reaction mixture, thereby limiting the effectiveness of this approach.

We envisaged that it would be possible to overcome the issues described above by directly synthesizing CL from cyclohexanol, which is an unavoidable by-product of the oxidation of cyclohexane. Thus, the oxidation of cyclohexanol in the liquid phase using H₂O₂, followed by sequential oximation and Beckmann rearrangement reaction in a single pot would represent an attractive alternative for the synthesis of CL (Scheme 1). This route would be particularly interesting from an industrial perspective, because all three steps, including (1) the oxidation of cyclohexanol to cyclohexanone, (2) the oximation of cyclohexanone to CHO, and (3) the rearrangement of CHO to CL could be performed as a one-pot procedure in the presence of a multifunctional catalysts.

The “green” oxidation of alcohols using tungsten peroxide as an oxidant, which may be prepared by the reaction of H₂O₂ with a catalytic amount of sodium tungstate (Na₂WO₄), has attracted considerable attention [15]. However, it is only possible to obtain high yields of the alcohol products in this way under acidic conditions with a phase transfer catalyst [15,16]. We recently investigated the direct synthesis of ϵ -caprolactam from cyclohexanol using [*n*-C₁₆H₃₃N(CH₃)₃][H₂PW₁₂O₄₀] as a catalyst [17].

In this study, we synthesized nine Brønsted acidic ILs (Fig. 1) and investigated their use as catalysts for the one-pot synthesis of CL from cyclohexanol using H₂O₂ and hydroxylamine. In addition to CL, we also obtained several other valuable

Fig. 1. Structures of nine acidic ionic liquids.

products, including cyclohexanone and CHO. The results ultimately revealed that Na₂WO₄-sulfonic acid-functionalized ionic liquids could be used as catalyst for the synthesis of CL. Furthermore, the final products were readily separated from the catalyst system by a simple extraction.

2. Experimental

2.1. Preparation of ionic liquids

All of the chemicals used in the current study were purchased as the AR grade from The Tianjin Fu Chen Chemical Reagent Factory (Tianjin, China).

[Hnmp]HSO₄, [Hmin]HSO₄, [Tma]HSO₄, [Tea]HSO₄, [BSMin]HSO₄, [BSTea]HSO₄, [BSTma]HSO₄, [BSTma]H₂PO₄ and [BSTma]*p*-TA were prepared using previously reported procedures [18–24]. The resulting ILs were identified by ¹H NMR and IR analyses.

2.2. Catalytic testing

In a typical procedure, Na₂WO₄ (2.75 mmol) and an ionic liquid were mixed with cyclohexanol (50 mmol) in a 100-mL three-necked flask equipped with a reflux condenser, magnetic stirrer and a thermometer. The resulting mixture was then heated to the required temperature, and treated with 30% H₂O₂ (75 mmol), which was added in a dropwise manner to the reaction mixture with vigorous stirring over 5 h. Hydroxylamine sulfate (25 mmol) was then added to the flask with vigorous stirring over a certain period of time. Upon completion of the reaction, the mixture was allowed to settle to give two phases. The aqueous phase was collected and extracted with dichloromethane, and the extracted products were identified by gas chromatography-mass spectrometry using a Thermo Trace DSQ gas chromatograph-mass spectrometer (Thermo Electron, Massachusetts, America). The products were analyzed on an SP-3420A gas chromatograph equipped with a KB-Wax column (30 m × 0.32 mm × 0.25 μm).

The cyclohexanol conversion (*X*_{ANOL}), product selectivity (*S_i*) and carbon balance were calculated as follows:

$X_{ANOL} = (\text{Moles of cyclohexanol added} - \text{moles of unconverted cyclohexanol}) / \text{moles of cyclohexanol added} \times 100\%$

Scheme 1. One-pot conversion of cyclohexanol to CL.

S_i = Moles of product i / (moles of cyclohexanol added – moles of unconverted cyclohexanol) $\times$ 100%.

Carbon balance = (Moles of unconverted cyclohexanol + moles of carbon in cyclohexanone + moles of carbon in CHO + moles of carbon in CL) / moles of carbon in cyclohexanol $\times$ 100%.

3. Results and discussion

3.1. Effect of ionic liquid structure on selective oxidation of cyclohexanol to cyclohexanone

The direct synthesis of CL from cyclohexanol would require three steps. The first step would involve the selective oxidation of cyclohexanol to cyclohexanone. The product cyclohexanone would then react with hydroxylamine to form CHO, which would undergo a rearrangement reaction to give CL. To identify a suitable catalytic system for the oxidation of cyclohexanol to cyclohexanone using Na_2WO_4 , we screened a variety of different ionic liquids (Table 1). In the absence of the catalyst, the yield of cyclohexanone was only 1.08% (Table 1, entry 1). Among the four non-sulfonic acid-functionalized ILs tested in the current study (Table 1, entries 2–5), [Tma]HSO₄ showed the highest catalytic activity. The catalytic activities of ILs featuring alkanesulfonic acid groups (Table 1, entries 6–10) were much higher than those of the ILs without an alkanesulfonic acid group (Table 1, entries 2–4). In particular, [BSTma]HSO₄· Na_2WO_4 gave an excellent catalytic performance with a cyclohexanol conversion of 97.7% and a selectivity for cyclohexanone of 96.2%.

The oxidation reaction proceeded smoothly in an organic-aqueous biphasic system. In the aqueous phase, the catalyst precursor Na_2WO_4 was rapidly oxidized by H_2O_2 , as follows: $\text{Na}_2\text{WO}_4 + 2\text{H}_2\text{O}_2 = \text{Na}_2[\text{WO}(\text{O}_2)_2(\text{OH})_2] + 2\text{H}_2\text{O}$ [25]. According to Noyori's report [25], the resulting bisperoxotungstate compound **A** would exist in equilibrium with compounds **B** and **C** during the oxidation process (Fig. 2). Noyori et al. [25] also indicated that the dianion in **A** exhibited very little activity toward alcohols, whereas the mono- and di-protonated forms in **B** and **C** were sufficiently reactive. The bisperoxotungstate

Fig. 2. Bisperoxotungstate compounds involved in the oxidation process.

compound was readily transferred to the organic phase by a $\text{Na}^+ - \text{Q}^+$ ion exchange mechanism. The catalytic activity observed during the oxidation process would therefore be highly dependent on the acidity of the reaction medium, whereas the efficiency of the aqueous–organic phase transfer would be dependent on the active species aided by Q^+ (Q refers to the cation of the ILs) [25]. The high catalytic performance of sulfonic acid-functionalized ionic liquids can therefore be attributed to the improved hydrophobicity of their cation, whilst their improved acidity can be attributed to the introduction of alkanesulfonic acid groups. A similar effect was also observed for changes in the alkyl chain length during a study of the selective oxidation of cyclohexanol to cyclohexanone [26,27].

As shown in Table 1, the catalytic activities of [BSTma] H_2PO_4 and [BSTma] p -TA were poor. The acidity of an IL is dependent on the nature of its cations and anions. The acidities of ILs bearing the same cations are dependent on the difference in their anions. ILs featuring [H_2PO_4] $^-$ as a conjugate base are much less acidic than those featuring [HSO_4] $^-$ as a conjugate base, according to H_0 [27]. The catalytic activity of [BSTma] p -TA was poor, most likely because its p - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ anion cannot provide protons, resulting in the low acidity of the IL. Based on these results, we concluded that the hydrophobic cation, hydrophilic anion and acidity characteristics of the ILs were responsible for the oxidation of cyclohexanol [28].

3.2. One-pot conversion of cyclohexanone to CL

It seems almost contradictory to suggest that a strong acid and dehydrating media are required to ensure the protonation of the oxime intermediate during the rearrangement step, when water from the H_2O_2 could lead to the hydrolysis of the oxime or the formation of undesirable by-products under the strongly acidic conditions [29,30]. With this in mind, we investigated the effect of the molar ratio of cyclohexanone to [BSTma]HSO₄ on the outcome of the one-pot conversion of cyclohexanone to CL (Fig. 3). In the absence of [BSTma]HSO₄, the yields of CL and CHO were 62.7% and 26.8%, respectively. The yield of CL increased as the molar ratio of cyclohexanone to [BSTma]HSO₄ increased from 1:0.04 to 1:0.08. However, further increasing the molar ratio to 1:0.16 did not lead to any further changes in the yield of CL and the carbon balance gradually decreased, which was attributed to the formation of a high boiling condensation by-product. The one-pot conversion of cyclohexanone to CL most likely proceeds via the non-catalytic oximation of cyclohexanone to CHO, followed by the Beckmann rearrangement of CHO to CL. The mechanism for

Table 1

Effect of the structure of the ionic liquid on the oxidation of cyclohexanol.

Entry	Ionic liquid	X_{ANOL} (%)	Y_{ANON}^a (%)	Carbon balance (%)
1	None	1.08	1.06	99.5
2	[Hnmp]HSO ₄	92.2	91.2	98.7
3	[Hmin]HSO ₄	91.6	90.4	98.8
4	[Tma]HSO ₄	92.5	92.0	98.2
5	[Tea]HSO ₄	91.7	90.5	98.5
6	[BSMin]HSO ₄	96.2	95.2	98.3
7	[BSTea]HSO ₄	97.1	93.2	93.6
8	[BSTma]HSO ₄	97.7	96.2	98.1
9	[BSTma] H_2PO_4	26.8	26.3	99.0
10	[BSTma] p -TA	10.6	10.0	99.2

Reaction conditions: cyclohexanol: H_2O_2 : Na_2WO_4 : $2\text{H}_2\text{O}$:ionic liquid (molar ratio) = 1.00:1.50:0.06:0.04, 80 °C, oxidation time 5 h.

^aYield of cyclohexanone.

Fig. 3. Effect of the molar ratio of cyclohexanone to [BSTma]HSO₄ on the one-pot conversion of cyclohexanone to CL. Reaction conditions: cyclohexanone:H₂O:(NH₂OH)₂·H₂SO₄:Na₂WO₄·2H₂O (molar ratio) = 1.00:6.60:0.50:0.06, 80 °C, oximation and arrangement time 2.5 h.

the rearrangement of CHO involves the Brønsted acid-mediated protonation of the nitrogen atom of the oxime, followed by a proton transfer from the nitrogen atom to the oxygen atom of the oxime [31,32]. The formation of an O-protonated oxime in this way is a 1,2-H-shift reaction, and reactions of this type generally require a high activation energy. For this reason, this step is considered to be the rate-determining step in the Beckmann rearrangement.

According to previous reports from the literature, solvents with high dielectric constants such as benzonitrile, DMSO and MeCN can play an important role in lowering the activation energy of a Beckmann reaction by interacting directly with the *N*-protonated oxime to form a cyclic transition state [33–35]. In the one-pot solvent free conversion of cyclohexanone to CL, the sulfonic acid groups associated with the cations on the sulfonic acid-functionalized ionic liquid could facilitate the formation and stabilization of the positively charged intermediate based on their strong acidity and high polarity [36]. A cyclohexanone to [BSTma]HSO₄ molar ratio of 1:0.08 was therefore selected as the optimum molar ratio for the one-pot conversion of cyclo-

hexanone to CL.

3.3. One-pot conversion of cyclohexanol to CL

Finally, we investigated the one-pot conversion of cyclohexanol to CL using Na₂WO₄·[BSTma]HSO₄ as a catalyst (Table 2). In the absence of a catalyst, this reaction did not afford any CL (Table 2, entry 1). When the same reaction was conducted in the presence of Na₂WO₄·[BSTma]HSO₄, the yield of CL reached 49.1% (Table 2, entry 3). Na₂WO₄·[BSTma]HSO₄ was therefore used as a catalyst in the one-pot synthesis of CL. During the oxidation process, the catalyst acted as a phase-transfer catalyst based on its ion exchange behavior, and the acidity of the catalyst system improved the coordination of the substrate to bisperoxotungstate. Our newly developed catalyst also lowered the activation energy for the Beckmann rearrangement by stabilizing the charged intermediate formed during the rearrangement, to ultimately afford CL [14].

We subsequently proceeded to investigate the effects of several key parameters, including the reaction temperature, reaction time and the molar ratio of cyclohexanone to [BSTma]HSO₄ on the outcome of the Na₂WO₄·[BSTma]HSO₄-catalyzed one-pot conversion of cyclohexanol to CL. The tandem reaction was divided into three steps. The first and the third steps were determined to be exothermic, whereas the second one was slightly exothermic. The cyclohexanol conversion and yield of CL increased with increasing temperature from 70 to 80 °C, where the yield of CL reached its maximum value of 49.1% (Table 2, entries 2 and 3). Although further increases in the temperature resulted in a decrease in the yield of CL (Table 2, entries 4 and 5), the selectivity for cyclohexanone continued to increase. The high selectivity for cyclohexanone, which was formed by the hydrolysis of the CHO, resulted in a decrease in the selectivity for CL for reaction temperatures above 80 °C.

The cyclohexanol conversion remained unchanged for oximation and rearrangement reaction times in the range of 60 to 180 min. The CL yield initially increased and reached its maximum value of 49.1% (Table 2, entries 3, 6, and 7), before decreasing to 41.4% after extending the reaction time by 30 min

Table 2

One-pot conversion of cyclohexanol to CL using Na₂WO₄·[BSTma]HSO₄.

Entry	<i>T</i> (°C)	Time ^a (min)	Cyclohexanol to [BSTma]HSO ₄ molar ratio	<i>X</i> _{ANOL} (%)	Selectivity (%)			Carbon balance (%)
					Ketone	Oxime	Amide	
1	80	150	—	1.58	5.67	41.9	0.5	96.8
2	70	150	1:0.04	96.1	23.2	49.8	24.2	93.3
3	80	150	1:0.04	100	10.3	36.6	49.1	93.7
4	90	150	1:0.04	100	32.4	39.4	23.0	92.5
5	100	150	1:0.04	100	31.4	39.5	21.6	90.1
6	80	60	1:0.04	100	23.1	50.2	23.0	93.8
7	80	120	1:0.04	100	15.4	37.2	44.3	94.0
8	80	180	1:0.04	100	19.1	31.5	41.4	90.1
9	80	150	1:0.08	97.3	11.0	9.6	76.0	93.3
10	80	150	1:0.12	96.0	7.88	42.0	46.7	92.4
11	80	150	1:0.16	52.5	13.4	40.0	32.0	85.4

Reaction conditions: cyclohexanol:H₂O₂:(NH₂OH)₂·H₂SO₄:Na₂WO₄·2H₂O (molar ratio) = 1.00:1.50:0.50:0.06, oxidation time 5 h.

^a Oximation and arrangement time.

(Table 2, entry 8). Furthermore, the selectivity for cyclohexanone increased from 10.3% to 19.1% during this period. This result indicated that the CHO formed during the reaction was being hydrolyzed in the presence of [BSTma]HSO₄ and water during the prolonged reaction times [37]. When the molar ratio of cyclohexanone to IL7 was 1:0.08, Na₂WO₄·[BSTma]HSO₄ showed high catalytic activity, with the conversion of cyclohexanol and yield of CL reaching 97.3% and 76%, respectively.

3.4. One-pot conversion of various alcohols to amides using Na₂WO₄·[BSTma]HSO₄ as a catalyst

With the optimized reaction conditions in hand, we proceed to investigate the scope of this reaction by synthesizing a series of *N*-substituted amides (Table 3). Pleasingly, a wide range of alcohol substrates, including various aromatic and cyclic alcohols, reacted smoothly under the optimized conditions to give the desired products in excellent yields. Furthermore, these results compared well with those previously reported for the reactions of the corresponding ketoximes using [*n*-C₁₆H₃₃N(CH₃)₃]H₂PW₁₂O₄₀ [17], Cs_xH_{3-x}PW₁₂O₄₀ [33], propane sulfonic acid-functionalized imidazolium salt of phosphotungstate [34], CL-based Brønsted acidic ionic liquid [38], heteropolyanion-based ionic liquid [39] and H₃PW₁₂O₄₀ [40] as catalysts (shown in Table 3).

Notably, our newly developed catalyst gave an excellent performance for the conversion of isopropanol and sec-butyl alcohol. This result was particularly impressive because previous reports had suggested that it was not possible to convert these substrates to amides using novel Brønsted acidic ILs bearing double –SO₃H cations [41]. The CL yield achieved in this work was lower than that reported by Zhang et al. [29] (99%), where cyclohexanone was directly converted to CL using trifluoroacetic acid as a catalyst with acetonitrile as an additive.

Table 4 summarizes the catalytic performance of various catalysts previously reported for the synthesis of CL. The yield of CL over Na₂WO₄·[BSTma]HSO₄ was much higher than that of Nb-MCM-41 using cyclohexanone as a reactant (Table 4, entry 1). The yield of CL over Na₂WO₄·[BSTma]HSO₄ was higher than that of Pd-Sc(OTf)₃/[bmim]PF₆ (Table 4, entry 2), where 300 mol% 1-butyl-methylimidazolium hexafluorophosphate

Table 3

Direct conversion of various alcohols to amides using Na₂WO₄·[BSTma]HSO₄ as a catalyst.

Entry	Substrate	<i>X</i> _{Alcohol} (%)	Selectivity (%)		
			Ketone	Oxime	Amide
1		100	0	18.0	80.8
2		100	7.39	12.2	80.1
3		97.3	11.0	9.6	76.0
4		91.5	26.7	36.0	36.3
5		100	38.9	37.0	20.1
6		100	31.5	65.6	1.33

Reaction conditions: cyclohexanol:H₂O₂:(NH₂OH)₂·H₂SO₄:Na₂WO₄·2H₂O (molar ratio) = 1.00:1.50:0.50:0.06, oxidation at 80 °C for 6 h, oximation and rearrangement at 80 °C for 5 h.

([bmim]PF₆) was used as an additive. The yield of CL over Na₂WO₄·[BSTma]HSO₄ was much lower than that of cyclohexanone when cyclohexanone was used as a reactant (Table 4, entry 4). However, the application of this process is limited by the difficulties associated with the recovery of the homogeneous CF₃COOH catalyst from the reaction mixture. Na₂WO₄·[BSTma]HSO₄ exhibited comparable catalytic activity to all of the other catalysts using CHO as a reactant (Table 4, entries 5–10). These results therefore demonstrate that Na₂WO₄·[BSTma]HSO₄ is an efficient catalyst for the one-pot conversion of cyclohexanol to CL.

3.5. Catalyst recycling

Upon completion of the reaction, the mixture was allowed to settle to form two distinct phases. The aqueous phase was collected and extracted with dichloromethane, with the ILs and Na₂WO₄ completely dissolving in the aqueous phase. To investigate the reusability of the catalyst, the aqueous phase from the first run was concentrated to dryness using a rotary evap-

Table 4

Comparison of the catalytic performances of various catalysts for synthesis of CL.

Entry	Catalyst	Reaction conditions	Reactant	Yield (%)	Ref.
1	Nb-MCM-41	1 atm of H ₂ , 20 °C, HONH ₃ ⁺ Cl [−]	Cyclohexanone	4.82	[11]
2	Pd-Sc(OTf) ₃ /[bmim]PF ₆	H ₂ O ₂ :NH ₃ :cyclohexanone = 1.32:1.5:1	Phenol	67.0	[14]
3	[<i>n</i> -C ₁₆ H ₃₃ N(CH ₃) ₃]H ₂ PW ₁₂ O ₄₀	Oxidation at 80 °C for 6 h, oximation and rearrangement at 80 °C for 5 h	Cyclohexanol	73.9	[17]
4	CF ₃ COOH	Solvent acetonitrile, 70 °C, 4 h	Cyclohexanone	99.0	[29]
5	Cs _x H _{3-x} PW ₁₂ O ₄₀	Solvent benzonitrile, 130 °C, 6 h	Cyclohexanone oxime	56.0	[33]
6	[MIMPS] ₃ PW ₁₂ O ₄₀ + ZnCl ₂	Solvent acetonitrile, 90 °C, 1 h	Cyclohexanone oxime	83.0	[34]
7	[NHC]BF ₄	100 °C, 4 h	Cyclohexanone oxime	82.3	[38]
8	[DPySO ₃ H] _{1.5} PW ₁₂ O ₄₀	Solvent benzonitrile, 130 °C, 2 h	Cyclohexanone oxime	73.0	[39]
9	H ₃ PW ₁₂ O ₄₀	Solvent acetonitrile, reflux, 2 h	Cyclohexanone oxime	89.0	[40]
10	[Bis-BsImD][OTf] ₂ ·ZnCl ₂	Solvent acetonitrile, 5 h	Cyclohexanone oxime	37.0	[41]
11	Na ₂ WO ₄ ·[BSTma]HSO ₄	Cyclohexanol:H ₂ O ₂ :(NH ₂ OH) ₂ ·H ₂ SO ₄ :Na ₂ WO ₄ ·2H ₂ O = 1.00:1.50:0.50:0.06, 5 h, oximation and rearrangement for 5 h	Cyclohexanol	76.0	this work

orator, and the resulting residue was stored at 60 °C under vacuum to obtain the recycled catalyst. This process was repeated for four cycles. Notably, the yield of CL obtained using the recycled catalyst decreased only slightly (3.5%) after four runs. This loss in activity can most likely be attributed to the physical losses incurred during the recycling process.

4. Conclusions

A new process has been developed for the one-pot synthesis of CL from cyclohexanol using H_2O_2 and hydroxylamine in the presence of a Na_2WO_4 -acidic ionic liquid catalyst. Sulfonic acid-functionalized ionic liquids bearing HSO_4^- anions showed excellent catalytic activities. Under the optimized conditions, we achieved a cyclohexanol conversion of 97.3% with a CL yield of 76.0%. This new reaction system has several advantages such as ease of operation, mild reaction conditions and environmental friendliness. Furthermore, the catalyst can be readily recycled without suffering any major losses in its catalytic activity. Notably, the results of our one-pot procedure are comparable with the yield achieved for the three-step synthesis of CL, highlighting its potential application. We have therefore shown that the sequential oxidation of cyclohexanol to cyclohexanone, oximation of cyclohexanone to CHO and rearrangement of CHO to CL can be conducted as a one-pot reaction.

References

- [1] R. Beerthuis, G. Rothenberg, N. Shiju, *Green Chem.*, **2015**, 17, 1341–1361.
- [2] D. M. Zhang, Y. J. Guan, E. J. M. Hensen, L. Chen, Y. M. Wang, *Catal. Commun.*, **2013**, 41, 47–51.
- [3] M. Anilkumar, W. F. Hoelderich, *J. Catal.*, **2012**, 293, 76–84.
- [4] K. Y. You, L. Q. Mao, L. Chen, D. L. Yin, P. L. Liu, H. A. Luo, *Catal. Commun.*, **2008**, 9, 2136–2139.
- [5] K. Y. You, B. H. Wu, L. Q. Mao, D. L. Yin, P. L. Liu, H. A. Luo, *Catal. Lett.*, **2007**, 118, 129–133.
- [6] P. L. Liu, H. A. Xie, K. Y. You, F. Hao, X. F. Li, H. A. Luo, *Catal. Lett.*, **2010**, 136, 150–154.
- [7] F. Hao, J. Zhong, P. L. Liu, K. Y. You, C. Wei, H. J. Liu, H. A. Luo, *J. Mol. Catal. A*, **2011**, 351, 210–216.
- [8] F. Hao, J. Zhong, P. L. Liu, K. Y. You, H. A. Luo, *J. Mol. Catal. A*, **2012**, 363–364, 41–48.
- [9] F. Hao, J. Zhong, P. L. Liu, K. Y. You, C. Wei, H. A. Luo, *Chin. J. Catal.*, **2012**, 33, 670–676.
- [10] P. L. Liu, H. K. Zhang, S. H. Liu, Z. J. Yao, F. Hao, K. Y. You, H. A. Luo, *React. Kinet. Mech. Catal.*, **2012**, 107, 383–391.
- [11] M. Anilkumar, W. F. Hoelderich, *Appl. Catal. B*, **2015**, 165, 87–93.
- [12] T. Hirabayashi, S. Sakaguchi, Y. Ishii, *Angew. Chem. Int. Ed.*, **2004**, 43, 1120–1123.
- [13] R. Raja, M. E. Potter, S. H. Newland, *Chem. Commun.*, **2014**, 50, 5940–5957.
- [14] J. Y. Shin, D. J. Jung, S. G. Lee, *ACS Catal.*, **2013**, 3, 525–528.
- [15] G. Chatel, C. Monnier, N. Kardos, C. Vorion, B. Andrioletti, M. Draye, *Appl. Catal. A*, **2014**, 478, 157–164.
- [16] R. A. Sheldon, *Catal. Today*, **2015**, 247, 4–13.
- [17] H. F. Wang, R. B. Hu, Y. F. Yang, M. D. Gao, Y. J. Wang, *Catal. Commun.*, **2015**, 70, 6–11.
- [18] C. Zhang, X. Y. Pan, M. J. Yu, L. Jin, G. Wu, *Chem. Eng. J.*, **2012**, 209, 464–468.
- [19] H. Mehdi, A. Bodor, D. Lantos, I. T. Horvanth, D. E. D. Vos, K. Binnemans, *J. Org. Chem.*, **2007**, 72, 517–524.
- [20] P. Attri, P. Venkatesu, T. Hofman, *J. Phys. Chem. B*, **2011**, 115, 10086–10097.
- [21] P. Attri, P. Venkatesu, *Phys. Chem. Chem. Phys.*, **2011**, 13, 6566–6575.
- [22] J. Z. Gui, H. Y. Ban, X. H. Cong, X. T. Zhang, Z. D. Hu, Z. L. Sun, *J. Mol. Catal. A*, **2005**, 225, 27–31.
- [23] J. Z. Gui, X. H. Cong, D. Liu, X. T. Zhang, Z. D. Hu, Z. L. Sun, *Catal. Commun.*, **2004**, 5, 473–477.
- [24] D. Fang, J. Luo, X. L. Zhou, Z. L. Liu, *Catal. Lett.*, **2007**, 116, 76–80.
- [25] R. Noyori, M. Aoki, K. Sato, *Chem. Commun.*, **2003**, 34, 1977–1986.
- [26] L. Chen, T. Zhou, L. F. Chen, Y. M. Ye, Z. W. Qi, H. Freund, K. Sundmacher, *Chem. Commun.*, **2011**, 47, 9354–9356.
- [27] D. Liu, J. Z. Gui, F. Lu, Z. L. Sun, Y. K. Park, *Catal. Lett.*, **2012**, 142, 1330–1335.
- [28] Y. Y. Wang, X. X. Gong, Z. Z. Wang, L. Y. Dai, *J. Mol. Catal. A*, **2010**, 322, 7–16.
- [29] J. S. Zhang, Y. C. Lu, K. Wang, G. S. Luo, *Ind. Eng. Chem. Res.*, **2013**, 52, 6377–6381.
- [30] L. Ronchin, M. Bortoluzzi, A. Vavasori, *J. Mol. Struct.-Theochem.*, **2008**, 858, 46–51.
- [31] K. Y. You, L. Q. Mao, D. L. Yin, P. Liu, H. A. Luo, *Catal. Commun.*,

Graphical Abstract

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One-pot conversion of cyclohexanol to ϵ -caprolactam using a multifunctional Na_2WO_4 -acidic ionic liquid catalytic system

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Na_2WO_4 -acidic ionic liquid was used as a simple, ecofriendly, recyclable and efficient catalytic system in the one-pot synthesis of ϵ -caprolactam from cyclohexanol, hydrogen peroxide, and hydroxylamine.

- 2008, 9, 1521–1526.
- [32] M. T. Nguyen, G. T. Raspoet, L. G. Vanquickenborne, *J. Am. Chem. Soc.*, **1997**, 119, 2552–2562.
- [33] N. R. Shiju, H. M. Williams, D. R. Brown, *Appl. Catal. B*, **2009**, 90, 451–457.
- [34] X. Zhang, D. Mao, Y. Leng, Y. Zhou, J. Wang, *Catal. Lett.*, **2013**, 143, 193–199.
- [35] C. Ngamcharussrivichai, P. Wu, T. Tatsumi, *J. Catal.*, **2004**, 227, 448–458.
- [36] M. C. Wu, H. F. Duan, J. G. Cao, D. P. Liang, F. Jiang, H. Gao, X. D. Jia, Y. J. Lin, *Chem. Res. Chin. Univ.*, **2011**, 27, 973–976.
- [37] R. X. Ren, W. Ou, *Tetrahedron Lett.*, **2001**, 42, 8445–8446.
- [38] S. Guo, Z. Y. Du, S. G. Zhang, D. M. Li, Z. P. Li, Y. Q. Deng, *Green Chem.*, **2006**, 8, 296–300.
- [39] D. Mao, Z. Y. Long, Y. Zhou, J. Li, X. C. Wang, J. Wang, *RSC Adv.*, **2014**, 4, 15635–15641.
- [40] G. Kaur, J. K. Rajput, P. Arora, N. Devi, *Tetrahedron Lett.*, **2014**, 55, 1136–1140.
- [41] X. F. Liu, L. F. Xiao, H. Wu, Z. Li, J. Chen, C. G. Xia, *Catal. Commun.*, **2009**, 10, 424–427.

多功能 Na_2WO_4 -离子液体催化体系催化环己醇一锅合成己内酰胺

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摘要: 己内酰胺是合成尼龙-6和工程塑料的关键中间体. 工业上己内酰胺的合成工艺分三步: 以环己醇为原料合成环己酮, 环己酮肟化合成环己酮肟, 环己酮肟重排生成己内酰胺. 该工艺存在工艺流程长、重排过程中使用发烟硫酸腐蚀设备、形成大量低值副产物硫酸铵等问题. 随着人们对环境保护意识的提高, 发展环境友好、经济效益高的直接合成己内酰胺工艺已经迫在眉睫. 多步串联反应具有设备投资少、中间分离步骤少、反应效率高等优点, 其关键问题之一是多功能催化剂的开发. 环己醇作为环己烷氧化反应的副产物, 能够直接用于己内酰胺的合成, 具有理论研究价值和工业应用意义.

本文构建了以环己醇氧化、环己酮肟化和环己酮肟重排反应构成的串联反应系统, 可缩短己内酰胺合成工艺流程, 降低能耗, 减小环境污染. 合成了九种离子液体, 并与 Na_2WO_4 组成催化体系, 以环己醇、过氧化氢和羟胺为原料, 催化环己醇直接合成己内酰胺.

首先研究了不同 Na_2WO_4 -离子液体催化体系对环己醇直接氧化合成环己酮反应的影响. 反应介质的酸性和离子液体水油两相中的相转移功能是影响氧化过程的两个主要因素. Na_2WO_4 -磺酸基功能化的离子液体催化剂具有较高的氧化活性. 这是由于磺酸基的引入提高了催化剂酸性, 另外磺酸基功能化的离子液体随碳链的增长, 催化剂的亲油性增强, 即该催化剂相转移功能增强. 考察了九种离子液体对氧化过程的影响, 其中 Na_2WO_4 -[BSTma]HSO₄在氧化过程中催化活性最高, 因此将其用于催化环己酮与羟胺合成己内酰胺的反应, 并考察了环己酮与[BSTma]HSO₄的摩尔比对该反应的影响, 发现该摩尔比为1:0.08时, 反应效果最好.

最后, 将 Na_2WO_4 -[BSTma]HSO₄体系用于催化环己醇直接合成己内酰胺的反应. 考察了反应温度、反应时间和环己醇与[BSTma]HSO₄摩尔比的影响. 在氧化时间为300 min, 肟化和重排时间为150 min, 反应温度为80 °C, 环己醇: H_2O_2 :(NH_2OH)₂· H_2SO_4 : Na_2WO_4 ·2 H_2O :[BSTma]HSO₄的摩尔比为1.00:1.50:0.50:0.06:0.08的条件下反应效果最好, 环己醇转化率为97.3%, 己内酰胺收率为76.0%. Na_2WO_4 -[BSTma]HSO₄催化体系活性较高的原因是离子液体阳离子的相转移作用, 以及在氧化过程中离子液体与过氧钨酸盐的配位作用和对Beckmann重排过程中中间产物的稳定作用. 研究了 Na_2WO_4 -[BSTma]HSO₄催化体系的普适性, 发现该催化体系对所考察的脂肪醇和芳香醇直接合成酰胺均具有较好的催化活性. 另外, 回用的 Na_2WO_4 -[BSTma]HSO₄催化剂仍具有较好的催化活性. 因此, 该催化体系具有高效易回收、操作简单和反应条件温和的优点.

关键词: 环己醇; 己内酰胺; 一锅合成; 酸性离子液体; 环己酮肟

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