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Direct catalytic synthesis of ε-caprolactam from cyclohexanol using $[n\text{-}C_{16}H_{33}N\ (CH_3)_3]H_2PW_{12}O_{40}$ as a catalyst

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ABSTRACT

ε-Caprolactam was synthesized directly from cyclohexanol via a tandem catalytic process using $[n\text{-}C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ as a catalyst. The highly efficient performance of the catalysts is due to the phase-transfer function of cation, improved coordination with peroxotungsten during oxidation and stabilization function of heteropoly anion on the intermediate formed during Beckmann rearrangement. A ε-caprolactam yield of 73.9% was obtained with a cyclohexanol conversion of 97.1% under optimized conditions.

1. Introduction

Tandem processes that involve multiple chemical transformations in a single-pot with minimal work-up and less waste generation have revolutionized synthetic chemistry in recent years. Tandem catalytic processes can replace multi-step syntheses with efficient catalytic reactions that can have significant impact on the manufacture of fine chemicals and pharmaceutical intermediates [1].

ε-Caprolactam(CL) is an important precursor of nylon-6 and plastics and the global market is forecasted to reach 5 million metric tonnes by the year of 2015 [2]. CL is currently manufactured using cyclohexanone as starting reactant, which is converted into cyclohexanone oxime and finally rearranged to give CL in a three step process. The yield of Beckmann rearrangement of cyclohexanone oxime to CL is high, using fuming sulfuric acid as both solvent and catalyst. However, this process has several disadvantages, such as formation of large amount of ammonium sulfate as a by-product due to the neutralization of the hazardous sulfuric acid with ammonia, and corrosion of the reactors and environmental pollution caused by the use of fuming sulfuric acid. Though cyclohexanone can be obtained by hydrogenation of phenol, the preferred industrial route involves the direct oxidation of cyclohexane. However, the aerobic oxidation of cyclohexane to cyclohexanone limits the whole efficiency of the three step process owing to the low yield per pass. Only yields of 8% and 10% were received in the cases of homogeneous cobalt complex [2] and heterogeneous Co-HZSM-5 [3] as catalysts respectively.

Increase in awareness of environmental protection has led to the development of eco-friendly and economical procedure for one-pot synthesis of CL. Several efforts have been made to synthesize CL in the presence of nitrosyl sulfuric acid from cyclohexane [4–7], nitrocyclohexane [8], or cyclohexanone [9,10]. The yield of CL in those processes was about 10%. Our previously work reported the utilization of the novel $(NH_2OH)_2$-IL in the one-step, solvent-free synthesis of CL from cyclohexanone with the 91% yield of CL, but using $ZnCl_2$ as a catalyst [11]. High yielding one-pot oximation–Beckmann rearrangement of ketones to amides using trifluoroacetic acid or $FeCl_3 \cdot 6H_2O$ as a catalyst was reported by Aricò and Mahajan respectively [12,13]. More recently, Lee reported a multifunctional $Pd/Sc(OTf)_3$/ionic liquid catalyst for the tandem one-pot conversion of phenol to CL, in 67% overall yield, using 300 mol% 1-butyl-methylimidazolium hexafluorophosphate ($[bmim][PF_6]$) as an additive [14]. Though very high phenol conversion and CL selectivity were achieved, this catalyst system suffered from the problems of difficult separation of the ionic liquid from the reaction mixture.

Polyoxometalates (POMs) with oxygen clusters of early transition metals have drawn wide attention because of high Brønsted acidity and redox properties [15]. A variety of different catalytic systems for hydrogen peroxide oxidation of alcohols catalyzed by POMs have been developed [16–21].

In recent years, $H_3PW_{12}O_{40}$ [22], propane sulfoacid-functionalized imidazolium salt of phosphotungstate [23], and $CsxH_3\text{–}xPW_{12}O_{40}$ [24] as catalysts in Beckmann rearrangement have been reported, affording a new approach for liquid phase Beckmann rearrangement. However, environmentally undesirable solvents such as benzonitrile and acetonitrile were used.

To overcome these abovementioned problems, the synthesis of CL directly from cyclohexanol, being an unavoidable side-product during

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oxidation of cyclohexane, by oxidation in liquid phase using H_2O_2 combined with simultaneous oximation and Beckmann rearrangement in a pot type reactor is an alternative route. This route is very interesting from an industrial point of view, because the oxidation of cyclohexanol to cyclohexanone, oximation of cyclohexanone to CHO and CHO rearrangement to CL will take place in presence of multifunctional catalysts.

In this paper, a more efficient tandem catalytic process to synthesize CL directly from cyclohexanol using $[n\text{-}C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ as a catalyst was reported. $[n\text{-}C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ effectively promotes tandem reactions without the requirement of any additional catalyst and the final products are easily separated by simple extraction.

2. Experimental

2.1. Material and methods

$H_3PMo_{12}O_{40}$, $(NH_2OH)_2{\cdot}H_2SO_4$, $H_3PW_{12}O_{40}$, cyclohexanol, $n\text{-}C_{16}H_{33}N(CH_3)_3Br$, $n\text{-}C_{14}H_{29}N(CH_3)_3Br$, and $n\text{-}C_{12}H_{25}N(CH_3)_3Br$, Na_2WO_4 were purchased from Tianjin Guangfu Fine Chemical Research Institute. 30% H_2O_2 aqueous was purchased from Tianjin Bodi Chemical Co. Ltd.

2.2. Preparation of quaternary ammonium decatungstates

Hexadecyl trimethyl ammonium decatungstate $[n\text{-}C_{16}H_{33}N(CH_3)_3]_4W_{10}O_{32}$ (CTAW), myristyl trimethyl ammonium decatungstate$[n\text{-}C_{14}H_{29}N(CH_3)_3]_4W_{10}O_{32}$ (TTAW), and dodecyl trimethyl ammonium decatungstate $[n\text{-}C_{12}H_{25}N(CH_3)_3]_4W_{10}O_{32}$ (DTAW) were synthesized according to previously reported methods respectively [18].

2.3. Preparation of quaternary ammonium heteropolyacid salts

Hexadecyl trimethyl ammonium phosphomolybdate ($[n\text{-}C_{16}H_{33}N(CH_3)_3]_3PMo_{12}O_{40}$) (CTAPMo) was synthesized according to reported methods [25]. $[n\text{-}C_{16}H_{33}N(CH_3)_3]_2HPMo_{12}O_{40}$ (CTAHPMo), $[n\text{-}C_{16}H_{33}N(CH_3)_3]H_2PMo_{12}O_{40}$ (CTAH$_2$PMo), $[n\text{-}C_{16}H_{33}N(CH_3)_3]_3PW_{12}O_{40}$ (CTAPW), $[n\text{-}C_{16}H_{33}N(CH_3)_3]_2H\text{-}PW_{12}O_{40}$ (CTAHPW) and $[n\text{-}C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ (CTAH$_2$PW) were also prepared accordingly by controlling molar ratios of cation and anion.

2.4. Characterization of catalysts

The POMs were characterized by ^1H NMR, FT-IR, UV, TGA and XRD. ^1H and ^{31}P NMR were obtained on an AVAVCE 400 instrument in DMSO. Chemical shifts of ^{31}P NMR were referenced to 85% H_3PO_4 as external standard. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using FT-IR spectrometer (BRUKER TENSOR 27). Ultraviolet–visible (UV) absorption spectra were obtained using a UV INESA L5 in acetonitrile. TGA–DTA measurements were conducted on a DuPont TA 2000 with 10 k/min heating rate under atmosphere. Powder X-ray diffraction (XRD) data were recorded on a D/max-2500 diffractometer operated at 45 kV and 40 mA, using Nickel filtrated CuKα radiation with 1.5406 Å between 5° and 40°(2 theta), with a scanning speed of 5°/min.

2.5. Catalytic test

In a typical experiment, the catalyst (0.25 mmol) was mixed with cyclohexanol (50 mmol) in a 100 mL three-necked flask equipped with a reflux condenser, a magnetic stirrer and a thermometer. When the required temperature reached, 30% aqueous hydrogen peroxide (75 mmol) was then added dropwise to the reaction mixture, with vigorous stirring for 300 min. Hydroxylamine sulfate (25 mmol) was added to the flask with vigorous stirring for a certain time. After the completion of reaction, the reaction mixture was divided into two phases. Water phase was extracted with dichloromethane and the products were identified by a Thermo Trace DSQ gas chromatograph–mass spectrometer. The products were analyzed by a SP-3420A gas chromatograph equipped with a KB-Wax column (30 m, 0.32 mm id, 0.25 μm film thickness) with toluene as internal standard.

$$\text{Cyclohexanol conversion}(\%) = [(\text{moles of cyclohexanol added–moles of unconverted cyclohexanol}) / \text{mole cyclohexanol added}] * 100$$

$$\text{Product selectivity}(\%) = [\text{moles of the product} / (\text{moles of cyclohexanol added–moles of unconverted cyclohexanol})] * 100$$

$$\text{Carbon balance } (\%) = [\text{sum of moles of carbon in the identified products} / \text{moles of carbon in converted cycloh}-\text{exanol}] * 100$$

3. Results and discussion

3.1. Catalytic performances of various POM catalysts during oxidation of cyclohexanol to cyclohexanone

Direct synthesis of CL from cyclohexanol involves three steps. The first step is the selective oxidation of cyclohexanol to cyclohexanone. Cyclohexanone then reacts with hydroxylamine to form oxime and oxime rearranges to CL. First, the oxidation of cyclohexanol catalyzed by quaternary ammonium decatungstate was investigated. The results are shown in Fig. 1. In the absence of any catalysts, the yield of cyclohexanone was only 1.08% (Fig. 1, none). After the addition of the quaternary ammonium decatungstate, the yield of cyclohexanone increased dramatically compared with that of the absence of a catalyst. Based on the results above, a series of POM catalysts with phosphotungstic acid (PW:$H_3PW_{12}O_{40}$) and 12-phosphomolybdic acid (PMo:$H_3PMo_{12}O_{40}$) as anion were prepared respectively and used for the reaction(Fig. 1). CTAPW, CTAHPW and CTAH$_2$PW showed good catalytic activities. The conversions of cyclohexanol were extremely low in the cases of quaternary ammonium phosphomolybdic acids (Fig. 1, CTAPMo, CTAHPMo, CTAH$_2$PMo) as a catalyst. Actually, the different catalytic activities resulted from different heteropoly anions with a similar organic modifier have been also observed in the oxidation of benzyl alcohol with aqueous H_2O_2 previously [26]. In order to determine the role of long-chain alkylammonium cations in the oxidation of cyclohexanol, same mol of

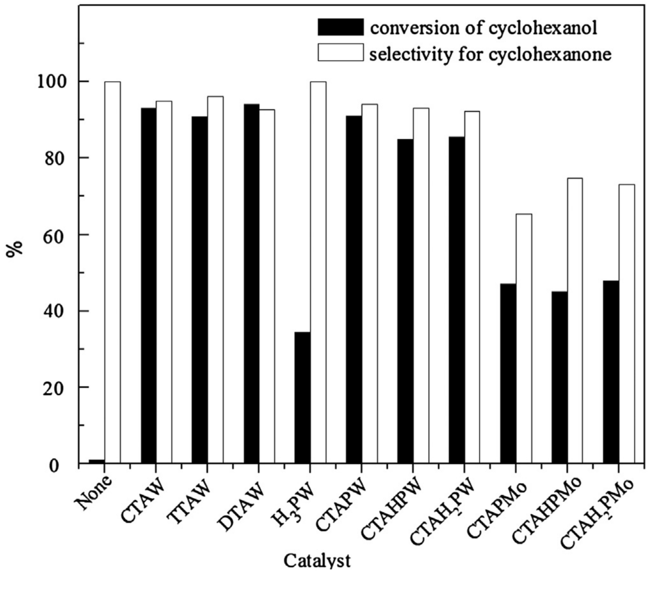


Fig. 1. Catalytic performance of various POM catalysts during oxidation of cyclohexanol. The reaction conditions: alcohol: H_2O_2: $(NH_2OH)_2{\cdot}H_2SO_4$: catalyst (molar ratio) = 1.00: 1.50:0.500: 0.005, T = 80 °C, oxidation time = 360 min.

$H_3PW_{12}O_{40}$ was used as a catalyst under the same reaction condition (Fig. 1). The conversion of cyclohexanol was 34.5%, which was lower than alkylammonium 12-phosphotungstate. Although the Keggin heteropoly anion is the active center for oxidation, alkylammonium is still considered to play a very significant role during reaction. The increase in the yield of cyclohexanone with long-chain alkylammonium cations of the POM catalyst is attributed to the higher phase-transfer ability in the oil–water two-phase reaction, which is in agreement with the results of Zhang [20].

For the three quaternary ammonium tungstophosphoric salts (CTAPW, CTAHPW and $CTAH_2PW$), the yield of cyclohexanone increased from 85.0% to 91.0% with an increase of the content of $C_{16}H_{33}N(CH_3)^{2+}$ cations. The same results have been obtained by using heteropolyacids in conjunction with phase transfer catalysts in the oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide as the oxidizing agent. The catalytic activity is found to increase gradually with the decrease of acidity by replacement of protons in the heteropolyacid with sodium ions [27].

3.2. One-pot conversion of cyclohexanol to CL

The direct synthesis of CL was investigated with POM as catalysts (Fig. 2). In the absence of any catalysts, no CL was produced (none, Fig. 2). Compared with the results obtained in the oxidation reaction above, the conversion of cyclohexanol increased over POM catalysts, especially for CTAPMo, CTAHPMo, and $CTAH_2PMo$. In the periods of oximation and arrangement, cyclohexanone obtained during the oxidation process reacted with hydroxylamine in situ to form CHO, which was favorable for cyclohexanol being oxidized with the removal of cyclohexanone.

In the previously proposed mechanism for the rearrangement of CHO, the rearrangement is initiated by the formation of a N-protonated oxime by the interaction of the proton from a Brønsted acid site with the nitrogen atom of oxime, followed by the proton transfer from nitrogen to oxygen atom [24]. The formation of O-protonated oxime by proton transfer from nitrogen to oxygen is a 1, 2-H-shift reaction with high activation energy and is considered as the rate-determining step in Beckmann rearrangement. In this process, heteropoly anion can play an important role in lowering the activation energy by interacting directly with the N-protonated oxime and forming a cyclic transition state. Such a stabilizing interaction between the heteropoly anion and the migrating hydrogen in the transition structure would lower the energy barrier of 1, 2-H-shift. Hence heteropoly anion may accelerate the 1, 2-H-shift of the N-protonated oxime due to the higher ability to stabilize the transition structure or to reduce the energy barrier of the transition state.

As shown in Fig. 2, the maximum yield of CL was 73.9% along with 7.4% of cyclohexanone oxime interaction with $CTAH_2PW$ as a catalyst. However, the maximum yield of ε-caprolactam was 19.1% with CTAPMo as a catalyst. The order of softness of heteropoly anions in aqueous solution was estimated as follows: $PW_{12}O_{40}^{3-} > PMo_{12}O_{40}^{3-}$. The softness of heteropoly anions is assumed to play an important role in stabilizing organic intermediates [28]. It is known that the stabilization of organic intermediates is closely relative to the performance of the catalyst, which accounts for the lower conversion of cyclohexanol for CTAPMo than that for $CTAH_2PW$.

For the three quaternary ammonium tungstophosphoric salts (CTAPW, CTAHPW and $CTAH_2PW$), the yield of CL increased from 54.5% to 73.9% with a decrease of the content of $C_{16}H_{33}N(CH_3)_3^+$ cations. Fig. 3 shows the XRD pattern of $CTAH_2PW$, CTA_2HPW and CTA_3PW. The free acid HPW(a) shows the main diffraction peaks, which are consistent with Joint Committee on Powder Diffraction Standards (JCPDS)50-0656. Compared with HPW, the $CTAH_2PW$, CTAHPW and CTA_3PW show the main diffraction peaks in which some differences occur because of the partial exchange of the H ion with the CTA ion. The diffraction peaks at 2θ (in degree) = 8–11°,18–22°, 24–30° and 33–40° are characteristic of HPA anions with Keggin structure [28,29]. The average particle size was calculated by X-ray diffraction line broadening using the Debye–Scherrer equation. The particle sizes of $CTAH_2PW$, CTA_2HPW and CTA_3PW were 22.2 nm, 24.0 nm and 47.2 nm respectively. Small particle size facilitates the permeation of the organic intermediates into the bulk of the hybrid. This proposal consists with the well-established view point of “pseudo-liquid behavior” for the bulk-type catalysis of a HPA catalyst [26,30].

The fresh catalyst and recovered catalysts in oxidation stage and Beckmann rearrangement stage were characterized by ^{31}P NMR (Fig. 4). A single peak at −15.6 ppm (shown in Fig. 4a) was attributed to the structure of $[PW_{12}O_{40}]^{3-}$ [19]. The spectrum of the recovered catalysts in oxidation stage (Fig. 4b) shows two peaks, which suggests

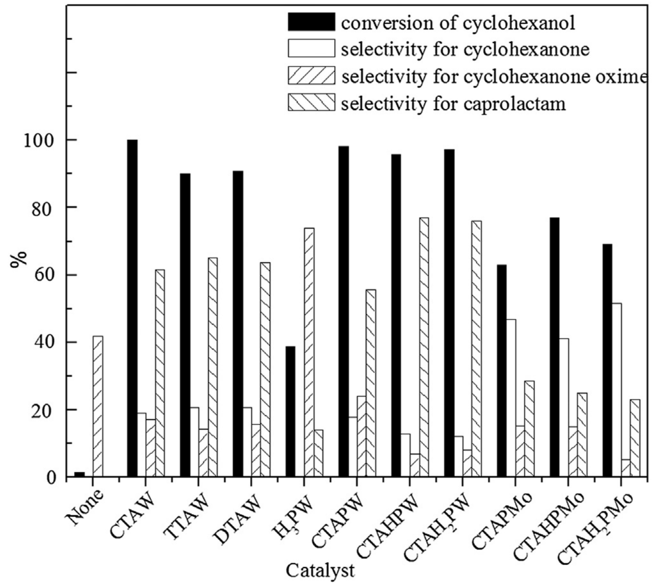


Fig. 2. Catalytic performance of various POM catalysts during direct synthesis of CL. The reaction conditions: alcohol: H_2O_2: $(NH_2OH)_2 \cdot H_2SO_4$: catalyst (molar ratio) = 1.00: 1.50:0.500: 0.005, T = 80 °C, oxidation time = 360 min, oximation and arrangement time = 300 min.

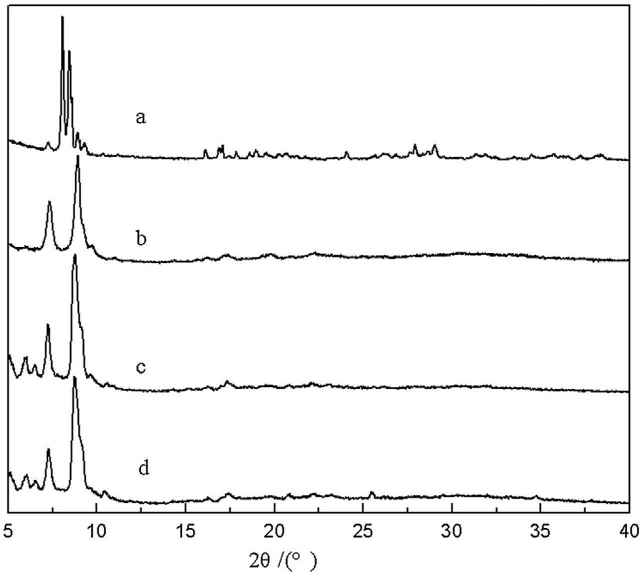


Fig. 3. XRD patterns of HPW(a),$(CTA)_3PW$(b),$(CTA)_2HPW$(c) and $(CTA)H_2PW$(d).

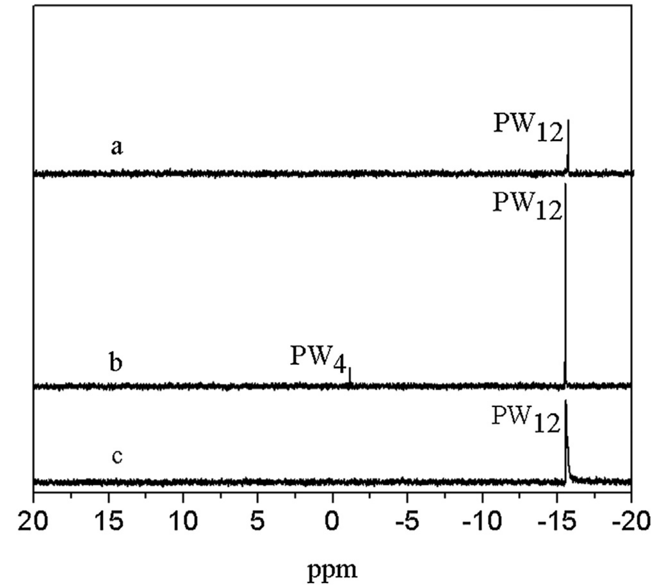


Fig. 4. ^{31}P NMR spectra of the fresh catalyst of $CTAH_2PW$ (a); $CTAH_2PW$ in oxidation stage(b); in Beckmann rearrangement stage(c).

that the catalyst is a mixture of different polytungstophosphate species. The main peak at 1.2 ppm can be attributed to active tungsten-peroxo complex, which is the real active species in oxidation stage. After the oxidation of cyclohexanol, the peroxo species lost its active oxygen completely or partly and were converted into large stable compounds with a Keggin structure by forming intermolecular W–O–W bonds when all H_2O_2 was consumed [31].

The effect of the amount of H_2O_2 and catalyst, rearrangement temperature, and rearrangement time on the direct synthesis of CL was shown in Fig. 2. The conversion of cyclohexanol increased drastically from 90.2% to 97.1% with an increase of the molar ratio of H_2O_2 to cyclohexanol from 1.2 to 2.1. The selectivity for CL first increased from 63.6% to 76.1%, then decreased from 76.1% to 67.5% with an increase of the amount of H_2O_2. In order to determine the residual hydroxylamine in the aqueous phase after reaction, cyclohexanone together with $NH_3 \cdot H_2O$ (25 wt.%) was added to induce the oximation of cyclohexanone with residual hydroxylamine to produce oxime. Fig. 5 showed the decomposition rate of hydroxylamine with different amounts of H_2O_2. The main reason for low selectivity for CL and high selectivity for cyclohexanone was the decomposition rate of hydroxylamine with an increase amount of H_2O_2. Oximation was promoted with the increase amount of catalyst, increase of rearrangement temperature, and prolong of rearrangement time. The selectivity for CL decreased, mostly due to the hydrolysis cyclohexanone oxime.

3.3. Direct synthesis of various alcohols to amide catalyzed by $CTAH_2PW$

Under the optimized reaction conditions, a series of N-substituted amides was prepared to establish the scope of this method (Table 1). To our delight a wide range of alcohol substrates including various aromatic and cyclic alcohols gave desired products in excellent yield compared to previous results from corresponding ketoximes over the catalysts of $H_3PW_{12}O_{40}$ [10], propane sulfoacid-functionalized imidazolium salt of phosphotungstate [23], $CsxH_3{-}xPW_{12}O_{40}$ [24], ε-caprolactam-based Brønsted acidic ionic liquid [32], and heteropolyanion-based ionic liquid [33].

In addition, the catalyst had a good catalytic performance in the conversation of isopropanol and sec-butyl alcohol, which is in contrast to the early report that these substrates were inert in the conversion to amides [34]. The yield of CL in this work is lower than that reported by Zhang (99%), which converted cyclohexanone to CL directly catalyzed by trifluoroacetic acid with acetonitrile as an additive [35].

3.4. Catalyst recycling

After the reaction, the reaction mixture was clearly divided into two phases. The aqueous phase was extracted with dichloromethane. The

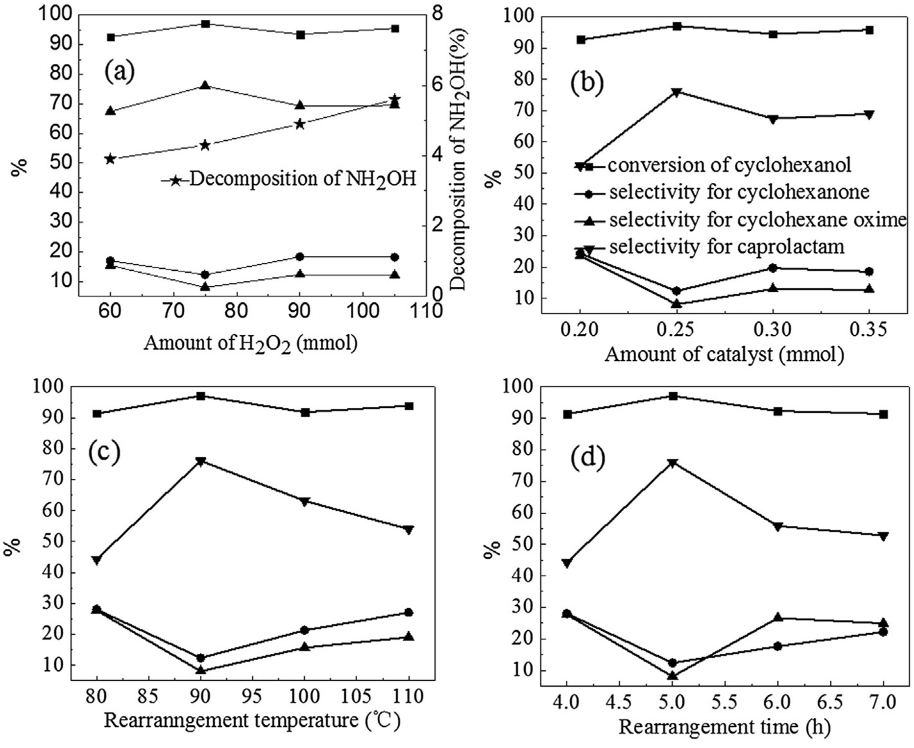
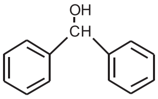
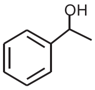
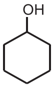
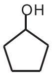
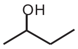
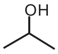


Fig. 5. Influence of reaction conditions on direct synthesis of CL catalyzed by $CTAH_2PW$.

Table 1
Direct conversion of various alcohols to amide catalyzed by CTAH$_2$PW.

Entry	Substrate	$X_{Alcohol}$ (%)	S_{Keton} (%)	S_{Oxime} (%)	S_{Amide} (%)	Carbon balance (%)
1[a]		100.0	0.0	17.1	81.9	99.4
2[a]		100.0	12.3	11.6	75.3	98.9
3[a]		95.8	13.0	7.0	77.1	99.1
4[b]		82.8	14.5	10.8	72.6	98.7
5[b]		92.6	25.2	40.1	34.6	98.8
6[b]		100.0	27.1	42.6	29.4	99.0

Reaction conditions: alcohol: H$_2$O$_2$: (NH$_2$OH)$_2$·H$_2$SO$_4$: catalyst (molar ratio) = 1.00: 1.50:0.500: 0.005, oxidation temperature = 80 °C, oxidation time = 360 min, oximation and rearrangement time = 300 min.

[a] Oximation and rearrangement temperature = 80 °C.

[b] Oximation and rearrangement temperature = 100 °C.

solid catalyst could be easily recovered by filtration of aqueous phase with a high recovery ratio of above 90% and directly reused for the next run. These procedures were repeated for four cycles. After four times of recycle, the yield of CL only slightly decreased to 70.1%. The loss of activity is probably due to the catalyst loss in the recycling process, which is proportional to reused-catalyst amount. Furthermore, due to the catalyst low protonation ability of the catalyst, the resulting amides can be easily recovered as pure compounds. High carbon balances with different alcohols were obtained (Table 1).

4. Conclusions

[n-(CH$_3$)$_3$NC$_{16}$H$_{33}$]H$_2$PW$_{12}$O$_{40}$ as a multifunctional catalyst, catalyzes three mechanistically distinct processes in a single-pot under the same reaction conditions. The highly efficient performance of this family of catalysts is due to the phase-transfer function of [n-C$_{16}$H$_{33}$N(CH$_3$)$_3$] H$_2$PW$_{12}$O$_{40}$ cation, improved coordination with peroxotungsten during oxidation and stabilization function of heteropoly anion on the intermediate formed during Beckmann rearrangement. Conversion of cyclohexanol and yield of CL were 97.10% and 73.90% respectively without the requirement of any additives or solvent in this reaction. Operational simplicity and minimal waste generation of this process should be beneficial for industrial applications. Furthermore, the catalysts can be easily recycled without loss of performance.

Acknowledgments

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