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A Novel Route to One-step Formation of ε-caprolactam from Cyclohexane and Nitrosyl Sulfuric Acid Catalyzed by VPO Composites

**Kuiyi You · Bohua Wu · Liqiu Mao · Dulin Yin ·
Pingle Liu · He'an Luo**

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Abstract A series of VPO composites were employed to catalyze the reaction of cyclohexane with nitrosyl sulfuric acid in the presence of fuming sulfuric acid. To our delight, ε-caprolactam was for the first time directly obtained through such one-step catalytic process. VPO composite catalysts were proven to be efficient for the reaction, especially, the transition metals introduced to Al–VPO composite catalysts could improve the reactions selectivity to some extent. Among them, the Mn–Al-VPO composite catalyst gave the best results with 11.65% of conversion and 34.70% of selectivity to ε-caprolactam. While the conversion and selectivity are too low at this time to be commercially viable, this discovery establishes a potential new single step process for making ε-caprolactam from cyclohexane. A reaction mechanism is proposed.

Keywords Cyclohexane · Nitrosyl sulfuric acid · ε-Caprolactam · One-step process · VPO composite catalyst

1 Introduction

ε-Caprolactam (CL or CPL) is an important monomer for the production of nylon-6 synthetic fibers and resins. Most of current caprolactam production methods involve the conversion of cyclohexanone with hydroxylamine (in its sulfate or phosphate form) into cyclohexanone oxime, followed by Beckmann rearrangement by the action of fuming sulfuric acid, and then treatment with ammonia giving ε-caprolactam [1, 2] (see *Route 1*, Scheme 1). However, this liquid-phase process suffers from many problems such as the formation of large quantities of low-value ammonium sulfate, the corrosion of equipment and environmental pollution caused by the use of fuming sulfuric acid.

In order to overcome the above-mentioned problems, many research groups have extensively studied on the vapor-phase Beckmann rearrangement using solid acid catalysts instead of fuming sulfuric acid [3–7]. The further improvement for production of ε-caprolactam was direct ammoximation of cyclohexanone with NH_3 and H_2O_2 catalyzed by TS-1, followed by vapor-phase Beckmann rearrangement of the formed cyclohexanone oxime over solid acid catalyst [8–10]. The vapor-phase reaction, however, suffers from its intrinsic features such as the requirement of high temperature and the need to use a fluidized bed due to coke formation on the catalyst.

Cambridge chemists have reported a bifunctional molecular sieve catalyst for one-step process for making ε-caprolactam from cyclohexanone, O_2 and ammonia without any by-products. The bifunctional catalyst is a zeolyte aluminum phosphate containing cobalt that generates the hydroxylamine, plus acidic sites that promote the Beckmann rearrangement [11].

Another industrial process for production of ε-caprolactam employed cyclohexanecarboxylic acid, which was obtained from toluene as the starting material (see *Route 2*). It is easy to obtain the raw material for this technique with the advantages of low investment and safety, however, this process still underwent the multi-step conversion from elementary material and the atom economical utilization

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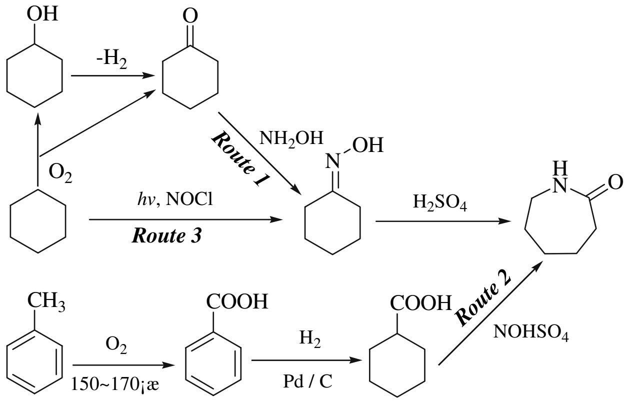
K. You · L. Mao · P. Liu · H. Luo (✉)
College of Chemical Engineering, Xiangtan University,
Xiangtan 411105, P.R. China
e-mail: heanluo@126.com

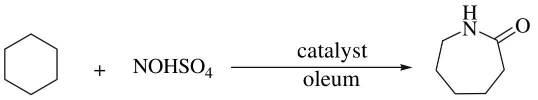
B. Wu · L. Mao · D. Yin (✉)
Institute of Fine Catalysis and Synthesis,
Hunan Normal University, Changsha 410081, P.R. China
e-mail: dulinyin@126.com

was not desirable. From both synthetic and industrial points of view, it is very attractive that cyclohexane can be used as the starting material for the production of ε-caprolactam*via* one-step process. Up to now, only Japan Toray Ltd have developed PNC (Photonitrosation of cyclohexane) process in which cyclohexane was reacted with nitrosyl chloride with the aid of UV radiation in the presence of hydrogen chloride to give cyclohexanone oxime hydrochloride [12] (see *Route 3*). This photochemical synthesis is most effective with regards to the material costs compared to important thermochemical processes, and the overall selectivity to caprolactam is higher than the selectivity of the classical routes. However, the formation of NOCl is very problematic and environmentally not benign. Also chlorinated compounds are formed in this process, which have to be taken rid off. Therefore, the development of a new system for the nitrosation or oximation of cyclohexane to overcome these drawbacks is highly desirable.



Scheme 1 The routes currently used for the manufacture of ε-caprolactam

Recently, in development of such one-step process, we found that VPO composites could efficiently catalyze the reaction of cyclohexane with nitrosyl sulfuric acid to obtain ε-caprolactam directly in the presence of fuming sulfuric acid [13] (see Scheme 2). Herein, we will report the remarkable results obtained from the one-step catalytic process.



Scheme 2 The liquid phase nitrosation reaction of cyclohexane and nitrosyl sulfuric acid

2 Experimental

2.1 Reagents and Instrument

Cyclohexane (AR) and other reagents were used as purchased. Nitrosyl sulfuric acid (73.54%) was purchased from chemical reagent factory of Shijiazhuang. The oleum (50%–53%) was purchased from chemical reagent factory of Shanghai. Gas chromatography was performed on Agilent 6890 equipped with an DB-5 (30 m × 0.25 mm × 0.25 μm) column and liquid chromatograph was performed on Agilent 1100 with an Eclipse XDB-C18 (4.6 × 250 mm) column; Mass spectra were run on an America Varian Saturn 2100T GC-MS spectrometer and a Surveyor liquid chromatography coupled with a TSQ Quantum Discovery Max triple quadruple mass spectrometry (Thermo Electron Corporation, USA). The XRD patterns of various VPO composite catalysts were recorded with Japan Rigaku D/Max 2550 VB^{+} 18 kw X-ray diffractometer, using nickel-filtered Cu K_{α} radiation with a scanning rate of 1°min^{-1}

2.2 Preparation of Composite Catalysts

A series of VPO composite catalysts were prepared according to the following procedure. Firstly, 0.025 mol of $Cr(Ac)_3(Mn(Ac)_2 \cdot 4H_2O$, $Fe(NO_3)_3$, $Co(Ac)_2 \cdot 4H_2O$, $Ni(Ac)_2 \cdot 4H_2O$ or $Cu(Ac)_2)$, 0.0125 mol of γ-Al_2O_3 and 0.0125 mol of V_2O_5 were added into flask, followed by dropwise addition of 85% H_3PO_4 (M:Al:V:P (molar ratio) = 1:1:1:7). The obtained mixture was heated at 100 °C for 12 h. After cooling to room temperature, the mixture was filtered under reduced pressure and calcined in dry air at 600 °C for 5 h (heating rate 75 °C h^{-1}).

2.3 Typical Experimental Procedure

The catalytic reaction was carried out in a glass reactor under atmospheric pressure over the catalysts. A mixture of cyclohexane, nitrosyl sulfuric acid and catalyst was stirred at 354 K for 24 h in the presence of 50–53% fuming sulfuric acid. After cooling to room temperature, the inorganic phase is dissolved by water in ice-water bath and successively treated with $Ba(OH)_2$ to neutralize H_2SO_4. The pH value of solution was adjusted to 7–8. The final product was analyzed using an Agilent-1100 liquid chromatograph with 10:90 of $CH_3OH:H_2O$ as eluant and detected at wavelength of 210 nm. The identification of products was done by GC-MS and LC-MS.

3 Results and Discussion

3.1 The Characterization of Composite Catalysts

All XRD patterns of VPO composite catalysts were shown in Fig. 1. The sole VPO catalyst shows high intensity peaks at 2θ values of 23.1°, 28.4° and 29.9°, characteristic of the $(VO)_2P_2O_7$ phase, and also low intensity peaks at 2θ values

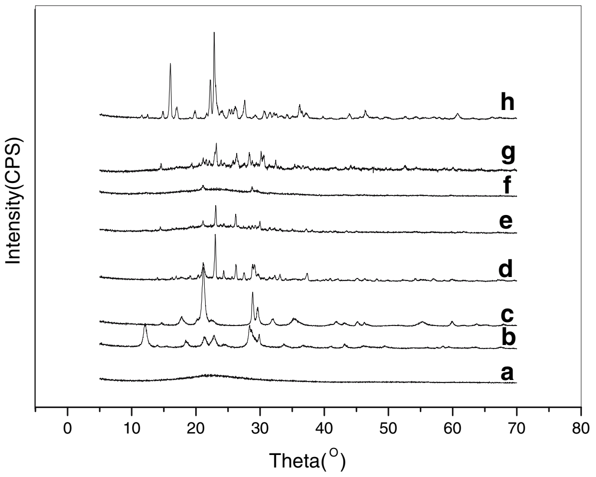


Fig. 1 XRD patterns of various VPO composite catalysts: (**a**) stands for Fe–Al-VPO, (**b**) stands for VPO, (**c**) stands for Co–Al-VPO, (**d**) stands for Mn–Al-VPO, (**e**) stands for Ni–Al-VPO, (**f**) stands for Cr–Al-VPO, (**g**) stands for Cu–Al-VPO and (**h**) stands for Al-VPO

of 22.0°, 26.0°, and 28.9°, characteristic of the $VOPO_4$ phase. This shows that the vanadium in the sole VPO catalyst sample is predominantly in the V^{4+} state with a small amount of V^{5+} species. In VPO composite catalyst combined aluminum, the high intensity peaks at 2θ values of 21.2°, which is the characteristic of the aluminum phosphate ($AlPO_4$) phase was observed. Except for the Fe–Al–VPO catalyst with noncrystal structure, the XRD patterns of the other composite catalysts combined transition metals show not only the presence of characteristic peaks of Al–VPO, but also the presence of their respective phosphates and oxides species. These results indicate that the VPO composite catalyst presented here consist of various crystal phases.

3.2 The Liquid Phase Nitrosation Reaction of Cyclohexane Catalyzed by Composite Catalysts

Table 1 summarizes representative results for the nitrosation reaction of cyclohexane over the catalysts. Cyclohexane was mainly converted to benzene sulfonic acid, and ε-caprolactam was not obtained in the absence of any catalysts, which indicates that the catalyst plays an extraordinarily important role in the formation of ε-caprolactam. In this catalytic system, the catalytic performances of the present catalysts were different. ε-Caprolactam could be formed from the nitrosation reaction of cyclohexane catalyzed by sole VPO catalyst, however, the selectivity to ε-caprolactam was only 3.14%. The selectivity to ε-caprolactam was slightly improved when the aluminum introduced to VPO composite catalyst. Especially, the Al–VPO catalysts combined transition metals could further improve the reactions selectivity to some extent. Among these composite catalysts, the Mn–Al–VPO composite catalyst gave the best results. Under our conditions, a conversion of 11.65% with the selectivity of 34.70% to ε-caprolactam was observed. These illustrate that the transition metals introduced to VPO composite catalysts play a critical role in the conversion of cyclohexane and the selectivity of ε-caprolactam. In addition, cyclohexylnitrite, nitroso cyclohexene, dimmer of nitroso cyclohexane and an extremely small quantity of oligomers of ε-caprolactam were also observed in this catalytic

Table 1 Effect of various composite catalysts on the nitrosation reaction of cyclohexane

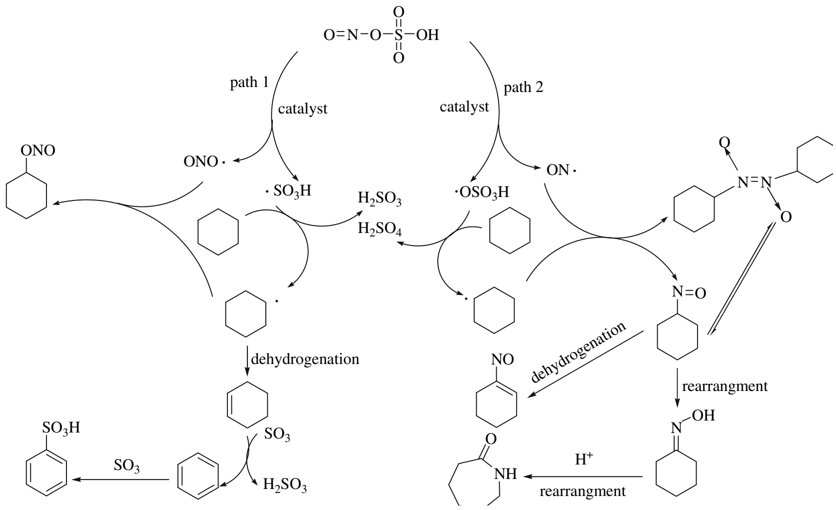
Entry	Catalyst	Conversion (%)	Selectivity (%)		
			ε-caprolactam	Benzene sulfonic acid	Other
1	None	9.56	0	95.42	4.58
2	VPO	14.95	3.14	46.51	50.35
3	Al-VPO	16.45	7.78	59.02	33.20
4	Cr–Al-VPO	17.01	11.90	41.88	46.22
5	Mn–Al-VPO	11.65	34.70	54.53	10.77
6	Fe–Al-VPO	17.99	15.80	49.87	34.33
7	Co–Al-VPO	25.75	19.17	47.66	33.17
8	Ni–Al-VPO	12.63	22.30	31.10	46.60
9	Cu–Al-VPO	33.01	9.80	45.99	44.21

Note: Reaction conditions: C_6H_{12}: $NOHSO_4$: Oleum = 5:1:1 (molar ratio); Reaction temperature: 354 K; Reaction time: 24 h; Catalyst mass: 0.5 g; Cyclohexane mass: 10 g

$$\text{Conversion}(\%) = \frac{[\text{the amount (mol) of starting cyclohexane}] - [\text{the amount (mol) of cyclohexane recovered}]}{\text{the amount (mol) of nitrosyl sulfuric acid}} \times 100\%$$

$$\text{Selectivity}(\%) = \frac{\text{the amount (mol) of caprolactam}}{[\text{the amount (mol) of starting cyclohexane}] - [\text{the amount (mol) of cyclohexane recovered}]} \times 100\%$$

Scheme 3 The possible reaction mechanism of liquid phase nitrosation of cyclohexane



reaction. However, the selectivity to benzene sulfonic acid formed by the O–S bond cleavage was relatively higher than ε-caprolactam formed by the N–O bond cleavage, which illustrates that the rate of the O–S bond cleavage was faster than the N–O bond cleavage. The relative amount of benzene sulfonic acid just reflects the amount of O–S bond cleavage versus N–O bond cleavage (see Table 1). The results of the catalytic test show that the VPO composite catalysts could alter efficiently the relative rate of the O–S bond cleavage and the N–O bond cleavage.

3.3 Proposed Possible Reaction Mechanism of Liquid-phase Nitrosation of Cyclohexane

On the basis of these results in this work, the possible reaction mechanism of liquid-phase nitrosation of cyclohexane with nitrosyl sulfuric acid over the VPO catalysts was proposed (see Scheme 3). The nitrosyl sulfuric acid could be decomposed by following two paths. In the first path, nitrosyl sulfuric acid could be decomposed to $ONO^\cdot$ and $HO_3S^\cdot$ free radical *via* the O–S bond cleavage. The formed $HO_3S^\cdot$ free radical would react with cyclohexane, giving cyclohexyl radical and sulfurous acid. In such way, cyclohexyl radical either reacts with $ONO^\cdot$ free radical forming cyclohexylnitrite ($C_6H_{11}ONO$), or is dehydrogenated to cyclohexene with the formation of sulfurous acid (H_2SO_3) and nitrous acid (HNO_2) with the aid of $ONO^\cdot$ and $HO_3S^\cdot$ free radical. The resulting cyclohexene in fuming sulfuric acid is further dehydrogenated to benzene with the formation of H_2SO_3, and, finally, the benzene is sulfonated by SO_3 to benzene sulfonic acid. In the second path, nitrosyl sulfuric acid could be decomposed to $NO^\cdot$ and $HO_3SO^\cdot$ free radical *via* the N–O bond cleavage. The formed $HO_3SO^\cdot$ free radical reacts with cyclohexane giving sulfur acid and cyclohexyl radical. Then the obtained cyclohexyl radical reacts with nitroso radical ($NO^\cdot$) forming nitroso cyclohexane ($C_6H_{11}NO$) as an important intermediate, which is easy to isomerize to cyclohexanone oxime, followed by Beckmann rearrangement to afford ε-caprolactam. It should be noted that, under the conditions of the reaction, the intermediate, nitroso cyclohexane, is easily dehydrogenated by SO_3 to nitroso cyclohexene or itself polymerized to dimmer.

4 Conclusion

A novel approach for one-step formation of ε-caprolactam from cyclohexane has been for the first time developed. A series of VPO composites were successfully prepared and employed to catalyze the reaction of cyclohexane with nitrosyl sulfuric acid to afford ε-caprolactam in the presence of fuming sulfuric acid. VPO composite catalysts were proven to be efficient for such reaction. Especially, the transition metals introduced to Al-VPO composite catalysts could improve the reactions selectivity to some extent. In addition, the reaction mechanism had been proposed and further studies for the optimization of the reaction conditions are now in progress. In summary, assuming that better catalysts can be developed, the method provides a novel strategy for the synthesis of caprolactam.

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References

1. Wassen WJ, Geottsch R (1978) US Patent 4, 081 442
2. Brand U, Schmitz R, Deuker E, Fuchs H (1989) US Patent 4, 806 638
3. Chaudhari K, Rajaram B, Chandwadkar AJ, Sivasanker S (2002) J Mol Catal A: Chemical 177:247

4. Ishida M, Suzuki T, Ichihashi H, Shiga A (2003) Catal Today 87:187
5. Zhang YJ, Wang YQ, Bu YF, Mi ZT, Wu W, Min EZ, Han S, Fu SB (2005). Catal Commun 6:53
6. Heitmann GP, Dahlhoff G, Niederer JP, Hoelderich WF (2000) J Catal 194:122
7. Heitmann GP, Dahlhoff G, Hoelderich WF (1999) J Catal 186:12
8. Wu CT, Wang YQ, Mi ZT, Xue L, Wu W, Min EZ, Han S, He F, Fu SB (2002) Catal Letts 77:73
9. Liu TF, Meng XK, Wang YQ, Liang XH, Mi ZT, Qi XJ, Li SY, Wu W, Min EZ, Fu SB (2004) Indian Eng Chem Res 43:166
10. Tanabe K, Holderich WF (1999). Appl Catal A: General 181:399
11. Thomas JM, Raja R (2001) Chem Commun 36:675
12. Ritz J, Fuchs H, Kieczka H, Moran WC (1986) Ullman's Encyclopedia of Industrial Chemistry A5:31
13. Luo HA, Mao LQ, Yin DL, You KY , Kuang YJ, LiuPL (2006) CN patent 10031284.6