

RESEARCH PROGRESS OF CAPROLACTAM INTERMEDIATE HYDROXYLAMINE PRODUCTION METHODS

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Abstract

This paper mainly discusses the production process of hydroxylamine, a caprolactam intermediate, including three traditional processes, namely, Rasching synthesis, nitric oxide-catalyzed reduction, and hydroxylamine phosphate, as well as the modern green process of hydroxylamine production by H_2O_2 -catalyzed oxidation, and hydroxylamine hydrolysis from cyclohexanone oxime. This work compares the advantages and disadvantages of the three traditional hydroxylamines and provides design ideas for the modern green chemical production of hydroxylamines, with a special focus on the one-step ammonia oxidation process based on H_2O_2 -catalyzed oxidation by Fujian Eversun Technology Co., Ltd. This work provides an important reference for the subsequent engineers of the production of hydroxylamine and caprolactam green transformation process transformation.

Keywords: hydroxylamine; green process; Rasching synthesis method; H_2O_2 catalytic oxidation method

1 INTRODUCTION

Hydroxylamine, also known as hydroxylamine is a colorless, odorless, easily deliquescent crystals. The main hydroxylamine salts are hydroxylamine sulfate, hydroxylamine hydrochloride, hydroxylamine phosphate and so on. Industrial preparation of large quantities of hydroxylamine salts are Rasching method, nitric oxide method and hydroxylamine phosphate method for the preparation of solid hydroxylamine is synthesized in 3 steps. Hydroxylamine sulfate aqueous solution is acidic. 50% aqueous solution at $40\text{ }^\circ\text{C}$ below does not decompose. The solubility of hydroxylamine sulfate in water increases with increasing temperature: 30.7% at $-8\text{ }^\circ\text{C}$, 32.9% at $0\text{ }^\circ\text{C}$, 41.3% at $20\text{ }^\circ\text{C}$.^[1] Hydroxylamine hydrochloride can be used as a reducing agent and developer for color film in organic synthesis for the synthesis of oximes and anticancer drugs and sulfonamides. It is used as a short-term suspending agent without coloring in the synthetic rubber industry. Can also be used as an analytical reagent for aldehydes and ketones in the test of organic compounds and sulfonic acid microanalysis of electroanalysis as a depolarizing agent. Hydroxylamine sulfate is also used as rubber vulcanizing agent, which is an important raw material for the synthesis of caprolactam, and also an intermediate of medicine and pesticide for the production of a series of isoxazole derivatives, sulfonamide drugs and vitamin B6, B12. In addition, hydroxylamine derivatives can be used in the production of pesticides, insecticides, fungicides, and herbicides, and also used in the polymer synthesis of raw materials and compounds for the refining of the collection of catalysts and reagents, etc..^[2-5] The molecular formula of hydroxylamine (NH_2OH , CAS

7803-49-8) and hydroxylamine sulfate ($(\text{NH}_2\text{OH})_2\text{SO}_4$, CAS 10039-54-0) are shown in Figure 1, and hydroxylamine sulfate is the sulfate of hydroxylamine.

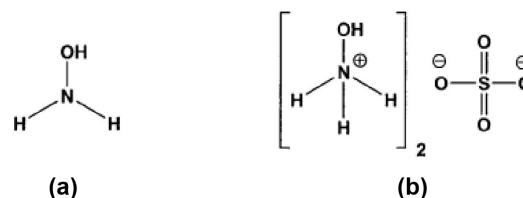


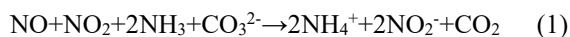
Figure 1. Molecular formulae of (a) hydroxylamine and (b) hydroxylamine sulfate

2 TRADITIONAL PROCESS OF HYDROXYLAMINE INDUSTRIAL PRODUCTION

2.1 Rasching synthesis method

Rasching synthesis method^[6] is the oldest method to produce hydroxylamine sulfate, and it is also the earliest industrialized production process of hydroxylamine salt. Since Germany and the United States in 1908 and 1911, respectively, the use of Rasching method for the production of hydroxylamine sulfate, the method has become the world's most important industrial production of hydroxylamine salts.^[7] Almost all of the domestic lactam manufacturers built in the early years have adopted the Rasching synthesis method to produce hydroxylamine sulfate. Typical Rasching production method, the first NH_3 by air-catalyzed hydrogenation of NO and NO_2 mixture, and then $(\text{NH}_4)_2\text{CO}_3$ solution to absorb, generating ammonium nitrite NH_4NO_2 , and then reduced with sulfur dioxide SO_2 , generating hydroxylamine disulfate, hydrolyzed under acidic

conditions to hydroxylamine sulfate hydroxylamine sulfate solution. The reaction principle is as follows:



The final product of hydroxylamine salt synthesized by the Raschig method is an aqueous solution containing NH_3OH^+ , NH_4^+ and H^+ as shown in equation (1) (3), which is called "Raschig solution". Typical Raschig solution contains 12% of hydroxylamine sulfate, 25% of ammonium sulfate and about 8% of sulfuric acid, the consumption cost of Raschig solution as a raw material of hydroxylamine salt is only 5000 RMB/ton (100% of hydroxylamine sulfate), but because of the large amount of inorganic salts and free sulfuric acid contained in it, this aqueous solution cannot be directly used in other industries. It can be said that the by-production of ammonium sulfate is too much (each ton of caprolactam by-production of ammonium sulfate is about 4.5 tons), is the biggest disadvantage of the Raschig method is that the method of hydroxylamine sulfate produced by the further expansion of the application of Raschig liquid as a low-grade hydroxylamine salt can only be used in special applications, such as the synthesis of lactam, acetaldehyde oxime and other processes.

2.2 Nitric oxide catalytic reduction method

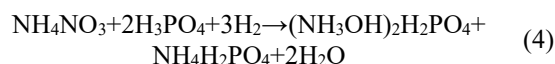
The method first NH_3 , in the Pt catalyst, high temperature conditions, through the air/ O_2 to generate NO, and the use of a sufficient amount of water diluted to below the explosion limit. Then in a dilute aqueous solution of inorganic acid (dilute sulfuric acid), with a special carrier loaded Pt catalyst suspended in the solution, at a higher temperature to NO catalytic hydrogenation, so as to produce hydroxylamine sulfate.

The hydroxylamine from the catalytic reduction method is of high purity and the by-products of the process are small amounts of ammonium sulfate and nitrous oxide (N_2O). Subsequent improvements to the process reduce production costs by incinerating the remaining combustible gases and generating steam for recycling. The process involves the use of specific precious metal catalysts at very high temperatures, making the actual production process more complex. The preparation of the catalyst is inherently cumbersome, and there is periodic replacement and regeneration of the catalyst, which further complicates the operation and increases operating costs. In addition, the presence of hazardous H_2 and N_2O gases in the process also puts the safety of large-scale production at risk^[8,9].

2.3 Hydroxylamine phosphate method

The method was originally proposed by the U.S. Spencer Chemical Company in 1953, the use of Pd/C catalyst with H_2 reduction of HNO_3 preparation of hydroxylamine salt. The reaction is carried out in a strong acid medium, the catalyst stability is poor, easy to dissolve resulting in deactivation, need to be protected by hydrogen, but hydrogen interruption of the supply of hydroxylamine decomposition caused by the inability of

industrial production. Later, the process was improved by the Dutch DSM company, using phosphoric acid and ammonium bisulfate to form a stable pH buffer system, nitrate ions can be provided by ammonium nitrate or alkali metal nitrate. The reaction formula is:



This process is suitable for application in the production of already lactam, called HPO method. The method was adopted in the nylon 6 production line introduced in China in the 1990s, such as the domestic manufacturers of Baling Petrochemical and Nanjing Dongfang. The biggest feature of this process is that there is no by-product ammonium sulfate, and the phosphate-containing mother liquor produced after the reaction can be recycled. The yield of hydroxylamine can reach 80%, the selectivity of cyclohexanone oximization is as high as 100%, and the conversion rate is 98%.

2.4 Traditional methods strengths and weaknesses

Raschig synthesis method as the oldest method to produce hydroxylamine sulfate is still used by many manufacturers, the advantages of this method are high process yield, low raw material and production cost, no catalyst contamination and deactivation problems, and simple industrial control. Moreover, the method directly obtains hydroxylamine sulfate with stable product properties. The disadvantages are that it produces a low-value by-product, ammonium sulfate, which is a low-value fertilizer with limited applications. In addition, the "Raschig liquid" product, hydroxylamine sulfate, is not easy to separate. Nitric oxide catalytic reduction method has the advantage of obtaining relatively pure hydroxylamine sulfate, but the disadvantage is that the NO reduction method uses platinum, rhodium and palladium and other precious metals as catalysts, the recycling of catalysts is a difficult problem to be solved, and also produces ammonium sulfate by-products. The advantage of the hydroxylamine phosphate method is that it does not produce ammonium sulfate by-products, but due to its poor production stability, more factors affecting the operation of the difficult to the specifications of raw materials and the control of the operating conditions are very strict, a small part of the improper handling will cause production problems. Due to the poor stability of hydroxylamine phosphate, the hydroxylamine phosphate produced by this method is only suitable for on-site use in specific lactam processes.

3 HYDROXYLAMINE GREEN PROCESS RENOVATION PROGRESS

3.1 H_2O_2 catalytic oxidation method

H_2O_2 plays an increasingly important role in the development of green chemistry, but the existing industrial anthraquinone preparation method is not "green" enough: it has significant drawbacks such as complexity of the process, high investment costs, potential environmental pollution by organic solvents,

use of large amounts of precious metal catalysts, high storage/transportation costs, and the need for additional dilution when used. This method has significant disadvantages such as complexity of the process, high investment costs, the use of large amounts of precious metal catalysts, high storage/transport costs and the need for additional dilution. If the in situ method can be used to generate H_2O_2 directly to complete the catalytic ammonia oxidation and other reactions, it can greatly save the energy consumption and equipment investment, which not only makes the whole process more economical and green, but also has great significance for the development of the new green chemical industry and chemical synthesis. The team from Cardiff Catalysis Centre of Cardiff University and Shanghai Jiaotong University used AuPd alloy and titanium-silicon molecular sieve (TS-1) as bifunctional catalysts.^[10] By optimizing the metal ratio and loading, AuPd alloy can effectively generate H_2O_2 under heating and weakly alkaline environment, while TS-1 can effectively utilize in-situ generated H_2O_2 to complete ammonia oxidation reaction. Single-component Au has no catalytic activity for this reaction, single-component Pd shows some conversion but relatively low selectivity, and simple physically-mixed catalysts have no catalytic activity, but once AuPd alloys are formed, the reaction activity is greatly enhanced. The AuPd-loaded alloy has excellent catalytic activity for the generation of H_2O_2 from H_2/O_2 but no catalytic ability for ammonia oxidation, whereas TS-1 is able to catalyze the generation of cyclohexanone oxime when a commercial H_2O_2 solution is used as the oxidant, but with poor selectivity. The simple physical mixing of the two catalysts yielded excellent catalytic performance, which demonstrated that in situ generation of H_2O_2 can be utilized to efficiently and conveniently accomplish the catalytic preparation of this important polymer monomer. The reaction process is shown in Figure 2:

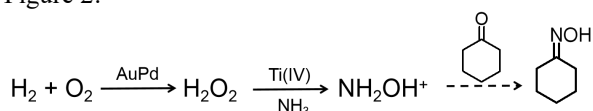


Figure 2. H_2O_2 -catalyzed oxidative synthesis of hydroxylamine reaction process

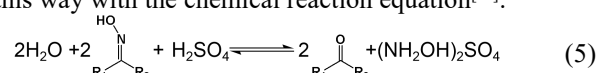
Fujian Eversun Technology Co., Ltd. developed a one-step ammonia oximization process based on H_2O_2 catalytic oxidation based on this process. The process includes an ammonia oximization unit, a membrane separation unit, a catalyst unloading unit, a solvent recovery unit, a toluene extraction unit, a toluene/oxime fractionation unit, a toluene separation unit, and a wastewater treatment unit. The process achieves >99.6% conversion of cyclohexanone and >99.5% selectivity of cyclohexanone oxime under optimized conditions.



Figure 3. Ammonia oxime chemical section of Fujian Eversun Technology Co., Ltd.

3.2 Hydroxylamine generation by oxime hydrolysis of cyclohexanone

With the chemical industry's increased awareness of production safety, product quality and environmental protection, the disadvantages of the traditional production process have become more and more obvious, oxime hydrolysis has received the attention of researchers in recent years. Semon reported the first detailed hydrolysis of acetone oxime to prepare hydrochloric acid. Of course, if caprolactam is to be synthesized, there is no need to prepare hydroxylamine when cyclohexanone oxime has already been obtained. If the final product is hydroxylamine it can be produced in this way with the chemical reaction equation^[11]:



Ketoxime hydrolysis is a typical thermodynamically limited reaction, its equilibrium conversion is generally only 10% to 20%, if you need to improve its hydrolysis conversion, a need to be coupled through the reaction-separation and reaction-crystallization technology to enhance the process, remove the resulting ketone and hydroxylamine sulfate, breaking the thermodynamic equilibrium limitations, increase the reaction conversion, but also by electrolysis, the process can be enhanced. The hydrolysis reaction can also be facilitated by electrochemical methods.

3.2.1 Reaction-separation and reaction-crystallization coupling technologies

Reaction-separation coupling enhanced technology mainly includes ion exchange, reaction-extraction, reaction-distillation, reaction-distillation, reaction-absorption, reaction-degradation, reaction-membrane separation, reaction-crystallization, and reaction-crystallization. reaction-crystallization, reaction-membrane separation and other coupling enhancement methods^[12]; Lin and Xu Shuqun et al. ^[13,14] prepared hydroxylamine salts using reaction-distillation coupling methods, but the sulfuric acid concentration used was low, and a large amount of water enrichment directly led to an increase in distillation energy consumption and wastewater discharge. In order to further reduce the energy consumption and wastewater discharge in the production of hydroxylamine sulfate, Du et al.^[15] addressed the problem of large water content in the reaction solution in the preparation of hydroxylamine salts by oxime hydrolysis. In this paper, by calculating the theoretical residual water and the mass of hydroxylamine sulfate generated by ketoxime hydrolysis under different sulfuric acid concentrations under a certain conversion rate, and combining with the results of the determination of the solubility of hydroxylamine sulfate in water at atmospheric pressure, we proposed to combine the reaction-distillation and reaction-crystallization coupling methods. The coupling of two reaction separation techniques, distillation and reaction-crystallization, was proposed for the preparation of hydroxylamine sulfate from ketoxime hydrolysis to

improve the reaction conversion rate by continuous in situ displacement of hydroxylamine sulfate and ketone as by-products, and to avoid the impact of the reaction solution on mass and heat transfer due to the high viscosity, to prevent the localization of overheating, to avoid the occurrence of side reactions, and to realize the preparation of hydroxylamine sulfate under the reaction system with a high concentration of sulfuric acid. Sulfuric acid reaction system to prepare hydroxylamine sulfate. The process flow diagram is shown in Figure 4.

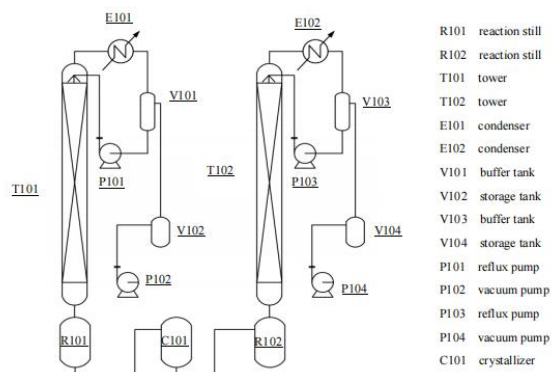


Figure 4. Reaction-distillation and reaction-crystallization coupling process schematic diagram.

The coupling of reaction-distillation and reaction-crystallization for the preparation of hydroxylamine sulfate from ketoxime hydrolysis can realize the preparation of hydroxylamine sulfate under high concentration sulfuric acid reaction system (initial addition of sulfuric acid concentration of 40%~60% (wt)), and avoid the reaction liquefaction of hydroxylamine sulfate, which can be prepared under high concentration sulfuric acid reaction system. At the same time, it can avoid the reaction liquid affecting mass and heat transfer due to high viscosity, preventing local overheating, avoiding the occurrence of side reactions, and improving the stability of the product; the process of initial addition of sulfuric acid with high concentration can avoid a large amount of water surplus leading to the increase in energy consumption of distillation and the subsequent purification of by-products, and effectively reduce the oxime hydrolysis to prepare hydroxyl amine sulfate process energy and wastewater discharge.

3.2.2 Coupled electro dialysis and oxime hydrolysis processes

NH_2OH can be regarded as the substitution of a hydrogen atom in H_2O by a highly electronegative group ($-\text{NH}_2$) or the substitution of a hydrogen atom in NH_3 by a strong electron absorbing group ($-\text{OH}$). As a result, NH_3OH^+ is formed even in aqueous solutions, especially in acid solutions. In addition, the ionic radius of NH_3OH^+ is similar to that of sodium ions. This means that NH_3OH^+ can penetrate ion exchange membranes as easily as sodium ions. In the external electric field of hydroxylamine sulfate, NH_3OH^+ and SO_4^{2-} migrate through the cation exchange membrane and anion exchange membrane to the cathode region and anode region, respectively. On the contrary, neutral butanone

and oxime do not migrate under the electric field or are intercepted by the ion exchange membrane, thus the product hydroxylamine sulfate is separated from the reaction zone to enhance the conversion of oxime hydrolysis^[16].

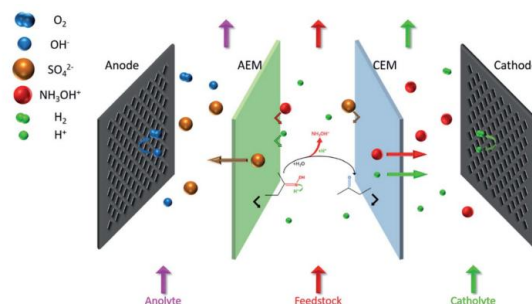


Figure 5. Electro dialysis coupled with oxime hydrolysis process schematic diagram.

Yu Rujun team of Shandong University of Science and Technology obtained the following conclusions through the small pilot plant test: the oxime hydrolysis decomposition voltage is higher than 1.93 V, at this time, the current density is $4.69 \times 10^2 \text{ A/cm}^2$, when the oxime concentration is 1.00 mol-L⁻¹, when the reaction time reaches 600 minutes, the yield of hydroxylamine sulfate is 67.59%. In addition, compared with the traditional method, this process has excellent mass transfer performance, mild reaction conditions and simple operation.

4. CONCLUSIONS AND RECOMMENDATIONS

Hydroxylamine is an important intermediate for the production of caprolactam, and it can also be used as a high-value product in the field of medicine and pesticide alone. The traditional methods for the production of hydroxylamine are mainly Rasching synthesis, nitric oxide catalytic reduction method and hydroxylamine phosphate method. Among the traditional methods, Rasching synthesis and nitric oxide catalytic reduction method are stable, but they produce a large number of low-value by-products of ammonium sulfate, and at the same time, they use H_2SO_4 reactants that do not meet the requirements of modern green chemistry. The modern green chemical synthesis of hydroxylamine mainly uses: H_2O_2 catalyzed oxidation of ammonia to prepare hydroxylamine and hydroxylamine through oxime hydrolysis. Fujian Eversun Technology Co., Ltd. developed a one-step ammonia oximization process based on H_2O_2 catalytic oxidation. The process includes an ammonia oximization unit, a membrane separation unit, a catalyst unloading unit, a solvent recovery unit, a toluene extraction unit, a toluene/oxime fractionation unit, a toluene separation unit, and an effluent treatment unit. The process was optimized to achieve a cyclohexanone conversion of >99.6% and a cyclohexanone oxime selectivity of >99.5%. For the preparation of hydroxylamine from oxime hydrolysis it is necessary to separate the product hydroxylamine by technical means in order to improve the conversion rate

of oxime hydrolysis. At present, there are mainly reaction-distillation and reaction-crystallization coupling process and electro dialysis and oxime hydrolysis coupling process, both achieved high hydroxylamine conversion.

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REFERENCES

- [1] Soler-Jofra A, Pérez J, van Loosdrecht M C M. Hydroxylamine and the nitrogen cycle: A review[J]. *Water Research*, 2021, 190(15): 116723.
- [2] Sharghi H, Sarvari M H. One-Step Beckmann Rearrangement from Carbonyl Compounds and Hydroxylamine Hydrochloride in Al_2O_3/CH_3SO_3H (AMA) as a New Reagent[J]. *Journal of Chemical Research*, 2001, 10: 446-449.
- [3] Zsolt S, Rita S F, Laszlo K, Zoltan B, Judit H, Zoltan T. Highly Efficient Synthesis of Steroidal Hydroxamic Acid Derivatives via Homogeneous Catalytic Carbonylation Reaction [J]. *Tetrahedron*, 2000, 56: 5253-5257.
- [4] Yasaki Gi, Xu Y.P, King S. B. An Efficient Synthesis of N-Hydroxyurea[J]. *Synthetic Communications*, 2000, 30: 2041-2047.
- [5] Takhi M., Murugan C., Munikumar M., Bhaskarreddy K. M, Singh G, Sreenivas K., Sitaramkumar M. Synthesis and Antibacterial Activity of Novel Oxazolidinones Bearing N-Hydroxyacetamide Substituent[J]. *Bioorganic & Medicinal Chemistry Letters*, 2006, 16(9): 2391-2395..
- [6] Raschig F. Process for the Manufacture of Alkali Earth Salts of Hydroxylamine Sulfonic Acid [P]. United State Patent, US 1010177, 1911.
- [7] Ritz J, Fuchs H., Perryman H.G. Hydroxylamine. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.[M]. Wiley: Chichester, 2000.
- [8] Paseka I. Hydrogenation of Nitric Oxide on Platinum Black in Acidic Solution [J]. *Reaction Kinetics and Catalysis Letters*, 1979, 11(1), 85-89.
- [9] Paseka I. Mechanism of Hydrogenation of Nitric Oxide on Platinum Catalysts in Acidic Solution [J]. *Reaction Kinetics and Catalysis Letters*, 1979, 11, 91-95.
- [10] Lewis R J, Ueura K, Liu X, Fukuta Y, Davies T E, Morgan D J, Chen L, Qi J, Singleton J, Edwards J K, Freakley S J, Kiely C J, Yamamoto Y, Hutchings G J. Highly efficient catalytic production of oximes from ketones using in situ-generated H_2O_2 . [J]. *Science*. 2022 May 6; 376(6593): 615-620.
- [11] Kovarik Z, Radić Z, Berman HA, Taylor P. Mutation of acetylcholinesterase to enhance oxime-assisted catalytic turnover of methylphosphonates. [J]. *Toxicology*, 2007, 233(1-3): 79-84..
- [12] Peng C, Wang Y, Deng C, Zhao F, You K. Preparation of hydroxylamine sulfate by continuous reaction-extraction coupling technology[J]. *CIESC Journal*, 2019, 70(5): 1842-1847.
- [13] Lin Y, Tian Y, Luo. Preparation method of hydroxylamine salt: CN, 101497433 [P]. 2009-08-05.
- [14] Xu S. Preparation method of hydroxylamine salt: CN, 103159191A [P]. 2013-06-19..
- [15] Du X Y, Long B, Liu L, Zhang W. Study on Low Energy Preparation of Hydroxylamine Sulfate[J]. *Journal of Chemical Engineering of Chinese Universities*, 2018, 32(1): 155-160.
- [16] Guan F, Chen Y, Zhang Y, Yu R. A coupling process of electro dialysis with oxime hydrolysis reaction for preparation of hydroxylamine sulfate. *RSC Adv*. 2021, 11(31): 19238-19247.