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Green Production Technology of the Monomer of Nylon-6: Caprolactam

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ABSTRACT

After two decades' endeavor, the Research Institute of Petroleum Processing (RIPP) has successfully developed a green caprolactam (CPL) production technology. This technology is based on the integration of titanium silicate (TS)-1 zeolite with the slurry-bed reactor for the ammoximation of cyclohexanone, the integration of silicalite-1 zeolite with the moving-bed reactor for the gas-phase rearrangement of cyclohexanone oxime, and the integration of an amorphous nickel (Ni) catalyst with the magnetically stabilized bed reactor for the purification of caprolactam. The world's first industrial plant based on this green CPL production technology has been built and possesses a capacity of 200 kt·a^{-1}. Compared with existing technologies, the plant investment is pronouncedly reduced, and the nitrogen (N) atom utilization is drastically improved. The waste emission is reduced significantly; for example, no ammonium sulfate byproduct is produced. As a result, the price difference between CPL and benzene drops. In 2015, the capacity of the green CPL production technology reached 3×10^6 t·a^{-1}, making China the world's largest CPL producer, with a global market share exceeding 50%.

1. Introduction

In the future, sustainable development of the chemical industry must be built on a foundation of green chemistry and green engineering, and the general concept must change from one of polluting first and treating later, to one of eliminating pollution at the source. The criteria of green chemistry are: to achieve overall atom economy of a reaction—that is, every atom of the source materials enters into the product, thus producing no waste or byproducts—and to avoid the use of toxic or harmful raw materials, catalysts, or solvents. In brief, the target of green chemistry is to produce chemicals in a clean manner that does not pollute the environment at any point in the entire life cycle.

Caprolactam (CPL), as the monomer for nylon-6 fiber and engineering plastics, is an important basic organic chemical that is widely used in textile, automobile, electronics, and other industries. In 2015, CPL consumption amounted to about 3×10^6 t in China and about 6×10^6 t around the world [1]. Two decades ago, CPL consumption in China relied almost completely on importation; therefore, China Petrochemical Corporation (Sinopec) invested 9 billion CNY to introduce three CPL production plants with a total capacity of 150 kt·a^{-1}. However, commercial CPL production technology has disadvantages such as low production capacity, high investment and production cost, and high waste emission, which are far from the criteria of green chemistry; thus, CPL production demands process improvement. This review outlines the green CPL production technology that was developed by the Research Institute of Petroleum Processing (RIPP) in recent years.

2. Existing CPL production technology

Of all the basic organic chemicals, CPL has the most complex production process, and the purity standard of its product is the most stringent. The existing CPL production technology was developed in the 1980s; it mainly consists of the hydrogenation of benzene to cyclohexane, the oxidation of cyclohexane to cyclohexanone, the

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oximation of cyclohexanone by hydroxylamine to cyclohexanone oxime, the liquid-phase Beckmann rearrangement of cyclohexanone oxime to CPL, and a multi-step purification process. The first key technology in this production is the oximation of cyclohexanone by hydroxylamine to cyclohexanone oxime (Table 1), which involves the oxidation of ammonia to NO_x, the absorption and reduction of NO_x to hydroxylamine, and the reaction of hydroxylamine and cyclohexanone to produce cyclohexanone oxime. This process has the shortcomings of high consumption of the noble metal catalyst, use of the highly toxic NO_x, and only 60% utilization of ammonia. The second key technology is the liquid-phase Beckmann rearrangement of cyclohexanone oxime to CPL (Table 1). In this process, fuming sulfuric acid is used as the solvent and the catalyst, resulting in the production of a large amount of low-value ammonium sulfate. The third key technology is the CPL purification process, which involves hydrogenation, distillation, and ion-exchange steps to reduce the impurity content to less than 5 $\mu g \cdot g^{-1}$. Thus, in addition to its complexity, the existing CPL production technology has harsh reaction conditions involving corrosive and highly toxic NO_x and SO_x, and its utilization of nitrogen (N) is only 60%. According to the statistical data of a 50 $kt \cdot a^{-1}$ CPL production plant using the existing technology, the production of one ton of CPL discharges 5000 m^3 of waste gas, 5 t of waste water, and 0.5 t of waste residue, in addition to producing 1.6 t of low-value ammonium sulfate. Therefore, there is a high demand for the development of a green CPL production technology.

3. The green CPL production technology

The green CPL production technology developed by RIPP comprises the integration of titanium silicate (TS)-1 zeolite with the slurry-bed reactor for the ammoximation of cyclohexanone, the integration of silicalite-1 zeolite with the moving-bed reactor for the gas-phase Beckmann rearrangement of cyclohexanone oxime, and the integration of amorphous nickel (Ni) catalyst with the magnetically stabilized bed reactor for the purification of CPL.

3.1. Integration of TS-1 zeolite with a slurry-bed reactor for the ammoximation of cyclohexanone

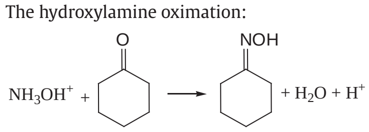
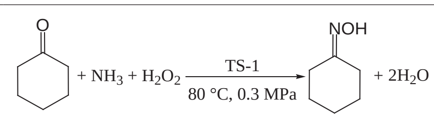
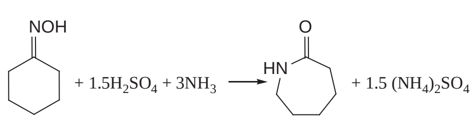
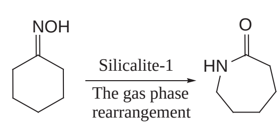
In the 1980s, EniChem Company developed TS-1 zeolite to catalyze the one-pot reaction of cyclohexanone, ammonia, and hydrogen peroxide to produce cyclohexanone oxime, as shown in Table 1, with an impressive selectivity. The advantages of this reaction are its highly simplified process, mild reaction conditions, and high atom economy, with water being the only byproduct. Subsequently, a 12 $kt \cdot a^{-1}$ industrial demonstration was accomplished in 1995. The technology employed spherical catalysts with a diameter of 20 μm and tanks-in-series slurry-bed reactors. The cyclohexanone conversion was no less than 99.9%, the cyclohexanone oxime selectivity was no less than 99.3%, and the hydrogen peroxide utilization was around 90%. Based on this technology, Sumitomo Chemical Co., Ltd. built a 65 $kt \cdot a^{-1}$ CPL production plant in 2003.

During the same period, RIPP developed a cyclohexanone ammoximation technology by integrating micro-sized hollow TS-1 zeolite with a slurry-bed reactor fitted with a membrane separation component. Fig. 1 provides a schematic diagram of the ammoximation of cyclohexanone based on this technology. RIPP began its investigation of this new technology in 1995 and achieved commercialization success in 2003.

To solve the problems of the poor preparation reproducibility of TS-1 zeolite and of its unstable activity and selectivity in the reaction, a state-of-the-art catalyst-preparation strategy was developed by combining hydrothermal synthesis with secondary structural modification, giving rise to the micro-sized hollow TS-1 zeolite [2]. A 100 $t \cdot a^{-1}$ production unit of the micro-sized hollow TS-1 zeolite was built at Sinopec Catalyst Co., Ltd. in 2002.

The cyclohexanone ammoximation technology developed by RIPP has two highlights. The first is the use of the micro-sized hollow TS-1 zeolite as the catalyst and the integration of a membrane separation component into the slurry-bed reactor. Directly synthesizing the micro-sized hollow TS-1 zeolite as the catalyst not only removes the need for the catalyst-forming process, but also enables a more effective utilization of the active centers. Moreover, with the aid of the membrane separation component, the micro-sized hollow TS-1 zeolite can be uninterruptedly separated and recycled. The second highlight is the improvement in controlling catalyst loss and in catalyst regeneration. It is known that silicon (Si) tends to dissolve from the TS-1 zeolite because the ammoximation of cyclohexanone is an alkalescent system. The loss of Si reduces the activity of the catalyst. The dissolved Si also blocks the separation membrane. Therefore, controlling the loss of Si is the key to the stable, safe, and long-term operation of the production plant. The new technology effectively suppresses the loss of Si based on a proprietary method and thus prolongs the lifetime of the catalyst. At the same time, it improves the catalyst renewability and reduces catalyst consump-

Table 1
The existing CPL production technology and the green CPL production technology.

Reaction process	Existing technology	Green technology
The oximation reaction	The oxidation of ammonia: $4NH_3 + 7O_2 \longrightarrow 4NO_2 + 6\,H_2O$ The reduction of NO_2 to hydroxylamine: $2NO_2 + 2H^+ + 5H_2 \longrightarrow 2NH_3OH^+ + 2H_2O$ The hydroxylamine oximation:  The decomposition of ammonium: $2NH_4^+ + NO + NO_2 \longrightarrow 2N_2 + 2H^+ + 3H_2O$	
The Beckmann rearrangement		
CPL refining	Raney nickel (Ni) catalyst, tank reactor	Amorphous Ni catalyst, magnetically stabilized bed reactor