

**The Third Green and Sustainable Chemistry Award**  
Awarded by the Minister of Economy, Trade and Industry

Sumitomo Chemical Company Limited

*The Development and Industrialization of the Vapor Phase Beckmann Rearrangement  
Process for the Production of  $\epsilon$ -Caprolactam*

$\epsilon$ -Caprolactam is an important intermediate used in the production of Nylon 6 fibers and resins, the worldwide production of which is estimated at about 3.8 million tons annually. Nylon 6 fibers and resins are used in a wide range of applications including clothes, automobiles, electric or electronic devices, as well as lapping films for foods. The production is expected to expand firmly from now on. All  $\epsilon$ -caprolactam is produced through the Beckmann rearrangement of cyclohexanone oxime, except a small amount that is produced through depolymerization of nylon 6 polymers.

The current caprolactam manufacturing processes produce large amounts of ammonium sulfate as a byproduct (at least 1.6 times of caprolactam by weight), because oleum or sulfuric acid is used for the reaction promoter in the Beckmann rearrangement process. A new process proceeded without sulfuric acid under vapor phase conditions, which is called the vapor phase Beckmann rearrangement, has been studied and developed world widely for more than 60 years for the purpose of cost reduction and lighten the burden to the environment.

This developed process produces only  $\epsilon$ -caprolactam and does not generate any ammonium sulfate, because it is conducted with a fine catalyst instead of sulfuric acid. It has been believed generally that the catalyst must possess acidity, because the Beckmann rearrangement reaction is one of the typical acid catalyzed ones.

Contrary to general expectations, it was discovered that a high silica MFI zeolite that did not possess acidity was the best candidate as a catalyst. And it was developed the know-how to make an effective catalyst suitable for industrial use, technology to improve the selectivity to  $\epsilon$ -caprolactam, a novel fluidized bed reaction system, and an effective purification technology. As a result, a new process avoiding any ammonium sulfate production has been established for the first time in the world. It can also reduce the consumption of resources and energy.

Large amounts of ammonium sulfate are also generated in the production of cyclohexanone oxime, the raw material for  $\epsilon$ -caprolactam production. In order to carry out the production of  $\epsilon$ -caprolactam without any ammonium sulfate production, Sumitomo Chemical commercialized for the first time in the world in April 2003, a combined process, with a first ammoximation step for obtaining cyclohexanone oxime, developed by EniChem (Italy), and a second step of vapor phase Beckmann rearrangement developed by Sumitomo Chemical, with a production scale of 60,000 metric tones annually.

This new technology not only realizes the Green Sustainable Chemistry, but also allows the reduction of construction cost, operating and maintenance expenses, because corrosive materials such as strong sulfuric acid are not employed. It is expected that this new technology will be widely accepted in the world in the future.