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Green Production Technology of Cyclohexanone oxime

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PURPOSE OF THE ABSTRACT

1 Introduction

Ideal of green chemistry is the reaction of "atom economy" and the production process of environment-friendly. After two decades' endeavor, the Research Institute of Petroleum Processing (RIPP-SINOPEC) has successfully developed a green production technology of caprolactam (CPL), in which the technology for producing cyclohexanone oxime by continuous ammoximation of cyclohexanone in single-reactor (CACS) is the key green technology. The first industrial plant based on CACS green technology with a capacity of 70kt/a has been built in 2003. In 2018, the production capacity of CACS green technology of cyclohexanone oxime reached 3,000kt/a, sharing 41% of the global market.

2 Production technology of caprolactam

Caprolactam is the monomer of nylon-6 fiber and nylon-6 engineering plastics. More than 90% of caprolactam worldwide is manufactured by rearrangement of cyclohexanone oxime. Cyclohexanone oxime is produced traditionally by the reaction of cyclohexanone with a hydroxylamine salt formed from oxidation of NH3 and then reduction. This process is not only complex and costly, but also has serious corrosion and pollution problem due to use or emission of NOx and /or SOx(fig.1 route 1). It is very important to develop green caprolactam production technology (fig.1 route 2).

3 Continuous ammoximation of cyclohexanone in single-reactor for Cyclohexanone Oxime Production (CACS)

The whole process of the ammoximation of cyclohexanone is a more simple and greener than the conventional one. Cyclohexanone oxime can be produced by a one-step reaction in which cyclohexanone reacts with NH3 and H2O2 using TS-1 as catalyst. High conversion and selectivity can be obtained with only water as the main by-product.

The technology for producing cyclohexanone oxime by continuous ammoximation of cyclohexanone in single-reactor (CACS), developed by RIPP-SINOPEC, is an innovative process, which has two important highlights.

The first is the use of the micro-sized hollow TS-1 zeolite (HTS) as the catalyst and the integration of a membrane separation component into the slurry-bed reactor. Directly synthesizing the micro-sized HTS 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 HTS zeolite can be uninterruptedly separated and recycled.

The second 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. 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 obviously. At the same time, it improves the catalyst renewability and reduces catalyst consumption. For the cyclohexanone ammoximation technology developed by RIPP, the cyclohexanone conversion was more than 99.9%, the cyclohexanone oxime selectivity was more than 99.5%.

4 Conclusion

The green cyclohexanone oxime production technology successfully developed by RIPP-SINOPEC, is an integrated innovation of new catalytic material and new reaction engineering. Based on the commercial application, the production process is simplified greatly, the plant investment is reduced by 70%, the utilization of NH3 increased from 60% to over 90%, the exhaust emission fall to 1/200, respectively. In 2018, China's CPL capacity based on this green production technology reached 3,000kt/a, sharing 41% of the global market. This green production technology produces great economic and social benefits, and also sets a successful example of green chemical engineering.

FIGURES

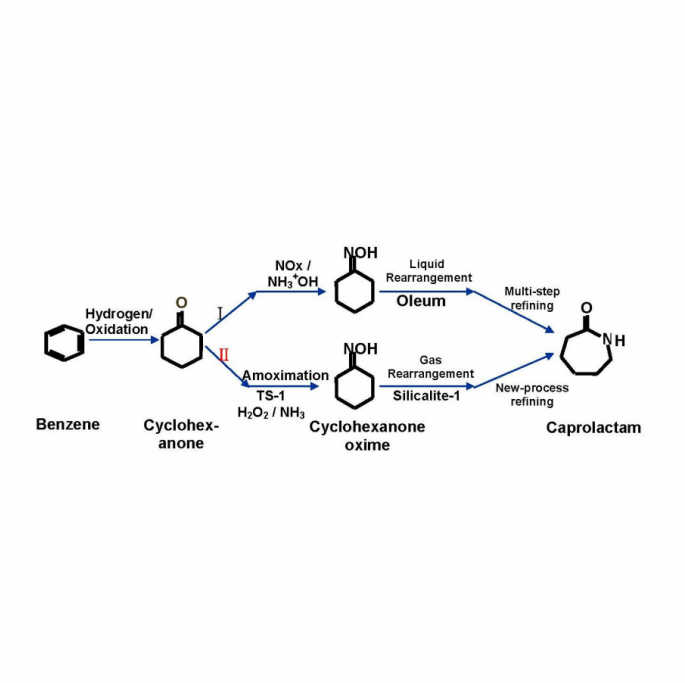

FIGURE 1

Production technology of caprolactam

Fig.1

FIGURE 2

KEYWORDS

Green Chemistry | Cyclohexanone oxime | Production Technology

BIBLIOGRAPHY