The 7th Green and Sustainable Chemistry Award
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The development of an environmentally benign THF polymerization process utilizing solid acid catalysis

An environmentally benign catalytic polymerization process for the production of polyoxy tetramethylene glycol (PTMG) has been developed and established industrially. Market demand for PTMG, a raw material produced for elastic fibers, is growing rapidly. This new continuous flow process includes the polymerization of tetrahydrofuran (THF) under the presence of acetic anhydride by solid acid catalysis on meso-porous support.

Conventional PTMG production technology is a batch process composed of three main steps, namely catalyzed polymerization by fluorosulfonic acid (FSO_3H), hydrolysis of polymers and neutralization of FSO_3H by Ca $(OH)_2$. FSO_3H is a very corrosive and harmful liquid and requires special materials for the reactors, which need periodical maintenance and renewal, and very careful attention throughout the operation. In addition, the use of FSO_3H generates a significant amount of fluolo-containing waste material (0.12kg waste per 1kg-PTMG). Therefore, a new environmentally benign technology to produce PTMG has been required to meet growing demand for the material.

In this new technology, a mixed solid oxide composed of ZrO_2 and SiO_2 was successfully introduced as the catalyst for the polymerization of THF under the presence of acetic anhydride. By using this non-corrosive and harmless catalyst, the technology has achieved near-zero emission levels of catalyst waste and therefore significantly reduces the load on the environment.

In general, heterogeneous catalyst can be easily separated from products and, compared with the homogeneous catalyst, has many advantages for industrial use. However, in the case of polymerization technologies, we can find few practical examples due to the declining performance of the catalysis in a longer term. This is caused by the hindered diffusion of the produced bulky molecules in the pores of the support. In this new technology, by using well-dispersed and well-defined solid acid on the SiO_2 support with meso-pores, in which a bulky polymer molecule can diffuse easily, the production of high-quality PTMG with stable polydispersity, less amount of oligomer and low product color-index, can be realized.

Furthermore, this new polymerization process has a much higher productivity rate and requires no special materials for the reactors. These two factors serve to reduce construction costs by more than 30% compared to the conventional process.

In summary, this technology realizes high productivity of high-quality product while reducing the amount of waste to zero by replacing conventional batch technology that utilizes catalysis with a high environmental load with continuous flow technology that is more easily handled and which enjoys more neutral catalysis. It has been concluded that this technology is a good example of industrialization of green sustainable chemistry.

Meso-porous materials have been investigated through the world since early 1990s and this technology strongly demonstrates the superiority and sound capabilities of meso-porous materials as a catalyst support in terms of easy diffusion of bulky product materials. Further research in this area is expected.