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Yasutaka Ishii
Department of Chemistry, Faculty of Engineering, Kansai University
Tetsuji Yanami and Tatsuya Nakano
Daicel Chemical Industries, LTD.

Development and Industrialization of Novel Environmentally Benign Aerobic Oxidation Method

In chemical industry, just over 60% of processes are related to the oxidation reactions. Therefore, the oxidation is very important in chemical industry for producing a wide range of oxygen-containing molecules including alcohols, ketones, epoxides, and carboxylic acids which are needed for the production of, in particular, plastics, and synthetic fiber materials. Nowadays, particularly important is the development of an environmentally benign oxidation method which satisfies the following issues, (1) high atom economy, (2) low environmental load, and (3) low E-factor. Over the past half-century, however, there has been no significant progress in alkane oxidations.

An innovative alkane oxidation through the catalytic carbon radical generation using *N*-hydroxyphthalimide (NHPI) as a key catalyst is developed. The NHPI method is capable to carry out the alkane oxidation under mild conditions that results in fewer by-product formations, saving energy costs, and reducing global warming substance generations and to considerably increase the product selectivities and yields in alkane oxidations which are difficult to be improved so far. For example, the oxidation of cyclohexane is successfully achieved by one-step using NHPI as the key catalyst to give adipic acid in 73% selectivity at 73% conversion, although the current method is performed via two-step reactions involving aerobic oxidation of cyclohexane in *ca.* 5% conversion followed by nitric acid oxidation of the resulting K/A oils that release a large amount of global warming gases exemplified as nitrous oxide. Now, the NHPI method is being received much attention as an environmentally benign method for producing adipic acid worldwide.

In contrast to the current oxidation of *p*-xylene to terephthalic acid by Mn/Co/Br system where the emission of bromine and the formation of brominated by-products are difficult to be avoided, the NHPI method is capable to remove halogen from the catalytic system and gives terephthalic acid in the yield over 95%.

The application of this strategy to the nitration of alkanes provides a very efficient nitration method under mild conditions, and the nitration of cyclohexane affords nitrocyclohexane in 70% yield. Since nitrocyclohexane is easily reduced to cyclohexanone oxime, this method leads to an ammonium sulfate-free route to cyclohexanone oxime which is a raw material of ε-caprolactam leading to nylon 6. In addition, the aerobic oxidation of K/A oils yielding the in situ generation of a hydroperoxide whose subsequent treatment with ammonia affords ε-caprolactam precursor without formation of ammonium sulfate.

The aerobic oxidation of adamantanes to polyols which provides key monomer materials for producing resist polymers in next generation is very attracted in industry. The NHPI method is expected to be widely adopted throughout the world as an innovative chemical technology from Japan.