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Environmentally benign catalytic technology for refining and petrochemical production A recent review of related R&D activities in China

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1. Introduction

The more and more stringent requirement for environmental protection becomes now the major driving force for technological progress. The impact is significant for refining and petrochemical industry in China as well as in the world. Looking forward to 21st century, the technologies for waste treatment should be continuously improved, and meanwhile, the technologies of green processes should be developed. The technologies of green processes are demanded both for revamping the existing units and for designing new units during the capacity expansion of China's petrochemical industry in the next century.

A green process is a highly selective chemical process using green raw materials, catalysts, and solvents, producing green products. Since most of the petrochemical processes were developed in 1940–1950s, technological breakthrough based on entirely new scientific knowledge is necessary for developing green processes. Catalysis, the key element for many chemical processes, will still play an important role in the development of green chemistry and hence in the greening of chemical processes or clean production. Historical review reveals that technological breakthrough occurs generally through the discovery and application of new catalytic materials or new reactor engineering.

The R&D activity in China in the field of catalysis has come to a rapid development stage since 1980s, which results in a series of technological innovations [1–3]. A number of unique catalytic technologies have been invented and commercialized in China, such as deep catalytic cracking (DCC) for maximum production of gaseous olefins, distillate selective cracking accompanied by alkene polymerization (DSCAP), liquid phase selective hydrogenation for propene fraction using a single stage adiabatic reactor, medium pressure hydro-upgrading process for production of low sulfur and low aromatics diesel fuel (MHUG), etc. A variety of new catalysts has been developed and commercially applied in refining and petrochemical industry. Scientists in China from universities and research institutions of Chinese Academy of Sciences and industrial sectors have also made contributions to the basic research and applied basic research in different areas of catalysis, including those areas related to green chemistry. In recent years, a state key applied basic research project, "Catalytic Chemistry and Reaction Engineering for Developing Environmentally Friendly Refining and Petrochemical Technology", has been established and jointly supported by Natural Science Foundation of China (NSFC) and China Petrochemical Corporation (SINOPEC). The present paper reviews the recent work related to developing environmentally benign refining and petrochemical technology.

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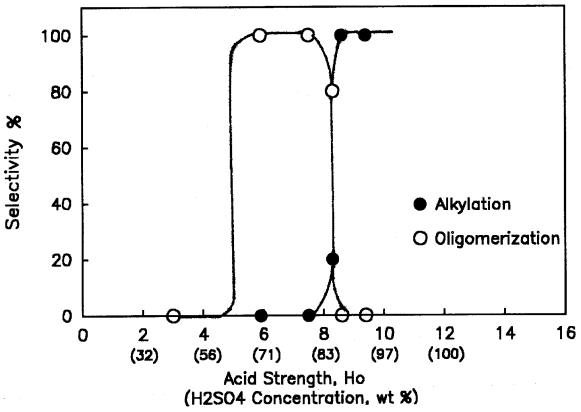

Fig. 1. Relationship between acid strength (H_2SO_4 concentration) and selectivity in the alkylation.

2. Alkylation of isobutane with butenes

Alkylation of isobutane with olefins is an important process in petroleum refining industry. The product, alkylate, is a valuable gasoline blending component with high octane number, low Reid vapor pressure (RVP), and no aromatics and olefins, and hence can be regarded as a clean-burning-paraffinic gasoline blending component. In current commercial practice, two kinds of liquid acids are used as catalysts for isobutane–butene alkylation, i.e., concentrated sulfuric acid and hydrofluoric acid. The disposition of spent sulfuric acid and the volatilization of hydrofluoric acid bring serious environmental concern. The challenge is obviously to develop effective solid acid catalysts for alkylation process. It is almost a worldwide effort for the researchers in the field of petroleum refining [4–6]. The requirement for a solid acid catalyst, which is effective for alkylation process, can be summarized as follows:

- High acid strength, as shown in Fig. 1.
- High density and homogeneous distribution of acid sites.
- Ability for catalyzing hydrogen transfer between C_8^+ carbonium ion and isobutane molecule.
- High surface area and large pore size.

Research Institute of Petroleum Processing, China Petrochemical Corporation (SINOPEC), has been working actively on the project for developing solid acid catalysts and related process for alkylation. A number of solid superacids are developed and tested for alkylation reaction [7]. The alkylation of isobutane with butene under supercritical condition using a selected solid acid has been carried out in a fixed-bed reactor for 1400 h with high stability for catalyst activity and selectivity [8]. The catalyst stability is shown in Fig. 2. The product distribution is comparable with that of liquid acid alkylation process as shown in Fig. 3.

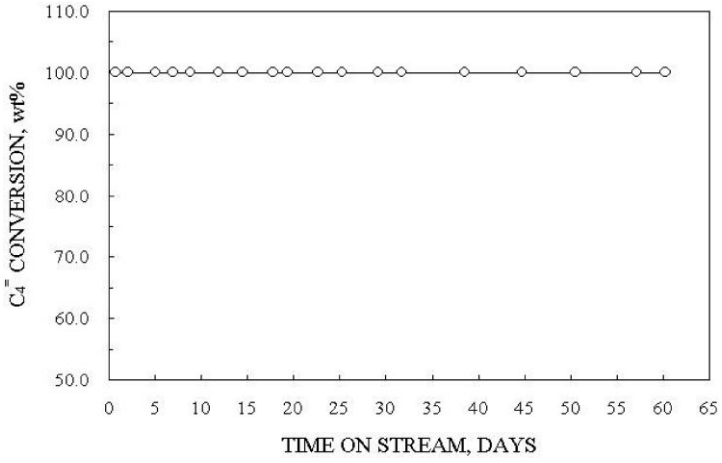

Fig. 2. Conversion of butene vs. time on stream during the lifetime test of solid acid catalyst under supercritical reaction condition.