Chinese Journal of Catalysis 37 (2016) 16–26

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Review (Special Column on New Porous Catalytic Materials)

Advances in development and industrial applications of ethylbenzene processes

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A R T I C L E I N F O

Article history:
Received 2 June 2015
Accepted 25 August 2015
Published 5 January 2016

Keywords:
Ethylbenzene
Alkylation
Transalkylation
ZSM-5 zeolite
MCM-22 zeolite
Beta zeolite
Y zeolite

A B S T R A C T

The benzene alkylation process for the production of ethylbenzene has undergone significant improvements during recent decades. Various environmentally benign zeolite-catalyzed ethylbenzene processes, including ZSM-5-zeolite-based vapor-phase ethylbenzene processes and Y-, β-, and MCM-22-zeolite-based liquid-phase processes, have been developed and commercialized. Pure ethylene, ethanol, and dilute ethylene have been used as ethylation agents. Here, the development and industrial application of alkylation catalysts and benzene ethylation techniques are summarized, and some other promising innovations are discussed. Recent advances in benzene alkylation over hierarchical zeolites with improved access to active sites and molecular transport are also covered. Zeolites with short diffusion lengths are promising candidates as better alkylation catalysts. The key point is how to obtain such materials easily and economically. The structure-activity relationships of commercial zeolites in these processes are discussed. Liquid-phase processes catalyzed by β and MCM-22 are more profitable than vapor-phase processes catalyzed by ZSM-5.

1. Introduction

Ethylbenzene is mainly used for the production of styrene, which is then used to produce polystyrene, acrylonitrile-butadiene-styrene resin, styrene-acrylonitrile resin, and other products [1]. More than half the world's ethylbenzene is produced and consumed by the US, Japan, Korea, China Taiwan, and Mainland China (Fig. 1). The production and consumption of ethylbenzene are growing continuously with the development of economy, especially in Mainland China (Fig. 2). In 2013, the overall ethylbenzene capacity of Mainland China was about 7 Mt, the largest in the world, and it is expected to exceed 9 Mt in 2015–2016.

The alkylation of benzene to ethylbenzene has been studied and commercially developed for more than 80 years since the 1930s, when a Friedel-Crafts catalyst ($AlCl_3$-HCl) was used [2]. The $AlCl_3$-HCl process causes corrosion problems, therefore UOP and Mobil-Badger developed supported catalysts [3,4] and zeolite-based catalysts in the 1960s and 1970s. The third-generation Mobile-Badger process was commercialized using ZSM-5 as a catalyst, and a second reactor was added for transalkylation in the 1990s. The zeolites used as catalysts for ethylbenzene processes are listed in Table 1. Research institutes and companies in Mainland China have done much work on the development of their own benzene alkylation techniques in the last two decades. The China Petroleum & Chemical Corporation (Sinopec) has performed a large amount of research and development on benzene alkylation in recent decades.

In this paper, we summarize the development and industrial application of benzene alkylation catalysts and processes for ethylbenzene production in Mainland China. The structure-activity relationships of zeolite catalysts in the corresponding processes are discussed. The results of research on benzene alkylation over catalysts with improved mass transfer are dis-

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DOI: 10.1016/S1872-2067(15)60965-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 1, January 2016

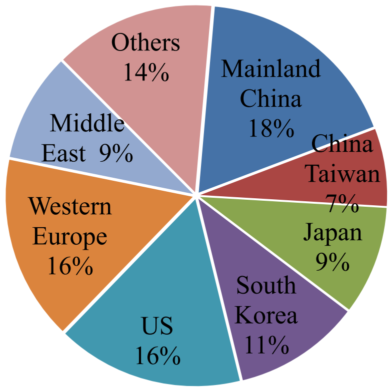


Fig. 1. Global ethylbenzene capacity in 2014.

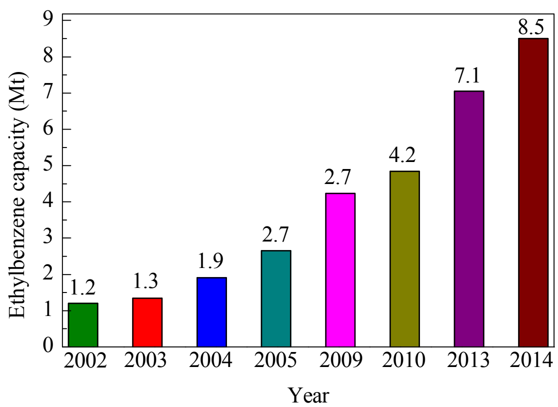
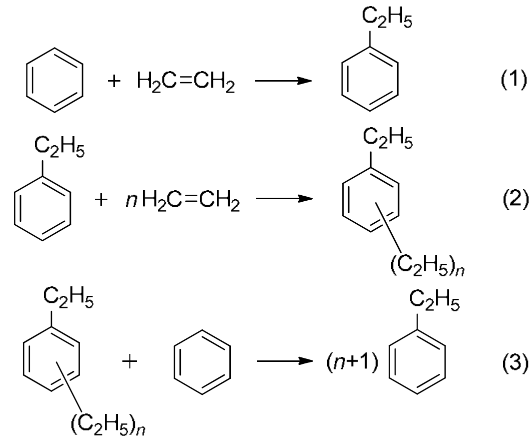


Fig. 2. Ethylbenzene capacity of Mainland China.

cussed, and some promising catalytic materials are proposed.

2. Benzene alkylation processes for ethylbenzene production

Ethylbenzene is produced by benzene alkylation, and ethylene is the most frequently used ethylation agent (Scheme 1(1)). Under the reaction conditions, the produced ethylbenzene further reacts with ethylene to form polyethylbenzenes (EBs, Scheme 1(2)), such as diethylbenzenes (DEBs) and triethylbenzenes (TEBs). Transalkylation of EBs with benzene is



Scheme 1. Alkylation of benzene to produce ethylbenzene.

performed to increase the yield of ethylbenzene (Scheme 1(3)). The addition of a transalkylation unit in ethylbenzene production increases the yield of ethylbenzene by about 10%. $AlCl_3$-catalyzed benzene alkylation was the first process to be developed for the production of ethylbenzene, and then solid-state acids (solid phosphoric acid, zeolites) were used as alkylation catalysts.

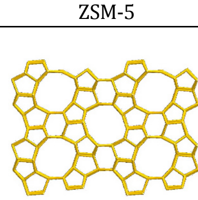
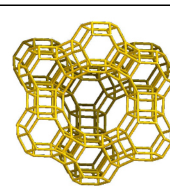
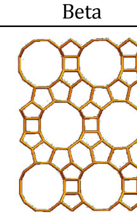
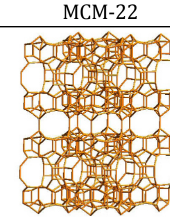
2.1. Liquid-phase benzene alkylation processes over $AlCl_3$-HCl catalyst

The $AlCl_3$-HCl-catalyzed liquid-phase process was developed in the 1930s. It was conducted at low benzene/ethylene molar ratios (about 2.5/1) and mild temperatures (160–250 °C). As mentioned above, processes using zeolite-based catalysts have attracted much attention in industry because of the corrosive effects of the $AlCl_3$-HCl catalyst and the solid phosphoric acid catalysts used since the mid-1960s [2–4].

2.2. Zeolite-catalyzed vapor-phase benzene alkylation processes

The ZSM-5 zeolite, which has the MFI structure (Table 1), is most effective in vapor-phase benzene alkylation [5]. It is one of the most important highly siliceous zeolites and was initially

Table 1
Commercial zeolites: structure and ethylbenzene processes.

Zeolite	ZSM-5	Y	Beta	MCM-22
Structure image	 along (010)	 along (111)	 along (100)	 along (001)
Framework type	MFI	FAU	BEA*	MWW
Ring size (# T-atoms)	10	12 (with cage, 1.3 nm × 0.74 nm)	12	10 (with cage, 1.82 nm × 7.1 nm)
Channel system	3 dimensional	3 dimensional	3 dimensional	2 dimensional
Ethylbenzene process	Vapor-phase	Liquid-phase, CD Tech	Liquid-phase	Liquid-phase