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Advances in development and industrial applications of ethylbenzene processes

Weimin Yang*, Zhendong Wang, Hongmin Sun, Bin Zhang

Sinopec Shanghai Research Institute of Petrochemical Technology, Shanghai 201208, China

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ABSTRACT

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.

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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 ($\text{AlCl}_3\text{-HCl}$) was used [2]. The $\text{AlCl}_3\text{-HCl}$ 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-

* Corresponding author. Tel: +86-21-68462197; Fax: +86-21-68462283; E-mail: yangwm.sshy@sinopec.com

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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

Table 2

Vapor-phase benzene alkylation processes.

Process (year of industrial application)		Mobil-Badger 2nd generation (1980)	Mobil-Badger 3rd generation (1990)	Sinopec (1999)	Sinopec (2007)	Sinopec (2009)	DICP-Sinopec-CNPC 3rd (2003)
Alkylation	Ethylation agent	Pure ethylene	Pure ethylene	Pure ethylene	Ethanol	Dilute ethylene	FCC off-gas
	Catalyst	ZSM-5	ZSM-5	AB-96, AB-97, AB-05HS	AB-AS, DF-AS	SEB-08, SEB-12	DL-0802A/DL-0802B
Transalkylation	Catalyst	—	ZSM-5	AB-97-T	DF-AS-T	AEB-1H	DL-0801
	Phase	—	Vapor	Vapor	Vapor	Liquid	Liquid

developed by Mobil [6]. There are two types of ten-membered ring (10-MR) channels in the structure: one straight elliptical pore system (0.53 nm × 0.56 nm) along the (010) axis and one zigzag circular pore system (0.51 nm × 0.55 nm) along the (100) axis [7]. ZSM-5 is thermally and hydrothermally stable, with adjustable acid amounts and strengths. Because of its unique pore structure and acidic properties, ZSM-5 zeolite is widely used in petrochemical processes such as fluid catalytic cracking (FCC), methanol-to-propylene conversion, methanol-to-gasoline conversion, MTA, and OCC [8].

In the last 20 years, Sinopec has commercialized several vapor-phase ethylbenzene processes using different ethylation agents (Table 2), including pure ethylene, dilute ethylene (including FCC off-gas), and ethanol. The Shanghai Research Institute of Petrochemical Technology (SRIPT), a subsidiary research facility of Sinopec, and the Dalian Institute of Chemical Physics (DICP, Chinese Academy of Sciences) have developed alkylation catalysts incorporating ZSM-5 and ZSM-5/ZSM-11 cocrystalline zeolites, respectively (Table 2).

2.2.1. Pure-ethylene processes

In the Mobil-Badger ethylbenzene process, which was the first to be commercialized, benzene alkylation with pure ethylene was conducted in a vapor-phase fixed-bed reactor to produce ethylbenzene and EBs (mainly DEBs). Ethylbenzene was separated as the product, and the EBs were recycled back into the reactor to undergo transalkylation. In the 1990s, the Mobil-Badger ethylbenzene process was improved by adding a transalkylation reactor. The service life of the catalyst increased from about 3 months to 1 year [9].

SRIPT launched research projects on the pure-ethylene process in 1994. There were two main issues to be addressed: catalyst deactivation caused by coke deposits from ethylene polymerization and removal of the xylene byproduct from ethylbenzene. SRIPT studied ZSM-5 catalysts with different SiO₂/Al₂O₃ molar ratios and crystal size for vapor-phase ben-

zene alkylation [10]. The data in Table 3 show that ethylene conversion decreased with increasing SiO₂/Al₂O₃ molar ratio, but the selectivity for ethylated benzenes (EBs, including ethylbenzene, DEBs, and TEBs) and the ZSM-5 stability were improved significantly. This is because ethylene polymerization decreased because of the decreased number of active sites resulting from higher SiO₂/Al₂O₃ molar ratios in the ZSM-5 zeolite.

As shown in Table 4, ZSM-5 zeolites with small crystals are more effective in benzene alkylation, because they give higher ethylene conversions and stability, although the selectivity for ethylated benzenes is slightly lower. A series of catalysts, i.e., AB-96, AB-97, and AB-05HS (vapor-phase alkylation catalysts), and AB-97-T (vapor-phase transalkylation catalyst), were developed using highly siliceous nano-sized ZSM-5 zeolite as the active component [11,12]; these catalysts were commercialized by SRIPT. There are several industrial plants in China using the pure-ethylene technique licensed by Sinopec.

2.2.2. Ethanol processes

Because of the high cost of ethylene derived from crude oil and advances in ethanol production by fermentation of crops such as maize, cassava, and crop straw [13], benzene alkylation with ethanol has attracted much attention recently [14]. However, water in either the bio-ethanol raw material or produced in the alkylation reaction causes loss of active Al sites, leading to poor catalytic performance [14,15]. Combined treatments with steam and phosphoric acid solution, based on the SRIPT pure-ethylene process, were therefore introduced to ensure that ZSM-5-zeolite-based catalysts have long lifetimes, high selectivities, and the ability to convert substantial amounts of ethanol to minimize generation of impurities such as xylene [16]. The zeolitic catalysts AB-AS and DF-AS (alkylation catalysts), and DF-AS-T (transalkylation catalyst) were developed and first used in an industrial plant in 2007; in 2010, they were used in the largest plant in Mainland China, with an annual capacity of 215 kt [17].

Table 3Effects of SiO₂/Al₂O₃ molar ratio on catalytic performance of ZSM-5 in benzene alkylation.

SiO ₂ /Al ₂ O ₃ molar ratio	Ethylene conversion (%)	Selectivity for EBs (%)	Deactivation rate (%/h)
55	91.85	87.58	0.85
91	81.23	94.37	0.31
120	74.31	94.86	0.30
165	55.34	95.85	0.26

Reaction conditions: 400 °C, 0.1 MPa, benzene/ethylene molar ratio = 1.0, ethylene WHSV = 8 h⁻¹, TOS = 100 h.

Table 4

Effects of crystal size on catalytic performance of ZSM-5 in benzene alkylation.

Size (μm×μm)	Ethylene conversion (%)	Selectivity for EBs (%)	Deactivation rate (%/h)
5×9	59.85	95.56	0.31
3×3	69.23	94.48	0.30
1×1	72.98	93.52	0.25

Reaction conditions: 400 °C, 0.1 MPa, benzene/ethylene molar ratio = 1.0, ethylene WHSV = 8 h⁻¹, TOS = 100 h.

As early as 1992, the Indian Petrochemicals Corporation introduced a benzene alkylation process using dilute ethanol rather than ethylene, and Fe-ZSM-5 was used as the alkylation catalyst [18]. However, the dilute-ethanol process has no distinct advantage over the ethylene process, and no commercial plants using this process have been reported.

2.2.3. Dilute-ethylene processes

FCC off-gas contains 10%–30% ethylene, which can be used as an ethylene source for ethylbenzene production. In China, about 5.5 Mt of FCC off-gas are produced every year, and the ethylene resource is estimated to be 1.0 Mt [19]. However, only some of the ethylene is recovered, and most of the ethylene is burned. The use of FCC off-gas as an ethylene feedstock would be of benefit to refineries and decrease carbon emissions. However, when FCC off-gas is directly fed into the alkylation reactor as the ethylene resource, impurities such as propylene cause side reactions and catalyst deactivation. The separation of ethylene from the FCC off-gas would facilitate benzene alkylation, but the overall investment and running costs would increase.

Mobil-Badger modified the pure-ethylene process for use with an FCC off-gas feed. The dilute-ethylene process involves a complex system for pretreating the raw material. After water removal, desulfurization, and propylene separation from the FCC off-gas feed, the stream is fed into the alkylation reactor to produce ethylbenzene. This process was first commercialized at Shell's Stanlow, UK refinery; it had an annual ethylbenzene capacity of 160 kt in 1991. The Dow Chemical Company built a larger industrial plant in the Netherlands, with a capacity of 450 kt/year [20]. There are still five plants using dilute ethylene as a feedstock.

In the early 1990s, DICP found that a ZSM-5/ZSM-11 co-crystalline zeolite gave a good catalytic performance in the alkylation of benzene with FCC off-gas. In cooperation with Sinopec and the China National Petroleum Corporation (CNPC), the DICP ethylbenzene process using FCC off-gas as the ethylation agent was developed and commercialized [19,21]. The feedstock pretreatment is simpler than that in the Mobil-Badger dilute-ethylene process. The first-generation technique used only one fixed-bed reactor, in which benzene alkylation and transalkylation of EBs took place simultaneously. The content of the main byproduct, xylene, was high, up to 3000 ppm. In the second-generation technique, vapor-phase alkylation and vapor-phase transalkylation were performed separately in two different reactors. The alkylation temperature was lowered from 410–430 °C to 360–390 °C, and the xylene content was reduced to ~2000 ppm. The third-generation technique was further improved by adding a propylene-removal unit and using β -zeolite-catalyzed liquid-phase PE-transalkylation instead of vapor-phase transalkylation [22,23]. The alkylation and transalkylation took place at 320–360 and 220–260 °C, respectively. The single-pass catalyst lifetimes for alkylation and transalkylation are 6–9 months and 18–24 months, respectively. The product quality is better, the xylene content is lower, <1000 ppm, and the ethylbenzene purity is higher than 99.8%. The third-generation technique has

been licensed to more than ten industrial plants.

SRIP's alkylation catalyst, SEB-08, for vapor-phase benzene alkylation with dilute ethylene was introduced in 2008, and was first used in an industrial plant in 2009 [24]. The SGEB dilute-ethylene process was then developed based on the SEB-08 alkylation catalyst and AEB-1H liquid-phase EB-transalkylation catalyst [25]. Benzene ethylation is performed at 320–380 °C and 0.7–1.3 MPa, with a benzene/ethylene feed molar ratio of (6.0–7.0)/1, and transalkylation is performed at 170–235 °C and 2.8–3.0 MPa with a benzene/DEB feed mass ratio of (5.0–8.0):1. The cycling lifetimes of the alkylation catalyst and transalkylation catalyst are more than 1 year and 2 years, respectively, and the total catalyst service lives are more than 2 years and 4 years, respectively. The ethylbenzene purity is higher than 99.8%, and the xylene content is lower than 800 ppm.

The SEB-08 alkylation catalyst contains ZSM-5 zeolite as the active component. The catalyst has abundant macropores and mesopores. Hydrothermal treatment and acid leaching modification are performed to remove Lewis acid sites to inhibit side reactions. The reactants can easily diffuse through the macropores and mesopores to reach the active sites located in the micropores. The catalyst showed stable performance in terms of ethylene conversion and selectivity, and the industrial runtime was beyond 12 months. The EB-transalkylation catalyst AEB-1H was developed by the Sinopec Research Institute of Petroleum Processing (RIPP), using an FAU zeolite as the active component. The overall ethylbenzene capacity using the SEB-08 alkylation catalyst and SGEB dilute-ethylene process is currently about 1.3 Mt annually. In 2014, a new alkylation catalyst, SEB-12, was used in industrial plants. The feed molar ratio of benzene/ethylene was lowered to (5.0–6.0)/1, and the energy consumption decreased.

2.3. Liquid-phase benzene alkylation

The energy consumption of vapor-phase benzene alkylation is high because of the high benzene/ethylene molar ratio and high reaction temperature. In addition, more xylene is produced, which lowers the ethylbenzene quality. In 1989, the liquid-phase benzene alkylation process was introduced by Lummus/Unocal/UOP using a Y-zeolite-based catalyst [26]. The Mobil-Raytheon EBMax process and Lummus/UOP EBOne liquid processes are now in operation. Sinopec has also developed and commercialized a liquid-phase benzene ethylation catalyst and liquid-phase ethylbenzene process (Table 5).

2.3.1. Liquid-phase alkylation of benzene catalyzed by FAU zeolite

Zeolite Y is a faujasite molecular sieve with a three-dimensional 12-MR pore structure [27]. The basic structural units of zeolite Y are sodalite cages, which form supercages that are large enough to accommodate spheres of diameter 1.2 nm (Table 1). Nanocrystalline zeolite Y has larger intercrystalline void spaces, a larger pore volume, more acid sites located on the external surface, higher activity, and better stability.

The liquid-phase ethylbenzene process catalyzed by zeolite

Table 5

Liquid-phase benzene alkylation processes.

Process (year of industrial application)		Lummus/Uonocal/UOP (1989)	Mobil-Raythen EBMax (1995)	Lummus/UOP EBOne (1996)	Sinopec (2000)
Alkylation	Ethylation agent	Pure ethylene	Pure/dilute ethylene	Pure ethylene	Pure ethylene
	Catalyst	Y	EM3300	EBZ-500, EBZ-800TL	AEB-2, AEB-6
Transalkylation	Catalyst	Y	EM3700	EBZ-100	AEB-1
	Phase	Liquid	Liquid	Liquid	Liquid

Y was first commercialized in 1990 [18]. Benzene alkylation took place at a much lower temperature, 240–270 °C, than that of the vapor-phase process, around 400 °C. EB transalkylation was performed in the liquid phase in a separate reactor using a Y-zeolite-based catalyst. Although the feed ratio of benzene/ethylene is high (about 7/1), the process is competitive because it has the advantages of better thermal control and a longer catalyst life (about 1 year). This process was licensed to several industrial clients, and their total ethylbenzene capacity is about 2.8 Mt annually.

2.3.2. Liquid-phase benzene alkylation catalyzed by β zeolite

β zeolite has a three-dimensional 12-MR pore structure consisting of perpendicular straight channels (0.66 nm $\times$ 0.67 nm), and the interconnections create narrow helical channels with effective pore diameters of 0.56 nm $\times$ 0.56 nm (Table 1) [28]. Since its discovery by Wadlinger et al. [29] in 1967, the use of β zeolite for catalytic reactions such as alkylation, alkane hydroisomerization, aromatic acylation, and methyl *tert*-butyl ether synthesis [30] has been extensively investigated because of its silica-rich framework and easy access to active sites in the pores.

β zeolite is highly active in benzene alkylation with ethylene and gives higher ethylene conversion and ethylbenzene selectivity than Y zeolite [31–33]. EBOne was developed and commercialized in 1996 by Lummus/UOP, using EBZ-500 as the alkylation catalyst and EBZ-100 as the transalkylation catalyst [34]. The active component of EBZ-500 is a modified β zeolite, which is also active in EB transalkylation [2,35]. Zeolite Y was used as the active component of EBZ-100. The feed ratio of benzene/ethylene is reduced to about 4/1, and the catalyst life is prolonged to 2 years.

RIPP began research on a liquid-phase circulating process for the production of ethylbenzene in 1990, and a highly active alkylation catalyst, AEB-2, with high ethylbenzene selectivity and stability was introduced and commercialized [36,37]. The process is operated with benzene/ethylene molar ratios of (3–6)/1 at 200–250 °C and 3.6 MPa. The catalyst life is 6 years. When operated with a feed ratio of 5, ethylene conversion is almost 100%, the selectivity for ethylbenzene is 86.5%, and the overall ethylbenzene yield is 99.9%. AEB-2 is also suitable for transalkylation processes. At 213–221 °C, EB conversion is about 80% and the ethylbenzene selectivity is 100%. After the commercialization of AEB-2, a new-generation benzene alkylation catalyst, AEB-6, was developed using a much smaller β zeolite as the active component. The alkylation can be operated with a low benzene/ethylene feed ratio of 3.5/1; the ethylben-

zene selectivity is about 88% and the total ethylbenzene yield is 99.7%. Use of AEB-6 as the catalyst greatly reduces the energy consumption [38]. A series of AEB catalysts are now being used in several industrial plants.

2.3.3. Liquid-phase benzene alkylation catalyzed by MWW zeolites

MWW zeolite is a general term for a series of zeolites formed by stacking basic layers with the MWW structure, such as MCM-22, PSH-3, SSZ-25, ERB-1, ITQ-1, MCM-49, MCM-56, ITQ-2, UZM-8, MCM-36, EMM-10, EMM-12, EMM-13, SSZ-70, and IEZ-MWW [39–43]. They differ in terms of the number of layers, stacking manner, and/or spacing between adjacent layers (Fig. 3). MWW zeolite, known as MCM-22, has attracted particular research attention because of its peculiar structure. It consists of two independent pore systems accessible via 10-MR windows, one of which is defined by two-dimensional sinusoidal channels with elliptical ring cross-sections of size 0.41 nm $\times$ 0.51 nm, and the other contains 12-MR supercages of dimensions 0.71 nm $\times$ 0.71 nm $\times$ 1.82 nm restricted by 10-MR openings of size 0.45 nm $\times$ 0.55 nm (Table 1). In addition, pocket-like semi-supercages are located on the crystal surfaces. These different types of pore systems play different roles in catalytic reactions [44].

MCM-22 zeolite shows comparable activity to that of zeolite Y in liquid-phase benzene alkylation, but it is less active than β zeolite. The advantage of MCM-22 zeolite is that the ethylbenzene selectivity is higher than those of Y and β zeolites; therefore, smaller amounts of EBs are produced during benzene alkylation with ethylene using MCM-22 zeolite as the catalyst [2]. Based on experiments, an MCM-22-zeolite-based alkylation catalyst and ethylbenzene process (EBMax) were developed by Mobil-Raytheon in 1995. The liquid-phase process was first commercialized in 1997. The feed ratio of benzene/ethylene is

Fig. 3. Typical zeolite materials with MWW structure.

lowered to only (3–4)/1, which in turn reduces the energy consumption. The catalyst is quite stable, and the lifetime is more than 3 years. Initially, EB transalkylation in the EBMax process was performed in the vapor phase using a ZSM-5-zeolite-based catalyst. The transalkylation process was improved by using a new zeolite catalyst, branded as Trans-4, which is also used in the liquid phase [34].

The performance of the EBMax ethylbenzene process is now even better. The optimum alkylation molar ratio of benzene/ethylene is only (2–4)/1. There are 28 plants operating with the liquid-phase EBMax process, and the overall annual ethylbenzene capacity is more than 16 Mt. Moreover, the EBMax ethylbenzene process can be easily adapted to accept dilute-ethylene feedstocks (ethylene accounts for more than 70%). The alkylation reactor is larger than that in the pure-ethylene process, to accommodate a higher catalyst load, and is operated under partial liquid conditions with a benzene to ethylene feed ratio of 3/1. The per-pass conversion of ethylene is higher than 99.5%.

The commercialized EBOne process was improved by Lummus/UOP, using a new catalyst with the UOP trade name EBZ-800TL. The active component is UZM-8 [45], a new MWW zeolite synthesized by UOP in 2004 using diethyldimethylammonium hydroxide as an organic template [40]. UZM-8 is formed through stacking of MWW structural layers, but stacking of the adjacent layers is not well organized. It is similar to MCM-56, another MWW zeolite. UZM-8 is efficient in liquid-phase benzene alkylation and gives better product yields [46].

2.4. Other processes

In addition to the abovementioned ethylbenzene processes, other ethylbenzene production techniques have been reported by the Dow Chemical Company, Indian Petrochemicals Corporation, and CD Tech.

2.4.1. CD Tech process

CD Tech was the first company to use catalytic distillation for the production of ethylbenzene [2]. In 1997, ABB Lummus Global and Chemical Research & Licensing (an affiliate of Shell) established a partnership and purchased the CD Tech company. The CD Tech process combines catalytic benzene alkylation and distillation in one reactor. There are two sections in the reactor. The liquid-phase benzene alkylation catalyst (Y zeolite) is placed in the upper section, and distillation trays are provided in another section. Ethylene is fed at the bottom of the catalyst bed, and benzene is introduced from the top. The heat generated during benzene alkylation is efficiently removed by distillation. After the reaction, ethylbenzene is separated from the mixture of products, and then EB transalkylation is performed in another reactor. The catalyst lifetime is 2 years and the total ethylbenzene yield is 99.5%. The energy consumption and equipment investment are low. The CD Tech ethylbenzene process was commercialized in 1994 at the Mitsubishi Chemical Corporation's ethylbenzene plant, with an annual capacity of 260 kt [20].

2.4.2. Ethane processes

The ethane content of FCC off-gas is about 10%, which is comparable to that of ethylene. However, in the dilute-ethylene process or FCC off-gas process for ethylbenzene production, ethane hardly reacts with benzene and is emitted as a waste gas. Great efforts have been devoted to developing catalytic processes for using ethane [47,48]. The Dow Chemical Company introduced a dual-stage ethylbenzene process that combined ethane dehydrogenation with benzene alkylation [18]. Ethane dehydrogenation is catalyzed by a Zn-, Ga-, or Pt-containing MOR catalyst, and benzene alkylation is catalyzed by β , Y, or ZSM-5 zeolite catalysts. However, there have been no reports of industrial applications of ethane processes.

3. Comparison

Zeolites with different framework structures have been extensively studied in benzene ethylation, with the aim of developing efficient ethylation catalysts. Among the tested zeolites, including MFI, MEL, MOR, FAU, BEA, MWW, FER, and MTT zeolites [49,50], only ZSM-5, Y, β , and MCM-22 zeolites have been successfully used in industrial plants.

ZSM-5 is more active than ZSM-23, ZSM-11, and ZSM-5/ZSM-11 cocrystalline zeolites in the vapor-phase alkylation of benzene [4]. The Mobil-Badger and SRIPT ethylbenzene processes both use ZSM-5 as the catalyst. However, ZSM-5/ZSM-11 cocrystalline zeolite is also effective in benzene alkylation [19], and several ethylbenzene plants are operated using it as the alkylation catalyst. These results seem almost contradictory. It is difficult to say which process is better, because each zeolite has its own optimum reaction conditions. Justification based on inversion of the catalytic performance of ZSM-5 and ZSM-5/ZSM-11 under different operating conditions is not convincing. Moreover, the zeolite composition and morphology are critical in the catalytic performance. Every zeolite is a potential candidate for industrial applications, provided the process is profitable. Scientists identify possibilities, and engineers realize them.

Vapor-phase benzene alkylation occurs at higher temperatures than liquid-phase processes. More xylene is therefore produced through cracking, which reduces the ethylbenzene quality. This is a problem because xylene is difficult to separate from ethylbenzene. The xylene content in ethylbenzene produced by vapor-phase processes is difficult to restrict to below 600 ppm, whereas it is only about 10 ppm for liquid-phase processes. Moreover, the benzene/ethylene feed ratio is significantly lower in liquid-phase processes. Less excess benzene has to be recycled and circulated. Liquid-phase ethylation of benzene also has other advantages such as a better thermal control and longer catalyst lifetimes, which allow off-site catalyst regeneration, thereby facilitating easier pollution control. The liquid-phase benzene alkylation process is therefore better than the vapor-phase technique.

However, diffusion resistance to mass transfer is stronger in the liquid-phase process than in the vapor-phase process. When ZSM-5 zeolite was tested in liquid-phase benzene alkylation with ethylene, its activity was rapidly lost. It is therefore

necessary to move from medium pore zeolites to large pore zeolites such as β and Y.

Zeolite Y has a three-dimensional 12-MR pore system with supercages at the pore interconnections (Table 1), and the pore openings are larger than those of ZSM-5 (10-MR). It is suitable for liquid-phase benzene alkylation and was commercialized by UOP/Lummus/Unocal in 1989. However, the supercages with 12-MR openings (0.74 nm) favor the formation of bulky by-products (higher alkylbenzenes such as biphenyl and diphenylethane), and this is a drawback of using zeolite Y as an alkylation catalyst. β zeolite also has a three-dimensional pore system with 12-MR openings, but no supercage structures. In liquid-phase benzene alkylation, β zeolite is more active than zeolite Y, and more DEBs and TEBs are produced. EBs can be transalkylated, therefore the overall selectivity for useful products is higher for β zeolite [31].

Similar to zeolite Y, MCM-22 zeolite has a supercage structure in the pore system, but MCM-22 is more selective, particularly in the formation of DEBs and TEBs, the amounts of which are significantly lower than with USY or β zeolites. Little heavy byproducts are produced. Benzene and ethylene can both diffuse into the supercages through the 10-MR windows, with no limitations [51]. EBs are produced without any constraints inside the supercages, but they can hardly diffuse through the 10-MR openings.

β and MCM-22 zeolites are more suitable than zeolite Y for liquid-phase operations. A liquid-phase process catalyzed by MCM-22 zeolite can be operated at lower benzene/ethylene feed ratios; β zeolite has the highest catalytic activity and poison tolerance. MCM-22 and β zeolites are both widely used in industrial plants. Again, only economic factors decide which is more competitive.

4. Outlook

Since the first industrial application of a zeolite-catalyzed ethylbenzene process, benzene alkylation technology has made significant progress. The reaction temperature, benzene/ethylene feed ratio, xylene content, and consumption of energy and materials have all been lowered, and the operating stabil-

ity, tolerance of diverse materials, and product quality have greatly improved. Further research on catalysts and processes will undoubtedly promote the development of ethylbenzene technology.

4.1. Ethylbenzene processes with lower consumption of energy and materials

The stoichiometric molar ratio of benzene to ethylene in benzene ethylation is 1:1. However, in order to improve the selectivity for ethylbenzene, the feed ratio of benzene/ethylene in industrial plants is much higher ($>2/1$), especially in vapor-phase processes ($>5/1$). This is because the selectivity for the desired product is not high enough. Figure 4 shows the influence of the benzene/ethylene molar ratio on the product selectivity in liquid-phase benzene ethylation over MCM-22 zeolite. The formation of byproducts such as DEBs can be effectively suppressed by raising the benzene/ethylene molar ratio. When the reaction is performed at a low benzene/ethylene molar ratio, dimerization and polymerization of ethylene take place easily, resulting in coke formation, which causes catalyst deactivation. The ethylbenzene selectivity of MCM-22 zeolite catalyst is higher than those of β and Y zeolites, as shown in Fig. 5 [52]. The EBMax process, which uses MCM-22 as the alkylation catalyst, therefore operates with the lowest benzene/ethylene feed ratio, about 2/1.

Recently, it has been observed that changes in the morphologies and mesoporosities of the zeolite crystals strongly influence the activity and selectivity in alkylation reactions [53–62]. Wang et al. [53] showed that the conversion of ethylene over MCM-22 zeolite nanoplates is higher than that over MCM-22 zeolite microspheres. When β zeolite with a nano-sponge morphology was used in benzene alkylation with benzyl alcohol, the maximum possible catalytic turnover was increased six-fold compared with that for bulk β zeolite [54]. This high catalytic performance was the result of alkylation reactions occurring on external surfaces. External active sites were able to perform the catalytic function even after the active sites inside the zeolite micropores were deactivated.

Studies of benzene alkylation over mesoporous zeolites show that zeolites with abundant mesopores are more active

Fig. 4. Influence of benzene/ethylene molar ratio on product selectivity in liquid-phase benzene alkylation over MCM-22 zeolite at 220 °C and 3.5 MPa.

Fig. 5. Catalytic performance of different zeolites in benzene ethylation at 220 °C and 3.4 MPa with benzene/ethylene ratio of 4.0/1.

Fig. 6. Dependence of ethylene conversion in liquid-phase benzene ethylation on SiO₂/Al₂O₃ molar ratio. Reaction conditions: catalyst 0.5 g, 200 °C, 4.5 MPa, benzene/ethylene molar ratio = 2.0/1, ethylene WHSV = 6.0 h⁻¹.

than conventional zeolites [55–61]. Figure 6 shows a comparison of ethylene conversions using conventional MCM-22 and mesoporous MCM-22 prepared at various SiO₂/Al₂O₃ molar ratios [58]. The mesoporous MCM-22 zeolites clearly gave higher ethylene conversions than did the conventional MCM-22 samples. Also, delaminated MWW zeolites and MFI zeolite nanosheets give better catalytic performance than the original zeolites [63–66]. As well as an improvement in the activity, increased selectivity for monoalkylated products is also observed.

In a typical reaction, several procedures are assumed to occur: a reactant molecule first diffuses to the active site, then adsorption, activation, and reaction take place, and then the formed product molecule desorbs and diffuses out to give an available active site. Compared with a conventional catalyst, where diffusion restraints are significant, less monoalkylbenzene is present in the interiors of the mesoporous zeolite crystals because of the improved mass transfer. The possibility of further reaction between monoalkylbenzene and alkylation agent molecules to produce polyalkylbenzenes is therefore reduced. This may be why the activity and selectivity are both improved for mesoporous zeolites.

In liquid-phase benzene alkylation, where mass transport limitations cause much greater problems than in vapor-phase processes, mesoporous zeolites have more potential applications.

Alkylation of benzene over MWW zeolite, which has internal 10-MR sinusoidal pores and external 12-MR semi-cages, is more complicated than the reactions over Y or β zeolites, which have 12-MR pore systems. Corma et al. [67], and Du and Olson [68] showed that the 10-MR pore system of the MCM-22 zeolite contributes little to the overall production of ethylbenzene and EBs in the liquid-phase alkylation of benzene with ethylene. This means that only some of the acid sites are active. This may be why MWW zeolite is less active than β zeolite.

The synthesis of materials with more semi-supercages or larger external surface areas is an effective way of obtaining better MWW-zeolite-based alkylation catalysts. Delaminated ITQ-2 [63,64,69] and pillared MCM-36 [70] zeolites represent

such materials. However, the complicated preparation procedures and high costs of ITQ-2 and MCM-36 restrict their use. The development of new preparation methods that can be easily used would benefit progress in ethylbenzene processes.

4.2. Ethylbenzene processes with various raw materials

Because of oil shortages and the requirements for sustainable development, it is necessary to develop new catalytic processes using a variety of raw materials such as benzene and ethylene from coal, ethanol from biomass, and ethane from FCC off-gas. The challenges are how to design and synthesize highly active catalysts that are tolerant of the impurities and poisons in low-quality feedstocks. The development of simple and efficient pretreatment processes is an alternative solution.

There is currently a trend to use unrefined ethylene produced in the methanol-to-olefin process as the ethylation agent to produce ethylbenzene. The content of ethylene is usually high, 75%–95%, and the main inert impurities are methane (about 3%), ethane (about 2%), CO, and H₂. There are also significant amounts of sulfide and nitrides, which can cause catalyst poisoning. Figure 7 shows the deactivation of ZSM-5 zeolite by a nitrogen-containing substance (2-aminoethanol) in vapor-phase benzene alkylation [71]. The use of ethanol from biomass faces the same poisoning problem. The use of poison-tolerant catalytic materials would therefore promote the use of low-quality raw materials.

The ethane content of FCC off-gas is low (about 10%) and it is relatively inert. The development of catalysts that can activate ethane or of bifunctional catalysts that have both dehydrogenation and alkylation activity would be worth investigating. Research on Pt/ZSM-5 as a catalyst for benzene alkylation with ethane has been performed for years [47]. An ethylbenzene process with separate ethane-dehydrogenation and benzene-alkylation processes was patented by the Dow Chemical Company. However, there has been no report of its commercialization.

4.3. Green routes for preparation of zeolite-based catalysts

Industrial catalytic processes using zeolite-based catalysts

Fig. 7. Effect of 2-aminoethanol on ethylene conversion in vapor-phase benzene alkylation.

are usually considered to be environmentally benign. However, procedures for the preparation of zeolite-based catalysts cause environmental pollution [72]. Zeolite synthesis is usually performed in the presence of a nitrogen-containing organic template, and only some of the used template is recyclable. Plenty of water is needed to wash the zeolite. NO_x is formed during zeolite calcination. Salt-containing wastewater is produced during the ion-exchange procedure. Moreover, the catalyst loses activity after years of operation, and is no longer suitable for industrial use, and becomes industrial waste.

It would be useful to produce catalysts in more effective ways, to reduce environmental pollution. Template-free or even solvent-free methods for zeolite synthesis need to be developed [73–76]. Direct synthesis of H-form zeolites would avoid the ion-exchange procedure [77]. The development of ways of using waste catalysts, for example by reusing them as raw materials for zeolite synthesis, would benefit the environment [78,79].

4.4. Other application of benzene alkylation

Aromatic hydrocarbons are usually added to gasoline as octane enhancers. However, aromatics such as benzene can be toxic to human organs and should be strictly limited or removed from gasoline [80]. BenzOut is a commercial process for the removal of benzene from gasoline, developed by modern refineries, and involves alkylation with olefins [81–83]. The abovementioned alkylation catalysts that have been commercialized, i.e., ZSM-5, Y, MCM-22, and β zeolites, are all candidates for the BenzOut process. One important factor that needs to be considered is that gasoline rather than benzene is fed into the catalyst bed. The feed ratio of benzene/olefin is low, and more multi-alkylated benzene is produced, which causes catalyst deactivation. Also, Lewis acids cause side reactions such as oligomerization. The selection of reaction conditions and modification of the acidic properties is therefore critical for the removal of benzene from gasoline through alkylation.

5. Conclusions

The development of ethylbenzene processes has been rapid during the last few decades, especially in China. Various alkylation and transalkylation catalysts based on different zeolites have been commercialized by Mobil, UOP, DICP, Sinopec, and some other companies.

Along with the development of catalytic materials, vapor-phase and liquid-phase ethylbenzene processes have been developed and commercialized. Vapor-phase processes are more flexible, because pure ethylene, dilute ethylene, ethanol, and even ethane can be used as the feedstock. The dilute-ethylene process is widely used in China, but the production capacity of every plant is limited. Liquid-phase processes have several advantages such as low energy consumption, low benzene/ethylene feed ratios, low alkylation temperatures, and high product quality.

Zeolites with different pore structure and acidic properties give different catalytic performance. Each has its own distinc-

tive features. ZSM-5 is the most widely used vapor-phase benzene ethylation catalyst. Among all the liquid-phase catalysts, β zeolite is the most active and poison tolerant, and MCM-22 zeolite has the highest ethylbenzene selectivity and longest catalyst lifetime. Use of a combination of two or more zeolite catalysts may therefore provide a significant breakthrough in the development of ethylbenzene processes.

In the future, the development of ethylbenzene processes will focus on the development and application of new catalytic materials and the use of different feedstocks, which would meet the requirements of sustainable development.

References

- [1] N. Mimura, M. Saito, *Catal. Today*, **2000**, 55, 173.
- [2] C. Perego, P. Ingallina, *Catal. Today*, **2002**, 73, 3.
- [3] K. Tanabe, W. F. Hölderich, *Appl. Catal. A*, **1999**, 181, 399.
- [4] A. A. O'Kelly, J. III Kellett, J. Plucker, *Ind. Eng. Chem.*, **1947**, 39, 154.
- [5] W. M. Yang, H. M. Sun, S. J. Yang, H. F. Zhu, *Shanghai Chem. Ind.*, **2002**, (9–10), 16.
- [6] J. R. Argauer, R. G. Landolt, US Patent 3 702 886, **1972**.
- [7] G. T. Kokotailo, S. L. Lawton, D. H. Olson, W. M. Meier, *Nature*, **1978**, 272, 437.
- [8] Z. K. Xie, *Porous Catalytic Materials with New Structure and Improved Performance*, China Petrochem. Press, Beijing, **2010**, 4.
- [9] N. Y. Chen, W. E. Garwood, *Catal. Rev.-Sci. Eng.*, **1986**, 28, 185.
- [10] W. M. Yang, H. M. Sun, Q. L. Chen, *Adv. Fine Petrochem.*, **2002**, 3(4), 12.
- [11] H. M. Sun, W. M. Yang, Q. L. Chen, Z. L. Xu, M. Jin, X. F. Shi, *Ind. Catal.*, **2001**, 9(5), 23.
- [12] H. M. Sun, W. M. Yang, B. X. Liao, J. C. Zheng, *Chem. React. Eng. Technol.*, **2006**, 22, 206.
- [13] M. Ni, D. Y. C. Leung, M. K. H. Leung, *Int. J. Hydrogen Energy*, **2007**, 32, 3238.
- [14] K. H. Chandawar, S. B. Kulkarni, P. Ratnasamy, *Appl. Catal.*, **1982**, 4, 287.
- [15] X. W. Nie, X. Liu, C. S. Song, X. W. Guo, *Chin. J. Catal.*, **2009**, 30, 453.
- [16] W. M. Yang, H. M. Sun, W. J. Liu, B. Zhang, Z. H. Shen, M. Y. Huan, H. Y. Zhang, US Patent 8 519 208, **2013**.
- [17] Y. J. Zhao, X. Zhang, C. L. Zhou, X. J. Jin, *Contemp. Chem. Ind.*, **2011**, 40, 1149.
- [18] T. F. Degnan Jr, C. M. Smith, C. R. Venkat, *Appl. Catal. A*, **2001**, 221, 283.
- [19] F. C. Chen, X. X. Zhu, S. J. Xie, P. Zeng, Z. J. Guo, J. An, Q. X. Wang, S. L. Liu, L. Y. Xu, *Chin. J. Catal.*, **2009**, 30, 817.
- [20] Y. Q. Wang, *Petrochem. Technol.*, **2001**, 30, 479.
- [21] Q. X. Wang, S. R. Zhang, G. Y. Cai, F. Li, L. Y. Xu, Z. X. Huang, Y. Y. Li, US Patent 5 869 021, **1999**.
- [22] J. W. Li, J. Wang, X. L. Liu, G. Chen, C. L. Guo, J. Cong, L. Wang, L. Chen, Y. B. Wang, *Chem. Ind. Eng. Progr.*, **2010**, 29, 1790.
- [23] S. Q. Gao, *Nat. Gas Chem. Ind.*, **2010**, 35(4), 55.
- [24] Y. Zhang, Q. J. Tian, X. B. Ma, *Petrol. Refinery Eng.*, **2012**, 42(10), 59.
- [25] J. L. Gou, *Ind. Catal.*, **2014**, 22, 397.
- [26] C. G. Wight, US Patent 4 169 111, **1979**.
- [27] M. Rasouli, N. Yaghobi, S. Chitsazan, M. H. Sayyar, *Microporous Mesoporous Mater.*, **2012**, 152, 141.
- [28] J. B. Higgins, R. B. LaPierre, J. L. Schlenker, A. C. Rohrman, J. D. Wood, G. T. Kerr, W. J. Rohrbach, *Zeolites*, **1988**, 8, 446.
- [29] R. L. Wadlinger, G. T. Kerr, E. J. Rosinski, US Patent 3 308 069, **1967**.

Graphical Abstract

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Advances in development and industrial applications of ethylbenzene processes

Weimin Yang*, Zhendong Wang, Hongmin Sun, Bin Zhang
Sinopec Shanghai Research Institute of Petrochemical Technology

Advances in catalysts and processes for benzene ethylation with pure/dilute ethylene or ethanol to produce ethylbenzene are summarized. Some promising techniques and applications are discussed.

- [30] J. Aguado, D. P. Serrano, J. M. Rodríguez, *Microporous Mesoporous Mater.*, **2008**, 115, 504.
- [31] G. Bellussi, G. Pazzuconi, C. Perego, G. Girotti, G. Terzoni, *J. Catal.*, **1995**, 157, 227.
- [32] L. Forni, G. Gremona, F. Missineo, G. Bellussi, C. Perego, G. Pazzuconi, *Appl. Catal. A*, **1995**, 121, 261.
- [33] J. C. Cheng, A. S. Fung, D. J. Klocke, S. L. Lawton, D. N. Lissy, W. J. Roth, C. M. Smith, D. E. Walsh, US Patent 5 557 024, **1996**.
- [34] J. N. Armor, *Appl. Catal. A*, **2001**, 222, 407.
- [35] G. J. Gajda, R. T. Gajek, US Patent 5 522 984, **1996**.
- [36] J. Wang, F. M. Zhang, M. L. Li, C. Zhang, *Petrol. Process Petrochem.*, **2002**, 33(9), 13.
- [37] Z. Y. Huang, S. X. Tian, Y. L. Xu, B. Zhu, W. D. Wang, F. M. Zhang, X. Wang, US Patent 5 600 050, **1997**.
- [38] H. L. Dai, *Aromatic Technology*, China Petrochem Press, Beijing, **2014**, 524.
- [39] Y. Wang, Y. M. Liu, L. L. Wang, H. H. Wu, X. H. Li, M. Y. He, P. Wu, *J. Phys. Chem. C*, **2009**, 113, 18753.
- [40] L. M. Rohde, G. J. Lewis, M. A. Miller, J. G. Moscoso, J. L. Gisselquist, R. L. Patton, S. T. Wilson, D. Y. Jan, US Patent 6 756 030, **2004**.
- [41] W. J. Roth, T. Yorke, D. L. Dorset, M. Kalyanaraman, M. C. Kerby, S. C. Weston, US Patent 8 110 176, **2012**.
- [42] W. J. Roth, D. L. Dorset, G. J. Kennedy, T. Yorke, T. E. Helton, US Patent 8 704 025, **2014**.
- [43] W. J. Roth, D. L. Dorset, G. J. Kennedy, T. Yorke, T. E. Helton, P. Ghosh, Y. V. Joshi, US Patent 8 704 023, **2014**.
- [44] M. E. Leonowicz, J. A. Lawton, S. L. Lawton, M. K. Rubin, *Science*, **1994**, 264, 1910.
- [45] D. Y. Jan, J. A. Johnson, R. J. Schmidt, G. B. Woodle, US Patent 7 268 267, **2007**.
- [46] D. Y. Jan, J. A. Johnson, R. J. Schmidt, M. P. Koljack, US Patent 8 518 847, **2013**.
- [47] D. B. Lukyanov, T. Vazhnova, *J. Catal.*, **2008**, 257, 382.
- [48] S. Kato, K. Nakagawa, N. O. Ikenaga, T. Suzuki, *Catal. Lett.*, **2001**, 73, 175.
- [49] T. Odedairo, S. Al-Khattaf, *Appl. Catal. A*, **2010**, 385, 31.
- [50] M. Raimondo, G. Perez, A. De Stefanis, A. A. G. Tomlinson, O. Ursini, *Appl. Catal. A*, **1997**, 164, 119.
- [51] M. Bevilacqua, D. Meloni, F. Sini, R. Monaci, T. Montanari, G. Busca, *J. Phys. Chem. C*, **2008**, 112, 9023.
- [52] J. C. Cheng, T. F. Degnan, J. S. Beck, Y. Y. Huang, M. Kalyanaraman, J. A. Kowalski, C. A. Loehr, D. N. Mazzone, *Stud. Surf. Sci. Catal.*, **1999**, 121, 53.
- [53] Z. D. Wang, Y. X. Zhang, B. Zhang, H. M. Sun, W. M. Yang, *Acta Petrol. Sin. (Petrol. Process Sect.)*, **2014**, 30(1), 110.
- [54] J. C. Kim, K. Cho, R. Ryoo, *Appl. Catal. A*, **2014**, 470, 420.
- [55] N. N. Gao, S. J. Xie, S. L. Liu, W. J. Xin, Y. Gao, X. J. Li, H. J. Wei, H. Liu, L. Y. Xu, *Microporous Mesoporous Mater.*, **2015**, 212, 1.
- [56] J. Pérez-Ramírez, C. H. Christensen, K. Egeblad, C. H. Christensen, J. C. Groen, *Chem. Soc. Rev.*, **2008**, 37, 2530.
- [57] K. F. Liu, S. J. Xie, G. L. Xu, Y. N. Li, S. L. Liu, L. Y. Xu, *Appl. Catal. A*, **2010**, 383, 102.
- [58] B. Zhang, Z. D. Wang, P. Ji, Y. M. Liu, H. M. Sun, W. M. Yang, P. Wu, *Microporous Mesoporous Mater.*, **2013**, 179, 63.
- [59] M. Horňáček, P. Hudec, K. Velebná, P. Lovás, *Catal. Commun.*, **2015**, 64, 1.
- [60] Y. Y. Sun, R. Prins, *Appl. Catal. A*, **2008**, 336, 11.
- [61] C. H. Christensen, K. Johannsen, I. Schmidt, C. H. Christensen, *J. Am. Chem. Soc.*, **2003**, 125, 13370.
- [62] M. S. Holm, E. Taarning, K. Egeblad, C. H. Christensen, *Catal. Today*, **2011**, 168, 3.
- [63] R. C. Runnebaum, X. Ouyang, J. A. Edsinga, T. Rea, I. Arslan, S. J. Hwang, S. I. Zones, A. Katz, *ACS Catal.*, **2014**, 4, 2364.
- [64] W. Kim, J. C. Kim, J. Kim, Y. Seo, R. Ryoo, *ACS Catal.*, **2013**, 3, 192.
- [65] A. Corma, V. Fornés, J. Martínez-Triguero, S. B. C. Pergher, *J. Catal.*, **1999**, 186, 57.
- [66] J. Aguilar, S. B. C. Pergher, C. Detoni, A. Corma, F. V. Melo, E. Sastre, *Catal. Today*, **2008**, 133–135, 667.
- [67] A. Corma, V. Martínez-Soria, E. Schnoefeld, *J. Catal.*, **2000**, 192, 163.

- [68] H. W. Du, D. H. Olson, *J. Phys. Chem. B*, **2002**, 106, 395.
- [69] A. Corma, V. Fornés, J. M. Guil, S. Pergher, Th. L. M. Maesen, J. G. Buglass, *Microporous Mesoporous Mater.*, **2000**, 38, 301.
- [70] C. T. Kresge, W. J. Roth, US Patent 5 278 115, **1994**.
- [71] X. B. Ma, F. C. Ruan, *Ind. Catal.*, **2014**, 22, 632.
- [72] X. J. Meng, F. S. Xiao, *Chem. Rev.*, **2014**, 114, 1521.
- [73] B. Xie, H. Y. Zhang, C. G. Yang, S. Y. Liu, L. M. Ren, L. Zhang, X. J. Meng, B. Yilmaz, U. Müller, F. S. Xiao, *Chem. Commun.*, **2011**, 47, 3945.
- [74] B. Xie, J. W. Song, L. M. Ren, Y. Y. Ji, J. X. Li, F. S. Xiao, *Chem. Mater.*, **2008**, 20, 4533.
- [75] L. M. Ren, Q. M. Wu, C. G. Yang, L. F. Zhu, C. J. Li, P. L. Zhang, H. Y. Zhang, X. J. Meng, F. S. Xiao, *J. Am. Chem. Soc.*, **2012**, 134, 15173.
- [76] Y. Y. Jin, Q. Sun, G. D. Qi, C. G. Yang, J. Xu, F. Chen, X. J. Meng, F. Deng, F. S. Xiao, *Angew. Chem. Int. Ed.*, **2013**, 52, 9172.
- [77] S. Q. Wei, F. F. Qu, CN Patent 102 092 740, **2011**.
- [78] Y. C. Shi, E. H. Xing, W. H. Xie, F. M. Zhang, X. H. Mu, X. T. Shu, *RSC Adv.*, **2015**, 5, 13420.
- [79] E. H. Xing, Y. C. Shi, A. G. Zheng, J. Zhang, X. Z. Gao, D. Y. Liu, M. D. Xin, W. H. Xie, F. M. Zhang, X. H. Mu, X. T. Shu, *Ind. Eng. Chem. Res.*, **2015**, 54, 3123.
- [80] A. Galadima, O. Muraza, *Microporous Mesoporous Mater.*, **2015**, 213, 169.
- [81] M. C. Clark, B. S. Umansky, E. A. Nye, M. J. Reichensperger, W. C. Lewis, US Patent 8 395 006, **2013**.
- [82] A. A. Chin, N. A. Collins, M. N. Harandi, R. T. Thomson, R. A. Ware, US Patent 5 491 270, **1996**.
- [83] O. Graf P., L. Lefferts, *Chem. Eng. Sci.*, **2009**, 64, 2773.

乙苯工艺技术开发及工业应用进展

杨为民*, 王振东, 孙洪敏, 张 斌

中国石油化工股份有限公司上海石油化工研究院, 上海201208

摘要: 乙苯是重要的基本有机化工原料, 主要用于生产苯乙烯, 进而作为合成橡胶和塑料等高分子材料的单体。乙苯的生产主要采用苯和乙烯的烷基化工艺。传统的 AlCl_3 法由于存在设备腐蚀和环境污染等问题已逐步被环境友好的分子筛烷基化法取代。分子筛烷基化法分为气相法和液相法。气相烷基化催化剂为ZSM-5分子筛, 例如Mobil-Badger气相烷基化工艺; 液相烷基化催化剂有Y, Beta和MCM-22分子筛, 例如Lummus/UOP的EBOne工艺和Mobil-Raythen的EBMax工艺。

近年来, 随着经济的发展, 全球范围内乙苯需求量逐年增加, 产能也逐渐扩大。尤其在中国大陆, 目前乙苯产能居世界首位, 其乙苯工艺技术的开发也最为活跃。经过20多年的发展, 苯烷基化制乙苯工艺取得了长足发展。中国科学院大连化学物理研究所在成功合成ZSM-5/ZSM-11分子筛的基础上, 与中国石化、中国石油联合开发了苯与干气气相烷基化制乙苯工艺; 中国石化上海石油化工研究院则以ZSM-5分子筛为基础, 开发了适应原料多样性的苯气相烷基化制乙苯催化剂和工艺技术, 可以采用石油苯、焦化苯、纯乙烯、乙醇和稀乙烯为原料; 石油化工科学研究院则开发了基于Beta分子筛的苯与乙烯液相烷基化催化剂及液相循环烷基化工艺。以上催化剂及工艺技术均已工业化应用。此外, 实现催化烷基化与分离同时进行的催化蒸馏工艺以及乙烷脱氢再与苯烷基化的两段法制乙苯工艺的研究也取得了一定进展。

在苯烷基化制乙苯工艺中, 气相法操作温度高, 苯与乙烯进料摩尔比高, 因而能耗高, 同时二甲苯含量高, 产品纯度低。液相烷基化工艺则具有温度低和苯/烯比低的特点, 其能耗控制及产品质量均优于气相法工艺。但是, 液相反应中的扩散阻力大, 孔道为10元环的ZSM-5分子筛失活迅速, 因而选用了具有12元环孔道的Y, Beta和具有表面12元环碗状半超笼的MCM-22分子筛为催化剂。然而, 液相法工艺的苯与乙烯进料摩尔比仍然远高于理论化学计量比, 其产品中含有一定比例的多乙基苯(主要是二乙苯), 需采用烷基转移过程将多乙基苯与苯反应生成乙苯。

进一步降低苯/烯比、提高单乙苯选择性是未来乙苯工艺开发的努力方向。研究表明, 介孔分子筛及纳米片状分子筛在苯烷基化反应中具有优于常规分子筛的催化表现, 即更高的乙烯转化率和乙苯选择性。其原因在于, 扩散是影响苯烷基化反应性能的关键因素, 扩散性能的改善使得产物从活性位解吸后更容易扩散出去, 进而空出活性位并进一步催化新的底物。同时, 单烷基化产物与新的烷基化试剂进一步发生烷基化的几率降低, 提高了单烷基化产物的选择性。因而, 采用扩散性能更好的催化剂催化苯烷基化反应前景看好, 关键在于如何简单并廉价地获取该类材料。

另外, 虽然分子筛催化苯烷基化是一个环境友好的工艺过程, 但是在分子筛催化剂制备过程中会产生环境污染。同时, 失活催化剂的处理也是需要考虑的问题。开发分子筛的绿色合成技术, 减轻甚至消除环境污染是一个值得努力的方向; 开发失活催化剂的综合利用技术, 如采用失活催化剂为原料用于分子筛的合成, 可以作为环境保护的有效手段。

关键词: 乙苯; 烷基化; 烷基转移; ZSM-5分子筛; MCM-22分子筛; Beta分子筛; Y分子筛

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*通讯联系人. 电话: (021)68462197; 传真: (021)68462283; 电子信箱: yangwm.sshy@sinopec.com

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