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Promoting Xylene Production in Benzene Methylation using Hierarchically Porous ZSM-5 Derived from a Modified Dry-gel Route[☆]

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ABSTRACT

Methylation of benzene is an alternative low-cost route to produce xylenes, but selectivity to xylene remains low over conventional zeolitic catalysts. In this work, a combined dry-gel-conversion and steam-assisted-crystallization method is used to synthesize hierarchically porous zeolite ZSM-5 with varied Si/Al malar ratios. X-ray diffraction (XRD), N_2 physisorption, NH_3-temperature programmed desorption (TPD), scanning electronic microscopic (SEM) measurement and Fourier transform infrared (FT-IR) are employed to characterize the structure and acidity of both hierarchically porous zeolites and their conventional counterparts. The method is found to be applicable to ZSM-5 with molar ratios of Si/Al from 20 to 180. The ZSM-5 zeolites are used as catalysts for benzene methylation at 460 °C to investigate the effect of additional porosity and Si/Al ratios. At low Si/Al ratios, the benzene conversions over conventional and hierarchical ZSM-5 are close, and selectivity to toluene is high over hierarchical ZSM-5. It is found that hierarchical porosity markedly enhances the utility of zeolite and the selectivity towards xylenes *via* improved mass transport at higher Si/Al ratios. Under an optimized hierarchical ZSM-5 catalyst, xylene selectivity reaches 34.9% at a Si/Al ratio of 180.

1. Introduction

Xylenes are important feedstock for the industrial production of terephthalic acid, isophthalic acid, dimethyl terephthalate, polyester resins, and the synthesis of vitamins or other pharmaceutical products. Nowadays, most xylenes are mass produced in industrial scale *via* either naphtha catalytic reforming or toluene disproportionation [1]. Separation of xylene isomers and the ethylbenzene mixture co-product is expensive due to their close boiling points. In the established toluene disproportionation process, a large amount of benzene is produced simultaneously, which was previously added to gasoline as co-fuels. Nonetheless, governments are imposing stringent guidelines to reduce benzene content in gasoline, with the awareness of its toxicity to public health and our ecological system. An alternative route to produce xylenes is through the methylation of toluene or benzene, and zeolites are the preferred solid acidic catalyst for their shape-selectivity [1–9]. For toluene methylation, since the pioneering work by Yashima *et al.* [2] over various cation modified Y-zeolite (FAU) catalysts in the 1970s, Kaeding and co-workers have optimized the modification methods of ZSM-5 (MFI structure) with a wide range of modifiers (Mg, P, Si, *etc.*) to maximize the *p*-xylene yields [3,4,11–16]. Later on, other zeolites, such as ZSM-11 (MEL), MCM-22 (MWW) [17], ITQ-2 (MWW) [17], Mordenite (MOR) [18,19], β-(BEA) [20], SAPO-34 (CHA) [18], SAPO-11/MnAPO-11 (AEL) [6,18], and SAPO-5/MnAPO-5 (AFI) [8,18,21] have been extensively explored for catalyzing methylation of toluene. In most cases, valuable *p*-xylene is the major product because *p*-xylene diffusivity in ZSM-5 channels is 3 orders of magnitude faster than *m*- or *o*-xylene, which endows desirable product selectivity [3,22]. On the other hand, there are only sporadic reports on benzene methylation using methanol compared with that of toluene; a complicated product spectrum with high selectivity to toluene and low selectivity towards xylenes is normally observed [5–10,23,24]. It is demanding to design a single intensified process to convert low-cost benzene and methanol through consecutive methylation to value added xylenes, for which the current selectivity to xylene remains low (≤20%) [5,23].

As the crystal size of most zeolites is in the range of micrometers, and molecular transport within microporous channels is solely governed by configurational diffusion [25]. One side effect of using zeolitic catalysts is the restriction of diffusion that limits the utility of zeolites or accessibility to and from the internal active centers. In the past decade or so, it has been recognized that creating additional porosity to zeolitic crystals or decreasing crystal size can alleviate the diffusion limitations and thereby promote the catalytic performance of zeolitic catalysts [25–34]. The

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zeolite with at least two types of porosity is called a hierarchically porous zeolite (HPZ), which normally contains both meso- (2–50 nm) and micro-porosity in one crystalline material. The merits of using HPZs with respect to their conventional analogues include high activity, high catalytic lifetime, higher activity towards bulky molecules, as well as improved stability, that has recently been highlighted in a recent review by Egeblad *et al.* [35]. The product distribution can also be altered due to the different shape or size of their controlled mass transport inside zeolitic architectures [26,35]. In the case of toluene methylation, however, there are controversial conclusions. For instance, Jahn *et al.* reported no size effect of ZSM-5 to production distribution for toluene methylation [36], whereas Wang and co-workers [13] showed the merits of using nanosized ZSM-5 by promoting activity (conv. 4%) in both toluene disproportionation and methylation. Ding and co-workers [37] have observed a jump of 10% in conversion when ZSM-5 after steaming treatment was used to catalyze the methylation of toluene; however, the zeolitic size effect is not clearly shown as steaming affects both porosity and acid strength. From early studies by Christensen *et al.* [26], it has been observed that over HPZ ZSM-5, benzene alkylation with ethylene to ethylbenzene is enhanced in terms of benzene conversion and ethylbenzene selectivity. The rate limiting process for the reaction over conventional ZSM-5 is intracrystalline diffusion of ethylbenzene, because the ethylbenzene molecule is larger in size than other reactants. On the other hand, the rate limiting process on HPZ ZSM-5 is shifted to the intrinsic reaction controlled process. These findings inspire us to find the effect of product distribution by HPZ, but no report on crystal size effect for benzene methylation has been known thus far.

From the point of view of mass transport, it was once believed that the shape-selectivity stems from the intracrystal diffusion of products and thereby a larger crystal size enhances selectivity [38]. However, recent transport studies show that benzene, toluene and xylene (BTX) transport depends on crystal sizes. Lercher and co-workers [39–41] found that the rate-controlling step in mass transport is switched from intracrystal diffusion to the surface process as the primary sizes of ZSM-5 are reduced down to below 100 nm, as a result of small values ($\leq 10^{-6}$) for the BTX sticking probability. As small molecules (*i.e.*, CH_3OH) access pore apertures *via* both sinusoidal/straight channels and BTX enters mainly *via* straight channels, traffic-control can also play a role in mass transport [42]. Keeping in mind that the majority of the conventional ZSM-5 crystal is covered by sinusoidal channels as a result of subunit intergrowth, only traces of straight channels are exposed to external surfaces [43]. Moreover, the pore mismatch in boundaries of intergrowth subunits can incur a more intricate effect to mass transport in conventional ZSM-5 [43]. From a kinetic angle of recent studies by Svelle *et al.* [5], it is evident that as the apparent reaction rate is first-order with respect to benzene partial pressure, improving BTX transport is expected to influence the concentration of BTX in the vicinity of active sites, and thereby the kinetic process. Although the reaction rate is zeroth order with respect to CH_3OH pressure, excessive CH_3OH adsorbed strongly on acidic sites can block the aperture to channels and lead to slow mass transport [5]. Changing the Si/Al ratio will adjust the concentration of pre-adsorbed CH_3OH. Inspired with the above knowledge, one can expect that both additional porosity and Si/Al ratio can influence the catalytic performance to benzene methylation [38].

Herein, we adopt H-ZSM-5, a widely employed archetypal zeolitic catalyst to explore the effect of hierarchical porosity and Si/Al ratio on the catalytic performance for the methylation of benzene. As the methylation of benzene is also an important step to understand methanol to hydrocarbon (MTH) [5] or methane methylation with benzene [7,8], these results can also be fundamentally important to these relevant reactions. We demonstrate here that HPZ ZSM-5 enhances both benzene methylation to toluene and its consecutive methylation to xylene at high Si/Al ratios. HPZ ZSM-5 is thereby a catalyst that intensifies the benzene methylation selectivity to xylene, which constitutes another merit of using hierarchical zeolites to consecutive reactions.

2. Experimental

2.1. Materials and syntheses

2.1.1. Materials

Tetraethyl orthosilicate (TEOS, 99%) and tetrapropylammonium hydroxide [TPAOH, 25% (by mass) aqueous solution] were obtained from Meyer Chemical, China. Ethanol (90%), aluminum tritertbutoxide (ATTB, 99%) and ammonium hydroxide (28%–30%) solutions were purchased from Shanghai Lingfeng Chemicals, while hexadecyltrimethoxysilane (HTS) was obtained from Gelest, USA. Distilled H_2O was used throughout this work. All commercial chemicals were used directly without further purifications.

2.1.2. Synthesis

Hierarchical ZSM-5 (denoted as ZSM-5-HTS-*x*, *x* is the molar ratio of Si/Al) was prepared *via* a modified approach developed by the author [44]. In a typical synthesis of ZSM-5-HTS, 3.12 g TEOS, 0.21 g HTS and 0.035 g ATTB were dissolved in 20.0 ml ethanol under stirring. This mixture was further stirred for 30 min to form a solution, followed by the addition of another solution of 2.0 g TPAOH in 5.0 g ethanol under vigorous stirring; hydrolysis occurred at this stage as evidenced by heat release, although a stable so-called "clear solution" is produced (the transparent "clear solution" is stable up to one month in a closed vial). The "clear solution" was stirred for 1 h before being transferred to a petri dish where the solvent was allowed to evaporate overnight. A transparent dry gel resulting from solvent evaporation was ground, then moved to a teflon cup. The cup was placed in a teflon-lined autoclave of 150 ml, and 10.0 g of water is added outside the cup to create steam for the hydrothermal synthesis conditions. The autoclave was moved into an oven set at 180 °C and kept there for 3 days for a steam-assisted crystallization. The final solid, retaining the shape of the original dry gel particles, was filtrated and washed with water, and then calcined at 550 °C for 20 h by a ramp of 3 $°C\cdot min^{-1}$ in air.

To prepare a conventional ZSM-5 with the same Si/Al ratio, 3.24 g TEOS, 0.07 g ATTB, 2.0 g TPAOH and 7.7 ml ammonium hydroxide were mixed in 30.0 g DI-H_2O and stirred for 4 h, then transferred to an autoclave and allowed to crystallize for 72 h at 180 °C [44]. Combustion to remove the template was conducted using the same procedure as for ZSM-5-HTS. For both samples, the Si/Al molar ratio was controlled to be 20, 40, 70 and 180.

2.2. Characterizations

X-ray diffraction patterns of powders were carried out on a Rigaku D/max 2550 VB/PC (40 kV, 100 mA) X-ray diffractometer operated with a monochromatized Cu K_α radiation ($\lambda = 0.15406$ nm) enabled by nickel filtration of Cu K_β. The scan rate was $8(°)\cdot min^{-1}$, ranging from 5–50°. N_2 physisorption was employed to analyze the surface area and pore architecture of both powders. The specific surface areas of both conventional ZSM-5 and HPZ ZSM-5-HTS were deduced from the Langmuir method and the Brunauer–Emmett–Teller (BET) method, respectively, for the purpose of comparison by using a Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry System. A micropore volume is calculated from the standard *t*-plot approach, while the total volume pores were based on the adsorption capacity at a relative pressure of 0.99. The macro- plus meso-pore volume was referred to as the subtraction of the micropore volume from the total pore volume. Mesopore size distribution was calculated from a Barrett–Joyner–Halenda (BJH) model using the adsorption branch of an isotherm. Scanning electronic micrographic (SEM) images were taken from a Hitachi S-4800(II) field-emission SEM apparatus (FESEM). Ammonia temperature programmed desorption (NH_3-TPD) was measured using a PX200A type TPD/TPR instrument from Tianjin Pengxiang Tech. Corp., with 0.10 g conventional ZSM-5 and 0.25 g ZSM-5-HTS sampled respectively. Before measurement, each sample was heated under