Catalytic Activity of Pt Modified Hierarchical ZSM-5 Catalysts in Benzene Alkylation with Methanol

Hualei Hu · Qunfeng Zhang · Jie Cen · Xiaonian Li

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Abstract Hierarchical ZSM-5 zeolite showed an improved performance as compared to conventional ZSM-5 catalysts in the alkylation of benzene with methanol. However, ethylbenzene yet remains as a major problem. In this study, we modified hierarchical ZSM-5 with Pt to evaluate the alkylation of benzene with methanol in a fixed-bed continuous flow reactor. It was found that Pt modified hierarchical ZSM-5 could successfully combine the catalytic advantages of hierarchical ZSM-5 and the high suppression of Pt to ethylbenzene formation. Moreover, employing direct reduction could improve the utilization of Pt by avoiding Pt particles sintering.

Keywords Hierarchical ZSM-5 \cdot Pt \cdot Ethylbenzene \cdot Xylene \cdot Benzene alkylation

1 Introduction

The alkylation of benzene with methanol is a promising technology in petrochemical industry for the production of toluene and xylene, which are important chemical intermediates [1–4]. While using conventional ZSM-5 zeolite as the catalyst for the alkylation of benzene with methanol, the formation of ethylbenzene was difficult to be eliminated [5–7]. Moreover, the separation or removal of ethylbenzene from C8 aromatic still remains as a major challenge [8–10]. Recently, researchers found that Pt

H. Hu · Q. Zhang · J. Cen · X. Li (🖂)

State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, Industrial Catalysis Institute of Zhejiang University of Technology, Hangzhou 310032, People's Republic of China e-mail: xnli@zjut.edu.cn modified ZSM-5 could exhibit high suppression ability towards the formation of ethylbenzene in benzene alkylation with methanol, which effectively avoided the difficulty of separating ethylbenzene from xylene [11]. However, low conversion of benzene and low selectivity to xylene was observed over the conventional ZSM-5 and this might be attributed to the diffusion limitation of micropores [5, 7].

Hierarchical materials can enhance the diffusion of bulky substrates during the catalytic reactions as the result of introducing mesopores into zeolite materials without destroying the catalytic feature of zeolitic micropores [12, 13]. Not surprisingly, hierarchical zeolites could dramatically improve the catalytic performance in the methylation of toluene and the ethylation of benzene as compared to conventional zeolite catalysts [14–16]. Recently, Lu et al. and Deng et al. had reported that hierarchical ZSM-5 displayed higher benzene conversion and xylene selectivity in benzene alkylation with methanol than conventional ZSM-5 [17, 18]. Unfortunately, hierarchical ZSM-5 still cannot exterminate the formation of ethylbenzene [19]. Consequently, combining the suppressing ability of Pt towards the ethylbenzene formation and the catalytic advantages of hierarchical ZSM-5 would be of great interests. On the other hand, it is well known that calcination at high temperatures in air causes Pt particle sintering, which decreases the dispersion of Pt and further influences its hydrogenation activity [20, 21]. Direct reduction of the supported Pt precursor in hydrogen flow could reduce the change of Pt particle caused by calcinations [22]. Therefore, employing direct reduction method might be able to improve the utilization efficiency of Pt.

In present work, the catalytic performance of Pt modified hierarchical ZSM-5 in benzene alkylation with methanol was investigated. The structural and textural properties of the catalysts were systematically characterized by different techniques (including SEM, TEM, XRD, BET and TG–DTA) and the selectivity to ethylbenzene product versus Pt content was also investigated. We observed that Pt modified hierarchical ZSM-5 catalysts could retain excellent catalytic activity of hierarchical ZSM-5, as well as significantly suppressing the formation of ethylbenzene.

2 Experimental

2.1 Catalyst Preparation

Hierarchical ZSM-5 was prepared via solvent evaporation assisted dry-gel route was reported by the author [17, 18, 23]. The molar composition of the reaction mixture was as follows:

	TEOS	AIP	ТРАОН	HTS	EtOH
Molar ratio	1	0.0056	0.2	0.05	15.

where *TEOS* tetraethylorthosilicate, *AIP* aluminum isopropoxide, *TPAOH* tetra-n-propylammonium hydroxide, *HTS* hexadecyltrimethoxysilane, *EtOH* ethanol

Firstly, AIP, 1/2 of the EtOH and TPAOH were mixed together and stirred until AIP was completely dissolved. Then TEOS, HTS and the rest of the EtOH were added to the solution and stirred briefly to obtain a solid gel. Then the solid gel was placed into stainless steel autoclave equipped with a PTFE liner and small amount of water. The synthesis temperature and time were 180 °C and 72 h, respectively. The resulting solid material was obtained by filtration, then dried at 110 °C and calcined at 550 °C for 7 h (heating rate of 10 °C/min).

Pt modified hierarchical ZSM-5 catalysts with a nominal Pt loading of 0.01–0.1 wt% were prepared by impregnating method. The hierarchical ZSM-5 was firstly tableted, crushed and screened to the particles with diameters of 0.45–0.90 mm. The catalyst was then impregnated with quantitative amounts of aqueous solution of H₂PtCl₆·6H₂O at ambient temperature for 24 h before dried at 110 °C overnight. The dried sample was later divided into two parts. One part was calcined in air at 500 °C for 7 h (heating rate of 10 °C/min) and reduced in hydrogen at 400 °C for 2 h (heating rate of 10 °C/min). The other part was directly reduced in hydrogen at 400 °C for 2 h (heating rate of 10 °C/min).

Conventional ZSM-5 powder $(nSiO_2/nAl_2O_3 = 360)$ were purchased from the Catalyst Plant of Nankai University (Tianjin, China). The sample was tableted, crushed and screened to the size of 0.45–0.90 mm, and then calcined in air at 550 °C for 7 h.

2.2 Catalyst Characterization

The catalysts were characterized using a transmission electron microscopy (TEM) (Tecnai G2 F30 S-Twin) and scanning electron microscopy (SEM) (Hitachi S-4700(II)). X-ray diffraction (XRD) (SCINTAG X" TRA) was operated using Cu K-radiation (1,542 A) at 30 mA and 40 kV high voltage source with scanning angle (2 θ) from 5° to 80°. BET surface area and porous structure of catalysts were determined by nitrogen physical adsorption–desorption at 77 K. Nitrogen adsorption isothermal was measured using a NOVA 1000e surface area analyzer (Quantachrome Instruments Corp.). The differential thermal analysis (TG–DTA) (Netzsch STA 449 C) was evaluated using a temperature ramp from 25 to 850 °C with a heating rate of 5 °C/min in oxygen atmosphere.

2.3 Catalytic Activity Test

All evaluation experiments were carried out in a continuous-flow fixed-bed reactor with a stainless steel tube (8mm i.d.) at atmospheric pressure. In each test, 0.5 g catalyst diluted with inert quartz sand in 10 times volume as that of catalyst was loaded at the middle of the tube reactor and a thermocouple was positioned in the center of the catalyst bed in order to monitor the temperature. The catalyst was first reduced in situ using a temperature ramp from ambient temperature to 400 °C at 10 °C/min and maintained at 400 °C for 3 h in H₂ flow having a space velocity of 2,400 h⁻¹. Then benzene and methanol mixture (B/M molar ratio = 1:1) was fed into the reactor (WHSV = 2.0 h⁻¹) at 400 °C with a co-feed H₂ flow of 40 mL/min. The effluent from the reactor was analyzed online by the gas chromatography (Fuli GC9790) with a DB-1 capillary column (30 m \times 0.25 mm \times 1.00 μ m) and a flame ionization detector. In order to ensure all of the products were in gas phase, the temperature of the effluent line was maintained at 200 °C by heating belt. Conversion of benzene, utilization of methanol and selectivity to toluene, xylene and ethylbenzene were defined as follows:

Conversion of benzene

$$= \frac{benzene infeed - benzene in product}{benzene infeed} \times 100\%$$

Selectivity of toluene
$$= \frac{n(toluene)}{n(alkyl aromatics)} \times 100\%$$

Selectivity of xylene
$$= \frac{n(xylene)}{n(alkyl aromatics)} \times 100\%$$

Selectivity of ethylbenzene
$$= \frac{n(ethylbenzene)}{n(alkyl aromatics)} \times 100\%$$

3 Results and Discussion

3.1 Catalyst Characterization

Figure 1 presents XRD patterns of conventional ZSM-5 and hierarchical ZSM-5 catalysts. Both types of catalysts displayed two distinct diffraction peaks in 8°-10° and 20°-25° (2θ) ranges, all consistent with the typical pattern of MFI crystal structure. The SEM images in Fig. 2a and b clearly show the crystal morphology of conventional ZSM-5 zeolites and synthesized hierarchical ZSM-5 zeolites. As shown in Fig. 2a, the crystals of conventional ZSM-5 are hexagonal-shaped crystal rods, while the shape of hierarchical ZSM-5 crystals is roughly ellipsoidal aggregates with a size of about 200-300 nm (Fig. 2b). A high-magnification TEM image (Fig. 2c) indicated that the aggregates were made of nanoparticles ranging from 10 to 50 nm and a higher resolution micrograph (Fig. 2d) further reveals that the nanoparticles were crystalline in nature. It should be noted that the nanoparticles in the same aggregate exhibited the same direction of lattice fringes, indicating that these nanoparticles were crystallographically aligned like a single crystal. This phenomenon was quite similar to the result reported by Zhu et al. [23]. The difference morphology of zeolite could be attributed to different synthesis conditions of ZSM-5 zeolites. It has long been recognized that when different synthesis conditions were used, the growth orientation of crystals was different, resulting in the crystals with different morphologies. For the synthesis of hierarchical ZSM-5, the formation mechanism had detailed description by Zhu et al. [23]. Organic aluminum source, organic silicon source, HTS and TPAOH were dissolve in ethanol to hydrolyze to form small hydrophilic moieties (such as AIO_{x-} and SiO_{x-}). The



Fig. 1 XRD patterns of conventional ZSM-5 and hierarchical ZSM-5 catalysts

hydrolyzed HTS (with hydrophobic tails and hydrophilic silane head) acted as the surfactant in stabilizing the solutions. With the evaporation of ethanol, the mixture became more concentrated, accompanying a self-assembly and condensation process of the moieties, and eventually produced a solid dry gel which was made of particles separated by the organic assemblies from HTS. In the hydrothermal treatment, these organic assemblies inhibited the growth of crystals as well as created additional porosities via occupying a certain space between the walls of zeolitic.

Figure 3 shows the N₂ adsorption/desorption isotherms and the pore size distribution corresponding to synthesized hierarchical ZSM-5 zeolites with $nSiO_2/nAl_2O_3$ ratio of 360. The samples exhibited the characteristic features of type-IV isotherm, an obvious hysteresis loop which is associated with capillary condensation taking place in mesopores and the limiting uptake over a range of high p/p_0 [24] (Fig. 3a). Moreover, the sizes of mesopores were all about 4 nm according to the pore size distribution (Fig. 3b).

3.2 Catalytic Tests

3.2.1 Catalytic Alkylation of Benzene with Methanol over Conventional ZSM-5 and Hierarchical ZSM-5

The catalytic performance of synthesized hierarchical ZSM-5 was investigated in benzene alkylation with methanol and the results were compared to that of conventional ZSM-5 with same silica-alumina ratio $(nSiO_2/nAl_2O_3 =$ 360). The presence of alkane and alkene in the reaction products indicated that the side reaction of methanol had occurred in methanol alkylation, which was attributed to the effect of strong acid sites on the external surface of conventional ZSM-5 [25]. As shown in Table 1, the presence of methanol was not observed in the products means that methanol has been completely converted. Moreover, hierarchical ZSM-5 gave higher contents of alkyl aromatics and fewer contents of light alkenes and alkanes, suggesting that hierarchical ZSM-5 could effectively reduce the side reaction of methanol. Many literatures had investigated the parameters of conventional ZSM-5 and hierarchical ZSM-5 and compared their catalytic properties for the reactions such as the alkylation of benzene and the aromatization of methanol [17, 18, 23, 25-27]. Rownaghi et al. [25] had observed that as compared to conventional ZSM-5, Nano-ZSM-5 catalyst gave the highest activity which could be attributed to the lower diffusion limitation and higher concentration of strong acid sites on the surface, while Meso-ZSM-5 gave higher yields of alkyl aromatics and paraffins and fewer light olefins due to the channel structure of mesoporos ZSM-5 crystals provided easier access to the active sites in micropores. Zhu et al. [23] had reported



Fig. 2 SEM image of conventional ZSM-5 zeolites (a) and hierarchical ZSM-5 zeolites (b), TEM image of the hierarchical ZSM-5 zeolites (c, d)



Fig. 3 N₂ adsorption/desorption isotherms (a) and pore size distribution (b) of hierarchical ZSM-5 zeolites

that the mesoporosity of hierarchical ZSM-5 was formed from the voids between crystallites and aggregates and the hierarchical ZSM-5 exhibited better performance due to the high connectivity between meso- and micropores which would facilitate mass transfer and provide more accessible acidic sites in the zeolites. Deng et al. [18] had found that with increasing the Si/Al ratios of catalyst, the xylene selectivity over conventional ZSM-5 did not show remarkable change while the benzene conversion and xylene selectivity over hierarchical ZSM-5 increased. They proposed that the intracrystal diffusion no longer limits the mass transport process due to the presence of additional porosity. According to these literatures, we could conclude that although the parameters (including the primary particle size, the extra-framework Al species, the properties of the external surface and so on) were different between hierarchical ZSM-5 and conventional ZSM-5, the excellent catalytic activity and xylene selectivity to hierarchical ZSM-5 mainly attributed to the presence of mesopore which promoted the diffusion of reactants and products and provided easier access to the active sites in micropores.

 Table 1
 Products content of benzene alkylation with methanol over conventional ZSM-5 catalyst and hierarchical ZSM-5 catalyst

Components	Content (wt)/%			
	Conventional ZSM-5	Hierarchical ZSM-5		
Methane	0.40	0.10		
Ethylene	0.17	0.12		
Ethane	0.18	0.08		
C3	2.45	0.59		
C4	0.90	0.22		
C5	0.32	0.20		
Benzene	48.22	41.84		
Toluene	26.43	22.05		
Ethylbenzene	3.10	1.50		
Xylene	10.3	17.86		
Trimethylbenzene	3.25	5.46		
Other	4.28	9.98		

Reaction conditions: 400 °C, H_2 , 1 atm, WHSV = 2.0 h⁻¹, methanol to benzene molar ratio = 1:1

As shown in Fig. 4, the benzene conversion and xylene selectivity over hierarchical ZSM-5 (48.4 and 33.4 %, respectively) are relatively higher than those of conventional ZSM-5 catalysts (43.1 and 20.4 %, respectively), indicating that the acid sites for catalysing the alkylation of benzene were retained after introducing the mesopores into zeolite materials. On the other hand, the increase of xylene selectivity indicated that the existence of mesopores could promote the diffusion of bulky aromatics in the reactions. The same phenomenon could be observed in trimethylbenzene selectivity (5.6 % for conventional ZSM-5 and 9.0 % for hierarchical ZSM-5). It is noteworthy that the selectivity to ethylbenzene dropped from 6.2 to 2.8 % possibly due to the decrease of ethylene in the reaction products as ethylbenzene was formed by the alkylation of



Fig. 4 Catalytic performances of conventional ZSM-5 and hierarchical ZSM-5 in benzene alkylation with Methanol

benzene and ethylene. This result suggested that suppressing the side reaction of methanol would help to reduce the formation of ethylbenzene.

The stability of hierarchical ZSM-5 and conventional ZSM-5 was also investigated. As seen in Fig. 5, the stability of hierarchical ZSM-5 (320 h) is obviously higher than that of conventional ZSM-5 (80 h). There are two reasons to explain the higher stability of hierarchical ZSM-5. One relates to the coke location of hierarchical ZSM-5. Schmidt had reported that the coke distribution for the microporous ZSM-5 showed a gradient over the particle and the carbonaceous species mainly accumulated in the outer particle layers which lead to the rapid deactivation of the catalyst, while hierarchical ZSM-5 showed a homogeneous distribution of coke residuals over the whole particle [28]. The other reason relates to the coke formation from alkenes by polymerization, so the decease of alkenes could reduce the coke deposit rate [20]. In addition, comparing the TG-DTA profiles (Fig. 6) of the hierarchical ZSM-5 catalyst after 320 h reaction on stream with that of the conventional ZSM-5 catalyst after 80 h reaction on stream, the amount of coke deposit (removed within 200-800 °C) of the hierarchical ZSM-5 is obvious lower than that of the conventional ZSM-5 and this further proves the inference above.

Above all, hierarchical ZSM-5 catalyst performed excellently in the alkylation of benzene with methanol. However, it still could not solve the problem of ethylbenzene formation.

3.2.2 Pt Modified Hierarchical ZSM-5 Catalysts for Suppressing the Formation of Ethylbenzene in Benzene Alkylation with Methanol

The effect of Pt modification on the catalytic performance of hierarchical ZSM-5 catalysts in benzene alkylation with



Fig. 5 Stability of conventional ZSM-5 and hierarchical ZSM-5 in benzene alkylation with methanol



Fig. 6 TG-DTA profiles of the catalysts after successive reaction time: conventional ZSM-5, 80 h; hierarchical ZSM-5, 320 h

methanol was shown in Figs. 7 (using calcination method) and 8 (using direct reduction method). We could see that Pt modified catalysts prepared by calcination or direct reduction method both could effectively reduce the selectivity to ethylbenzene and improve the selectivity to xylene. According to our previous report, the hydrogenation of ethylene to ethane could restrain the alkylation of benzene with ethylene to form ethylbenzene [11]. The change of ethylene and ethane content in the products (Fig. 9) clearly showed that Pt modified catalysts could effectively decrease the content of ethylene and increase the content of ethane. Therefore, we concluded that the high suppressing of ethylbenzene formation on Pt modified hierarchical ZSM-5 could be attributed to the hydrogenation of ethylene to ethane on Pt clusters. It should be noted that the decrease of ethane content in the products of 0.05 and 0.1 wt% Pt modified catalysts prepared by direct reduction was due to the decreasing of benzene conversion improved the content of benzene in the products. We also



Fig. 7 Catalytic performance of Pt modified hierarchical ZSM-5 prepared by calcination method



Fig. 8 Catalytic performance of Pt modified hierarchical ZSM-5 prepared by direct reduction method

noted that the selectivity to ethylbenzene gradient decrease from 2.8 to 0.15 % with the increasing content of Pt (0–0.1 wt%) in modified hierarchical ZSM-5 by calcinations (Fig. 7). As for the modified hierarchical ZSM-5 catalysts prepared by direct reduction method, loading with 0.01 wt% Pt could notably decrease the selectivity to ethylbenzene to 0.18 % (Fig. 8). Obviously, direct reduction method was helpful to reduce the required amount of Pt on the modified catalyst. In addition, although many literatures [29–32] had reported that Pt/ZSM-5 could catalyze the hydrogenation of aromatic hydrocarbons, the hydrogenation of benzene was not occurred due to that the high temperature and low pressure used in this work was unfavorable for this reaction.

As mentioned earlier, calcinations could influence the size of Pt metal particle, which in turn influenced the hydrogenation activity of Pt [20]. When the supported



Fig. 9 Content of ethylene and ethane in the products of Pt modified hierarchical ZSM-5 prepared by different method

precursor was calcined in air and then reduced in hydrogen (calcination method), aggregated large particles were observed in TEM (Fig. 10a, b). Moreover, the degree of sintering increased with increasing the content of Pt from 0.01 to 0.1 wt%. In contrast, when the supported precursor was directly reduced (direct reduction method), aggregated large particles was no longer observed even when increasing the content of Pt to 0.1 wt% (Fig. 10c, d). This outcome could be ascribed to that chloroplatinic acid precursor after being calcined in air formed Pt oxides which enabled the growth of platinum particles through vapor phase transport [33, 34]. While employing direct reduction, the hydrogen atmosphere suppressed the generation of volatile Pt oxides and formed Pt particles without the migration of Pt species [22]. In addition, removing the chlorine is necessary as chlorine would cause metal poisoning and surface corrosion [35]. However, compared to direct reduction in hydrogen, chlorine was retained at much higher temperatures during calcinations in air [33]. Moreover, high temperatures will cause more particles sintering due to that small metal particles have lower melting point than bulk metal. Considering the suppressing ability of Pt/ ZSM-5 for the formation of ethylbenzene and the content of Pt, we can draw a safe conclusion that direct reduction could improve the utilization efficiency of Pt by avoiding the Pt particle sintering and the resulted Pt particles with smaller sizes were conducive to hydrogenate ethylene into ethane. On the other hand, the well dispersed Pt particles would cover more acid sites of the catalyst, which caused the decrease of benzene conversion over the directly reduced catalyst (48.4–39.0 %) higher than that over the calcined catalyst (48.4–45.5 %).

Although the reaction temperature (400 °C) was lower than the calcination temperature (500 °C), the Pt particles sintering of Pt modified hierarchical ZSM-5 prepared by direct reduction might still occur which could further influence the hydrogenation activity of Pt. Thus, investigating the stability of Pt modified hierarchical ZSM-5 prepared by direct reduction is necessary. 0.02 wt% Pt modified hierarchical ZSM-5 could reduced the selectivity to ethylbenzene to a relatively low amount and at the same times remained high activity (Fig. 8), so we investigated it in the following experiment. It could be seen that the selectivity to ethylbenzene maintains under 0.1 %, benzene conversion maintains 48-51 % and xylene selectivity maintains about 35.5 % during 50 h reaction on stream (Fig. 11). The hold of the performance for suppressing the formation of ethylbenzene indicated that the Pt particles



Fig. 10 TEM images of Pt modified catalysts hierarchical ZSM-5 by different method: **a** 0.01 wt% Pt, calcination, **b** 0.1 wt% Pt, calcination; **c** 0.01 wt% Pt, direct reduction, **d** 0.1 wt% Pt, direct reduction



Fig. 11 Stability of 0.02 wt% Pt modified hierarchical ZSM-5 prepared by direct reduction method

were without big changes during the reaction. This could be ascribed to the hydrogen atmosphere in alkylation reaction was similar to that in direct reduction, while Pt dispersion was independent of the reduction temperature [22], and this avoids the migration of Pt particles.

4 Conclusions

Pt modified hierarchical ZSM-5 successfully combined the catalytic advantages of hierarchically ZSM-5 and the high suppression of Pt towards ethylbenzene formation. Employing direct reduction method could improve the utilization of Pt by avoiding the migration of Pt particles causing particle sintering. These technologies would help to improve the commercial viability of the process of benzene alkylation with methanol into toluene and xylene.

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