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Effect of mesoporosity on selective benzylation of aromatics with benzyl alcohol over mesoporous ZSM-5

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ABSTRACT

The effect of mesoporosity on product distribution in benzylation of aromatics such as benzene, toluene, anisole and mesitylene with benzyl alcohol was investigated over various ZSM-5 catalysts with different degree of mesoporosity, which were prepared by microwave-induced assembly via ionic interaction between sulfonic acid-functionalized or non-functionalized ZSM-5 nanozeolites and counter cationic surfactant, and hydrothermal synthesis with or without sulfonic acid functionalization and surfactant. The product distribution of the aromatic benzylation was found to vary with the different mesoporosity. The selectivity of desired monobenzylated aromatic was increased from 19.8% to 75.5% with increasing mesopore volume from 0.11 to 0.75 cm³/g. Meso ZSM-5 (SO₃H-CTAB)-MW with the highest external acid sites and mesopore volume showed better conversion as well as much higher selectivity of desired bulky monobenzylated aromatics than those of other catalysts, whereas microporous ZSM-5 mainly showed dibenzyl ether as major product due to diffusion limitation of bulky product.

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1. Introduction

Catalytic benzylation of aromatics with benzyl alcohol or benzyl chloride is one of the commercial significance reaction processes to produce benzylated aromatics (diphenylmethane and substituted diphenvlmethane), which are key intermediates in fine chemicals and pharmaceuticals such as analgesic or anti-inflammatory agent. reagent for inhibiting agglomeration of blood, backbone, and skeleton [1-4]. To control the selective formation of desired monobenzylated aromatics is quite challenging in this reaction process. Zeolites such as ZSM-5 [5], Zeolite X, Y [6,7] and Zeolite BETA [8] are used as heterogeneous acid catalysts in the benzylation process instead of mineral acid (e.g., AlCl₃) due to less corrosiveness, strong acidity, shape-selectivity and high hydrothermal stability [9–13]. However, zeolites with small pore size (<1 nm) cause diffusion limitation for bulky substrates [14]. This diffusion limitation in microporous zeolites is also responsible for poor selectivity and loss in lifetime of the catalysts. Hence, mesoporous zeolites having periodic mesoporosity, strong acidity and stability like microporous zeolites and shape-selectivity in catalysis are desirable without sacrificing acidity [15,16].

Mesoporous zeolites containing both structured microporosity and secondary mesoporosity inside of zeolite single crystals exhibit high catalytic activity of bulky reactants in various organic reactions due to diffusion alleviation [17]. Moreover, these mesoporous

* Corresponding author. E-mail address: separk@inha.ac.kr (S.-E. Park). zeolites show the remarkable change in product selectivity compared with microporous zeolites due to improved diffusion to and/or from active sites in micropores through the mesopores [18,19]. Recently, Sun and Prins [20] have reported the enhanced catalytic activity of hierarchical mesoporous ZSM-5 in the alkylation of benzene with benzyl alcohol, which is 23 times larger than that for microporous ZSM-5. The similar phenomenon is observed in case of mesoporous mordenite obtained by acid–base leaching [21]. Groen et al. have found the superior performance of alkaline-mediated mesoporous mordenite in the alkylation of benzene with ethylene compared with mordenite [22]. The enhanced catalytic performance indicates that the existence of mesopore remarkably overcomes the diffusion limitation from micropore, and suggests the mesoporous zeolites have potential application in alkylation reactions of bulky molecules.

Recently, microwave irradiation has been considered as a useful method for synthesis of nanoporous materials such as zeolites, mesoporous materials and mesoporous zeolites [23]. According to our previous works, microwave synthesis could provide distinct advantages [9,24,25] over the conventional hydrothermal synthesis such as fast crystallization, homogeneous heating and nucleation, morphology control and enhanced hydrophobicity, moreover it is efficient for mesopore generation by desilication [26], carbon templating method [27,28] and supramolecular self-assembly [29]. In this regard, we have developed a new synthetic strategy for synthesis of mesoporous ZSM-5 with enhanced mesoporosity by microwave-induced assembly via ionic interaction between sulfonic acid-functionalized ZSM-5 nanoparticles



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and counter cationic alkyltrimetyl ammonium surfactant. Sulfonic acid group plays an important role as negative charge enhancer on the surface of zeolite nanoparticles that interact with cationic surfactants to create the mesoporosity inside of the zeolite single crystals [30].

In the present study, we report a novel investigation on the effect of mesoporosity on the catalytic activity and selectivity of desired monobenzylated aromatics in the aromatic benzylation. For this analysis, mesoporous ZSM-5 were synthesized by assembly via ionic interaction between sulfonic acid-functionalized or non-functionalized ZSM-5 nanozeolites and counter cationic surfactant under microwave [Meso ZSM-5 (SO₃H-CTAB)-MW and Meso ZSM-5 (CTAB)-MW], and hydrothermal synthesis with or without sulfonic acid functionalization and surfactant [ZSM-5 (SO₃H-CTAB)-HT] and ZSM-5 (HT)] (Scheme 1). The catalytic performances of these ZSM-5 catalysts with different degree of mesoporosity were studied in benzylation of aromatics such as benzene, toluene, anisole and mesitylene with benzyl alcohol as benzylating agent. Furthermore, the effects of mole ratio of aromatic to benzyl alcohol, reaction time and recyclability have also been investigated.

2. Experiment

2.1. Catalysts preparation

The chemicals used for the preparation of materials were tetraethyl orthosilicate (TEOS, 98%; Aldrich) as silica source, aluminum isopropoxide (AIP; Aldrich) as alumina source, tetrapropylammonium hydroxide (TPAOH, 20–25%; TCI) as a template for micropore, 3-mercaptopropyltriethoxysliane (MPTES; TCI) as anionic functional group, hydrogen peroxide (H_2O_2 , 30% in the water; Duksan) as oxidizing agent, cetyltrimethylammonium bromide (CTAB; TCI) as supramolecular template and distilled water.

The ZSM-5 catalysts were prepared according to following procedure.

2.1.1. Meso ZSM-5(SO₃H-CTAB)-MW

As an initial stride, ZSM-5 nanozeolites were pre-crystallized from a clear solution with the following molar composition: $1Al_2O_3$: $60SiO_2$: 11.5TPAOH: $1000H_2O$ (20.8 g TEOS, 19.1 g TPAOH, 0.33 g AIP, 15 g H₂O) under microwave irradiation (600 W, 120 °C and 30 min) followed by functionalization with MPTES (5 mol% of silica) under MW (600 W, 120 °C and 60 min). The precursor solution was continuously treated by 5 g H₂O₂ in order to oxidize thiol group for obtaining sulfonic acid–functionalized zeolite nanoparticles. The resultant solution was added to CTAB solution (1.78 g

CTAB with 15 g H_2O) and stirred 3 h, then moved to MW (600 W, 165 °C for 2 h) as [Meso ZSM-5(SO₃H-CTAB)-MW].

2.1.2. Meso ZSM-5(CTAB)-MW

A similar procedure to that of [Meso ZSM-5(SO₃H-CTAB)-MW] with omission of steps for functionalization with MPTES and oxidation with H_2O_2 has been adopted for the synthesis of [Meso ZSM-5(CTAB)-MW].

2.1.3. ZSM-5(SO₃H-CTAB)-HT

The synthesis procedure was same with that of [Meso ZSM- $5(SO_3H-CTAB)-MW$] except the final step, whereby the resulted solution in the vessel is subjected to hydrothermal treatment (HT) at 165 °C for 3 days instead of microwave irradiation.

2.1.4. ZSM-5 (HT)

The conventional microporous ZSM-5 [ZSM-5 (HT)] was synthesized from a clear solution with the following molar composition: $1Al_2O_3$: $60SiO_2$: 11.5TPAOH: $1500H_2O$ under hydrothermal treatment at165 °C for 3 days.

2.2. Characterization methods

Crystallinity of obtained materials was determined by powder X-ray diffraction (XRD) using a Rigaku X-ray diffractometer with CuK α radiation (40 kv and 20 mA). N₂ adsorption and desorption isotherms were conducted on a micromeritics ASAP 2020 at -196 °C. The Brunauer–Emmett–Teller (BET) surface areas were calculated from the liner part of the BET plot according to IUPAC recommendations. Pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method from adsorption branch of the isotherm.

Temperature-programmed desorption (TPD) of NH₃ was carried out with a Micromeritics TPD/TPR/TPO 2900 apparatus with thermal conductivity detector (TCD). The samples were first outgassed in a He flow (20 ml/min) under 500 °C for 1 h with heating rate of 20 °C/min before the measurement. After cooling to 100 °C, the samples were saturated in an NH₃ stream (5% in He) for 1 h with 30 ml/min flow and consequently treated in He (50 cm³/min) for 120 min for removing physisorbed NH₃. Finally, the TPD profile was determined by increasing temperature from 100 to 500 °C with a heating rate of 5 °C/min while recording NH₃ desorption with a thermal conductivity detector.

The number of external acid sites (i.e., acid sites at the mesopore walls) in ZSM-5 catalysts was measured by the chemisorption of 2,6-di-tert-butylpyridine (DTBPy) in a thermoanalyzer (Bruker axs 2000SA) equipped with high resolution balance



Scheme 1. Schematic representation of the synthesized ZSM-5 catalysts.

(Sensitivity = 0.1 μ g). Prior to the adsorption of DTBPy, the samples were pretreated at 350 °C overnight under vacuum. Followed by exposure to 2,6-DTBPy at room temperature for 1 h, desorption of DTBPy was carried out at 150 °C for 4 h under vacuum to remove physisorbed DTBPy. The amount of adsorbed DTBPy was obtained from weight loss before and after adsorption. The external acid sites were calculated with assumption of one DTBPy molecule per acid site [31].

2.3. Catalytic benzylation

Prior to the catalytic experiments, all the catalysts were activated at 450 °C for 90 min and then cooled down in a desiccator.

The benzylation reactions were carried out with aromatics such as benzene, toluene, anisole and mesitylene (16 mmol) and benzyl alcohol (4 mmol) in the presence of catalysts (0.05 g) in a 25-ml single-necked flask at 100 °C for 1 h. The mole ratio of the aromatics with benzyl alcohol was varied as 1:2, 1:1, 2:1, 3:1 and 4:1. The reaction time was varied from 15 to 120 min. The catalyst was filtered after the reaction and washed with acetone followed by drying and calcining in air at 450 °C for 6 h prior to reuse. The course of the reaction was followed by analyzing the reaction mixture periodically using a gas chromatograph (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (HP 5% silicone gum). The products were also identified by GC/MS.

3. Results and discussion

3.1. Catalysts characterization: porosity and acidity

The wide-angle XRD patterns of all ZSM-5 catalysts displayed well-resolved peaks that were characteristic reflections for typical crystalline MFI structure as shown in Fig. 1. The Meso ZSM-5 (SO₃H-CTAB)-MW prepared with sulfonic acid–functionalized ZSM-5 nanoparticles and CTAB by microwave showed much higher intensity of the diffraction peak in low-angle XRD patterns compared with mesoporous ZSM-5 synthesized by using non-function-alized ZSM-5 nanoparticles, which were used to reflecting the mesopore arrays, whereas the low-angle XRD pattern of ZSM-5 (SO₃H-CTAB)-HT exhibited no distinct peak. This inferred that mesoporous ZSM-5 with improved mesoporosity could be preferably synthesized by the microwave-induced rapid assembly through the ionic interaction between anionic enhanced zeolite



Fig. 1. XRD patterns of ZSM-5 catalysts (a) Meso ZSM-5 (SO₃H-CTAB)-MW, (b) Meso ZSM-5 (CTAB)-MW, (c) ZSM-5 (SO₃H-CTAB)-HT and (d) ZSM-5 (HT).

nanoparticles and counter cationic surfactants. As shown in Fig. 2A, the Meso ZSM-5 (SO₃H-CTAB)-MW showed type IV N₂ adsorption–desorption isotherm with H4 hysteresis capillary condensation at $0.2 < (P/P_0) < 0.5$ due to the presence of mesopores (2–3 nm size) with narrow distribution (Fig. 2B). However, the ZSM-5 (SO₃H-CTAB)-HT showed type I isotherm, which was similar to microporous ZSM-5. The surface area and mesopore volume of Meso ZSM-5 (SO₃H-CTAB)-MW were 529 m²/g and 0.75 cm³/g, respectively, which were much larger than those of other ZSM-5 catalysts (Table 1).

Acidic properties of the ZSM-5 catalysts were investigated by NH₃ TPD. The TPD profiles of ZSM-5 catalysts given in Fig. 3 showed two desorption peaks of NH₃ in the range below 500 °C. These desorption peaks were corresponding to two different type of acid sites of varving strengths. The low temperature desorption peak (100-300 °C) was due to NH₃ bound to weak acid sites, and the high temperature desorption peak in the range of 300–500 °C was caused by NH₃ desorption from strong acid sites (Brønsted and Lewis acid sites). The number of acid sites of the catalysts was calculated by peak area with the assumption of one NH₃ molecule per acid sites as depicted in Table 2. The strong acid sites of Meso ZSM-5 (SO₃H-CTAB)-MW were 8% less than the ZSM-5 (HT). The acid strengths were found to be approximately similar. This result indicated that mesoporous ZSM-5 catalysts could be prepared without significantly sacrificing acidity during microwave-induced assembly through ionic interaction, which was in good agreement with earlier report regarding the acidity of hierarchical porous zeolites by Suzuki et al. [32].

3.2. Benzylation of aromatics with benzyl alcohol (BA)

Benzylation of aromatics with benzyl alcohol is presented schematically in Scheme 2, where R is -H, $-CH_3$, $-OCH_3$, $-(CH_3)_3$ group corresponding to benzene, toluene, anisole and mesitylene, respectively. This reaction mainly produces dibenzyl ether and monobenzylated aromatic in different competitive reaction pathways. The dibenzyl ether was formed by self-condensation of benzyl alcohols. On the other hand, benzylation reaction was occurred between aromatics and benzyl alcohol to produce desired monobenzylated aromatic. The monobenzylated aromatic further reacted with benzyl alcohol to produce bulky dibenzylated aromatics at high reaction temperature or strong acidity.



Fig. 2. (A) N_2 adsorption–desorption isotherms and (B) pore size distribution of ZSM- 5 catalysts (a) Meso ZSM-5 (SO₃H-CTAB)-MW, (b) Meso ZSM-5 (CTAB)-MW, (c) ZSM-5 (SO₃H-CTAB)-HT and (d) ZSM-5 (HT).

Table 1

Textural properties of various ZSM-5 catalysts.

Catalysts	S_{BET}	S_{Ext}	V _{total}	V _{Meso}
	(m ² /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)
Meso ZSM-5 (SO ₃ H-CTAB)-MW	529	400	0.81	0.75
Meso ZSM-5 (CTAB)-MW	500	390	0.40	0.35
ZSM-5 (SO ₃ H-CTAB)-HT	388	226	0.30	0.21
ZSM-5 (HT)	348	145	0.23	0.11

Table 2

Acidic properties of ZSM-5 catalysts.

Catalysts	NH3 chemisorbed ^a (mmol/g)	Strong acidity (300–500 °C) NH ₃ desorbed ^b (mmol/g)	External acid sites ^c (mmol/g)
Meso ZSM-5 (SO ₃ H-CTAB)-MW Meso ZSM-5 (CTAB)-MW ZSM-5 (SO ₃ H-CTAB)-HT ZSM-5 (HT)	0.73 1.03 0.64 0.90	0.32 (44%) 0.50 (49%) 0.42 (65%) 0.46 (52%)	0.08 0.07 0.04 0.03

^a Determined by NH₃ desorption (chemisorbed at 100 $^{\circ}$ C).

^b Determined by NH₃ desorption (chemisorbed at 100 °C).

^c Determined by the chemisorption of 2,6-di-tert-butylpyridine (DTBPy).



Fig. 3. NH_3 TPD profiles of ZSM- 5 catalysts (a) Meso ZSM-5 (SO₃H-CTAB)-MW, (b) Meso ZSM-5 (CTAB)-MW, (c) ZSM-5 (SO₃H-CTAB)-HT and (d) ZSM-5 (HT).

3.2.1. Effect of substituent on aromatic

Benzylation of substituted aromatics such as benzene, toluene, anisole and mesitylene with benzyl alcohol over Meso ZSM-5 (SO₃H-CTAB)-MW and ZSM-5 (HT) was performed in order to demonstrate the role of mesoporosity and electronic or molecular size effect of substrates on catalyst performance. The conversion of all substrates and benzyl alcohol over Meso ZSM-5 (SO₃H-CTAB)-MW was much higher than those of ZSM-5 (HT) as shown in Fig. 4A and B. Meso ZSM-5 (SO₃H-CTAB)-MW without diffusion restriction exhibited the increasing aromatic conversion from benzene to mesitylene, which was mainly due to ring activation by electron donating effects ($-(CH_3)_3 > -OCH_3 > -CH_3 > -H$). In case of the ZSM-5 (HT), the conversion of anisole and mesitylene was less than those of benzene and toluene due to diffusion limitation of large molecular size. The molecular size of benzene (0.49 nm) and toluene (0.54 nm) is smaller than the pore size of ZSM-5 $(5.4 \times 5.6 \text{ A})$ [33]. However, the molecular size of anisole [34]

and mesitylene (0.87 nm) [35] is close to or much larger than the size of micropore. It indicated that benzene and toluene reacted in both micropores and mesopores; however, in case of anisole and mesitylene, the reaction mainly occurred in mesopore wall and pore mouth of micropores. This significant difference in catalytic activity indicated that the presence of mesopore remarkably enhanced the accessibility of reactants and products to overcome the diffusion limitation from micropore.

Fig. 5A and B showed the selectivity of benzylation product (monobenzylated aromatic) and self-condensation product (dibenzvl ether), respectively. Meso ZSM-5 (SO₃H-CTAB)-MW showed much higher selectivity of monobenzylated aromatic compared with the ZSM-5 (HT), which showed dibenzyl ether as major product. However, the selectivity of dibenzyl ether in benzylation of benzene over Meso ZSM-5 (SO₃H-CTAB)-MW is rather higher than that of monobenzylated aromatic (diphenylmethane). It indicated that the self-condensation of benzyl alcohol is more favorable than benzylation of aromatic in case of benzene benzylation due to less reactivity of benzene. According to early report by Prins and coworkers [21], the alkylation reaction mainly occurred in the mesoporous parts of zeolite due to diffusion limitation of bulky molecules; hence, the mesitylene was chosen for the detail study of benzylation, which can prove the effect of mesoporosity on the catalytic activity and selectivity.

3.2.2. Effect of mole ratio of mesitylene to benzyl alcohol (BA)

Benzylation of mesitylene with benzyl alcohol was carried out by varying the mole ratio of mesitylene to benzyl alcohol from 1:2 to 4:1 over Meso ZSM-5 (SO₃H-CTAB)-MW to assess its effect on the catalytic activity and selectivity. The conversion of both mesitylene and BA was found to increase with an increase in reactant mole ratio from 1:2 to 2:1 as can be seen in Fig. 6A. Further increase in mole ratio has no significant effect on conversion of both reactants. The conversion of BA was significant in the mole ratio of 1:2 and 1:1. However, the rate of benzylation of mesitylene with benzyl alcohol was guite slow, and dibenzyl ether was formed mainly due to self-condensation of benzyl alcohol. With increase in the mole ratio of mesitylene to benzyl alcohol, the selectivity of monobenzylated mesitylene (2-benzyl-1,3,5-trimethylbenzene, 9.6×6.8 Å) was found to increase from 15.5% at mole ratio of 1:2 to 75.5% at mole ratio of 4:1. 2-Benzyl-1,3,5-trimethylbenzene was shown as predominant product over Meso ZSM-5 (SO₃H-CTAB)-MW at higher mole ratio of mesitylene to benzyl alcohol (Fig. 6B). Thus, all the reactions were performed with a mole ratio of 4:1.

3.2.3. Effect of catalyst porosity

The catalytic performance of four different ZSM-5 catalysts for the benzylation of mesitylene with benzyl alcohol was investigated to examine the role of mesoporosity on selective production of monobenzylated aromatics (Table 3). The conversion of mesitylene over Meso ZSM-5 (SO₃H-CTAB)-MW and Meso ZSM-5 (CTAB)-MW was 30.7% and 27.8%, respectively, which was nearly 5 times higher than ZSM-5 (SO₃H-CTAB)-HT and ZSM-5 (HT). The most active catalyst for the reaction was Meso ZSM-5 (SO₃H-CTAB)-MW with the highest external surface area and mesopore volume. These observations were in line of report by Candu et al. [36,37] that zeolite behavior was dictated not only by their acidity but also by their porosity in benzylation of benzene with benzyl alcohol. The different porosities caused certain surface chemical composition changes (acidity) again the product distribution. A similar phenomenon was observed by de long and co-workers [38] in the alkylation of benzene with propylene to produce cumene over mesoporous mordenite. The catalytic activity was increased due to enhanced accessibility and the selectivity of cumene/DIPB and was mainly affected by the acid site on the external surface of



Scheme 2. Benzylation reaction mechanism of aromatics with benzyl alcohol.



Fig. 4. Conversion of (A) aromatics and (B) benzyl alcohol in benzylation of benzene, toluene, anisole and mesitylene with benzyl alcohol over Meso ZSM-5 (SO₃H-CTAB)-MW and ZSM-5 (HT).

crystallites. Pérez-Ramírez and co-workers [39] also stated that in alkylation of toluene with benzyl alcohol, the selectivity to (methylbenzyl)benzene was mainly affected by the acidity and the alkylation activity was dominated by the mesoporous surface area. Based upon these reports, we measured the external acid sites (i.e., acid sites at mesopore walls) by chemisorption of 2,6-ditert-butylpyridine as shown in Table 2. The external acid sites were increased with increasing external surface area and mesopore volume. These observations indicated the improved mesoporosity affected the external acid sites. The Meso ZSM-5 (SO₃H-CTAB)-MW gave around 4 times higher selectivity of benzylated mesitylene (2-benzyl-1,3,5-trimethylbenzene) than the microporous ZSM-5. In case of ZSM-5 (HT), the dibenzyl ether was mainly formed due to self-condensation of benzyl alcohol. This significant difference in catalytic selectivity resulted from the existence of mesopores, which definitely allowed the mesitylene benzylation by acid sites in mesopores. The selectivity of benzylated mesitylene was increased with increasing mesopore volume which



Fig. 5. Selectivity of (A) monobenzylated aromatic and (B) dibenzyl ether in benzylation of benzene, toluene, anisole and mesitylene with benzyl alcohol over Meso ZSM-5 (SO₃H-CTAB)-MW and ZSM-5 (HT).



Fig. 6. (A) Conversion and (B) product distribution plotted as a function of various mole ratio of mesitylene to benzyl alcohol from 1:2 to 4:1 for benzylation of mesitylene with benzyl alcohol over Meso ZSM-5 (SO₃H-CTAB)-MW.

inferred that it was mainly due to the improved external acid sites which were affected by mesopore generation. This investigation revealed that the mesoporosity played a significant role on controlling the selectivity of desired monobenzylated product.

3.2.4. Effect of reaction time and recyclability

To further investigate the catalytic performance of Meso ZSM-5 $(SO_3H-CTAB)-MW$, the effect of reaction time and reusability of catalyst was tested through the benzylation of mesitylene with benzyl alcohol. The conversion of both reactants was increased with increasing reaction time from 15 min to 30 min and stabilized after 30 min as presented in Fig. 7A. The selectivity of 2-benzyl-1,3,5-trimethylbenzene was increased with increasing reaction

time, whereas that of dibenzyl ether was decreased. This result indicates that the benzylation of mesitylene with benzyl alcohol is predominant reaction, whereas the formation of dibenzyl ether through the self-condensation of benzyl alcohol is side reaction and dibenzyl ether generated can act as benzylating agent to participate in the benzylation reaction (Fig. 7B).

The reusability of Meso ZSM-5 (SO_3H -CTAB)-MW as heterogeneous catalysts in the benzylation of mesitylene with benzyl alcohol was investigated for three cycles. Table 4 shows the catalytic activities of fresh and reused Meso ZSM-5 (SO_3H -CTAB)-MW. The fresh catalysts gave 100% of BA conversion and 75.2% of 2-benzyl-1,3,5-trimethylbenzene selectivity, respectively, which was maintained even after reusing catalysts two times. These results



Fig. 7. (A) Conversion and (B) product distribution plotted as a function of reaction time for benzylation of mesitylene with benzyl alcohol over Meso ZSM-5 (SO₃H-CTAB)-MW.

Table 3

Benzylation of mesitylene (MES) with benzyl alcohol (BA) over various ZSM-5 catalysts.



Reaction conditions: MES:BA = 4:1; Catalyst = 50 mg; 100 °C, 1 h. (A) 2-Benzyl-1,3,5-trimethylbenzene; (B) dibenzyl ether; (C) others: (2,4,6-trimethyl-1,3-phenylene)-bis(methylene)-dibenzene; (2-benzylphenyl)methanol; 9,10-dihydroanthracene.

Table 4

Reusability of Meso ZSM-5 (SO_3H -CTAB)-MW in the benzylation of mesitylene (MES) with benzyl alcohol (BA).

Catalysts	BA conv. (%)	2-Benzyl-1,3,5-TMB Select. (%)
Fresh	100	75.2
1st reuse	100	77.6
2nd reuse	100	75.0

Reaction conditions: MES: BA = 4:1; catalyst = 50 mg; 100 °C, 1 h.

indicated that the Meso ZSM-5 (SO_3H -CTAB)-MW can be reused without a significant change in the activity and selectivity and has potential for industrial application.

4. Conclusions

In this investigation, the selectivity of desired monobenzylated aromatic was mainly controlled by the external acid sites that were affected by degree of mesoporosity of various ZSM-5 catalysts. The selectivity of desired monobenzylated aromatic increased with the increase of mesoporosity was confirmed.

The Meso ZSM-5 (SO₃H-CTAB)-MW showed nearly 5-fold increase in catalytic activity in aromatic benzylation compared

with microporous ZSM-5 due to enhanced intracrystalline mesoporosity. Moreover, this Meso ZSM-5 (SO₃H-CTAB)-MW with the highest external acid sites and mesoporosity showed much higher selectivity of desired monobenzylated aromatic than those of other ZSM-5 catalysts. The microporous ZSM-5 produced dibenzyl ether as major product due to diffusion limitation of bulky reactant or product. Controllable mesoporosity play an important role on controlling the selectivity of desired monobenzylated aromatic. The Meso ZSM-5 (SO₃H-CTAB)-MW can be reused for three cycles without loss of acidity. This Meso ZSM-5 (SO₃H-CTAB)-MW can be regarded as promising heterogeneous acid catalyst to improve the selectivity of desired monobenzylated product in aromatic benzylation and has potential application for pharmaceutical industry.

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References

[1] B. Viswanathan, B. Jacob, Catal. Rev. 47 (2005) 1.

- [2] C. Perego, P. Ingallina, Catal. Today 73 (2002) 3.
- [3] E. Aleksandrova, G. Nosova, N. Solovskaya, K. Romashkova, V. Luk'yashina, E. Konozobko, V. Kudryavtsev, Semiconductors 38 (2004) 652.
- [4] S. Van der Beken, E. Dejaegere, K.A. Tehrani, J.S. Paul, P.A. Jacobs, G.V. Baron, J.F.M. Denayer, J. Catal. 235 (2005) 128.
- [5] G. Mirth, J. Cejka, J. Krtil, J.A. Lercher, Stud. Surf. Sci. Catal. (1994) 241.
- [6] U. Sridevi, B.K. Bhaskar Rao, N.C. Pradhan, Chem. Eng. J. 83 (2001) 185.
- [7] H.-j. Dong, L. Shi, Ind. Eng. Chem. Res. 49 (2010) 2091.
- [8] G. Girotti, F. Rivetti, S. Ramello, L. Carnelli, J. Mol. Catal. A: Chem. 204–205 (2003) 571.
- [9] Y.K. Hwang, J.-S. Chang, S.-E. Park, D.S. Kim, Y.-U. Kwon, S.H. Jhung, J.-S. Hwang, M.S. Park, Angew. Chem. Int. Ed. 44 (2005) 556.
- [10] C.H. Christensen, K. Johannsen, E. Törnqvist, I. Schmidt, H. Topsøe, C.H. Christensen, Catal. Today 128 (2007) 117.
- [11] A. Corma, Chem. Rev. 95 (1995) 559.
- [12] J. Čejka, B. Wichterlová, Catal. Rev. 44 (2002) 375.
- [13] S. Barman, N.C. Pradhan, J.K. Basu, Ind. Eng. Chem. Res. 44 (2005) 7313.
- [14] A. Corma, Chem. Rev. 97 (1997) 2373.
- [15] J. Pérez-Ramírez, C.H. Christensen, K. Egeblad, C.H. Christensen, J.C. Groen, Chem. Soc. Rev. 37 (2008) 2530.
- [16] X. Gu, T. Jiang, H. Tao, S. Zhou, X. Liu, J. Ren, Y. Wang, G. Lu, W. Schmidt, J. Mater. Chem. 21 (2011) 880.
- [17] V.N. Shetti, J. Kim, R. Srivastava, M. Choi, R. Ryoo, J. Catal. 254 (2008) 296.
 [18] C.H. Christensen, K. Johannsen, I. Schmidt, C.H. Christensen, J. Am. Chem. Soc.
- 125 (2003) 13370. [19] J.S. Jung, J.W. Park, G. Seo, Appl. Catal. A: Gen. 288 (2005) 149.
- [20] Y. Sun, R. Prins, Appl. Catal. A: Gen. 336 (2008) 11.
- [21] X. Li, R. Prins, J.A. van Bokhoven, J. Catal. 262 (2009) 257.

- [22] J.C. Groen, T. Sano, J.A. Moulijn, J. Pérez-Ramírez, J. Catal. 251 (2007) 21.
- [23] S.-E. Park, J.-S. Chang, Y.K. Hwang, D.S. Kim, S.H. Jhung, J.S. Hwang, Catal. Sur. Asia 8 (2004) 91.
- [24] H. Jin, N. Jiang, S.-E. Park, J. Phys. Chem. Solids 69 (2008) 1136.
- [25] H. Jin, N. Jiang, S.-M. Oh, S.-E. Park, Top. Catal. 52 (2009) 169.
- [26] S. Abello, J. Pérez-Ramírez, PCCP 11 (2009) 2959.
- [27] N. Jiang, D.-S. Han, S.-E. Park, Catal. Today 141 (2009) 344.
- [28] J.-B. Koo, N. Jiang, S. Saravanamurugan, M. Bejblová, Z. Musilová, J. Cejka, S.-E. Park, J. Catal. 276 (2010) 327.
- [29] Sujandi, S.-E. Park, D.-S. Han, S.-C. Han, M.-J. Jin, T. Ohsuna, Chem. Commun. (2006) 4131.
- [30] H. Jin, M. Bismillah Ansari, S.-E. Park, Chem. Commun. 47 (2011) 7482.
- [31] J. Kim, M. Choi, R. Ryoo, J. Catal. 269 (2010) 219.
- [32] K. Suzuki, Y. Aoyagi, N. Katada, M. Choi, R. Ryoo, M. Niwa, Catal. Today 132 (2008) 38.
- [33] J.J. Vijaya, L.J. Kennedy, G. Sekaran, K.S. Nagaraja, Mater. Lett. 61 (2007) 5213.
- [34] M. Álvaro, D. Das, M. Cano, H. Garcia, J. Catal. 219 (2003) 464.
- [35] S. Nakashima, Y. Takahashi, M. Kiguchi, Beilstein J. Nanotech. 2 (2011) 755.
- [36] N. Candu, M. Florea, S.M. Coman, V.I. Parvulescu, Appl. Catal. A: Gen. 393 (2011) 206.
- [37] N. Candu, S. Wuttke, E. Kemnitz, S.M. Coman, V.I. Parvulescu, Appl. Catal. A: Gen. 391 (2011) 169.
- [38] A.N.C. van Laak, S.L. Sagala, J. Zečević, H. Friedrich, P.E. de Jongh, K.P. de Jong, J. Catal. 276 (2010) 170.
- [39] M. Milina, S. Mitchell, Z.D. Trinidad, D. Verboekend, J. Pérez-Ramírez, Catal. Sci. Technol. (2012).