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Comparative study of zeolite catalyzed alkylation of benzene with alcohols of different chain length: H-ZSM-5 versus mordenite

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ABSTRACT

Alkylation of benzene with light alcohols offers opportunities for a more environmental friendly gasoline by removing considerable portions of benzene. The performances of ZSM-5 and mordenite zeolites as catalysts were tested in the alkylation reaction of benzene with different light alcohols (methanol, ethanol and isopropanol). The experiments were carried out in a fluidized-bed reactor with a 1/1 mol ratio of benzene/alcohol at 200, 250, 300, 350 and 400 °C for 3, 5, 7, 10, 13, 15 and 20 s. The reaction temperature, nature of the alcohol molecule and the BrØnsted to Lewis acid ratio of the catalysts, play an important role in the alkylation reactions. For benzene alkylation with methanol to toluene and xylene (XY), both mordenite and ZSM-5 are active and selective catalysts, while for benzene ethylation to ethylbenzene (EB), ZSM-5 exhibits higher EB selectivity than mordenite. Isopropanol presents higher difficulty to be activated as compared with other alcohols at the higher temperature, while the lower temperature favors benzene isopropylation to cumene over both catalysts. By studying the alkylation of benzene with alcohols of different chain length, it has been found that as the alkyl size (i.e. methyl, ethyl, and propyl) increases, the optimum temperature for alkylation reaction decreases.

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1. Introduction

The U.S. Environmental Protection Agency (EPA) reported in 2008 that gasoline from the catalytic reforming process contributes with 70–85% of the benzene in the gasoline pool [1]. Pre-treatment and post-treatment technologies have been developed to reduce the benzene content from this source [2,3]. Utilization of a suitable catalyst that could exploit this fraction of the refinery stream for the production of useful higher polybranched aromatics would be of great importance. Recently, Mobil Source Air Toxics rule, requires that refiners and importers in the USA should produce gasoline that has an average benzene content of 0.62 volume percent (vol%) or less, beginning in 2011 [4,5].

Zeolites were first introduced as acid catalysts for oil refining in the late 60s, improving the catalytic behavior of the previous amorphous silica–alumina [6–9]. Zeolite acidity, the size of channels and their dimensionality influence the activity and selectivity in transformations of organic compounds [10–13]. Reactions of alkyl and dialkyl-aromatics hydrocarbons represent an interesting group of reactions both from the practical petrochemical viewpoint as well as model reactions usually influenced by shape selectivity [14–17]. Zeolites with 10 rings usually exhibit restricted transition-state and product shape selectivity being particular important in para-selective reactions such as toluene disproportionation, xylene isomerization, and toluene alkylation with methanol, ethylene/ethanol, and propylene/propanol [17–29]. Large pore zeolites of the type Y, mordenite, Beta and MCM-22 do not exhibit para-selectivity, but are advantageously used in the synthesis of monoalkyl benzenes like ethylbenzene and cumene [30,31].

Alkylation of benzene is a vital reaction in the petrochemical industry. Benzene alkylation technologies offer improvements in octane number and gasoline volume [32,33]. Ethylbenzene, diethylbenzene, toluene and xylenes are important raw materials for many intermediates of commodity petrochemicals and valuable fine chemicals [34]. The use of zeolite catalysts for production of these valuable aromatics offers environmentally friendly route and opportunity of achieving superior product selectivity through pore size control [35]. The different pore window size of zeolites ranging from 5 Å to 12 Å cause a mass transfer effect excluding certain reactant molecules based on size relative to the zeolite pore window size. Several types of zeolites have been reported to provide high activity in benzene alkylation, for example, faujasite, beta, HZSM-5, mordenite, TNU-9 and SSZ-33 [36–43]. A number of alkylation processes has been proposed to enhance the benzene alkylation processes [44]. For example, Mobil-Badger process uses the ZSM-5 zeolite catalyst in order to increase the ethylbenzene diffusion while it prevents the polyethylbenzene to diffuse through the catalyst [45].

Abbreviations: B, benzene; T, toluene; XY, xylene; M, methanol; TMB, trimethylbenzene.

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Nomenclature

C_i	concentration of specie i in the riser simulator (mol/m^3)
CL	confidence limit
E_i	apparent activation energy of ith reaction (kJ/mol)
k_1	rate constant of reaction 1 (m^3/(kg of catalyst s))
k_2	rate constant of reaction 2 (m^3/(kg of catalyst s))
k_3	rate constant of reaction 3 (m^3/(kg of catalyst s))
k	apparent kinetic rate constant (m^3/(kg of catalyst s))
k_0	pre-exponential factor in Arrhenius equation defined at an average temperature [m^3/(kg of catalyst s)], units based on first order reaction.
MW$_i$	molecular weight of specie i
R	universal gas constant (kJ/(kmol K))
t	reaction time (s)
T	reaction temperature (K)
T_0	average temperature of the experiment (°C)
V	volume of the riser (45 cm^3)
W_c	mass of the catalysts (0.60 g cat)
W_{hc}	total mass of hydrocarbons injected in the riser
Y_i	mass fraction of ith component (wt%)

Subscripts

0	at time $t = 0$
1	for reaction (1)
2	for reaction (2)
3	for reaction (3)
cat	catalyst
i	for ith component

Although previous studies have tested series of zeolites for the conversion of benzene, the detailed understanding of the ease of alkylating benzene with different light alcohols, has not been extensively documented. In this work, we examine the performance of ZSM-5 and mordenite in the alkylation of benzene with light alcohols (methanol ethanol, isopropanol), with the aim of searching for a more suitable catalyst for benzene conversion. The purpose is to compare the behavior of a 10-ring pore zeolite such as ZSM-5 with that of 12-ring pore mordenite under indistinguishable reaction conditions, using a fluidized-bed reactor. Benzene was chosen due to the fact that environmental regulations demand lower proportion of this aromatic in the gasoline pool. Also, for the purpose of this study, this aromatic makes monitoring of the alkylation reaction easier as compared to other alkylaromatics (such as toluene or ethylbenzene), where side reactions occur on the aromatic compound itself. Furthermore, this work presents a kinetic model describing the dominant steps in the alkylation of benzene with these alcohols over the zeolite catalysts. The proposed model will be tested with the obtained experimental data and the model parameters estimated using nonlinear regression analysis.

2. Experimental

2.1. Catalyst preparation

The ZSM-5 zeolite and mordenite zeolite used in this work was obtained from Tosoh Chemicals, Japan. All zeolites were ion-exchange with NH_4NO_3 to replace the Na cation with NH_4^+. Following this, NH_3 was removed and the H form of the zeolites was obtained by calcination for 2 h at 600 °C.

2.2. Catalyst characterization

The catalysts were characterized by X-ray power diffraction (XRD), FT-IR of pyridine adsorption and nitrogen adsorption–desorption to understand the textural and chemical properties of the catalysts. Powder X-ray diffraction (XRD) was recorded on a Mac Science MX18XHF-SRA powder diffractometer with monochromatized Cu Kα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. Scanning electron microscopy (SEM) image was recorded using a JEOL, JSM-5500LV scanning electron microscope.

Concentration of Lewis and BrǾnsted acid sites was determined after adsorption of pyridine by FTIR spectroscopy (Nicolet 6700 FTIR). Samples were pressed into self-supporting wafers with a density of 8.0–12 mg/cm^2 and activated in situ at 430 °C overnight. Pyridine adsorption was carried out at 150 °C for 20 min at partial pressure 800–1000 Pa, followed by desorption for 15 min.

Nitrogen sorption isotherms were performed at liquid nitrogen temperature (−196 °C) on a Quantachrome AUTOSORB-1 (model ASI-CT-8) instrument to determine surface area and pore volume. Prior to the sorption measurements, all samples were degassed at 250 °C for at least 24 h until pressure of 10^{-3} Pa was attained.

2.3. Catalytic experiments

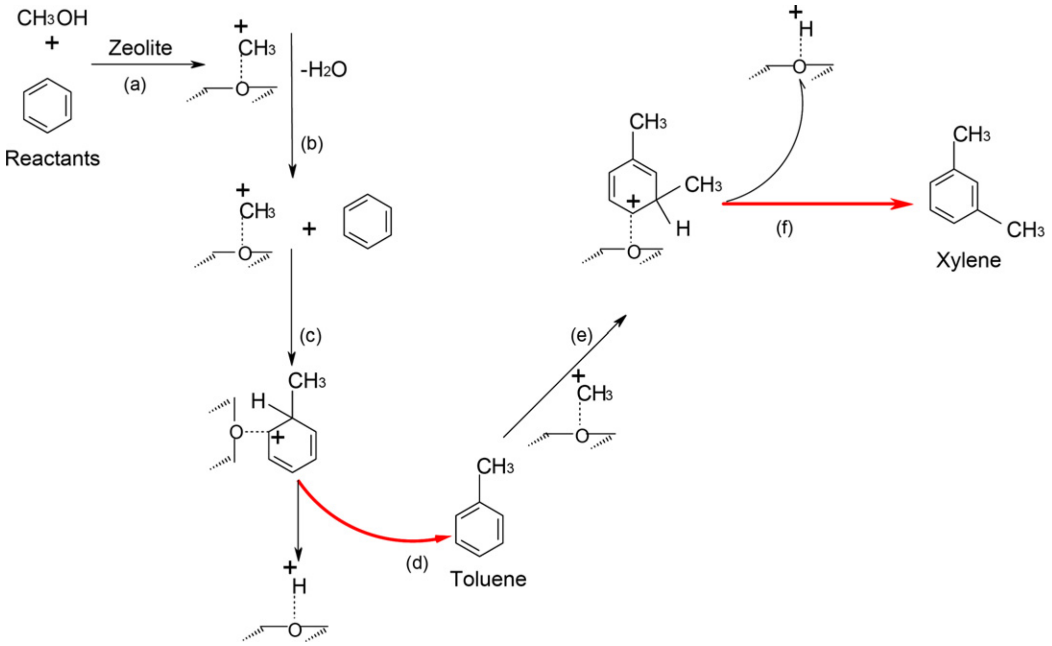
Alkylation of benzene with these alcohols was carried out in a riser simulator under atmospheric pressure. This reactor is novel bench-scale equipment with an internal recycle unit invented by de Lasa [46]. Catalytic experiments were performed at a catalyst/reactant ratio of 3.75 (weight of catalyst = 0.60 g) for different residence times of 3, 5, 7, 10, 13, 15 and 20 s and at reaction temperatures of 200, 250, 300, 350 and 400 °C. Analytical grade (99% purity) benzene, isopropanol, ethanol and methanol were obtained from Sigma–Aldrich. These chemicals were used as received. The feed molar ratio of benzene to alcohol is 1:1. A four-port valve enables the connection and isolation of the 45 cm^3 reactor and the vacuum box, and a six-port valve allows for the collection of a sample of reaction products in a sampling loop. The products were analyzed in an Agilent model 6890N gas chromatograph with a flame ionization detector and a capillary column INNOWAX, 60-m cross-linked methyl silicone with an internal diameter of 0.32 mm. During the course of the investigation, a number of runs were repeated to check for reproducibility in the experiment results, which were found to be excellent. Typical errors were in the range of ±2%.

3. Results and discussion

3.1. Characterization of catalysts

Zeolite structures were confirmed by powder X-ray diffraction. X-ray powder patterns of all zeolites under study exhibited good crystallinity and characteristic diffraction lines (not shown here). The particle morphology of the materials was investigated using scanning electron microscopy. The SEM images of the zeolites evidence the absence of impurities including an amorphous one.

The acidic properties of the zeolite catalysts can be measured by means of different basic probe molecules [47–49]. For application of zeolites in acid catalyzed reactions, the concentration of acid sites (BrǾnsted and Lewis types) is of utmost importance. Quantitative evaluation of FTIR spectra of ZSM-5 and mordenite is presented in Table 1. Over both zeolite catalysts, adsorption of pyridine resulted in the formation of bands at 1545 cm^{-1} and 1455 cm^{-1} (not shown here). The absorption band at 1545 cm^{-1} stems from the interaction of pyridine with BrǾnsted acid sites while the absorption band at



Scheme 1. Possible mechanism for benzene alkylation with methanol.

1455 cm^{-1} is characteristic for pyridine interacting with Lewis acid sites.

3.2. Alkylation of benzene with methanol

The results of the alkylation of benzene with methanol using mordenite and ZSM-5 as catalysts are presented in Tables 2 and 3. Formation of toluene, xylenes, trimethylbenzenes and ethylbenzene via alkylation of benzene with methanol was investigated over ZSM-5 and mordenite-based catalyst at 200, 250, 300, 350 and 400 °C for reaction times of 3, 5, 7, 10, 13, 15 and 20 s. The mechanism of the methylation of aromatic rings on zeolite catalysts was first reported by Venuto and Landis [50], and the analogous mechanism was presented by Kaeding et al. [51]. A possible mechanism to represent the alkylation of benzene with methanol over the zeolite catalysts is illustrated in Scheme 1. The reaction is initiated when a proton from the acidic bridging OH group attacks methanol to form water and methoxy cation. A methoxy cation then attacks benzene molecule to form protonated toluene. Toluene is formed when a protonated toluene returns a proton to the surface. The xylene is formed in a similar manner, where methoxy cation attacks toluene ring carbon atom at ortho or para position atom to form a surface protonated xylene.

Fig. 1 shows benzene conversion in alkylation with methanol over mordenite and ZSM-5. The conversions of benzene increased with increasing reaction temperature and time over both catalysts. A maximum benzene conversion of ~32.8% and ~19.1% were observed over mordenite and ZSM-5, respectively, at 400 °C for a reaction time of 20 s. Benzene conversion has been obtained at a short time-on-stream (TOS = 20 s) over both mordenite and ZSM-5 to minimize the deactivation effect of the catalysts. The catalyst based on mordenite showed a much higher activity as compared with the ZSM-5 catalyst, which may be related to the topology of each zeolite. The channels in mordenite catalyst provide larger reaction volume for formation of more xylenes (XY) and trimethylbenzenes (TMB) as compared with ZSM-5 having a smaller reaction volume.

The main products of benzene alkylation with methanol are toluene, xylenes and trimethylbenzenes. Tables 2 and 3 present complete conversion and product yields for benzene alkylation with methanol over ZSM-5 and mordenite. Formation of toluene represents the primary alkylation step, while the alkylation reaction of toluene with methanol represents the secondary alkylation reaction. A tertiary alkylation reaction was also noticed over mordenite catalyst, which led to the formation of trimethylbenzenes at the higher temperature (400 °C). In the alkylation reaction, higher toluene selectivity was obtained over ZSM-5 catalyst as compared with mordenite (Fig. 2A), while the mordenite catalyst was found to be more selective towards xylene (Fig. 2B). Toluene selectivity over ZSM-5 at 250 °C, decreased progressively with benzene conversion, which is due to the formation of xylenes with increasing benzene conversion. In the case of mordenite, toluene and xylene selectivity were fairly stable with increasing benzene conversion at the higher temperatures. The product selectivity during the alkylation of benzene with methanol over ZSM-5 and mordenite is compared in Fig. 3 at constant conversion level of ~11%. Higher toluene selectivity was noticed over ZSM-5 as compared with mordenite, when both catalysts were compared at the same conversion level. As could be anticipated, mordenite produces larger amount of polyalkylated product (Fig. 3).

Table 1
Acidic and textural properties of the catalysts under study.

	ZSM-5	Mordenite
Particle properties		
SiO_2/Al_2O_3 ratio	27	180
Channel dimensions (Å)	5.1 × 5.5 and 5.3 × 5.6	6.5 × 7.0 and 2.6 × 5.7
Pore topology	3D, 10-rings	1D, 12 and 8-rings
Textural properties		
BET area (m^2/g)	295	420
Pore volume (cm^3/g)	0.17	0.27

	Acidity (mmol of pyridine/g)				
	C_{Br}/C_{Le} ratio	C_{Br} (mmol/g)	C_{Le} (mmol/g)	C_{Br} (%)	C_{Le} (%)
ZSM-5	1.9	0.240	0.130	65	35
Mordenite	15	0.030	0.002	94	6

C_{Br}, concentration of BrØnsted acid sites; C_{Le}, concentration of Lewis acid sites.

Table 2
Product distribution (wt%) at various reaction conditions for alkylation of benzene with methanol over ZSM-5 based catalyst.

Temp. (°C)	Time (s)	Benzene conv. (%)	Toluene	EB	*m*-Xy.	*p*-Xy.	*o*-Xy.	Total xylene
300	3	2.56	2.17	–	0.16	0.11	0.05	0.32
	5	4.50	3.46	–	0.42	0.35	0.13	0.90
	7	5.12	4.10	–	0.45	0.40	0.16	1.02
	10	6.78	4.56	0.76	0.52	0.45	0.17	1.14
	13	9.59	6.53	1.04	0.81	0.75	0.19	1.75
	15	10.06	6.71	1.36	0.77	0.71	0.28	1.77
	20	13.79	8.27	2.47	1.38	1.03	0.51	2.92
350	3	4.02	2.85	–	0.52	0.39	0.19	1.10
	5	6.79	4.70	–	0.90	0.63	0.33	1.86
	7	7.35	5.30	–	1.00	0.72	0.33	2.05
	10	11.24	6.97	1.13	1.36	0.89	0.50	2.75
	13	12.49	7.48	1.89	1.42	0.93	0.54	2.89
	15	14.76	8.66	2.34	1.83	1.11	0.71	3.65
	20	16.99	9.96	2.73	2.14	1.22	0.85	4.21
400	3	5.50	3.86	–	0.80	0.47	0.33	1.60
	5	7.55	5.27	–	1.10	0.62	0.45	2.17
	7	10.85	6.85	0.99	1.46	0.78	0.62	2.86
	10	12.81	7.96	1.37	1.71	0.90	0.71	3.32
	13	15.30	9.65	1.58	2.04	1.06	0.84	3.94
	15	15.59	9.92	1.65	2.06	1.06	0.87	3.99
	20	19.05	11.72	2.35	2.53	1.30	1.06	4.89

T = 300–400 °C, benzene to methanol molar ratio 1 and catalyst/feed = 3.8; Xy., xylene.

3.3. *Alkylation of benzene with ethanol*

Benzene alkylation with ethanol can be considered as an electrophilic substitution on the aromatic ring, and over acidic zeolites it is commonly considered as proceeding via a carbonium ion-type mechanism [52]. The ethylation of benzene with ethanol has been proposed to take place by the reaction of the activated alkene (formed by dehydration of the alcohol) on the acid sites of the zeolite [37,40]. Benzene conversions in the alkylation reaction of benzene with ethanol at 300, 350 and 400 °C over mordenite and ZSM-5 based catalyst are presented in Fig. 4. It is evident from Fig. 4 that the conversions of benzene increased with increasing time to ~28.8% and ~20.8%, for a reaction time of 20 s over mordenite and ZSM-5, respectively. At reaction temperatures of 350 and 400 °C, mordenite shows higher conversion in the alkylation reaction as compared with the ZSM-5 based catalyst, while comparable benzene conversions were noticed at 300 °C, over both catalysts.

Ethylbenzene (EB), diethylbenzenes (DEBs) and toluene were obtained as major products in the alkylation of benzene with ethanol over ZSM-5 and mordenite catalyst. Negligible amounts of xylene and gaseous hydrocarbons were also detected. From an industrial point of view, Perego and Ingallina [53] reported that formation of byproducts different from diethylbenzene has a negative effect, not only on the final yield, but also on the quality of the final product. Fig. 5 summarizes the product selectivity during the alkylation of benzene with ethanol over these catalysts at constant benzene conversion level of ~20%. Ethylbenzene was obtained as the most predominant product over both catalysts and might be attributed to its free diffusion without steric hindrance through the pores of the catalysts. Formation of ethylbenzene represents the primary alkylation step, while the alkylation reaction of ethylbenzene with ethanol led to the formation of diethylbenzene, representing the secondary alkylation reaction. Significant amounts of toluene noticed in the

Table 3
Product distribution (wt%) at various reaction conditions for alkylation of benzene with methanol over mordenite catalyst.

Temp. (°C)	Time (s)	Benzene conv. (%)	Toluene	TMB	*m*-Xy.	*p*-Xy.	*o*-Xy.	Total xylene	TetraMB
300	3	3.18	2.07	0.20	0.40	0.13	0.37	0.90	–
	5	7.58	4.83	0.54	1.04	0.43	0.65	2.12	–
	7	11.21	6.55	0.79	1.66	0.67	1.03	3.36	–
	10	14.34	8.18	0.98	1.96	0.88	1.29	4.13	–
	13	14.50	8.86	1.07	2.04	0.88	1.24	4.16	–
	15	15.32	10.02	1.15	2.03	0.91	1.17	4.11	–
	20	21.36	12.29	2.13	3.14	1.37	2.07	6.58	–
350	3	7.40	3.92	1.01	1.24	0.56	0.61	2.41	–
	5	10.93	5.47	1.59	1.85	0.83	0.90	3.58	–
	7	13.82	7.02	2.11	2.21	1.04	1.11	4.36	–
	10	16.53	8.37	2.64	2.74	1.24	1.34	5.32	–
	13	21.20	10.58	2.98	3.37	1.55	1.66	6.58	–
	15	22.57	11.59	3.09	3.47	1.57	1.73	6.77	–
	20	26.75	13.28	4.11	4.72	2.15	2.23	9.10	–
400	3	9.25	4.41	1.23	1.57	0.71	0.75	3.03	–
	5	12.33	6.06	1.61	2.04	0.92	0.97	3.93	–
	7	17.26	8.34	2.23	2.92	1.32	1.38	5.62	0.60
	10	20.88	9.70	2.67	3.41	1.54	1.58	6.53	0.98
	13	25.61	12.19	3.23	4.47	2.03	2.08	8.58	1.01
	15	25.88	12.39	3.30	4.49	2.04	2.07	8.60	1.31
	20	32.76	15.70	3.83	5.72	2.69	2.67	11.08	1.80

T = 300–400 °C, benzene to methanol molar ratio 1 and catalyst/feed = 3.8; Xy., xylene.

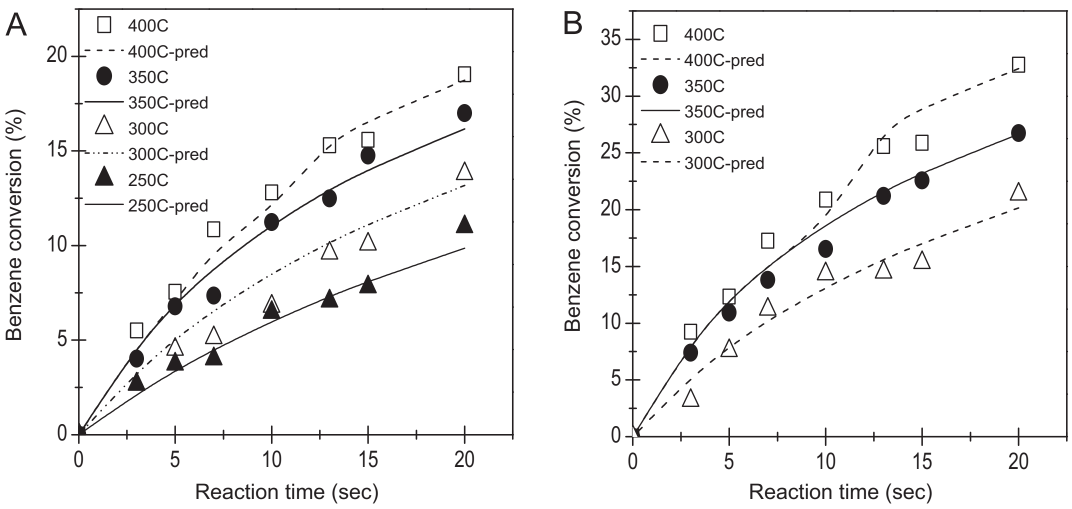


Fig. 1. Benzene conversion in the alkylation process versus reaction time over ZSM-5 (A) and mordenite (B) (benzene to methanol molar ratio = 1, catalyst/feed = 3.8, reaction temperature = 250, 300, 350 and 400 °C).

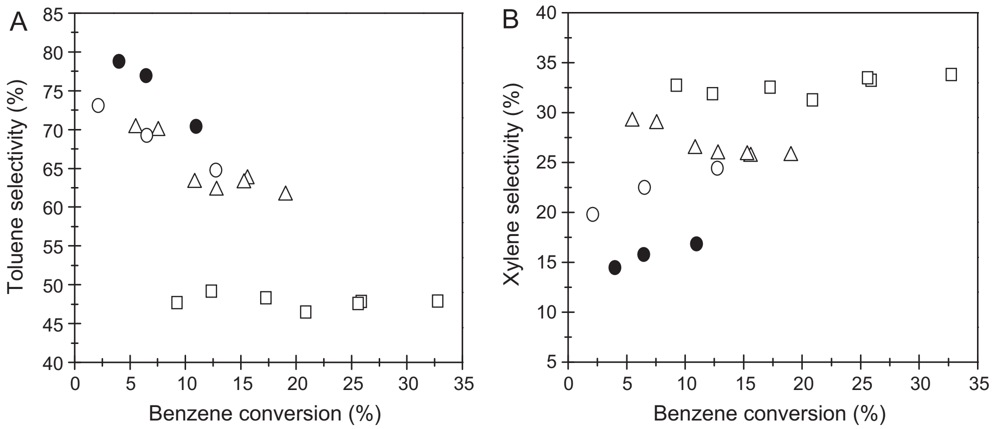


Fig. 2. Toluene (A) and xylene (B) selectivities versus benzene conversion for ZSM-5 (▲, △, ●) and mordenite (■, □, ○) at 250 (○, ●) and 400 °C (△, □) (benzene to methanol molar ratio = 1, catalyst/feed = 3.8).

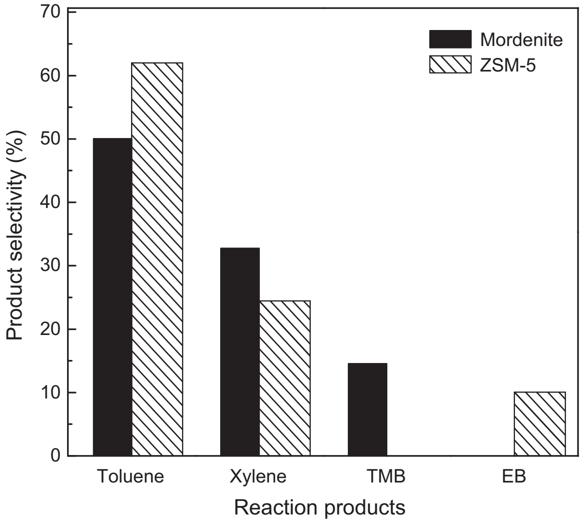


Fig. 3. Product selectivity of benzene alkylation with methanol over ZSM-5 (▨) and mordenite (■) at ∼11% benzene conversion (benzene to methanol molar ratio = 1, catalyst/feed = 3.8, reaction temperature = 350 °C).

reaction products over ZSM-5 are formed from the cracking of ethylbenzene.

The effect of benzene conversion on ethylbenzene, diethylbenzene and toluene selectivities at 250, 300 and 400 °C over mordenite and ZSM-5 based catalyst is given in Fig. 6. Ethylbenzene selectivity over mordenite decreased with increasing benzene conversion at all reaction temperatures studied, while its selectivity was found to increase with increasing conversion over ZSM-5 at 300 °C (Fig. 6A). This trend confirms the increasing diethylbenzene selectivity over mordenite (Fig. 6B), since production of diethylbenzene is at the expense of ethylbenzene conversion. Diethylbenzene selectivity over mordenite shows a high dependence on the conversion of benzene at 300 °C, and was found to increase with increasing benzene conversion (Fig. 6B). Higher toluene selectivity was achieved over mordenite as compared with ZSM-5, when both catalysts are compared at the same conversion level. However, higher toluene selectivity (∼40%) was found over ZSM-5, when the reaction temperature was increased from 300 to 400 °C (Fig. 6C). The trend of toluene selectivity noticed over ZSM-5 can be related to its acidity, leading to more cracking of ethylbenzene to toluene at the higher temperature. Catalytic behavior of zeolites with different pore diameter can be differentiated by para to ortho (*p*/*o*) ratio in the diethylbenzene fraction. Over both catalysts, the experimental results showed that the para to ortho ratio was found to be between 2.1 and 3.7 for mordenite, while the catalyst based

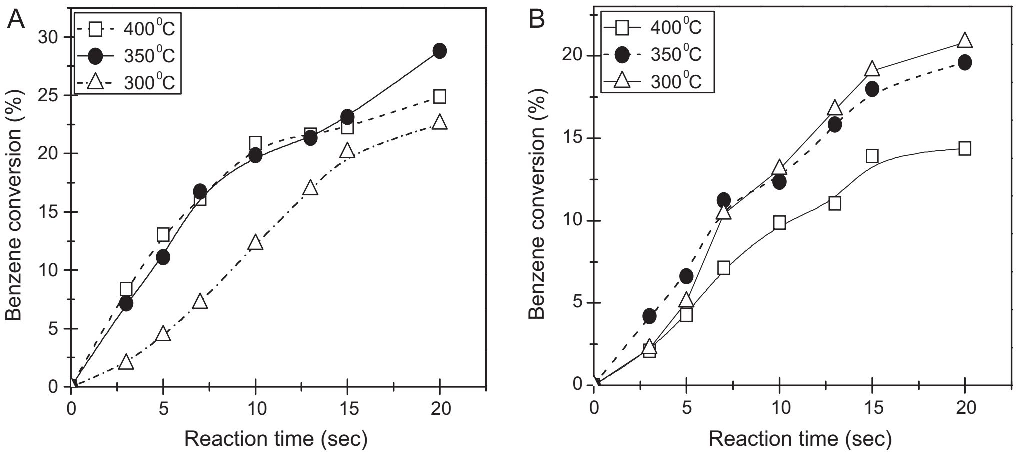


Fig. 4. Effect of reaction conditions on benzene conversion in the alkylation reaction of benzene with ethanol over mordenite (A) and ZSM-5 (B) (benzene to ethanol molar ratio = 1, catalyst/feed = 3.8, reaction temperature = 300, 350 and 400 °C).

on ZSM-5 gave *p*/*o* ratio between 2.6 and 11.9. The high *p*/*o* ratio observed over ZSM-5 is anticipated, because medium pore zeolites exhibiting channels with dimensions of about 0.55 nm have led to shape selectivity in the processing of alkylaromatics, particularly with respect to para isomers of dialkylaromatic hydrocarbons, while large pore zeolites do not exhibit para selectivity [54].

3.4. Alkylation of benzene with isopropanol

When isopropanol or propylene is contacted with benzene in the presence of a solid acid catalyst, the alkylating agent can follow two major reaction pathways: (a) alkylation with benzene to produce cumene, being able to further react to diisopropylbenzene and (b) oligomerization of olefin to produce C6 and C9 olefins [55]. In the alkylation reaction of benzene with isopropanol over mordenite and ZSM-5 based catalyst, benzene conversions were found to be less than 11% over both catalysts. The mechanism for the isopropylation of benzene with isopropanol is better exemplified in Scheme 2. A proton attacks isopropanol to initiate the start of the reaction, forming water and surface isopropyl cation. An isopropyl cation attacks benzene molecule to form protonated cumene and returning a proton to the surface result in the formation of cumene. Diisopropylbenzene (DIPB) is formed when isopropyl cation attacks cumene ring carbon atom. Benzene conversions of 14.0, 19.5, 10.5, 7.4 and 5.3% were obtained at 200, 250, 300, 350 and 400 °C in the alkylation reaction of benzene with isopropanol at 20 s over mordenite catalyst. On the other hand, a much lower benzene conversions were noticed in the alkylation reaction of benzene with isopropanol over ZSM-5. Conversions of approximately 3.0, 3.2, 4.3, 6.9 and 6.8% were noticed at 200, 250, 300, 350 and 400 over the catalyst based on ZSM-5 for a reaction time of 20 s. The higher benzene conversion noticed over mordenite as compared with ZSM-5, is in line with the findings of Cejka in the case of benzene alkylation with isopropyl alcohol [56], where the alkylation activity does not depend on the acidity of the molecular sieves, but mainly controlled by the desorption/transport rate of the bulky, strongly adsorbed cymenes and cumene.

Toluene and ethylbenzene were observed as the major products at the higher temperatures (350 and 400 °C) in the alkylation reaction over both catalysts (Table 4), while cumene, diisopropylbenzene and n-propylbenzene were noticed as the major products at the lower temperatures (200, 250, 300 °C). The product selectivity during the alkylation of benzene with isopropanol over ZSM-5 and mordenite is compared in Fig. 7 at reaction temperatures of 200, 250, 300, 350 and 400 °C, for a reaction time of 20 s. The results show that cumene is obtained as the most predominant product over both catalysts at all reaction temperature studied. The highest

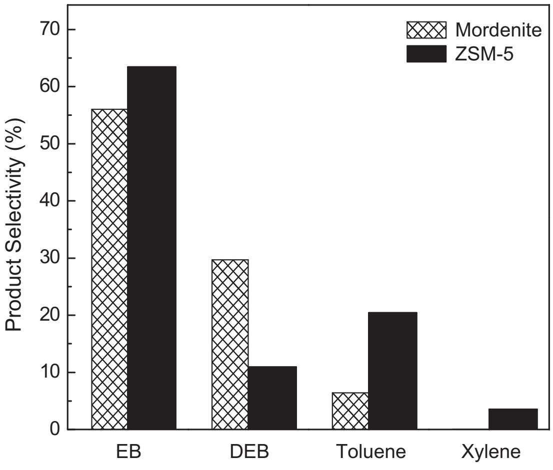


Fig. 5. Product selectivity of benzene alkylation with ethanol over ZSM-5 (■) and (▨) at $\sim$20% benzene conversion (benzene to ethanol molar ratio = 1, catalyst/feed = 3.8, reaction temperature = 350 °C).

Table 4
Conversion and product distribution in benzene alkylation with isopropanol over mordenite and ZSM-5 based catalyst.

Temperature (°C)	200	250	300	350	400
Mordenite catalyst					
Benzene conversion (%)	13.96	19.53	10.50	7.36	5.26
Product (wt%)					
Gases	–	0.26	0.95	1.02	1.05
Toluene	–	0.07	1.98	2.81	3.20
Ethylbenzene	–	0.99	1.59	1.51	0.70
Cumene	8.83	13.57	5.87	1.70	0.26
Diisopropylbenzene	4.78	4.11	–	–	–
n-Propylbenzene	0.30	0.50	–	–	–
ZSM-5 catalyst					
Benzene conversion (%)	3.05	3.17	4.30	6.91	6.79
Product (wt%)					
Gases	–	–	0.30	0.65	0.70
Toluene	–	–	0.41	2.16	3.43
Ethylbenzene	–	–	2.25	3.75	2.58
Cumene	1.93	2.38	1.30	0.21	0.05
Diisopropylbenzene	–	–	–	–	–
n-Propylbenzene	1.09	0.73	–	–	–

T = 200–400 °C, reaction time = 20 s, catalyst/feed = 3.8 and benzene to isopropanol molar ratio 1.

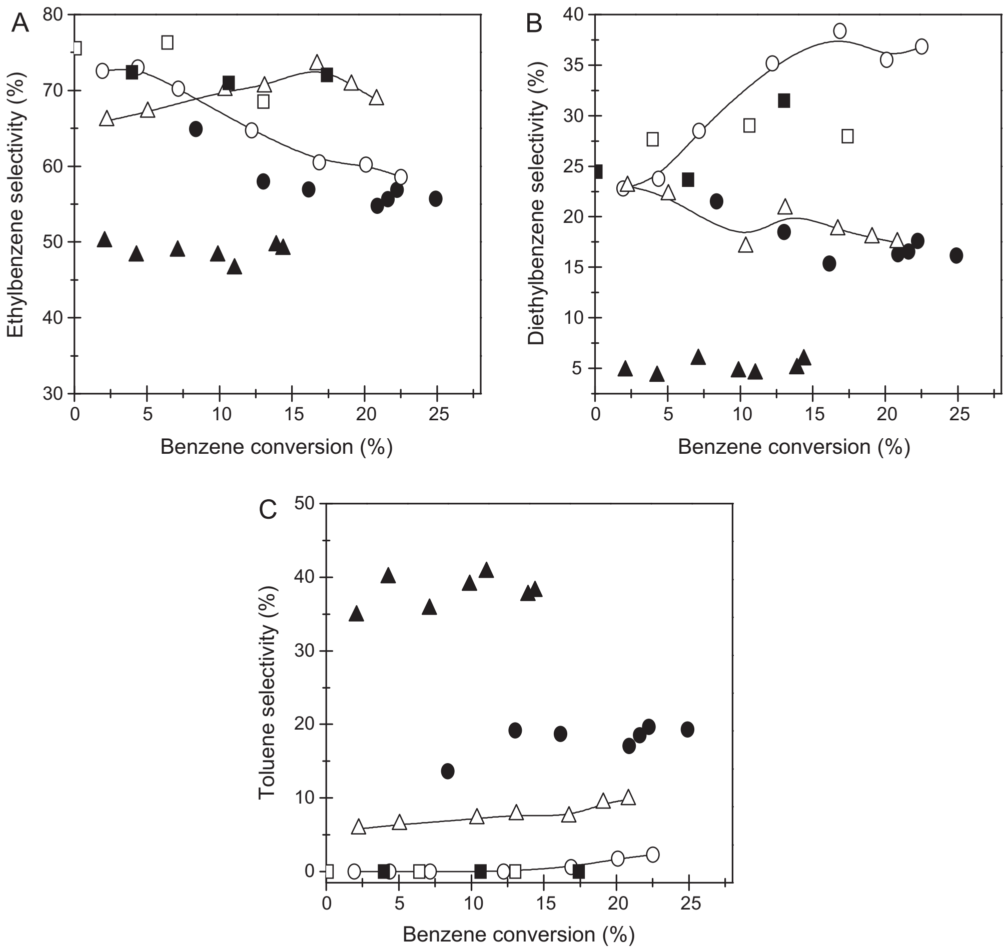
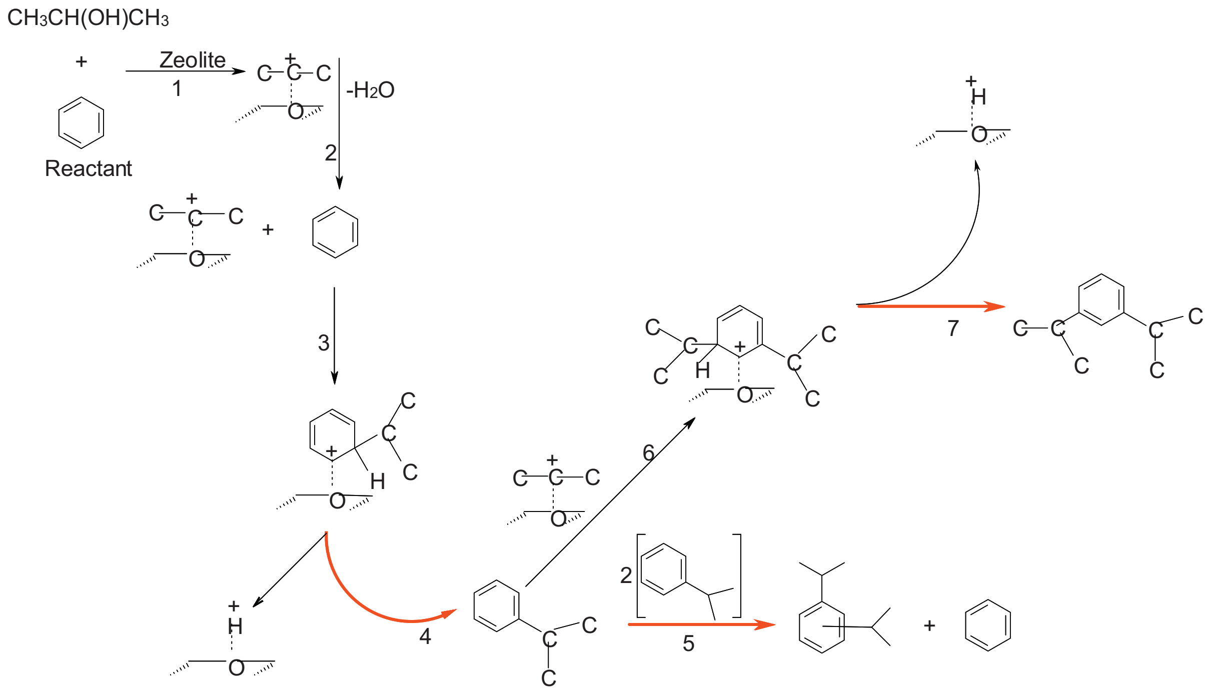


Fig. 6. Effect of benzene conversion on ethylbenzene, diethylbenzene and toluene selectivities over ZSM-5 (▲, △, ■) and mordenite (●, ○, □) (benzene to ethanol molar ratio = 1, catalyst/feed = 3.8, reaction temperature = 250 °C (□, ■), 300 °C (○, △) and 400 °C (●, ▲)).



Scheme 2. Possible mechanism for benzene alkylation with isopropanol.

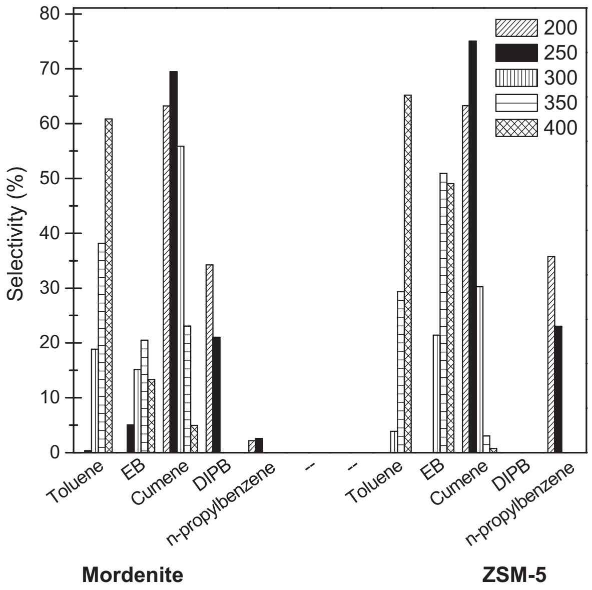


Fig. 7. Product selectivity of benzene isoproylation over ZSM-5 and mordenite (reaction temperatures = 200, 250, 300, 350 and 400 °C, reaction time = 20 s, benzene to isopropanol molar ratio = 1, catalyst/feed = 3.8).

selectivity of toluene and ethylbenzene were noticed at the higher temperatures, indicating dealkylation reaction as the major reaction taking place over both catalysts at these temperatures (350 and 400 °C). Both catalysts gave the highest isopropylbenzene (cumene) at the lower temperatures, confirming a low degree of dealkylation activity taking place at these temperatures. At 250 °C, catalyst based on ZSM-5 gave a cumene selectivity of ~75.1%, while mordenite gave a slightly lower cumene selectivity of ~69.5%. Similarly, mordenite gave diisopropylbenzene selectivity of ~21.0% at 250 °C; however, no diisopropylbenzene was detected over the catalyst based on ZSM-5. It is important to note that since the diisopropylbenzene formed are reconverted to cumene in the transalkylation units that are usually present in commercial cumene processes, it is interesting to consider the selectivity to cumene and diisopropylbenzene over mordenite.

With respect to the n-propylbenzene formed over both catalysts, it can be seen from Fig. 7 that n-propylbenzene selectivity of ~35.7% was observed over ZSM-5 as compared with only 2.2% over mordenite at 200 °C. It should be mentioned that in the industrial process the presence of n-propylbenzene has a negative effect on yield and on the product quality. The higher selectivity of n-propylbenzene noticed over ZSM-5 is not surprising, since the formation of n-propylbenzene by the transalkylation reaction between isopropylbenzene and benzene, is favored over 10MR zeolites such as ZSM-5 as compared with large pore zeolites such as mordenite [14,29,57]. The three-dimensional channel system of ZSM-5 permits the formation of n-propylbenzene, while the one-dimensional channel system of mordenite restricts the formation of the n-propylbenzene. The product selectivity over both catalysts clearly shows that reaction space, i.e., the zeolite inner volume, plays a crucial role in the n-propylbenzene formation.

3.5. *Comparison of catalysts in the alkylation reaction of benzene with the different alcohols*

Fig. 8 shows the benzene conversion for the alkylation with methanol, ethanol and isopropanol over mordenite and ZSM-5 based catalyst. The benzene conversions in the alkylation reactions over both ZSM-5 and mordenite catalyst carried out at 400 °C follow the order: methylation > ethylation > isopropylation. Benzene conversions of ~32.7%, 24.9%, and 5.3% were noticed for the methylation, ethylation and isopropylation reactions, respectively, over mordenite at 400 °C, for a reaction time of 20 s. Similarly, over the catalyst based on ZSM-5, benzene conversions of ~19.1%, 14.4%, and 6.8% were observed for the methylation, ethylation and isopropylation reactions, respectively, at the same reaction temperature. The mordenite catalyst presents high activity for both alkylation of benzene with methanol and ethanol, while comparable activity was noticed for both catalysts in the isopropylation reaction at 400 °C (Fig. 8A).

It was found that decreasing the temperature from 400 to 300 °C did change the order of benzene conversion (Fig. 8B). Similarly, the conversions of benzene in the alkylation reactions over mordenite catalyst at 300 °C, for a reaction time of 20 s, follow the order: ethylation (22.5%) > methylation (21.4%) > isopropylation (10.5%), while the benzene conversions at the same temperature over ZSM-5 catalyst follow similar order: ethylation (20.8%) > methylation (13.8%) > isopropylation (4.3%). At much lower reaction temperatures (200 and 250 °C), a completely different trend was noticed over mordenite in the alkylation reaction. Benzene conversions over mordenite in the alkylation reactions at 250 °C, follow the order: isopropylation (19.5%) > ethylation (13.0%) ≈ methylation (12.7%). The obtained results clearly show that dealkylation reaction plays a decisive role in the alkylation of benzene with isopropanol at the higher temperatures. Taking into consideration the physico–chemical properties of both catalysts, these results indicate that reaction temperature as well as the nature of the alcohol molecule plays an important role in the alkylation reactions. However, the Bronsted to Lewis acid ratio of mordenite as well as its pore architecture might have contributed to the ease of alkylation. Undoubtedly, a higher proportion of Bronsted acid sites improve the activation of alcohols towards benzene alkylation over oligomerization [58]. Furthermore, a linear correlation is known to exist between the conversion of catalyst and the Bronsted acid concentration in the alkylation reaction of benzene with methanol [59]. Under the present experimental conditions, it easier to activate methanol at the higher temperature (400 °C) over mordenite catalyst, while the lower temperatures (300 and 350 °C) favors the activation of ethanol over both catalysts (Fig. 9). This observation is in agreement with our previous study on benzene ethylation over TNU-9 and SSZ-33 zeolite catalysts, in which the highest selectivity towards ethylbenzene was obtained at a very low reaction temperature (250 °C) [40]. Also, isopropanol has been found to be more reactive than methanol and ethanol at lower reaction temperatures (200 and 250 °C) (Fig. 9).

4. Kinetic modeling

4.1. *Model development*

Developing a kinetic model which illustrates the alkylation of benzene with methanol over mordenite and ZSM-5 zeolite catalysts under study is the main objective of this section. The kinetic parameters obtained in the alkylation reaction of benzene with methanol in this present study will be compared with our previously reported kinetic parameters on the ethylation of benzene with ethanol [39,40]. To develop a suitable kinetic model representing the alkylation reaction over both catalysts, the reaction network shown in Scheme 3 was used.

In developing the reaction network we assumed the alkylation of benzene with methanol follows simple second-order kinetics and a pseudo-first order reaction kinetic was assumed for all species involved in the reactions. Catalyst deactivation is assumed to be a function of reactant conversion (RC) and a single deactivation function was defined for all reactions. Isothermal operating conditions

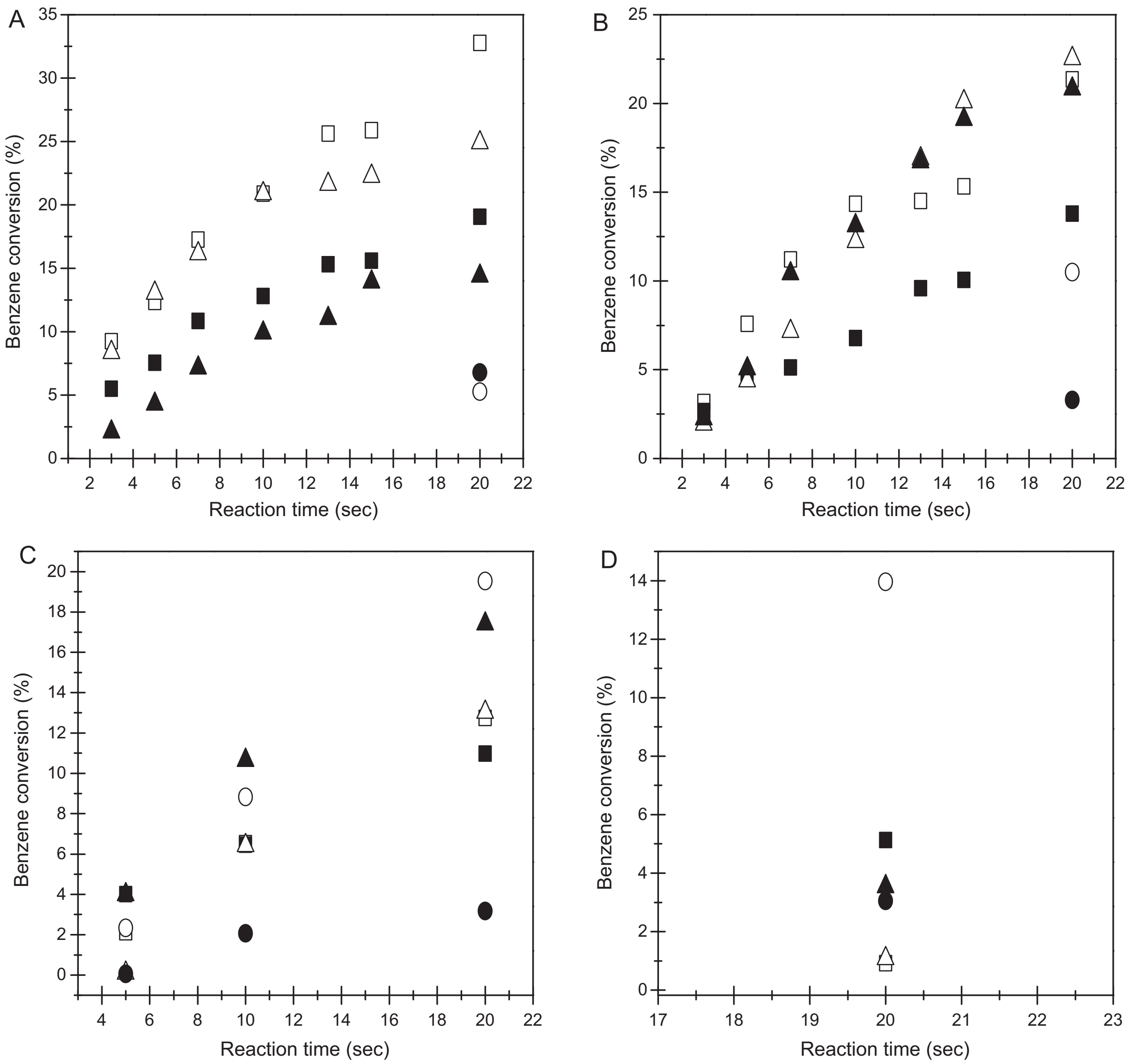


Fig. 8. Benzene conversion in the alkylation process versus reaction time at 400 °C (A), 300 °C (B), 250 °C (C) and 200 °C (D) with methanol (□, ■), ethanol (△, ▲) and isopropanol (○, ●) over ZSM-5 (■, ▲, ●) and mordenite (□, △, ○) (benzene to alcohol molar ratio = 1, catalyst/feed = 3.8).

can also be assumed given the design of the riser simulator unit and the relatively small amount of reacting species. Also, dealkylation reaction is inconsequential due to minor amount of gases in the reaction system. Based on the reaction products noticed in the alkylation of benzene with methanol over ZSM-5 catalyst, $k_{x3} \approx 0$, (where $x = z$ in the case of ZSM-5 and $x = \mathrm{M}$ in the case of mordenite) in Scheme 3. The formation of tetramethylbenzenes over mordenite as well as ethylbenzene and trimethylbenzenes over ZSM-5 based catalyst were neglected due to the inconsistency of these products.

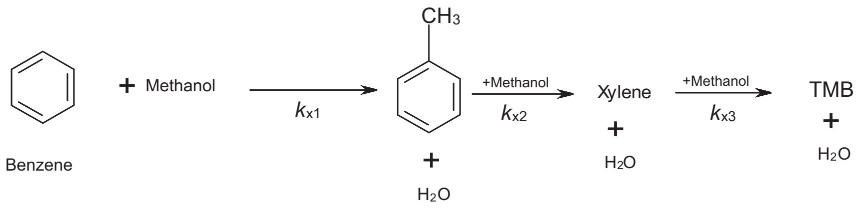
The following set of species balances and catalytic reactions can be written:

Rate of disappearance of benzene

$$-\frac{V}{W_c}\frac{dC_B}{dt} = k_{x1}C_BC_M \exp(-\lambda(1-y_B)) \tag{1}$$

Rate of formation of toluene

$$\frac{V}{W_c}\frac{dC_T}{dt} = (k_{x1}C_BC_M - k_{x2}C_TC_M)\exp(-\lambda(1-y_B)) \tag{2}$$



Scheme 3.

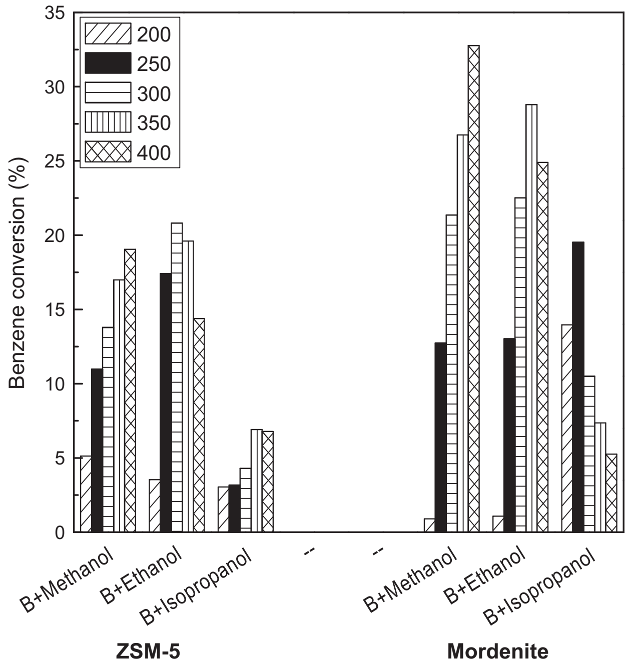


Fig. 9. Benzene conversion in the alkylation process over mordenite and ZSM-5 catalysts (reaction temperatures = 200, 250, 300, 350 and 400 °C, reaction time = 20 s, benzene to alcohol molar ratio = 1, catalyst/feed = 3.8).

Rate of formation of xylene

$$\frac{V}{W_c}\frac{dC_{XY}}{dt} = (k_{x2}C_T C_M - k_{x3}C_{XY}C_M)\exp(-\lambda(1-y_B)) \tag{3}$$

Rate of formation of trimethylbenzene

$$\frac{V}{W_c}\frac{dC_{TMB}}{dt} = (k_{x3}C_{XY}C_M)\exp(-\lambda(1-y_B)) \tag{4}$$

The measurable variables from our chromatographic analysis are the weight fraction of the species, y_x, in the system. By definition the molar concentration, c_x of every species in the system can be related to its mass fraction, y_x by the following relation:

$$c_x = \frac{y_x W_{hc}}{V\,\mathrm{MW}_x} \tag{5}$$

where W_{hc} is the weight of feedstock injected into the reactor, MW_x is the molecular weight of specie x in the system, V is the volume of riser simulator and λ is the catalyst deactivation constant.

The temperature dependence of the rate constants was represented with the centered temperature form of the Arrhenius equation, i.e.

$$k_i = k_{0i}\exp\left[\frac{-E_i}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{6}$$

Since the experimental runs were done at 250, 300, 350 and 400 °C, T_0 was calculated to be 325 °C. Where T_0 is an average temperature introduced to reduce parameter interaction [60], k_{0i} is the rate constant for reaction i at T_0, W_c is the weight of catalyst and E_i is the activation energy for reaction i.

4.2. Discussion of kinetic modeling results

Table 5
Estimated kinetic parameters based on reactant-converted (RC model) for alkylation of benzene with methanol over mordenite catalyst.

Parameters	Values		
	k_{M1}	k_{M2}	k_{M3}
E_i (kJ/mol)	33.34	22.08	14.85
95% CL	2.25	3.53	4.15
$k_{0i}^a \times 10^3$ (m^3/(kg of catalyst s))	0.231	1.137	0.833
95% CL × 10^3	0.079	0.405	0.311
	λ = 4.50 (95% CL of 0.93)		

Table 6
Estimated kinetic parameters based on reactant-converted (RC model) for alkylation of benzene with methanol over ZSM-5 catalyst.

Parameters	Values	
	k_{Z1}	k_{Z2}
E_i (kJ/mol)	23.86	18.71
95% CL	1.75	3.81
$k_{0i}^a \times 10^3$ (m^3/kg of catalyst s)	0.143	0.586
95% CL × 10^3	0.061	0.180
	λ = 4.80 (95% CL of 1.44)	

The kinetic parameters k_{0i}, E_i, and λ for the alkylation reaction of benzene with methanol over mordenite and ZSM-5 based catalyst under study were obtained using nonlinear regression (MATLAB package). The values of the model parameters along with their corresponding 95% confidence limits (CLs) are shown in Tables 5 and 6 (RC model) for both mordenite and ZSM-5 based catalyst, respectively, while the resulting cross-correlation matrices are also given in Table 7 for ZSM-5 based catalyst and Table 8 for mordenite based catalyst. Based on the correlation matrices of the regression analysis presented in Table 7 for alkylation of benzene with methanol over ZSM-5 based catalyst, it shows the very low correlations between k_{Z1}, k_{Z2} and E_{Z1}, E_{Z2} and the moderate correlation between k_{Z1}, k_{Z2} and λ. Likewise, Table 8 reports the very low correlations between $k_{M1}-k_{M3}$ and $E_{M1}-E_{M3}$. It is evident that in the cross-correlation matrices presented in this present study, most of the coefficients remain in the low level with only a few exceptions.

Table 5 presents the values of the optimized kinetic parameters for alkylation reaction of benzene with methanol over mordenite based catalyst. Apparent activation energies of 33.3, 22.1 and 14.9 kJ/mol were obtained for benzene methylation, toluene methylation and xylene methylation, respectively, over mordenite based catalyst. Comparing the obtained apparent activation energy for benzene methylation (33.3 kJ/mol) with our previously reported apparent activation energy for benzene ethylation (59.9 kJ/mol) over mordenite catalyst [40], much higher apparent activation energy was noticed in the ethylation reaction as compared with the methylation reaction. Two factors might have contributed to the difference in activation energy noticed over both reactions. The reaction temperature as well as the ratio of BrØnsted to Lewis acid ratio might have resulted in the lower apparent activation energy noticed for benzene methylation reaction as compared with the ethylation reaction. Comparing the obtained apparent activation energy for the first, second and third alkylation reactions over mordenite catalyst, the reactivity of the alkylbenzenes was noticed to increase with increasing methyl group per benzene ring. This trend is consistent with the observation made by Kaeding [61], that alkylation reactions of long substituted benzenes (diethylbenzene) generally occur with greater ease compared to their shorter substituted counterparts. Comparing the obtained apparent activation

Table 7
Correlation matrix for parameters of benzene alkylation with methanol over ZSM-5 catalyst.

	k_{Z1}	E_{Z1}	λ	k_{Z2}	E_{Z2}	λ
$k_{Z1,2}$	1.0000	0.4457	0.8190	1.0000	0.2572	0.7922
$E_{Z1,2}$	0.4457	1.0000	0.6477	0.2572	1.0000	0.3187
λ	0.8190	0.6477	1.0000	0.7922	0.3187	1.0000

Table 8
Correlation matrix for parameters of benzene alkylation with methanol over mordenite catalyst.

	k_{M1}	E_{M1}	λ	k_{M2}	E_{M2}	λ	k_{M3}	E_{M3}	λ
$k_{M1,2,3}$	1.0000	0.2170	0.7975	1.0000	0.1263	0.7895	1.0000	−0.0482	0.6283
$E_{M1,2,3}$	0.2170	1.0000	0.3258	0.1263	1.0000	0.4990	−0.0482	1.0000	0.2072
λ	0.7975	0.3258	1.0000	0.7895	0.4990	1.0000	0.6283	0.2072	1.0000

energy for benzene methylation over mordenite with the energy of activation for toluene isopropylation (37.3 kJ/mol) over another 12 ring zeolite [62], slightly lower apparent energy of activation is still observed in the benzene methylation reaction over mordenite, even though the aromatic compound is expected to be more reactivity in case of the isopropylation reaction.

Apparent activation energies of 23.9 and 18.7 kJ/mol were obtained for benzene methylation and toluene methylation, respectively, over the catalyst based on ZSM-5 (Table 6). Similar to the observation noticed in the alkylation reaction over mordenite, the reactivity of the alkylbenzenes increased with increasing methyl group per benzene ring over the ZSM-5 based catalyst. Lower apparent activation energy was obtained for benzene ethylation (17.1 kJ/mol) [40] over ZSM-5 based catalyst, as compared with the activation energy reported for benzene methylation reaction (23.9 kJ/mol) in this present study. Although, the BrØnsted to Lewis acid ratio of the ZSM-5 based catalyst used in this present study is higher than the BrØnsted to Lewis acid ratio of the ZSM-5 catalyst used previously, the reaction temperature might have played its part in the difference in apparent activation energy. It is a well established fact that the intrinsic activation energy is a function of catalyst acidity; however, the ethylation reaction over ZSM-5 based catalyst previously reported was carried out at a much lower reaction temperatures (250–300 °C) as compared with the reaction temperatures used in this present study.

Comparing the minimum energy required in alkylating methanol with benzene over mordenite and ZSM-5, lower apparent activation energy is required in the case of ZSM-5, as compared with mordenite. The difference in apparent activation energies for benzene methylation over both catalysts can be attributed to the acidity of these catalysts. The validity of the estimated kinetics parameters were checked by substituting the fitted parameters into the comprehensive model developed for this scheme and the equations were solved numerically using the fourth-order-Runge-Kutta routine. Graphical comparisons between experimental and model predictions for reactant-converted model (RC) based on the optimized parameters for Scheme 3 is shown in Fig. 1.

5. Conclusions

Zeolite mordenite and ZSM-5 are active catalysts for the synthesis of toluene, xylene and ethylbenzene by alkylation of benzene with methanol and ethanol in the vapor phase. By studying the alkylation of benzene with alcohols of different chain length, it has been found that as the alkyl size (i.e. methyl, ethyl, and propyl) increases, the optimum temperature for alkylation reaction decreases. The high reaction temperatures strongly favor the yields of xylenes and toluene with mordenite in benzene methylation, while low yield of cumene was noticed over both catalysts in benzene isopropylation. In the ethylation reaction, the catalyst based on ZSM-5 showed higher ethylbenzene selectivity, while comparable diethylbenzene selectivity was noticed over both catalysts at constant conversion level. When benzene is to be alkylated, there is no competitive reaction apart from the alkylation reaction and the effect of these alcohols as an alkylating agent plays an important role. The reaction temperature and the BrǾnsted to Lewis acid ratio of the catalysts, play a significant role in the alkylation reactions. Activation of methanol over mordenite catalyst was easier at high reaction temperature, while the low temperature favors the activation of ethanol over both catalysts. Isopropanol presents higher difficulty to be activated as compared with other alcohols at the higher temperature. Therefore, for the purpose of implementing an alkylation process for benzene content reduction in gasoline, and considering the real feedstock, mordenite will be a suitable catalyst for this particular process, under the present experimental conditions. Kinetic parameters of the benzene methylation (E_1), toluene methylation (E_2) and xylene methylation (E_3) with methanol were calculated using the catalyst activity decay function based on reactant-converted (RC). The apparent activation energies were found to decrease as follows: $E_1 > E_2 > E_3$. Additional studies involving catalyst preparation are needed for optimizing the BrǾnsted and Lewis acid acid properties of these materials.

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