PORE-SIZE REGULATED
ZSM-5 ZEOLITE FOR THE SYNTHESIS
OF *PARA*-DIALKYLBENZENES

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الخلاصــة :

يمكن تصنيع (ثنائي الكيل البنزينات) بواسطة (الكلة أحادي الكيل البنزين) بأحد عوامل الألكلة كالأوليفين

أو الكحول وحفاز فريدل – كرافت أو حفاز الزيوليت. يتألف (ثنائي الكيل البنزينات) الناتج عن التفاعل من

أيٍّ هذه من الحفازات وهو مزيج متوازن ثرمودينامكيا من كلٍّ من ايزوميرات الاورثو، والميتا والبارا. ويعتبر

ايزومر البارا، مثلُ كلٍّ من : (بارا الكومن – بارا اثيل البنزين – بارا الكزيلين – بارا ثنائي ايثيل البنزين) وهو

مهمٌ صناعياً، حيث تُعدُّ هذه المركبات الكيميائية مصدراً لمونوميرات عديدة. لذلك فمن الضروري العمل على

زيادة تركيز هذا الايزومر في ناتج عملية الألكلة. وقد ورد في نشرات علمية عدة طرق تقنية لتعديل خصائص

الانتشار في الزيوليت، كان من أهمها تلك التي لفتت نظر الباحثين بشدة، والتي تقوم على تنظيم قطر

مسامات الزيوليت بواسطة ترسيب البخار الكيميائي لرباعي ايثيل أورتو سيليكات. حيث يؤدي تعديل الزيوليت

هذا إلى خلق حاجز على فوهات مسامات الزيوليت يقوم بزيادة مقاومة انتشار الجزئيات كبيرة الحجم بشدة.

تتناول هذه الورقة أحد تطبيقات الزيوليت ذا حجم المسام المنظم في زيادة تركيز ايزومير البارا الناتج عن

تفاعل الكلة ايثيل البنزين والتولوين مع الايثانول.

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ABSTRACT

The dialkylbenzenes can be synthesized by alkylating monoalkylbenzene with an alkylating agent such as an olefin or alcohol over a Friedel–Craft or zeolite catalyst. On all these catalysts, the dialkylbenzenes mixture produced consists of a thermodynamic equilibrium composition of *ortho-*, *meta-*, and *para-*isomers. Among the various dialkyl-benzenes, the *para-*isomers such as *p*-cymene, *p*-ethyltoluene, *p*-xylene, *p*-diethylbenzene are industrially important. These chemicals are sources for various monomers. Hence it is of significance to enhance the concentration of the *para-*isomer in the dialkylbenzenes mixture during alkylation of monoalkylbenzene. Several techniques have been reported in the literature to modify the diffusion characteristics of the zeolite. One of the techniques most drawing the attention of researchers is pore size regulation by chemical vapor deposition of tetraethyl orthosilicate. This modification of the zeolite creates a barrier at the entrance to the zeolite pores, which dramatically enhances the diffusional resistance to the passage of bulkier molecules. The applications of pore-size regulated zeolite for enhancing *para-*isomer concentration during ethylation of ethylbenzene and toluene are discussed in this paper.

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INTRODUCTION

Para-dialkylbenzenes, such as *p*-xylene, *p*-ethyltoluene, *p*-diethylbenzene, *p*-cymene, are industrially important due to their use in various commercial processes. Purified terephthalic acid (PTA), a raw material for polyester fiber, is produced by the oxidation of *p*-xylene. *p*-Ethyltoluene is the starting material for *p*-methylstyrene: the polymer of this monomer possesses certain advantages over the conventional polystyrene. The adsorbent used in the selective separation of *p*-xylene from an isomeric C_8 aromatics mixture is *para*-diethylbenzene. *p*-Cymene is used in the production of fungicides, pesticides, perfumes, and flavors.

One of the ways to synthesize dialkylbenzenes is to alkylate a monoalkylbenzene with an alkylating agent such as an olefin or alcohol over a Friedel–Craft or zeolite catalyst. The latter is gaining importance as it is an environmentally benign system. On a ZSM-5 zeolite of normal crystal size or the Friedel–Craft catalyst, the dialkylbenzenes synthesized contain a nearly thermodynamic equilibrium mixture of *ortho*-, *para*-, and *meta*-isomers. An expensive separation process coupled with an isomerization process is needed to recover the desired *para*-isomer, which is not feasible economically. However, a higher *para*-isomer composition beyond thermodynamic equilibrium can be obtained by incorporating compounds like P_2O_5, MgO, or B_2O_3, by adsorbing a bulky organic base on the external surface sites, by coking or by increasing the crystallite size, or silica deposition [1–3]. Among the various techniques employed for enhancing the shape selectivity, chemical vapor deposition of silica has several distinct advantages over the other techniques. This technique involves blocking of non-selective external surface sites and fine-tuning the pore opening without altering the internal structure. The present paper discusses the details of chemical vapor deposition of tetraethyl orthosilicate on ZSM-5 zeolite and the application of the pore-size regulated zeolite for the synthesis of *para*-dialkylbenzenes. The alkylation reactions studied are ethylation of ethylbenzene and ethylation of toluene.

PORE SIZE REGULATION OF ZSM-5

ZSM-5 zeolites used in this study were synthesized by following a patented procedure [4, 5]. Two different silica sources *viz.* sodium silicate, Ludox and two different templating agents *viz.* tetrapropyl ammonium bromide and triethyl *n*-butyl ammonium bromide were used in zeolite synthesis. The gel composition and synthesis conditions are presented in Table 1. The zeolite samples were characterized for structural, morphological, and acidity features by physico-chemical techniques such as XRD, SEM, MASNMR, and TPD of ammonia (Table 2). The Si/Al ratio was determined by atomic absorption spectrophotometry. The as-synthesized zeolites were calcined at 813 K for 8 h to burn off the organic template and ion-exchanged with 1M ammonium nitrate four times. They were further converted to proton form by calcining at 813 K in the presence of air for 6 h. A tubular, fixed bed, down flow integral glass reactor was used for pore size regulation and alkylation reactions at atmospheric pressure.

The chemical vapor deposition of bulky silicone compound, tetraethyl orthosilicate was carried out in-situ to regulate the pore size of the zeolite as per the procedure reported earlier [6]. A 6.5% tetraethyl orthosilicate solution in 50:50 toluene and methanol was vaporized at 503 K and passed through the zeolite bed maintained at 503 K. The silica precursor solution was fed at a rate of 8 ml/h, and a flow of 50 ml/min nitrogen was maintained so that there was uniform contact of the vapor with the catalyst. After the vapor was in contact with the zeolite for the required period, the nitrogen flow was changed to air and the reactor temperature was raised to 815 K. This temperature was maintained for 10 h to decompose tetraethyl orthosilicate to SiO_2.

The molecular size of tetraethyl orthosiliacte is larger than the zeolite opening, so the chemical vapor deposition results in fine control of pore opening size, with the silica deposited on the external surface. The initial deposition reaction involves hydroxyl groups located on the external surface and pore mouth entrance of the zeolite, and subsequent reaction between gaseous alkoxide and surface residue or between deposited molecules. This process can be considered as a sort of polymerization accompanied by hydrolysis. During this process, the internal structure remains unaffected; only the pore entrance is narrowed [7].

According to Hibino *et al.*, silica deposits on the external surface as a thin layer, and simultaneously the silica layer deactivates the acid sites located there [8]. The deposited silica layer consists of siloxane bonds, whereas the zeolite is comprised of siloxane and Si–O–Al bonds. This results in a variation in bond lengths or angles between the silica layer and zeolite framework. The siloxane bond of the silica layer protrudes into the pore, causing a reduction in pore opening size. Murakami has discussed the thickness of deposited silica on the zeolite. XPS measurement of silica deposited zeolite has indicated an enrichment of silica on the external surface [9].

The change in reduction of pore opening size after chemical vapor deposition was monitored by a test reaction [10]. A mixture of two reactant probe molecules of different kinetic diameter was employed. The reaction mixture contained 80% *meta*-xylene and 20% ethylbenzene. Essentially two reactions take place on ZSM-5 zeolite: (*i*) *meta*-xylene isomerization to *para*- and *ortho*-isomers; and (*ii*) ethylbenzene dealkylation to benzene and ethylene. After the pore size regulation, there was almost no conversion of *meta*-xylene, whereas ethylbenzene conversion was still at an appreciable level (Figure 1). This can be ascribed to the smaller kinetic diameter of ethylbenzene compared to *meta*-xylene and the

Table 1. Gel Composition and Zeolite Synthesis Conditions.

Zeolite batch	Molar Composition of the Gel	Temperature (K)	Period of Crystallization (day)
A1	$[(TEBA)_2O]_{7.9} - (Na_2O)_{43.8} - (Al_2O_3)_{1.0} - (SiO_2)_{135} - (H_2O)_{7239}$	418	4
A2	$[(TPA)_2O]_{7.9} - (Na_2O)_{43.7} - (Rb_2O)_{0.66} - (Al_2O_3)_{1.0} - (SiO_2)_{135} - (H_2O)_{7237}$	413	3
A3	$[(TPA)_2O]_{11.5} - (Na_2O)_{17.4} - (Rb_2O)_{1.9} - (Al_2O_3)_{1.0} - (SiO_2)_{135} - (H_2O)_{7903}$	433	8
A4	$[(TPA)_2O]_{11.5} - (Na_2O)_{19.3} - (Al_2O_3)_{1.0} - (SiO_2)_{135} - (H_2O)_{7903}$	443	10
A5	$[(TPA)_2O]_{11.5} - (K_2O)_{12.4} - (Rb_2O)_{1.9} - (Al_2O_3)_{1.0} - (SiO_2)_{135} - (H_2O)_{7903}$	443	12

pH of the gel was adjusted to 10.5 using dilute sulfuric acid for all the batches.
Batch A1 was stirred during crystallization.
TPABr = Tetrapropyl ammonium bromide, TEBA = Triethyl *n*-butyl ammonium bromide.

Table 2. Characterization Data of the Zeolite Batches.

Zeolite batch	XRD phase	SEM crystal size		Si/Al	Acidity Mmol eq. Ammonia/g
		Length (μm)	Breadth(μm)		
A1	MFI	5.7	2.8	78	0.42
A2	MFI	15.9	----	75	0.42
A3	MFI	23.9	10.6	80	0.40
A4	MFI	27.1	15.9	73	0.41
A5	MFI	37.9	16.2	76	0.43

latter value is very close to the pore opening size of unmodified ZSM-5 zeolite. The chemical vapor deposition resulted in reduction of the pore opening dimension of zeolite; it was smaller than *meta*-xylene but still comparable to ethylbenzene, which is why *meta*-xylene could not diffuse inside the zeolite and react.

ETHYLBENZENE ETHYLATION

Figure 2 depicts the effect of pore size regulation by silica deposition on the *para*-diethylbenzene selectivity under the reaction conditions of temperature 623 K, mole ratio EB:Ethanol 5:1 and WHSV 3/h. It is obvious from this figure that *para*-diethylbenzene selectivity, which is defined as the fraction of *para*-isomer among the diethylbenzenes formed, as high as almost 100% can be attained by depositing the appropriate amount of silica on the zeolite.

During ethylation, it can be seen from the chemistry of alkylation that the carefully controlled diffusivity of the zeolite by chemical vapor deposition allows ethylbenzene and ethyl alcohol free access to the interior of the channels. The usual alkylation, isomerization, dealkylation, realkylation take place inside the pores of ZSM-5 zeolite. An equilibrium mixture of diethylbenzene isomers is formed in accordance with the laws of thermodynamics. Benzene is formed due to the dealkylation of ethylbenzene. It is the shape selectivity constraints imposed on diffusion of the products from within the pores to the outside, that brings about enhanced *para* selectivity. The smaller *para*-diethylbenzene, benzene, and ethylbenzene (unreacted) exit from the pores many times faster than *ortho*- and *meta*-diethylbenzene. Decrease in the *para* isomer concentration inside the channels causes the diethylbenzene mixture within the pore system to re-equilibrate
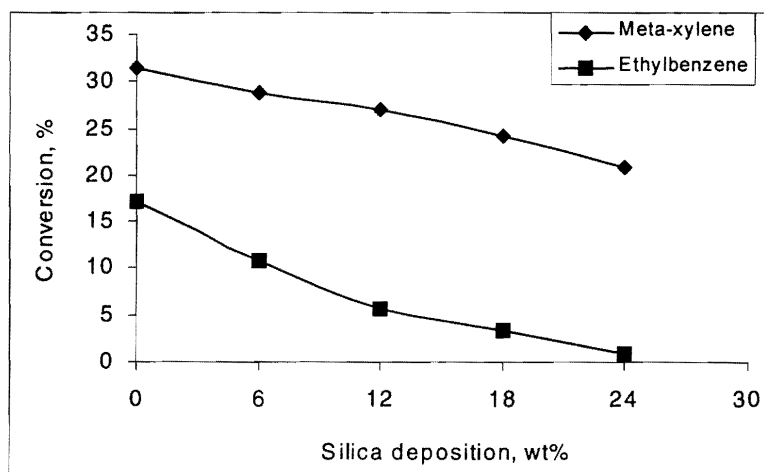

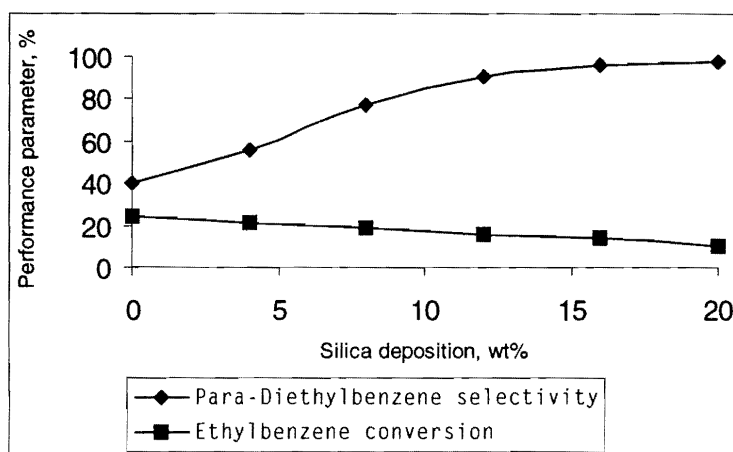*Figure 1. Standard activity test using probe molecules ethylbenzene and* meta-xylene.

Figure 2. The effect of silica deposition on ethylbenzene conversion and para-diethylbenzene *selectivity.*

forming more and more *para*-diethylbenzene. The overall effect of this is a very high *para* selectivity in the product stream.

It has been observed during monoalkylbenzene alkylation, only a fraction of the alcohol participated in the alkylation. In this context it was reported that the best results of alcohol utilization for alkylation can be obtained by using a mole ratio of monoalkylbenzene to alcohol in the range 4–6.

Figure 3 summarizes the effect of temperature on the performance of pore-size regulated zeolite during ethylation of ethylbenzene. The conversion of ethylbenzene increased from 9.5% to 20% by raising the temperature from 573 K to 673 K. The higher ethylbenzene conversion was accompanied by higher selectivity to benzene and lower selectivity to diethylbenzenes. In other words the dealkylation reactions are favored at elevated temperature and alkylation prevails at lower temperature. But there is no major effect of temperature on the proportion of *para* isomer in the diethylbenzene mixture, which remained higher at all the temperatures.

TOLUENE ETHYLATION

Toluene ethylation over five zeolite batches having nearly the same Si/Al ratio but different crystallite sizes is summarized in Table 3. On batches A1 and A2 containing smaller crystals of zeolite, formation of all three isomers of
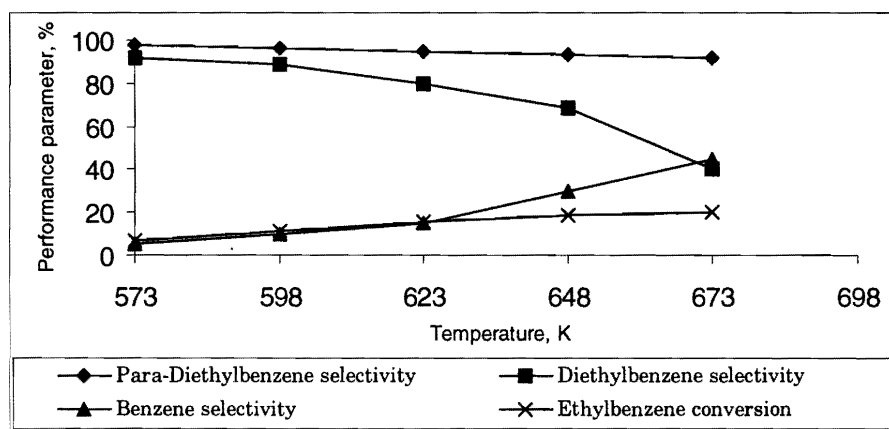

Figure 3. Influence of temperature on ethylbenzene ethylation activity of pore size regulated zeolite.

Table 3. Toluene Alkylation Over Unmodified Zeolites.

Performance Parameter	Batch A1	A2	A3	A4	A5
Toluene conversion	19.94	19.17	16.3	18.07	17.48
Ethanol conversion	100	100	100	100	100
Ethyltoluene, wt%	15.22	15.67	12.81	15.04	14.88
Ethyltoluene distribution:					
Ortho-	7.82	7.21	0.00	0.00	0.00
Para-	31.80	31.91	68.77	69.28	81.32
Meta-	60.38	60.88	31.23	30.72	18.68

Temperature = 598K, mole ratio Toluene/Ethanol = 6, WHSV = 2.5/h

ethyltoluene is favored, while the *ortho*-isomer is completely excluded on batches containing larger zeolite particles (A3–A5). During alkylation of toluene, the methyl group on the benzene ring activates *ortho* and *para* positions for alkylation. Due to space restrictions inside the zeolite channel, alkylation preferably takes place at the *para* position, while *ortho* alkylation can take place on the sites located at the external surface. Even that possibility is reduced due to steric factors as the alkyl group already present may hinder the movement of another alkyl group around the *ortho* position. Hence the *para* isomer is the primary product of alkylation. The formation of *ortho* isomer with ZSM-5 batches containing smaller crystallites may be attributed to the presence of more external surface sites than with the batches containing larger crystallites. There was a clear relationship between crystallite size and *para* selectivity exhibited by the zeolite of different batches. With an increase in crystallite length from 5.7 to 37.9 µm, the *para* selectivity enhanced from 32 to 81%.

Table 4 presents results of toluene alkylation over pore size regulated zeolite of five different batches. Except for zeolite of batch A3, there is a clear relationship between size, morphology of the zeolite, and the extent of silica deposition required to achieve a desired high *para* selectivity. It was interesting to analyze why zeolite of batch A3 could not fit into the crystallite morphology and catalytic activity relationship, even though the catalytic activity before pore size regulation correctly fit into the relationship. The zeolite of batches A1 and A2, having crystallites of smaller size and spheroidal morphology, required a higher extent of silica deposition than the zeolite of batches A4 and A5 to achieve a selectivity of 98%. This can be explained on the basis of the fact that in cases of A1 and A2 the specific external surface area is more due to the geometry of the crystal, hence there is more area to be covered by silica. But the geometry of the crystal clearly indicates a lesser specific external surface area in case of A3, therefore it should have required a lesser extent of silica deposition to achieve the same desired high *para* selectivity. The SEM micrographs at higher magnification showed that A3 contained longer crystals, surfaces which are not as clean as those of A1, A2, A4, and A5. Amorphous silica is present on the crystal surfaces making them rough. These particles prevented the accessibility of tetraethyl orthosilicate to the sites on the external surface. Hence, even with higher extent of silica deposition, the zeolite was not covered by silica enough to enhance *para* selectivity.

Table 4. Toluene Alkylation Over Pore Size Regulated Zeolites.

Performance parameter	Batch A1	A2	A3	A4	A5
Toluene conversion	13.25	12.80	11.15	13.57	13.28
Ethanol conversion	100	100	100	100	100
Ethyltoluene, wt%	9.03	8.55	8.99	11.42	11.22
Ethyltoluene distribution:					
Ortho-	0.00	0.00	0.00	0.00	0.00
Para-	98.89	99.18	86.76	99.65	99.73
Meta-	1.11	0.82	13.24	0.35	0.27
Silica deposition, wt%	15.12	0	21.46	2.97	2.5

Temperature = 598K, mole ratio Toluene/Ethanol = 6, WHSV = 2.5/h

CONCLUSIONS

It is possible to enhance the proportion of *para* isomer in dialkylbenzene mixture to as high as nearly 100% by pore size regulation of ZSM-5 zeolite. The required extent of pore size control can be achieved by depositing the appropriate quantity of tetraethyl orthosilicate. The extent of modification required to deactivate the external surface sites and regulate the pore size for the zeolite batches having smaller crystallite sizes was higher, while it was lower for zeolite batches containing twinned elongated prismatic crystals. Any covering of these crystals by foreign elements enhances the extent of inactivation needed to achieve a desired high *para* selectivity.

ACKNOWLEDGEMENT

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