Zeolite catalyzed alkylation of toluene by alcohol

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ABSTRACT

Vapor-phase methylation of toluene using methanol and its isopropylation with 2-propanol has been investigated in a down flow reactor under atmospheric conditions using N_2 carrier over a series of surface modified and unmodified ZSM-5 (Si/Al = 60–170) loaded with H_3PO_4, differing in the external surface treatment of the zeolites. The feed molar ratios of toluene/methanol and toluene/2-propanol were varied over a wide range (8–0.125), and the optimum feed ratio of toluene/alcohol was less than 0.5 in both cases. Space velocity employed in toluene methylation reported as WHSV (toluene) = 1.2h^{-1}, and the space velocity employed in toluene isopropylation reported as WHSV (toluene) = 0.8 h^{-1}. The methylation reactions were carried out in the temperature range of 623–773 K, and the isopropylation reactions were carried out in the temperature range of 483–583 K. Atmospheric pressures was maintained in all runs. Catalysts containing 0–4.9 wt.% P were prepared using modified and unmodified ZSM-5 zeolites, and their catalytic performance for vapor-phase alkylation of toluene with methanol and 2-propanol were investigated. The optimum phosphorous content for methylation was 2.1 wt.% P which was greater than the optimum phosphorous loading for isopropylation (0.7 wt.% P).

Keywords: Toluene alkylation; 2-Propanol; H3PO4; Modified ZSM-5; Cymene; Xylene; Catalyst

INTRODUCTION

Over the last decades of the 20th century, the shape-selective formation of substituted aromatic molecules over medium-pore zeolites was intensely studied by industrial as well as academic institutions [1–5]. The industrial interest was mainly focused upon ZSM-5 as catalyst, because of its unique properties for production of p-dialkylbenzenes in selectivities exceeding the thermodynamic values by far. The discovery of zeolites possessing acid sites of strong and medium strength, bound to the zeolite framework inside the pores and not aggressive to the environment, opened a new era of technologies in alkylation of aromatics, and reactions of alkyl aromatics in general. An objective of the work reported here, was to open a new era of shape selectivity by modifying the ZSM-5 zeolite with

surfactant, what we was expecting to demonstrate in this article. Alkylation of toluene with methanol to obtain p-xylene has been tested over various kinds of catalysts [6–8], and similar to the toluene disproportionation, the composition of xylene isomers in this reaction strongly depends on the inner volume of the zeolite. The alkylation of toluene with methanol was initially investigated over various cationic forms of zeolite Y [9,10] and later mainly medium-pore zeolites of ZSM-5 structure with silicon isomorphously substituted by trivalent cations like Al, Fe and B were used [11]. In general, alkylation of toluene with methanol, and toluene disproportionation to benzene and xylene are carried out over acidic

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zeolites [12–14]. The role of the acid–base properties of zeolite catalysts on the product distribution of aromatic alkylation reactions has been reviewed by Giordano et al. [15]. The acidity and structure of different zeolites varies greatly, so the selection of zeolites is the first step in finding suitable catalysts for methylation of toluene. The modification of acidity and structure of ZSM-5 as a common shape-selective zeolite has widely been investigated to reduce by-products and improve the selectivity of methylation of toluene to p-xylene [16–18]. Regarding the modification of zeolites, the work by Kaeding et al. [6,19] is worth mentioning. They observed an enhanced para-selectivity for the alkylation of toluene with methanol on phosphorus-modified H-ZSM-5 zeolites and suggested that the phosphorus reagent interacted with the acid sites of the zeolite and attached to the zeolite via framework oxygen atoms. This partially blocked the pore openings and, therefore, restricted the diffusion of meta and ortho-xylenes. The ring methylation with methanol over acid catalysts would proceed via the formation of methoxonium ion, which requires Brønsted acid sites [6, 20]. The surface concentration of methoxonium ion, and, therefore, the catalytic activity for ring alkylation would depend on the density and strength of the Brønsted acid sites. Molecular modeling studies [21] on the methanol interaction with zeolites have shown that physically adsorbed methanol is the most stable binding geometry while a methoxonium cation represents a transition state and not a local minimum. It has also been suggested that zeolite methoxy groups can form another adsorption complex with toluene [22]. This type of complex can be formed according to the Rideal-Eley mechanism where a toluene molecule, interacting with a methoxonium or methoxy group, is kept in the zeolite channel system by its strong electrostatic field. The formation of methoxoniumor methoxy groups bound to the zeolite framework depends strongly on the reaction conditions and the acid strength of the individual zeolite used. Although the nature of the alkylating species is not clear, but in this respect some researchers believe that methoxy species alkylate toluene [22–25], while the others favor methoxonium species [4, 22 and 26] and some authors reported dimethyether as the alkylating agent [27, 28]. As a mechanistic point

of view and because of the high selectivity that has been reached using the new modified ZSM-5 introduced in this article, it is necessary to mention the hypothesis of the "restricted transition state selectivity" represented by Yashima et al. [29]. They have suggested that high yields of p-xylene are obtained in the first alkylation step due to restricted transition state selectivity and the high para-selectivity can be achieved by preventing the isomerization of primarily formed p-xylene [30]. Also Mikkelsen et al. [31] by studying the alkylation of toluene with methanol using isotopic labeling have supported a "pool" mechanism in agreement with the Yashima hypothesis. As will be shown later, by modification of ZSM-5 with surfactant and then loading it with H_3PO_4, we have been able to bring about a new type of shape-selectivity in the ZSM-5 zeolite. The mechanism based on the difference in diffusion rates of xylene isomers was supported by the kinetics model proposed by Wei [32], and later more precisely explained by Hashimoto et al. and Masuda et al. [33]. Although this model is highly accepted by the people in this field, another explanation prevails and is frequently made [34,35]. It is the mechanistic interpretation based on the nonselective reaction on the external surface; i.e., para-xylene is isomerizes on the external surface into two other isomers, and if it occurs, it results in the low selectivity. It should be pointed out that one has to take notice of the nonselective reaction on the outer surface. However, it is difficult, in different samples of zeolite, to identify the deterioration of selectivity by the external surface acid sites because the external surface area can be correlated to the crystal size of the zeolite and, thus, to the diffusion property of zeolite. Alkylation of toluene with isopropyl alcohol to produce cymenes is also an industrially important reaction. Cymenes, specially the para and the meta isomers, are important starting materials for the production of a range of intermediates and products, such as cresols, fragrances, pharmaceuticals, herbicides, heat transfer media, etc. [36–38]. Some commercial units are operating with an installed capacity of around 40 kilo tonnes per year. The alkylation produces a mixture of cymene isomers (i.e. o-, m- and p-). The most preferred isomer distribution requires low ortho-cymene content, since orthocymene is difficult to oxidize and

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inhibits the oxidation of the other isomers. The highest para-selectivity in the synthesis of isopropyltoluene can be achieved with zeolites of MFI structures, the channel diameter of which is close to the kinetic diameters of aromatic molecules. Wichterlova et al. [11, 39] have studied alkylation of toluene with isopropanol in relation to time-on-steam with the large pore zeolites Y, beta, mordenite and ZSM-12 and medium pore MFI silicates with aluminum, iron in the framework. They have found that the conversion of toluene does not correlate with the number and strength of bridging OH groups, as it does for alkylation reactions leading to xylenes and ethyltoluenes. Moreover, on the basis of the TOS behavior of the conversion as well as the product composition, they have also concluded that the reaction rate is controlled by the desorption/transport rate of the bulky propyltoluenes being affected by the acidity and channel geometry of the zeolite. Based on the selectivity observed in the Fries rearrangement of phenylacetate which conducted on the externally modified H_3PO_4/ZSM-5 in compare with the unmodified H_3PO_4/ZSM-5[40], we decided to test this selectivity on other reactions. Therefore, the aim of this work is to demonstrate our idea for modification of ZSM-5 zeolite, and to carry out two typical catalytic reactions, toluene methylation with methanol and isopropylation with 2-propanol. The data has presented in this work are in good agreement with the effectiveness of our method for the generation of a very good shape-selective active sites on the ZSM-5 zeolites.

EXPERIMENTAL

Preparation of H_3PO_4/ZSM-5 zeolite modified by N-cetylpyridinium bromide

The ZSM-5 zeolite samples with Si/Al ratios of 60-170 were synthesized using tetrapropylammonium bromide (TPABr) as a template. The structure and surface characteristics of all synthetic ZSM-5 zeolites were determined using X-ray diffraction spectroscopy and scanning electron microscopy [41]. N-cetylpyridinium bromide (>0.98 mass fraction), a cationic surfactant from Merck with a concentration of 20 mmol dm^{-3} (higher than critical micelle concentration; >cmc), was used for modifying the external surface of the zeolites. Due to the relatively low solubility of CPB in water, a water–ethanol mixture of 8:2 (w/w) was used as solvent. For the modification of the external surface of the zeolites, in other words, for increasing the lipophilicity of the external surface of zeolites, we used the procedure mentioned in our previous study [40]. Briefly each batch of zeolite (1.0 g) was added to a vial (150 ml) and 100 ml of CPB solution (20 mmol dm^{-3}; higher than cmc) was poured into the vial. Then, the sample was placed on a shaker at room temperature for 48 h. The mixture was then centrifuged and the extracted solution analyzed for the CPB concentration, using a JASCOV-570 UV/vis/NIR spectrophotometer at λ_{max} = 259 nm. The amount of the surfactant adsorbed on the zeolite surface was determined by difference of initial concentration versus the concentration of surfactant in the filtrate solution [42]. The solid phase was washed with 150 ml of deionized water to remove unbound surfactant from the surface of the zeolite. The samples were dried at 383 K for 12 h. A series of catalysts with varying H_3PO_4 content were prepared by impregnating with calculated amounts of H_3PO_4 dissolved in deionized water on the surfactant modified ZSM-5 zeolites. The impregnated catalysts dried at 383 K for 12 h and then calcined in air at 873 K for 4 h. All the impregnated catalysts pressed into wafers, crushed and sieved to 20–40 mesh before use. These catalysts renamed hereafter as H_3PO_4/ZSM-5-surf followed by the ratio of Si/Al in the zeolite, e.g., H_3PO_4/ZSM-5-surf-170.

Preparation of unmodified H_3PO_4/ZSM-5 zeolite

A series of ZSM-5 zeolites (not treated with surfactant) with varying H_3PO_4 content were prepared by impregnating calculated amounts of H_3PO_4 dissolved in deionized water on unmodified ZSM-5 zeolites. The impregnated catalysts dried at 383 K for 12 h and then calcined in air at 873 K for 4 h. All the impregnated catalysts pressed into wafers, crushed and sieved to 20–40 mesh before use.

Toluene alkylation procedure and apparatus

Preliminary tests performed with modified H_3PO_4/ZSM-5-surf-170 (Si/Al = 170) allowed the identification of the best reaction conditions for methylation and isopropylation of toluene using

methanol and isopropanol as alkylation agents. The vapor-phase tests were carried out using approximately 500 mg of catalyst (20–40 mesh) in a flow Pyrex reactor (i.d. 8 mm), inserted in an electric oven controlled by a thermocouple and operating at atmospheric pressure. The feed (toluene/methanol in the methylation reaction, and toluene/2-propanol in the isopropylation reaction) was introduced by an infusion pump, GENIE, Kent Scientific Corporation, and nitrogen as the carrier gas, regulated by a mass-flow meter. The catalyst was previously activated in situ for 1 h at 573 K under a 25 ml min^{-1} of N$_2$ flow. In each experiment, the products were collected for 1.5 h by condensing them in a trap containing saltice (258 K), and analyzed off-line using a Shimadzu gas chromatograph, equipped with a wide bone OV-17 (60 m) capillary column and a FID detector.

Characterization techniques

Powder X-ray diffraction patterns were recorded on a Phillips diffractometer with Cu Ka radiation (40 kV, 30 mA) over a 2u range from 5 to 458. The equipment was connected to a DACO-MP microprocessor using a Diffract-AT software. Single point BET surface area was measured on a Micromeritics Digisorb 2600 system at liquid N$_2$ temperature using N$_2$ as adsorbate. Fourier transformed infrared spectra of the samples were recorded on a Perkin-Elmer, Paragon 1000 PC, FT-IR Spectrometer, in the range between 4000 and 400 cm^{-1}. In this regard, approximately 25 mg of the zeolite sample, plus 1 g of KBr was weighed out, milled and ground in an agate mortar and pestle for 5 min, until a fine smooth powder of even particle size was obtained. A quarter (0.25 g) of the catalyst and KBr mixture was then pressed with a steel die into a pellet (or wafer). Table 1 shows the surface area of Na-ZSM-5 and H$_3$PO$_4$ loaded samples before the catalytic tests. The other characterization data are presented in our previous study [40].

RESULTS

Toluene alkylation with methanol

Alkylation of toluene with methanol produces primarily a mixture of xylenes the distribution of which in the product largely depends on the characteristics of the catalyst. Side reactions might also take place, beside alkylation, namely, disproportionation and/or transalkylation (Scheme I).

Table 1. Surface area of blank ZSM-5 and H$_3$PO$_4$ loaded samples before the catalytic tests

Catalyst	Surface area (m^2/g)		
	NaZSM5	H$_3$PO$_4$-ZSM5 (modified)	H$_3$PO$_4$-ZSM5 (unmodified)
ZSM5-60	321	267	119
ZSM5-80	344	272	267
ZSM5-120	386	311	298
ZSM5-170	432	377	366
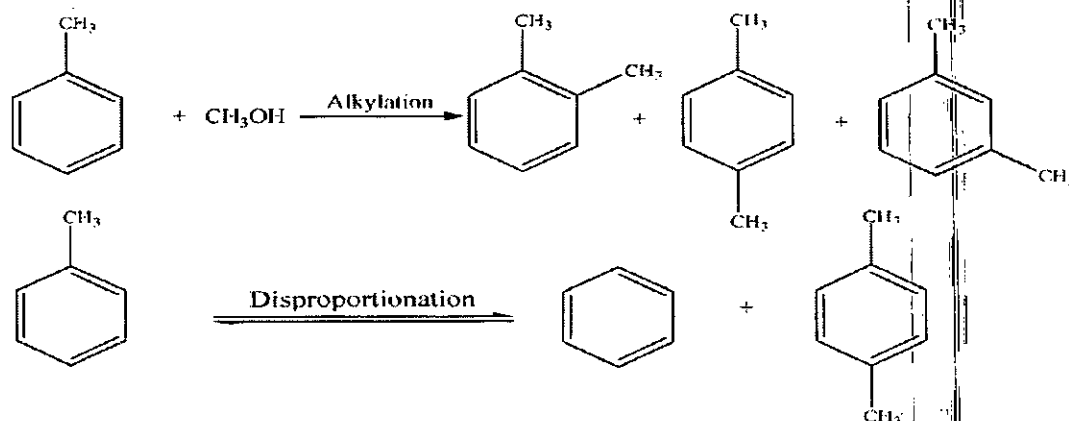
Scheme I

Effect of phosphorous content on the product distribution

The activity of the unloaded zeolite is lower than the activities of all H_3PO_4 loaded catalysts between 623 and 773 K. Hence, H_3PO_4 incorporation in the zeolite has a significant role for activating the catalysts during the methylation reaction. Table 2 show the changes in the total toluene conversion, and the yield of ortho, meta and para-xylenes on the unmodified catalysts as a function of phosphorous content. Data of this table shows that the unloaded zeolite is significantly less active for xylenes production. Interestingly no trimethylbenzenes (TMBs) were detected in our products. It should be mentioned that a small amounts of ethylbenzene was also detected.

Effect of reaction temperature on activity and selectivity of modified catalyst

Toluene methylation reaction was studied over 2.1 wt.% PZSM- -5 surf-170 in the temperature range of 623 773- K. The para-xylene selectivity using themodified zeolite catalyst loaded with 2.1 wt.%P reaches to about 100%at 698 K. This selectivity decreases with increasing temperature from 698 to 773 K .The results presented in Table 3, show the distribution of the reaction products for para, meta and ortho isomers. The maximum conversion of toluene was reached to 43%in 698 K. para-Xylene selectivity was over %90 in the all temperature range studied.

Time on stream and regeneration of the catalyst

Fig. 1 (left), shows the deactivation of the modified catalyst in a period of 8 h. In compare with the deactivation of the unmodified catalyst, it can be seen that more deactivation occurred on the modified catalyst. Fig. 2 (left). shows the deactivation of the unmodified catalyst. It can be seen from Figs. 1 and 2 that the 2.1 wt.% P/ZSM-5-surf-170 shows high selectivity toward para-xylene after 8 h time-on-stream (over 91% after 8 h), and also there is no significant decrease in paraxylene selectivity. It should be pointed out that the catalysts can be regenerated in a conventional manner to remove the coke deposits and restore its activity.

Table 2. Effect of the H_3PO_4 loading on the catalytic activity of the unmodified zeolite

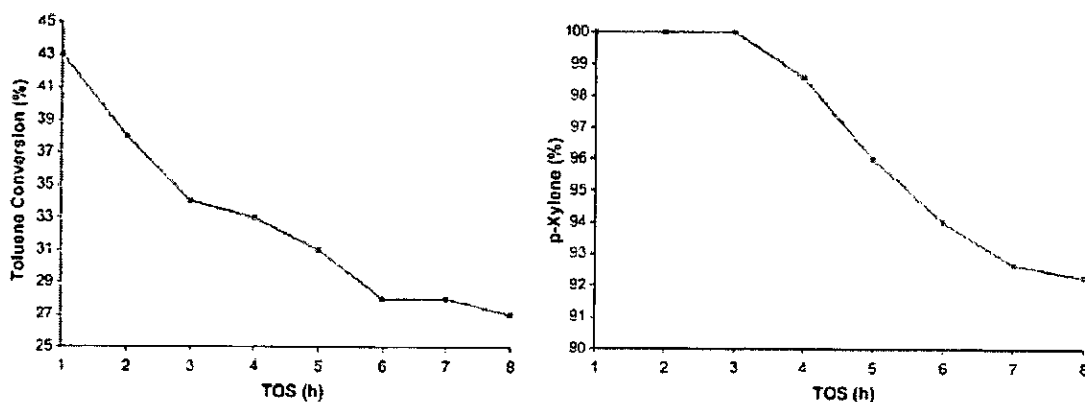| P(wt.%)	p-Xylene(%)	o-Xylene(%)	m-Xylene(%)	Ethylbenzene (%)	Benzene (%)	Toluene conversion (%)
0	46	27	18	<0.5	9	14
0.7	42	35	16	ND	7	21
2.1	30	48	21	<0.5	<0.5	46
3.5	32	49	18	ND	ND	40
4.9	37	39	18	ND	6	35

Fig. 1. TOS for H_3PO_4/ZSM-5-surf-170 (modified): T = 698 K, P content = 2.1 wt.%, WHSV = 1.2 h-1, flow rate = 25 ml min-1, toluene: methanol = 1:2.
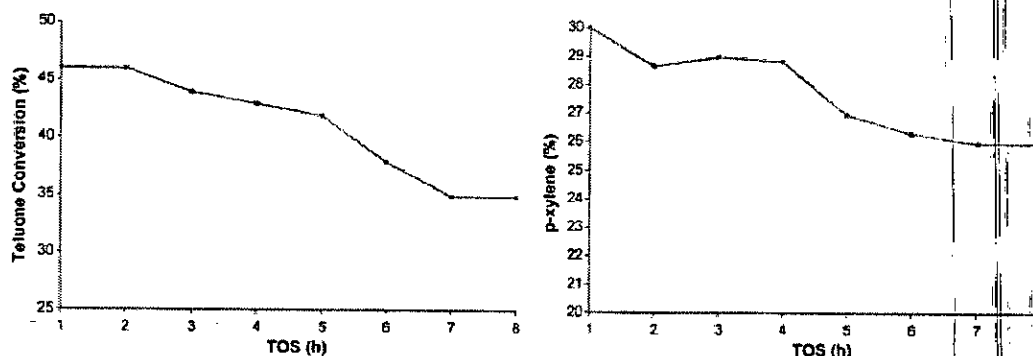
Fig. 2. TOS for H_3PO_4/ZSM-5-surf-170 (unmodified): T = 698 K, P content = 2.1 wt.%, WHSV = 1.2 h^{-1}, flow rate = 25 ml min^{-1}, toluene: methanol = 1:2.

Effect of toluene to methanol molar ratio on the catalytic activity

The effect of the amount of toluene on the methylation over modified 2.1 wt.% P-ZSM-5-surf-170 is presented in Fig. 3. The conversion of toluene increased with decreasing the amount of toluene in the feed, from toluene: methanol molar ratio of 8:1 to 1:2, and benzene (from disproportionation of toluene and/or toluene dealkylation) decreased from 7.8% to 0.0. When the toluene: methanol molar ratio of 1:2 was employed, the apparent conversion of toluene reached to its maximum value of 43%. This conversion might be marginal; however the conversion of toluene under an ample supply of methanol would decrease, because of the stronger tendencies of the surface of the catalyst for adsorption of methanol.
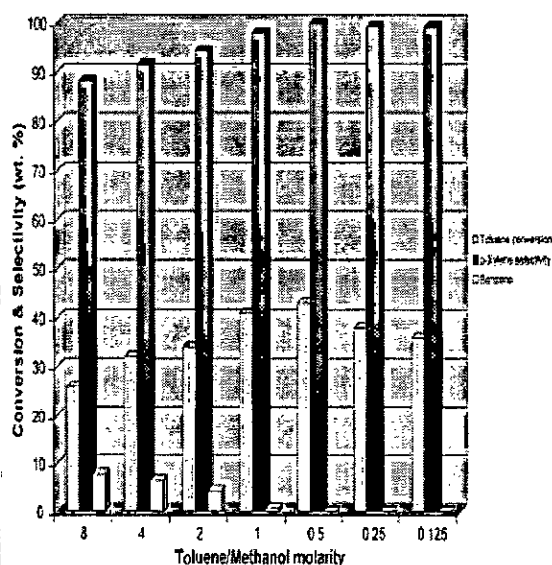

Fig. 3. Effect of toluene: methanol molar ratio on the catalytic activity of modified zeolites: Si/Al = 170, T = 698 K, P content = 2.1 wt.%, WHSV = 1.2 h^{-1}, flow rate = 25 ml min^{-1}.

Effect of the Si/Al ratio in the modified and unmodified catalysts on toluene conversion and p-xylene selectivity

A total of four ZSM-5 zeolites (Si/Al = 60, 80, 120, 170) are used, respectively, to support 2.1 wt.% P for the toluene methylation at 698 K. Tables 4 and 5 show the toluene conversion and xylenes selectivity's obtained for the unmodified and modified catalysts, respectively. For the unmodified catalyst, the toluene conversion and p-xylene selectivity increases by increasing the Si/Al ratio, as can be seen in the Table 4. Modified catalyst shows the same trend in toluene conversion but there is a big increase in p-xylene selectivity from 60.3% which reaches to maximum value of 100% in compare with unmodified catalyst. These results are in support of our previous study [40] and we decided to use the 2.1 wt.% P-ZSM-5-surf-170 for our detailed studies.

Isopropylation of toluene with 2-propanol

Cymene (methylisopropylbenzene) production is commercially carried out by alkylation of toluene with propene. The alkylation produces a mixture of cymene isomers (i.e. ortho, meta and para). The most preferred isomer distribution requires low ortho-cymene content, since ortho-cymene is difficult to oxidize and inhibits the oxidation of the other isomers. In the present study the alkylation of toluene with isopropanol (Scheme 2) to produce cymenes over ZSM-5 zeolite has been carried out on two series of H3PO4 loaded ZSM-5 zeolite catalysts, same as the catalysts which were prepared and used for toluene methylation and the results are presented in the following sections. Interestingly there is no formation of n-propyl and diisopropyl toluene in this case and p-cymene selectivity reaches up to 94% in the optimum conditions.

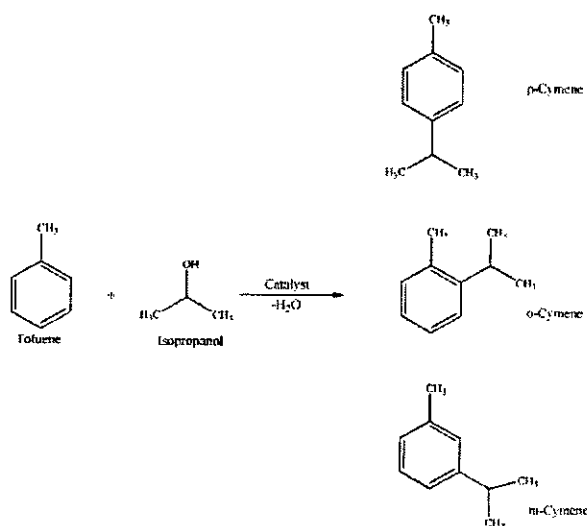**Table 3.** Effect of Si/Al ratio on the catalytic activity of unmodified zeolites

Si/Al	p-Xylene(%)	o- Xylene(%)	m- Xylene(%)	Ethylbenzene (%)	Benzene (%)	Toluene conversion (%)
60	21	59	18	ND	2	39
80	24	58	16	<0.5	1	40
120	27	52	19	<0.5	1	44
170	30	48	21	<0.5	1	46

Table 4. Effect of Si/Al ratio on the catalytic activity of modified zeolites

Si/Al	p-Xylene(%)	o- Xylene(%)	m- Xylene(%)	Ethylbenzene (%)	Benzene (%)	Toluene conversion (%)
60	60	23	16	<0.5	1	35
80	69	17	13	ND	ND	38
120	96	2	1	<0.5	ND	39
170	100	ND	ND	ND	ND	43

Table 5. Effect of the reaction temperature on the catalytic activity of the modified zeolite

Temperature/K	p-Xylene(%)	o- Xylene(%)	m- Xylene(%)	Ethylbenzene (%)	Benzene (%)	Toluene conversion (%)
483	82	3	13	1	1	48
508	87	4	6	1	2	62
533	94	1	2	1	2	75
558	91	1	1	2	4	59
583	90	1	1	3	5	52

Scheme 2. alkylation of toluene with isopropanol

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Effect of reaction temperature on toluene conversion and p-cymene selectivity

In order to achieve better toluene conversion and maximum p-cymene selectivity, we carried out toluene isopropylation in the temperature range of 483–583 K in steps of 25 K on the modified catalyst. The product distribution is presented in Table 6. All the reactions were carried out at optimized feed ratio toluene:2-propanol (1:4) and WHSV (0.8 h^{-1}). This clearly depicts that the toluene conversion increases up to 533 K. Maximum p-cymene selectivity reached to 94% in 533 K and it did not go up to 100% like toluene methylation reaction over this catalyst. m- and o-cymene selectivity decreased by increasing temperature and disproportionation and dealkylation products (benzene and xylene) were increased up to the total level of 8%. Toluene conversion reaches to its maximum level of 75% at 533 K over 0.7 wt.% P-ZSM-5-surf-170 catalyst.

DISCUSSION

Idea behind the ZSM-5 modification

Sorption of cationic surfactants from solution onto solid surfaces has undergone extensive study in the past [42,43]. Sorption on solids with high surface charge density includes some clay minerals, mica, and zeolites. Several mechanisms, including ion exchange, ion pairing, acid–base interaction, polarization of P electrons, dispersion force, and hydrophobic bonding, were attributed to the sorption of cationic surfactants onto solid surfaces. Among them, ion exchange and hydrophobic bonding were the important ones [44,45]. It is known that the dimensions of the open channels in ZSM-5 zeolite are large enough for a small exchangeable cation to enter and exit freely, but too small for N-cetylpyridinium bromide (CPB) head group. Thus the sorption of CPB on this zeolite is only limited to the external cation-exchange sites. It should be mentioned that the initial sorption encompassed sub-monolayer, full-monolayer, potential belayed and finally hemi micelles. Therefore by modifying the external surface of the zeolite with CPB, one could imagine at this stage that the surface of the zeolite has a dual character. The external surface with the exception of the pore entrances is hydrophobic and all of the internal surfaces are hydrophilic.

This is the question that we asked ourselves at this stage: what happen if we suspend the zeolite which has been modifies externally with CPB, in an aqueous solution containing H3PO4, and evaporating the mixture slowly presumably, in this solution we have different types of units with different lengths. The small units probably could penetrate into the pores and the long units has to deposit at the entrance of the pores and if we were lucky enough, these phosphate units do not land on the lipophilic sites loaded with the surfactant molecules. Therefore, if this happens, we should end up with a mass that has some phosphate units inside the pores of the zeolite and, if the phosphate units are being deposited around themouths of the pores, they might block the entrances or in the best case these phosphate units may have decorated the entrances with a new architecture. The new question in this stage would be: We think that by calcinating this zeolite at about 550–600 8C, it will loss the surfactant from its external surface and, one expects to get a ZSM-5 zeolite that on its external surface H_3PO_4 deposited on the mouths of the pores and the rest of the external surface probably contaminated with the coke residue of the surfactant without H_3PO_4 deposition. This zeolite has been called modified H_3PO_4/ZSM-5. Hence the ZSM-5, zeolite loaded with H_3PO_4 without any surface modification was called the unmodified H_3PO_4/ZSM-5. We has demonstrated this process schematically in Fig. 7. We did use FTIR spectroscopy and the experimental data of our previous article [40], and the data of this article to prove our idea, and in future we will try to gather more information in this respect. By treating the ZSM-5 zeolite with phosphoric acid several authors [46–50] proposed a model in which it is assumed that the bridged OH groups between Si and Al atoms are replaced by H_2PO_4 groups. The substitution of the Brønsted acidic hydroxyl groups by the H_2PO_4 groups implies to different consequences on the strength and density of the Brønsted acid sites: (1) strong Brønsted acid sites are converted into weak Brønsted acid sites, and it is clear that the resulting terminal hydroxyl groups have a lower acid strength than the bridged hydroxyl groups. It should be mentioned that the weak Brønsted acid sites are possibly AlOH groups on extra-lattice regenerated by deglutination during calcinations steps or SiOH groups of hydroxyl nests formed by

the same process. (2) The number of (weak) acid sites increased. (3) This substitution should not change the polar character of the surface. Interesting data were obtained by studying the FTIR spectra of the untreated ZSM-5-170, H_3PO_4/ZSM-5-surf-170 (2.1 wt.% P), and the unmodified H3PO4/ZSM-5-170 samples treated with different amounts of H3PO4 (0.7–3.5 wt.% P) which were measured with a diffuse reflectance type apparatus. We refer you to the IR measurements data presented in our previous article [40]. We have demonstrated that in the unmodified catalysts, H_3PO_4 becomes distributed on the outer surface as well as inside the pores, but in the case of the modified ZSM-5, H_3PO_4 distributed on the mouths of the pores with a new architecture, and probably inside the pores. It was summarized in our previous investigation [40] on Fries rearrangement that the external modification of ZSM-5 zeolite with surfactant and increasing the hydrophobicity of its outer surface has important effects on the shape selectivity of this industrially important zeolite. As we concluded in that work, in the unmodified catalysts, H_3PO_4 becomes distributed on outer surface as well as inside the pores, but in the case of modified H_3PO_4/ZSM-5 catalysts, only the mouths of the pores and the internal pores of the zeolite should function as host sites for H_3PO_4. Thus, we would expect to observe different acid sites distribution, and different pore mouth's diameter for the modified and unmodified zeolites. The IR data supported this hypothesis because by excluding the phosphoric acid from reaching to the hidden external Brønsted acid sites, we observed the corresponding absorption band (3610 cm^{-1}) in the modified samples in contrast with the unmodified samples. Hence, we should expect for the modified zeolites that there should be strong Brønsted acid sites on the external surface, but these modified zeolites have lost the strong Brønsted acid sites in the channels and at the entrance of the pores. Also, for the modified zeolites we expect to have more deposited aluminum phosphate because of dealumination, and more polymeric phosphate species in the channels. Therefore, we expect to observe lower conversion and higher selectivity (narrower pore size) for the modified ZSM-5 zeolites. In this regard, we carried out two typical alkylation reactions, toluene methylation and isopropylation,

perhaps to get a strong support for the effectiveness of our technique for the generation of a very good shape-selectivity on the ZSM-5 zeolites.

Toluene methylation

The toluene conversion on the H3PO4 loaded catalysts is found to follow the order of: 2.1 wt.% P-ZSM-5 > 3.5 wt.% PZSM-5 > 4.9 wt.% P-ZSM-5 > 0.7 wt.% P-ZSM-5 > ZSM-5.By accident the optimized phosphoric acid content is equal to that of our results in the Fries rearrangement [40]. Perhaps, by increasing the H_3PO_4 loading from 2.1 to 4.9 wt.% P, the activity of the catalyst decreased, because of the covering the most active sites by blocking the pore mouth with higher concentrations of phosphoric acid. As stated before, modification of the external surface of the ZSM-5 zeolite, should lead to lose of its internal strong Brønsted acid sites, but it keeps these acidic sites on the external surface of the catalyst. We think that the alkylation of toluene is catalyzed by the weak Brønsted acid sites and our judgment in this respect is that the modified ZSM-5 has the strong Brønsted acid sites on its external surface and if the alkylation occurs on the strong Brønsted acid sites, therefore one should not expect to observe any selectivity in the modified ZSM-5. However, why the alkylation of toluene with alcohol should not takes place on the strong Brønsted acid sites? Probably, the alcohol molecules cluster around the strong Brønsted acid sites through hydrogen bonding and there will be an inappropriate environment for toluene as a hydrophobic molecule. Therefore, one should not observe the occurrence of the alkylation reaction on the external surface of the modified ZSM-5. On the other hand, impregnation of phosphoric acid on the zeolite restricted the pore diameter (channel) and favors the formation of less voluminous components. The molecular diameter of p-xylene has been found to be 6.3 A° , whereas those of meta- and ortho-xylenes are 6.9 A°. Less voluminous reaction products will diffuse faster to the outside of the pore, so that pxylene diffuses 1000 times faster than o- and m-xylene, and thus p-xylene in the product might surpass the thermodynamic equilibrium values significantly [51]. Catalytic performance of modified and unmodified H_3PO_4/ ZSM-5 catalysts with time-on-stream is compared and the results are shown

in Figs. 1 and 2. It can be seen from Figs. 1 and 2 that the 2.1 wt.% P/ZSM-5-surf-170 shows high selectivity toward p-xylene even after 8 h time-on-stream (over 91% after 8 h). It indicates that modification of external surface of zeolite and loading with phosphoric acid restricted the pore a little more in compare with the zeolite loaded with the same level of phosphoric acid without external surface modification and favors the formation of less voluminous component, i.e., p-xylene. The narrower pore size of the modified zeolite causes poor diffusion of the reactant, results in higher retention of reactants inside the pores of the catalyst, which may result in faster deactivation of the catalyst. The results of variation in toluene/methanol molar ratio are shown in Fig. 3. The increase in xylene selectivity and the decrease in benzene selectivity with decreasing amount of toluene can be elucidated by the relative decrease in isproportionation reaction by abundance of toluene. The relative selectivity's for xylenes were not affected by lowering the molar ratio of toluene: methanol from 1:2 to 1:4 and 1:8. In the toluene methylation with methanol over acidic zeolite catalysts, methanol is strongly adsorbed in competitive adsorption with toluene [5]. The relative selectivities for xylenes were practically constant under kinetic control with an ortho, meta, and para-xylene selectivity of 2:1:1 [52,53]. On the whole, the selectivity profiles illustrated in Fig. 3 are reasonable. The conversion of toluene increased with increasing amount of methanol. However, the maximum conversion of toluene was not more than 43%, even when a 8-fold excess amount of methanol was employed, which also demonstrates that the adsorption of toluene was weaker than that of methanol. It is generally accepted that the alkylation of toluene with methanol proceeds via the formation of methoxonium ion, which requires Brønsted acid sites [6,20]. Thus, the surface concentration of methoxonium ion, and therefore the catalytic activity for ring alkylation would depend on the density and strength of the Brønsted acid sites. One of the remarkable features of the selectivities shown in Table 4 is that demethylation of toluene increased significantly with decreasing the amount of methanol. The results of toluene WHSV are summarized in Table 6. It was found that the conversion decreases from 49% to 36% over 2.1 wt.% P-ZSM-5-170, when the WHSV increased

from 0.5 to 2.32 h_1, the perceived low toluene conversion at higher space velocities could be accounted for in terms of the shorter contact time (faster diffusion) [54].

Toluene isopropylation

Although we optimized the P content of the catalyst for methylation of toluene and Fries rearrangement, because of the difference in molecular size of the reagents (primary alcohol reagent and secondary alcohol reagent) and their products, we decided to optimize the phosphorous content for cymene production too. The toluene conversion in isopropylation reaction on the H_3PO_4 loaded zeolite catalysts is found to follow the order of: 0.7 wt.% P-ZSM-5 > 2.1 wt.% P-ZSM-5 > 3.5 wt.% P-ZSM- 5 > 4.9 wt.% P-ZSM-5 >ZSM-5. This difference between optimum phosphorous content of the catalyst in the toluene methylation and the toluene isopropylation can be due to larger reagent size (2-propanol) in compare with less bulky toluene methylation reagents, which needs pores with wider diameters. As can be seen in Table 7, 0.7 wt.% P-ZSM-5-170 is the best catalyst for the toluene isopropylation while the best catalyst was 2.1 wt.% P ZSM-5-170 for the toluene methylation. Loading of catalyst with 0.7 wt.% of phosphorous resulted in less deposited phosphorous inside the channels and wider pore diameter for diffusion of cymenes. After this amount of P loading, the increase in phosphorous content up to 4.9 wt.% cause lower activity in the catalyst, because of covering the most active site and blocking the pore mouth with higher concentrations of phosphorous. One of the preferences of this new catalyst is that npropyltoluenes as an undesirable by-product do not produce. Wichterlova´ and C˘ ejka [39] clearly demonstrated that the reaction space, i.e., the zeolite inner volume plays a decisive role in the n-propyltoluenc formation. They have shown that the one-dimensional channel system of the mordenite structure restricts the formation of the n-propytoluenes, but because of the more convenient channel geometry of H-ZSM-5 the transalkylation process between p-cymene and toluene has a stronger tendency to produce n-propyltoluenes. Probably the reason that in the case of the modified H_3PO_4/ZSM-5-surf we do not get n-propyltoluenes, could be the deposition of some phosphoric acid in the channels of ZSM-5, so that, the channels have been tuned in a desire way. Also

we think the effect of acid site strength is important. As shown before [10], the Al-silicates in comparison with Fe-silicates produce more n-propyltoluenes that caused by the higher acidity of the Al-silicates compared to Fe-silicates. From the data presented in Table 6, it is clear that the reaction temperature has a significant effect on the toluene conversion. At the lowest temperature, 483 K, after 1.5 h of operation, the concentration of para isomer in the xylenes product was 82%, well above the equilibrium value. By increasing the temperature to 533 K, toluene conversion and para-selectivity had increased to 75% and 94%, respectively. Further increase in temperature leads to a fall in the toluene conversion over 0.7 wt.% P-ZSM-5-surf-170 catalyst. The decrease in toluene conversion at higher temperatures could be attributed to the coke deposition caused by the alcohol oligomerization or toluene dealkylation, which is favored at higher temperature, which in turn leads to the oligomerization of formed olefins. By optimizing the toluene/2-propanol molar ratio in this study (Fig. 4), we come to this conclusion that toluene has a weaker adsorption than 2-propanol on the catalyst. Among the isomers of cymene, p-cymene was found to predominate over all the other isomers and its selectivity was found to be 94% in this condition. With the decrease in the feed ratio from 8:1 to 1:4, the selectivity to p-cymene increases from 68% to 94% over 0.7 wt.% P-ZSM-5-surf-170. The lower selectivity to p-cymene in the feed ratio of 8:1 compared to 1:4 is due to the presence of more toluene content in the former, which leads to more chemisorption of toluene on the catalyst surface thereby suppressing the chemisorption of 2-propanol, which in turn facilitates the dealkylation rather than the isopropylation of toluene. Further increase in 2-propanol content in the feed leads to marginal decreases in p-cymene selectivity due to dilution. As mentioned above at the feed ratio of 8:1, toluene is more prone to chemisorption on the catalyst surface, but the intermittent chemisorption of 2-propanol would also be accomplished. This would aid the ortho position of aromatic ring, making it easily accessible for electrophilic substitution. Therefore, there is an enhanced selectivity to o-cymene at the feed ratio of 8:1 (24%.) The selectivity to m-cymene did not show any decreasing or increasing trend by varying the feed ratio. In contrast with the presumption [55] that the

isopropylation of cymene is faster than the isopropylation of toluene there was no diisopropyltoluene detected in our study. Of course, in this respect other factors such as the concentration of toluene and cymene and steric hindrances of the zeolite channel should be taken into account. The effect of Si/Al ratio of the unmodified and modified zeolites on the toluene conversion and p-cymene selectivity is shown in Tables 9 and 10, respectively. In modified zeolite disproportionation and dealkylation reactions took place slower with increasing the Si/Al ratios. We found out that the replacement of strong Brønsted acid sites in modified and unmodified ZSM-5 by H_3PO_4 resulted in decreased benzene and xylene by-products. The process of disproportionation and dealkylation has been obviously more inhibited because of the lower concentration of the Brønsted acid sites in the zeolite with higher Si/Al ratio. Also the amount of disproportionation and dealkylation products are more in compare with toluene methylation (2.1 wt.% P), because of the lower phosphoric acid concentration and probably higher residual strong Brønsted acid sites in the catalysts used in the toluene isopropylation (0.7 wt.% P).

CONCLUSION
We have demonstrated a unique process for modification of ZSM-5zeolite,which can enhance the selectivity of para-xylene, probably by deposition of phosphoric acid on the entrances of the pores and, inside of the pores of the zeolite. The 2.1 wt.% PZSM- 5-surf-170 and 0.7 wt.% P-ZSM-5-surf-170 are suitable catalysts for alkylation of toluene withmethanol and 2-propanol, respectively. The appropriate acidic sites, needed for catalyzing alkylation of toluene withmethanol and 2-propanol, are supplied by loading 2.1 and 0.7 wt.% P on ZSM-5 with optimum Si/Al ratio of 170. The large fraction of the loaded phosphoric acid led to narrowing of the pore openings of the zeolite, which probably suppressed the further penetration of oligomers of phosphoric acid into the pores of the zeolite. Based on the results obtained from the present study, we believe that the alkylation reactions over these new catalysts proceed mainly on the weak Brønsted acid sites within the pores of the zeolite. The external modification of catalyst with surfactant before

H_3PO_4 loading, led to passivation of the unselective Brønsted acid sites and to narrowing of the pores of the zeolite. Both effects resulted in enhanced shape selectivity of para-xylene in the toluene alkylation reaction. Therefore, this novel modification technique is a promising way to improve the selectivity of p-xylene and

pcymene of products in toluene methylation and isopropylation industrially important reactions.

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