

# Internal versus external surface active sites in ZSM-5 zeolite Part 2: Toluene alkylation with methanol and 2-propanol catalyzed by modified and unmodified H<sub>3</sub>PO<sub>4</sub>/ZSM-5

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## Abstract

Vapor-phase methylation of toluene with methanol and isopropylation of toluene with 2-propanol has been investigated in a down flow reactor under atmospheric conditions using N<sub>2</sub> gas carrier over a series of surface modified and unmodified ZSM-5 (Si/Al = 60–170) loaded with H<sub>3</sub>PO<sub>4</sub>, 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) = 1.2 h<sup>-1</sup>, and the space velocity employed in toluene isopropylation reported as WHSV (toluene) = 0.8 h<sup>-1</sup>. 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).

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## 1. 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 for 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 are 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 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 to get catalysts to be suitable 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]. In regard to the

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modification of zeolites, we should mention the work of Kaeding and his co-workers [6,19] that 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, which 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]. 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. 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 methoxonium or 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 [4,22,26] and some authors reported dimethylether as the alkylating agent [27,28].

As a mechanistic point of view and because of the high selectivity that has been reached by using the new modified ZSM-5 that is 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 the 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 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<sub>3</sub>PO<sub>4</sub>, 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 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 also.

Alkylation of toluene with isopropyl alcohol to produce cymenes is also an industrially important reaction. Cymenes, especially 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 *ortho*-cymene is difficult to oxidize and 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.

Wichterlová 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<sub>3</sub>PO<sub>4</sub>/ZSM-5 in compare with the unmodified H<sub>3</sub>PO<sub>4</sub>/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.

## 2. Experimental

### 2.1. Preparation of H<sub>3</sub>PO<sub>4</sub>/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<sup>-3</sup> (higher than critical micelle concentration; >cmc), was used for modifying the external surface of the

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