



Alkylation of toluene with ethanol to *para*-ethyltoluene over MFI zeolites: Comparative study and kinetic modeling



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ABSTRACT

The production of *para*-ethyltoluene (*p*-ET) from the alkylation of toluene with ethanol was investigated over three MFI zeolites with varying SiO₂/Al₂O₃ ratio (80, 280, and 2000). The ethylation reaction was conducted in a batch fluidized-bed reactor at a temperature range of 300–400 °C, reaction times of 5–20 s and molar feed ratio of toluene to ethanol at 1:1. Toluene conversion increased with temperature over all the MFI zeolites except for MFI-80, which showed a maximum conversion of 29% at 300 °C. The product distribution exhibited ethyltoluenes as major product with a maximum yield of 26% over MFI-80. At 400 °C, constant toluene conversion of 14% and 100% ethanol conversion, para-selectivity to *p*-ET was 100% over MFI-2000 compared with 27% and 48% over MFI-80 and MFI-280, respectively. The high para-selectivity over MFI-2000 is attributed to the combined effects of higher SiO₂/Al₂O₃ ratio, very weak acid sites and larger crystal size (longer diffusion length). The experimental data were analyzed for each MFI zeolite and suitable reaction mechanism for toluene ethylation was proposed based on the Langmuir–Hinshelwood model. The activation energy for the formation of *p*-ET over MFI-280 and MFI-2000 is 30 kJ/mol and 65 kJ/mol, while the heat of adsorption of ethanol is 19 kJ/mol and 29 kJ/mol, respectively.

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1. Introduction

The alkylation of toluene with ethanol produces ethyltoluenes which find applications in the petrochemical and chemical industries [1–5]. The ethylation of toluene with ethanol produces a wide range of hydrocarbon products which include C₁–C₄ gases (mostly obtained from dehydration and disproportionation reactions of ethanol and toluene, respectively), ethylbenzene, xylenes, and mixtures of ethyltoluene isomers [4–6]. In addition, other products such as styrene and methylstyrene could also be obtained as a result of side-chain alkylation, a condition favored by basic zeolites. The composition of the products may vary depending on the structural and morphological properties of the zeolites used [7–9].

Several researchers have investigated various parameters to enhance para-selectivity and catalyst activity. Parikh et al. studied the effects of crystal size and acidity on para-selectivity over A1-MFI

and B-, Fe-, Ga-isomorphously substituted zeolites of MFI structure with Si/metal ratios between 50 and 64 [10]. They reported that an increase in MFI crystal size results in a reduction in the active sites available on the external surface thereby inhibiting the isomerization of *p*-ET formed in the pores to other isomers. This is in conformity with the reaction mechanism proposed by Papparatto et al. using MFI (SiO₂/Al₂O₃ = 25, 58, 63) and MEL (SiO₂/Al₂O₃ = 40, 80). They concluded that *p*-ET is initially formed in the zeolite channels but undergoes isomerization if there are available acid sites on the external surface [8]. Wichterlova and Čejka [11] studied para-selectivity from the view point of the diffusion coefficient and coke deposition. It was observed that coke deposition did not influence para-selectivity, however, surface silylation with tetraethylorthosilicate (TEOS) could enhance *p*-ET due to pore narrowing.

Another important factor that could enhance para-selectivity is the external surface area. A correlation has been established between the crystal size and external surface area of MFI with SiO₂/Al₂O₃ ratios of 22 to 600 [11–14]. An increase in the crystal size translates to a reduction in the external surface which enhances the para-selectivity by impeding isomerization into meta and ortho isomers. Further improvement of para-selectivity over MFI can be

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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 the i th reaction (kJ/mol)
K_i	adsorption equilibrium constant of component i
k_i	apparent rate constant for the i th reaction (m ³ /kg of catalyst.s)
k_{oi}	pre-exponential factor for i th reaction after re-parameterization (m ³ /kg of catalyst.s)
MW_i	molecular weight of specie i
R	universal gas constant (kJ/kmol K)
t	reaction time (s)
T	reaction temperature (K)
T_o	average temperature of the experiment (K)
V	volume of the riser (45 cm ³)
W_c	mass of the catalyst (0.81 g)
W_{hc}	total mass of the hydrocarbon injected the riser (0.162 g)
$\Delta S_{ads,i}^0$	entropy for adsorption for component i
$\Delta H_{ads,i}^0$	enthalpy for adsorption for component i
Greek letters	
φ	apparent deactivation function
α	catalyst deactivation constant (time on stream model)

achieved by impregnation of the zeolite channels with metal or non-metal oxides [15–18]. Modification of MFI (SiO₂/Al₂O₃ = 50) with different elements (B, P, Mg, Si, La, or Cd) showed an increase in para-selectivity to p -ET due to the decreased concentration of strong acid sites and the sorption capacity of the zeolite [16–19].

The heat of adsorption for toluene and ethanol was reported at 56 kJ/mol and 35 kJ/mol, respectively, with surface activation energy of 62 kJ/mol [16]. Parikh reported the kinetics of the ethylation reaction using a monolith reactor on which MFI (SiO₂/Al₂O₃ = 24) was wash-coated [20]. The proposed rate expression indicated that p -ET is the primary product of the alkylation reaction. o -ET was not considered due to negligible quantities while the net rate of m -ET formation was a result of the total rate of toluene consumption to form p -ET and the subsequent isomerization rate of p -ET to m -ET.

Most of the zeolites that showed high para-selectivity for toluene ethylation were subjected to post-synthesis steps either by modification of zeolite channels or deactivation of external surface. Consequently, the aim of this paper is to present aspects related to the development of a para-selective MFI-zeolite for toluene ethylation to p -ET without the need to modify either the zeolite pore channels or external surface. The paper addresses the effects of SiO₂/Al₂O₃ ratio, crystal size and reaction temperature on p -ET formation. It also focuses on development of a kinetic model accounting for all reaction steps i.e. adsorption, surface reaction and desorption.

2. Experimental

2.1. Materials

Two of the MFI zeolites used in this work were procured from Zeolyst; MFI-80 (CBV8014, NH₄-form) and MFI-280 (CBV28014, NH₄-form). Prior to catalyst testing, the zeolites were calcined

in standing air at 550 °C for 5 h (ramping rate of 3 °C min⁻¹), in order to get the H-form. MFI with a SiO₂/Al₂O₃ of 2000 (MFI-2000) was prepared using hydrothermal techniques, in a typical synthesis of this sample 4.26 g tetrapropylammonium bromide, 0.7407 g ammonium fluoride and hydrated aluminium nitrate 0.0750 was dissolved in 72 ml of water and stirred well for 15 min. 12 g silica (381276 Aldrich) was added and stirred well until homogenized. The obtained gel was autoclaved and kept at 200 °C for 2 days. The molar composition of gel was 1 SiO₂: 0.08 (TPA) Br: 0.10 NH₄F: 0.0005 Al₂O₃: 20 H₂O. The solid product obtained was washed with water and dried at 80 °C overnight. The template was removed by calcination in air at 750 °C for 5 h. These zeolites are hereafter referred as MFI-80, MFI-280 and MFI-2000, where the number represents the nominal SiO₂/Al₂O₃ ratio. Silicalite-1 was synthesized by the same procedure as MFI-2000 but without addition of aluminium source i.e. aluminium nitrate.

Toluene and ethanol were obtained from Sigma-Aldrich and no further attempt was made to purify the chemicals.

2.2. Catalyst characterization

The MFI zeolites were characterized using several techniques. The amounts of SiO₂ and Al₂O₃ the catalysts were determined by atomic absorption spectrometer (Perkin-Elmer AAS Analyst 100). Textural properties were characterized by N₂ adsorption-desorption measurements at 77 K, using Quantachrome Autosorb 1-C adsorption analyzer. Samples were outgassed at 220 °C under vacuum (10⁻⁵ Torr) for 3 h before N₂ physisorption. The Brunauer–Emmett–Teller (BET) specific surface areas were determined from the desorption data in the relative pressure (P/P_0) range from 0.06–0.3, assuming 0.164 nm² for the cross-section of the N₂ molecule. Contribution of micropore and mesopores was derived from the t -plot method according to Lippens and de Boer [21].

High-angle X-ray diffraction patterns were recorded on a Rigaku Miniflex II XRD powder diffraction system using CuK α radiation ($\lambda_{K\alpha 1} = 1.54051 \text{ \AA}$, 30 kV and 15 mA). The XRD patterns were recorded in the static scanning mode from 1.2–60° (2 θ) at a detector angular speed of 2°/min and step size of 0.02°. The crystal sizes of the MFI zeolites were measured using a scanning electron microscopy (SEM) by Nova NanoSEM FEI with an accelerating voltage of 30 kV.

In order to assess the acid sites on the MFI zeolites and their properties, NH₃ temperature-programmed desorption (TPD) and FTIR spectroscopy of adsorbed pyridine were used. NH₃-TPD was carried out using Quantachrome Autosorb 1-C/TCD to determine total acid sites on the catalysts. Samples were pretreated at 450 °C in a stream of helium (25 ml min⁻¹) for 2 h. This was followed by the uptake of ammonia (5 vol. % in helium) at 100 °C for 30 min. The samples were then subjected to flow of helium for 2 h at 120 °C so as to remove loosely bound ammonia (i.e. physisorbed ammonia). After that, the samples were heated from 100–700 °C at a rate of 10 °C/min in a flow of helium (25 ml min⁻¹) while monitoring the evolved ammonia using TCD.

Infrared spectroscopy of adsorbed pyridine was used to identify the nature of available acid sites (i.e. Brønsted and/or Lewis acid sites). The measurements were conducted using a Fourier transform infrared with Nicolet FTIR spectrometer (Magna 500 model). The samples, as self-supporting wafers (ca. 60 mg in weight and 20 mm in diameter) were obtained by compressing a uniform layer of the powdered samples. The wafer was then inserted into an infrared vacuum cell equipped with KBr windows (Makuhari Rikagaku Garasu Inc., Japan), and preheated under vacuum (ca. 10⁻³ torr) at 450 °C for 2 h. The adsorption temperature of pyridine was 150 °C. The IR cell was then cooled down to ambient temperature and placed in an IR beam compartment while under vacuum

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