



Selective synthesis of linear alkylbenzene by alkylation of benzene with 1-dodecene over desilicated zeolites



Waqas Aslam^a, M. Abdul Bari Siddiqui^a, B. Rabindran Jermy^a, Abdullah Aitani^a, Jiří Čejka^{a,b}, Sulaiman Al-Khattaf^{a,*}

^a Center of Research Excellence in Petroleum Refining & Petrochemicals, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

^b J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic

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ABSTRACT

The alkylation of benzene with 1-dodecene to linear alkylbenzenes (LAB) was investigated over 12-ring zeolites MOR, BEA, and FAU with varying framework topologies and Si/Al ratios. The reaction was carried out under a high-pressure, 20 bar, in a fixed-bed flow reactor at 140 °C, using WHSV 4 h⁻¹, benzene/1-dodecene molar ratio of 6.0 and time-on-stream of 6.0 h. In contrast to MOR and BEA zeolites, FAU exhibited the lowest selectivity (24%) to the desired 2-phenyl dodecane (2-LAB) due to its large cavities. The MOR and BEA with different Si/Al ratios were further desilicated using alkali-metal treatments (0.2 M and 0.05 M NaOH) to create hierarchical porous structure. The desilication of both zeolites improved the conversion of 1-dodecene and the selectivity to 2-LAB. The excellent stability resulting from desilication is attributed to a better diffusivity of the LAB isomers, shortening of real contact time, due to the enhanced mesoporous structure in both zeolites and the higher Lewis acidity. The selectivity to 2-LAB increased to 70% over desilicated MOR (Si/Al ratio = 20) compared with a selectivity of 35% over desilicated BEA (Si/Al ratio = 24).

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1. Introduction

Linear alkylbenzenes (LAB) with appropriate chain length are predominantly used as synthetic detergent intermediates for the manufacture of LAB sulfonate (LAS), which replaced dodecylbenzenes in the 1960s. LAS is a synthetic surfactant that quickly and completely biodegrades and does not cause any environmental problems. Among six LAB isomers, 2-phenyl dodecane (2-LAB) is the most desirable product for the detergent industry [1]. Currently, most of the 3.6 million tons/year of LABs is produced using homogenous liquid phase catalysts such as hydrofluoric acid (HF) or aluminum chloride (AlCl₃) [2]. Unfortunately, these catalysts have major disadvantages related to environmental pollution, equipment corrosion, and separation problems. To avoid these drawbacks, the detergent industry looks for environmentally friendly processes, in particular utilizing solid acid catalysts. UOP and Cepsa developed the DETAL process for solid bed alkylation commercialized in 1995 [1,2].

Benzene alkylation with linear C₁₀–C₁₃ olefins to LAB, which is a mixture of C₁₀–C₁₃ alkylbenzenes, is performed at a high benzene/olefin ratio to suppress side reactions such as polyalkylation,

dealkylation, olefin isomerization and oligomerization reactions that co-produce heavy alkenes and other undesired coke precursor products. The oligomerization of 1-olefins, although usually insignificant, occurs simultaneously with the main alkylation reaction. Depending on the type of catalyst and olefin used, the reaction is conducted at temperatures less than 150 °C to minimize skeletal isomerization of olefins and to maintain high product linearity [3].

There are ongoing efforts to develop more active and stable solid acid catalysts for LAB synthesis with major emphasis on zeolites using either batch or flow reactors [4,5]. However, solid acids have significantly lower activities than homogeneous ones, although they provide improved reaction selectivity. The product selectivity to 2-LAB over non-zeolite acid catalysts does not exceed 50% and catalysts are subjected to fast deactivation and difficult regeneration. Zeolites with relatively small channels such as MFI showed a low activity for benzene alkylation and poor selectivity to LAB isomers because they easily deactivate by coking [2]. Among large-pore zeolites investigated, zeolites with three-dimensional topology such as FAU, MOR and BEA received the most attention [6–11]. The difference in the selectivity to LAB isomers over various zeolites was attributed to the product shape selectivity due to the zeolite pore structures and the relative rate constant of isomerization vs. alkylation of 1-dodecene [5]. The open pore structure of the dealuminated FAU appears suitable for the production of LAB isomers but it is not selective to 2-LAB.

* Corresponding author. Tel.: +966 13 860 1429.

E-mail addresses: skhattaf@kfupm.edu.sa, cejka@jh-inst.cas.cz (S. Al-Khattaf).

Table 1
List of parent and desilicated zeolites used in LAB alkylation reaction.

Zeolite sample	Pore structure	Sample code	Description ^a	Si/Al molar ratio
Ultra-stable Y Beta	3D, 7.4 Å 3D, 7.3 × 6.5 and 5.6 × 5.6 Å	FAU	Parent zeolite from Tosoh	8
		BEA-24	Parent BEA from Tosoh	29
		DBEA-24	Desilicated BEA-24, treated with 0.05 M NaOH solution for 1 h at 100 °C	26
		BEA-40	Parent BEA from Tricat	38
Mordenite	2D, 7 × 6.5 and 5.7 × 2.6 Å	DBEA-40	Desilicated BEA-40, treated with 0.2 M NaOH solution for 0.5 h at 60 °C	29
		MOR-18	Parent MOR from Tosoh	19
		DMOR-18	Desilicated MOR-18, treated with 0.2 M NaOH solution for 0.5 h at 60 °C	18
		MOR-40	Parent MOR from J. Heyrovský Institute of Physical Chemistry	40
		DMOR-40	Desilicated MOR-40 treated with 0.2 M NaOH solution for 0.5 h at 60 °C	36
		MOR-180	Parent MOR from Tosoh	180

^a All zeolites were calcined at 650 °C for 3 h (3 °C/min).

HF-modified MOR [12] and steam-treated MOR [13] have been investigated with varying successes. The improved behavior of the steam-treated MOR was attributed to its lower acid site concentration and less hydrophilic surface [13]. Tsai et al. showed that LAB production over MOR is an exothermic reaction, in which thermodynamic equilibrium was favorable at low temperature, approaching 100% conversion at 227 °C [14]. Using a steam-pretreated MOR, the selectivity to 2-LAB exceeded the thermodynamic equilibrium composition being higher than over catalysts such as zeolite FAU and AlCl₃. Compared with FAU zeolite, dealuminated MOR exhibited the selectivity to 2-LAB above 70% at the reaction temperature of 200 °C and at benzene/1-hexadecene molar ratio equal to 8.6 [11]. Desilication of MOR was found to improve catalytic stability in kinetic test up to 80 h as compared with dealumination or metal impregnation for an octadiene containing dodecene feed [15]. An optimum alkylation catalyst was obtained by the desilication of MOR under mild conditions (0.4 M NaOH) affording 100% conversion of 1-dodecene and selectivity of 98% to LAB of which 2-LAB isomer selectivity was around 78%.

Zeolite BEA showed lower conversion and selectivity to 2-LAB compared with MOR [17–19]. The lifetime of fluorinated BEA catalysts depended on the specific surface area and pore volume rather than strong Lewis acidity. At a fluorine content of 0.5%, the lifetime of BEA zeolite increased from 23 to 32 h at maximum BET area and pore volume [17]. Higher 1-dodecene conversion was reported at 180 °C for zeolite BEA with the lowest Si/Al ratio (12.5) [19]. At a higher Si/Al ratio, a greater portion of Lewis acid sites initialized undesired side reactions like dimerization or oligomerization of 1-olefins resulting in catalyst deactivation. Zeolite MTW [5,20] showed low activity while MWW modified with 0.5 wt% phosphorus showed improved selectivity to 2-LAB (52%) and increased catalytic stability for more than 33 h of T-O-S [21].

Introducing mesopores into zeolites by alkaline treatment (desilication) can improve zeolite stability against coking by enhancing the diffusivity of products and oligomer by-products [22,23]. Groen et al. demonstrated the effectiveness of desilication in making hierarchically structured micro-mesoporous MOR and BEA zeolites for improved transport properties of feed and product in benzene alkylation with ethylene [24,25]. Tsai and co-workers reported improved catalytic activity and diffusion properties of modified MOR for the LAB alkylation reaction and the transalkylation of heavy alkylbenzenes [15,26]. Similar results were also reported for mesoporous MFI zeolites prepared using carbon black pearls with microwave synthesis [27].

Nevertheless, there are no systematic studies of the stabilization effect of mesoporous structure of zeolites on benzene alkylation with long-chain olefins. Therefore, in this study, zeolites BEA and MOR with different Si/Al ratios are modified by desilication aiming to improve their catalytic performance in alkylation of benzene with 1-dodecene.

2. Experimental

2.1. Chemicals and catalysts

The parent zeolites used in this study included commercially available zeolites with varying Si/Al molar ratio: two NH₄-BEA (BEA-24, BEA-40), two H-MOR (MOR-18, MOR-40, MOR-180) and one USY zeolite (Si/Al = 8). The H-BEA was obtained by calcination of NH₄-BEA at 650 °C for 3 h. Table 1 presents descriptions of the parent zeolites, their pre-treatment procedures and Si/Al ratio.

GC grade LAB isomers (used for quantitative analysis) and laboratory grade benzene and 1-dodecene (used as feeds) were purchased from Sigma–Aldrich.

2.2. Desilication procedures

The parent BEA and MOR zeolites were desilicated to prepare mesoporous zeolites. Table 1 presents a description of the desilicated zeolites and their treatment procedures. The desilicated BEA (DBEA-40) and desilicated MOR (DMOR-18, DMOR-40) were prepared by treating the parent zeolites with a NaOH solution of 0.2 M at 60 °C for 0.5 h. The solid was then further ion exchanged with a 0.1 M NH₄Cl solution at 60 °C for 4 h. The desilicated BEA (DBEA-24) was prepared by slurrying the zeolite sample (5 g) in 350 ml of 0.05 M NaOH solution at 60 °C for 1 h. The zeolite/alkali slurry was immediately quenched in ice bath to stop further reaction, filtered, dried and ion exchanged. All the ion-exchanged zeolites were calcined at 650 °C for 3 h at a heating rate of 3 °C/min.

2.3. Catalyst characterization

The elemental analysis for Si and Al was measured using ICP Optical Emission Spectrometer, Ultima 2, Horiba Scientific. 50 mg catalyst sample was fused with 300 mg of Lithium metaborate in a muffle furnace at 950 °C for 15 min. The fused product was dissolved in 20 ml of 4% HNO₃. The solution was further diluted with deionized water to make a total volume of 50 ml. The X-ray powder diffraction (XRD) was recorded on a Rigaku Miniflex II X-ray diffractometer using nickel filtered Cu Kα radiation at 40 kV and 30 mA.

SEM images were taken on a Nova NanoSEM FEI with an accelerating voltage of 30 kV.

The surface area of the catalysts was measured using a Quantachrome NOVA 1200 gas sorption analyzer by the adsorption of nitrogen at –196 °C according to ASTM D3663 standard method. Prior to nitrogen adsorption, the catalyst was evacuated for 2 h at 350 °C. Micropore volume, V_{micro} , was determined using *t*-plot method. The mesopore volume, V_{meso} was estimated by subtracting micropore volume, V_{micro} , from the total pore volume, V_{tot} .

The acidic properties of the zeolites were measured using a Nicolet 6700 FTIR spectrophotometer (Thermo Scientific) equipped with a high temperature vacuum chamber using pyridine as a probe. The zeolite sample (50 mg) was pressed and placed in a

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