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

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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 mesporous 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).

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 ($AlCl_3$) [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 C_{10}–C_{13} olefins to LAB, which is a mixture of C_{10}–C_{13} 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.

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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	3D, 7.4 Å	FAU	Parent zeolite from Tosoh	8
Beta	3D, 7.3 × 6.5 and 5.6 × 5.6 Å	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
		DBEA-40	Desilicated BEA-40, treated with 0.2 M NaOH solution for 0.5 h at 60 °C	29
Mordenite	2D, 7 × 6.5 and 5.7 × 2.6 Å	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 $AlCl_3$. 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 NH_4-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 NH_4-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 NH_4Cl 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% HNO_3. 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 diffractomer 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 sample holder for pretreatment at 550 °C under vacuum for 1 h. The sample was then cooled to 100 °C and the spectrum was recorded. The physically adsorbed pyridine was removed by heating the sample at 150 °C under vacuum (10^{-5} mbar) for 40 min. The removed material was cooled to room temperature and then the spectrum was recorded again. The concentrations of Brønsted and Lewis acid sites were determined using the extinction coefficients from Ref. [28].

Temperature-programmed desorption (TPD) of ammonia was performed in BEL-CAT-A-200, chemisorption apparatus consisting of a gas mixing unit allowing both continuous and pulsed reactant dosing, U-tube quartz micro-reactor with a thermocouple placed inside the sample, and a thermal conductivity detector (TCD). The sample (50 mg) was pretreated in a flow of He (50 mL/min) at 500 °C for 1 h. Then the sample was exposed to He/NH_3 mixture (95/5 vol%) at room temperature for 30 min. TPD was performed in He flow (50 mL/min) at a heating rate of 10 °C/min, and the desorbed NH_3 was monitored by a TCD detector.

2.4. Catalytic reaction

Benzene alkylation reaction with 1-dodecene was performed using a continuous flow fixed bed BTRS-Jr Laboratory Reactor System (Autoclave Engineers). A stainless steel reactor tube of 30 cm length and 10 mm ID was operated in a down flow mode and its effluents were passed through a gas-liquid separator. Catalyst powder was pressed into a tablet, crushed and sieved to obtain uniform size of particles in the range of 16–20 mesh. One gram of catalyst was placed at the center of the reactor tube supported by alumina spheres and glass wool. The reactor was pressurized up to 20 bar with N_2 and heated in N_2 flow of 50 ml/min up to 140 °C at a rate of 10 °C per minute. The feed mixture consisted of benzene and 1-dodecene at a molar ratio of 6:1 with feed preheaters kept at 140 °C (reactant to catalyst weight ratio 10:1). The reaction was performed for 6 h time-on-stream (T-O-S) and liquid samples were collected at intervals of 0.5 to 1 h. An off-line gas chromatograph-mass spectrometer (GS-MS Agilent 5890) was used to identify the components of the reaction products. Quantitative analysis of products was done in a GC (Agilent 7890A) equipped with a flame ionization detector. A 30 m capillary column (Agilent HP-5) with 0.32 mm ID was used to separate the product components. Helium was used as carrier gas and the injector was operated in split mode with a split ratio of 100:1. The main reaction products of benzene alkylation with 1-dodecene are 2–6 LAB (Fig. 1) and dodecene isomers [29]. 1-LAB isomer was not detected due to its very low equilibrium concentration [30].

Conversion of 1-dodecene and LAB selectivity were determined as follows:

- 1-Dodecene conversion = $(N_{d0} - N_d)/N_{d0} \times 100$, where N_{d0} is number of moles of 1-dodecene before reaction, and N_d is number of moles of 1-dodecene after reaction.
- LAB selectivity (S_{LAB}) = $N_l/N_t \times 100$, where N_l is number of moles of LAB in the final products and N_t is sum of moles of all products including all dodecene isomers (1–6-dodecenes) and LAB isomers (2–6-phenyldodecanes) [4].

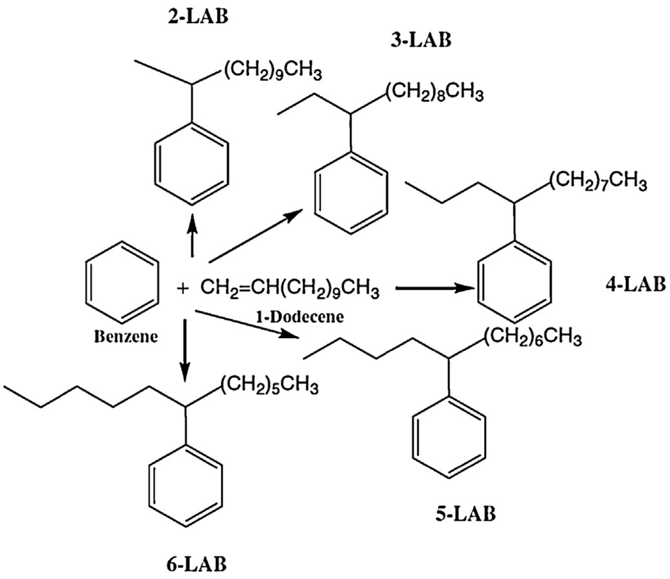

Fig. 1. LAB isomers formation in the alkylation of benzene with 1-dodecene [29].

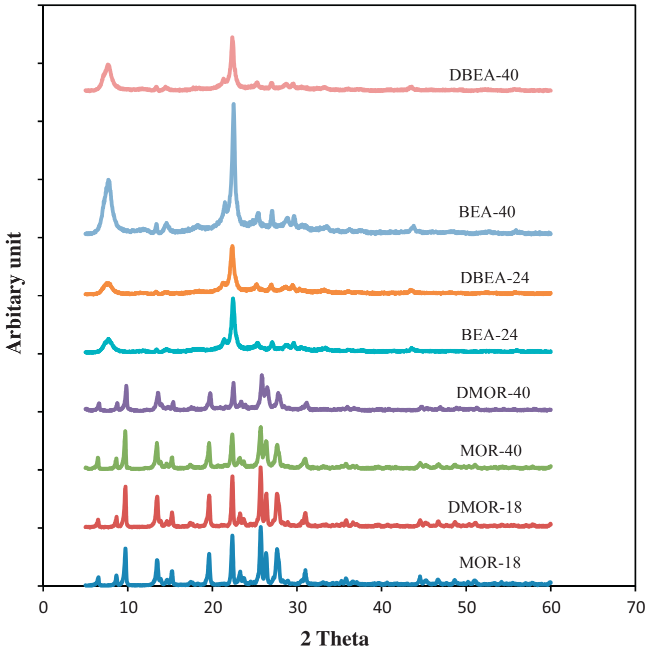

Fig. 2. X-ray diffraction patterns of parent and desilicated MOR (MOR-18, MOR-40, DMOR-18, DMOR-40) and BEA (BEA-24, BEA-40, DBEA-24, DBEA-40).

3. Results and discussion

3.1. Characterization results

The results of ICP-OES chemical analyses (Si/Al ratio), BET areas and concentrations of acid sites in parent and desilicated zeolites are presented in Tables 1 and 2. The XRD patterns of the parent and desilicated MOR (MOR-18, MOR-40, DMOR-18, DMOR-40), BEA (BEA-24, BEA-40 DBEA-24, DBEA-40) are shown in Fig. 2. The XRD patterns remain unchanged as for the position of individual diffraction lines while the intensity of some of them decreased as a result of desilication.

Fig. 3 shows the nitrogen adsorption–desorption isotherms for selected zeolite samples (as for textural characteristics, see Table 2). The desilicated MOR (DMOR-40) and BEA (DBEA-40) showed a Type IV isotherm with enhanced hysteresis loop compared with parent samples. Desilicated samples exhibited an increase in the BET area accompanied by a significant increase in the mesopore volume (Table 2). This phenomenon can be attributed to the formation for mesopores at the expense of micropores [31]. The BET area and total pore volume results show that FAU zeolite has the highest BET area (533 m^2/g) and total pore volume (0.41 cm^3/g).

Table 2
Chemical, physical and acidic properties of parent and desilicated zeolites.

Zeolite	N_2 adsorption characteristics				Acidity, pyridine (mmol/g)			Acidity TPD NH_3 (mmol/g)
	S_{BET} (m^2/g)	V_{meso} (cc/g)	V_{micro} (cc/g)	V_{tot} (cc/g)	B	L	B/L	
USY	533	0.21	0.20	0.41	–	–	–	0.33
Beta								
BEA-24	428	0.20	0.15	0.35	0.29	0.06	4.83	0.47
DBEA-24	470	0.24	0.14	0.38	0.20	0.48	0.42	0.57
BEA-40	436	–	0.18	0.18	0.24	0.11	2.18	0.34
DBEA-40	441	0.28	0.06	0.34	0.19	0.14	1.36	0.36
Mordenite								
MOR-18	264	0.04	0.15	0.19	0.93	0.07	13.28	0.54
DMOR-18	350	0.11	0.11	0.22	0.20	0.14	1.43	0.38
MOR-40	302	0.07	0.14	0.21	0.26	0.13	2.00	0.21
DMOR-40	362	0.29	0.12	0.41	0.18	0.28	0.64	0.14
MOR-180	514	0.05	0.24	0.29	0.05	0.22	0.23	0.04

S_{BET}: BET specific surface area; V_{micro}: micropore volume; V_{meso}: mesopore volume; V_{tot}: total pore volume.
L: Lewis acidity; B: Brønsted acidity.

Fig. 4A and B shows the IR absorption bands of hydroxyl stretching vibrations of both parent and desilicated zeolites MOR and BEA under study recorded at room temperature after activation at 400 °C (A) and after adsorption of pyridine at 100 °C (B). Parent and desilicated MOR zeolites showed distinctly two characteristic absorption bands around 3740 cm^{-1} and 3610 cm^{-1} due to terminal silanols (Si—OH) and bridging hydroxyl group associated with Brønsted acid sites, respectively [32]. For parent MOR (MOR-18), the peak at 3611 cm^{-1} corresponding to Brønsted acid sites was sharp and highly distinct compared with other zeolites. The impact of desilication is clearly reflected on the desilicated MOR samples (DMOR-18 and DMOR-40), where absorption band of Brønsted acid peak (3615 cm^{-1}) is almost disappeared. In addition, for both catalysts, formation of extra-framework aluminum species was observed at 3673 cm^{-1} [33]. In contrast with desilicated DMOR-18, DMOR-40 showed an apparent increase in the intensity of silanol bands indicating the formation of new isolated silanols groups associated with the formation of mesopores [34]. In the case of zeolite BEA (Fig. 4B), the peak at 3620 cm^{-1} was very weak and broader compared with MOR zeolites. The presence of such broad peak indicates a wide distribution of acid sites [35]. Apparently, the difference in the intensity of silanol groups after desilication clearly indicates the formation of mesopores.

Pyridine FTIR adsorption was used to characterize acidity of all zeolites studied. Fig. 4B shows the FTIR spectra of pyridine adsorbed for parent and desilicated MOR measured after evacuation at 150 °C. Adsorption of pyridine resulted in the formation of new absorption bands at 1545 (Brønsted) and 1454 (Lewis acid sites) cm^{-1}, respectively. The B/L ratios calculated from the IR absorbance intensities are shown in Table 2. Compared with parent zeolites, the concentration of Lewis acid sites increased whereas the concentration of Brønsted acid sites decreased after alkaline-treatment (Table 2). Holm et al. reported that upon zeolite treatment with NaOH strong Lewis acid sites are generated, presumably from dislodged framework aluminum [36]. It indicates the increase in the concentration of Lewis acid sites after desilication, which is further confirmed from the presence of absorption band in the region of Al—OH group around ~3673 cm^{-1} (Fig. 4).

The results of ammonia TPD of parent and desilicated zeolites are presented in Fig. 4C and Table 2. All samples showed two desorption peaks in the temperature range of 130–600 °C corresponding to the weakly adsorbed ammonia (mainly physisorption) and ammonia adsorbed on strong acid sites. The amount of desorbed NH_3 was calculated from the high-temperature peak. Tian et al. concluded that the acidity of zeolites is not only affected by the framework Si/Al ratio but it is also related to the coordination and distribution of framework Si and Al sites [37]. Some decrease in the concentration of strong acid sites with temperature maximum around 400 °C is observed for desilicated DMOR-18 and DMOR-40. The observed changes of the concentrations of acid sites may be attributed to the occurrence of framework dealumination [38]. In the case of desilicated beta (DBEA-24 and DBEA-40), only a little change in the concentration of strong acid sites was observed. This trend shows the possibility of some non-framework aluminum reinsertion into the framework upon desilication [39] or that desilication did not proceed in so large extent as for MOR.

The results of field emission-scanning electron microscopy (FE-SEM) images with energy-dispersive X-ray (EDX) spectroscopy analysis of parent and desilicated zeolites are presented in Fig. 5. In general, desilication of zeolites BEA and MOR originally with Si/Al

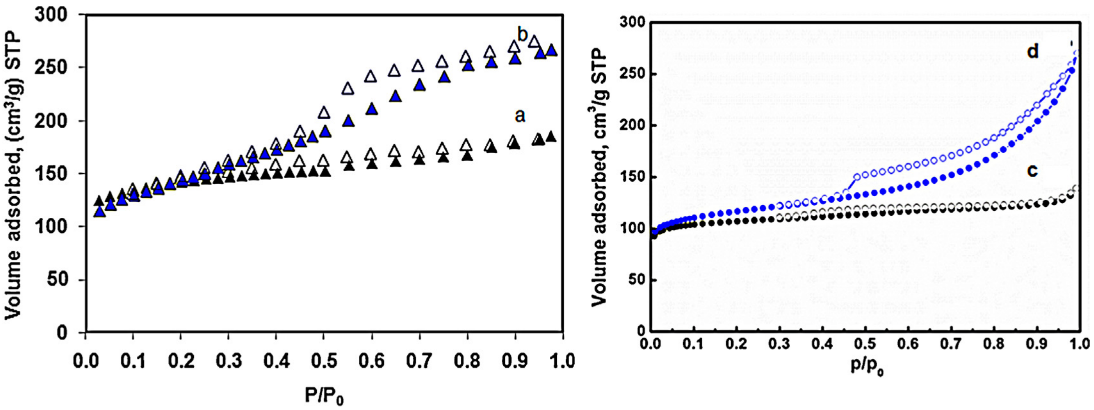

Fig. 3. Nitrogen adsorption (●, ▲) and desorption (○, △) isotherms of selected parent and desilicated samples: (a) BEA-40, (b) DBEA-40, (c) MOR-40, and (d) DMOR-40.

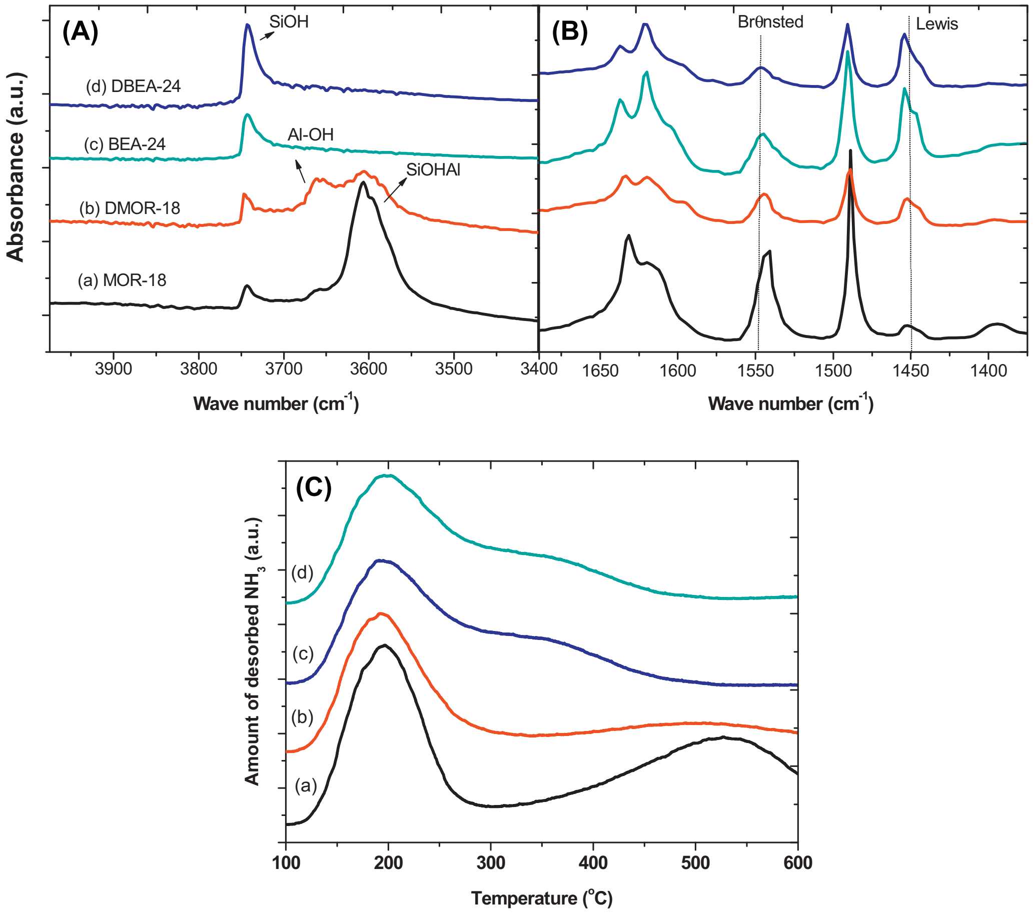

Fig. 4. FTIR spectra of parent zeolites: (A) prior to pyridine adsorption, (B) after pyridine adsorption (a) MOR-18, (b) MOR-40, red line: spectra of activated samples, black line: spectra after 20 min desorption at 150 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

ratios in the range 20–50 retains the morphology of parent zeolites. Similarly, in the present study, the morphological difference between parent and desilicated samples is less apparent. However, an agglomeration among the desilicated samples is seen. The observed characteristics are similar to those reported for desilicated BEA zeolite [24].

3.2. *Benzene alkylation over parent zeolites*

Fig. 6 and Table 3 present the catalytic performances of the parent FAU, BEA-24 and MOR-18 in terms of 1-dodecene conversion, stability, and selectivity to LAB isomers.

The FAU zeolite exhibited the highest 1-dodecene conversion (97%) and the highest selectivity to LAB isomers (97%) compared with MOR-18 (93%) and BEA-24 (60%). Moreover, FAU was the most stable catalyst with constant conversion and selectivity to LAB isomers during the 6 h of time-on-stream (T-O-S), Fig. 6. Selectivity to the desired 2-LAB over FAU zeolite was 26% and the 2-LAB/3–6 LAB ratio was 0.4 (Table 3). High selectivity to 3–6 LAB isomers may be attributed to FAU large pore opening of 7.4 Å permitting an easy access and diffusion of dodecene into the super-cages of 12.4 Å.

Zeolite BEA-24 exhibited a rapid deactivation; 1-dodecene conversion dropped from 73% to 45% at 6 h of T-O-S (Fig. 6). The selectivity to 2-LAB was less than 24% and the 2-LAB/3–6 LAB isomers ratio was 0.7. The selectivity to dodecene isomers was the highest over BEA-24 (39%) as compared with FAU (2%) and MOR-18 (6%). The drop in 1-dodecene conversion with T-O-S for BEA-24 is primarily due to its lower concentration of Brønsted acid sites (0.29 mmol/g), cf. Table 2.

On the other hand, the performance of MOR-18 showed that 1-dodecene conversion and selectivity to LAB isomers were both above 92% (Table 3). The selectivity to 2-LAB (68%) and the 2-LAB/3–5 LAB ratio (2.7) were the highest compared with FAU and BEA-24. At longer T-O-S, MOR-18 showed a gradual deactivation, as shown in Fig. 6A, which is probably due to the smaller MOR-18 pore diameter compared with BEA-24 and FAU (Table 1). During the 6 h T-O-S, the selectivities to total LAB, 2-LAB, and dodecene isomers for the three zeolites were constant regardless of any change in 1-dodecene conversion.

Conversion of 1-dodecene over three parent zeolites decreased in the order of: FAU > MOR-18 > BEA-24 with a constant selectivity to 2-LAB during 6 h of T-O-S. The difference in the selectivity to 2-LAB over the three zeolites is influenced by the ability of the individual zeolite active sites in promoting benzene alkylation versus isomerization of 1-dodecene (Table 3 and Fig. 6). Compared with FAU, MOR-18 selectively formed 2-LAB (68.1%), whereas the selectivity to 3–6 LAB isomers was 71.1% over FAU due to its three-dimensional network of large cavities and openings [5,40]. Moreover, the alkylation of benzene to LAB over zeolite catalysts involves the interaction of 1-dodecene with strong acid sites to form 2-dodecylcarbenium ion which undergoes a rapid rearrangement followed by the attack of benzene ring by alkylcarbenium to form LAB isomers [26,41]. Both Brønsted and Lewis acid sites are considered as active species in this reaction [42].

To further elucidate the performance of MOR-18 in a wide range of 1-dodecene conversion, benzene alkylation experiments were performed at 100 °C and WHSV between 5 and 40 h^{-1} using different catalyst weights. Fig. 7 shows the increase in 1-dodecene

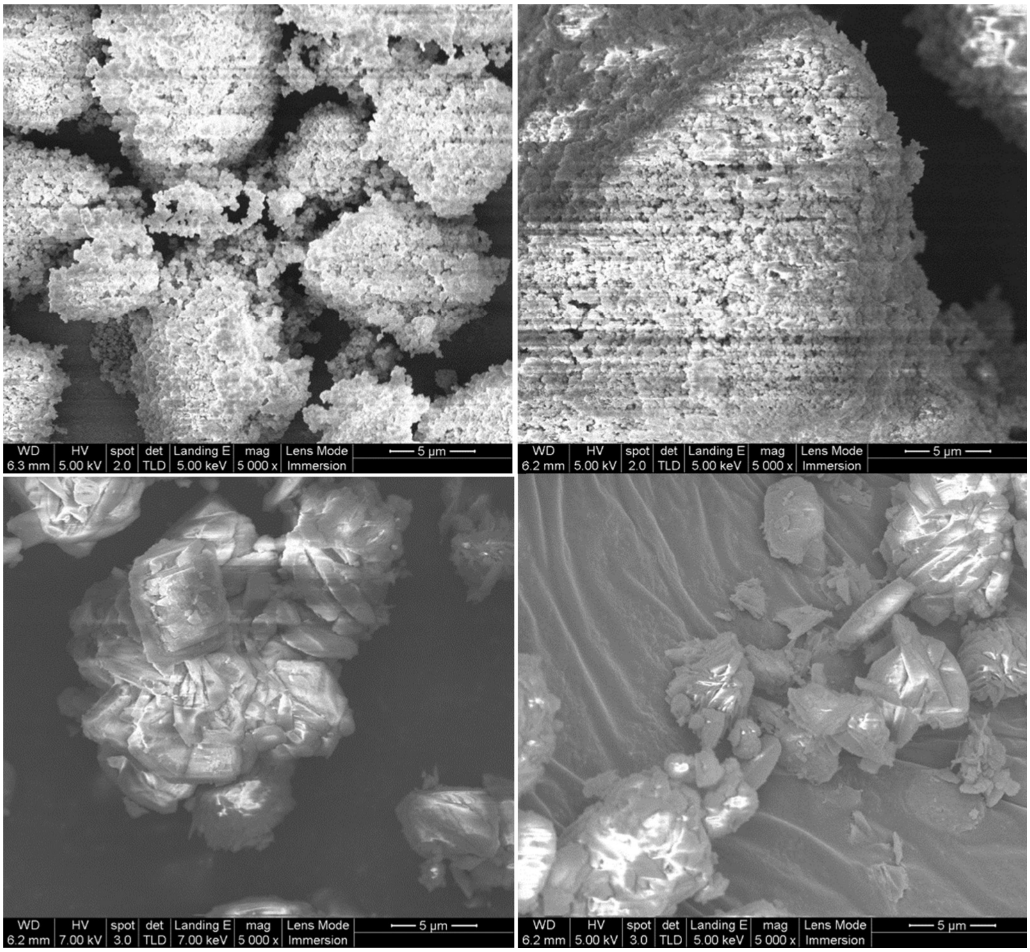

Fig. 5. FE-SEM images of parent and desilicated samples: (a) BEA-24, (b) DBEA-24, (c) BEA-40, (d) DBEA-40, (e) MOR-18, (f) DMOR-18, (g) MOR-40, and (h) DMOR-40. All the samples shown here are measured at 5 μm.

conversion from 25% to 86% with decreasing WHSV accompanied by a significant decrease in the selectivity to 1-dodecene (from 80% to 27%). As shown in Fig. 7, the selectivity to 2-LAB did not decrease with increasing 1-dodecene conversion but kept constant at about 86%.

3.3. *Effect of Si/Al ratio*

In the case of parent MOR samples with varying Si/Al ratios (MOR-18, MOR-40, MOR-180), the conversion of 1-dodecene and the selectivities to LAB versus T-O-S are presented in Fig. 8. There was no clear trend on the effect of Si/Al ratio on the behavior of MOR samples. While the conversion of 1-dodecene over MOR-40 gradually decreased from 77% to 60% during the 6 h of T-O-S, it was nearly constant over MOR-18 (90%) and MOR-180 (99%). After 1 h of T-O-S, the selectivity to 2-LAB was 68% over MOR-18 compared with 54% over MOR-180 and 34% over MOR-40. The selectivity to dodecene isomers over MOR-40 (38%) was the highest, indicating high isomerization activity compared with MOR-18 and MOR-180. The behavior of MOR-18 and MOR-40 may be attributed to the differences in the acidity characteristics of these two MOR samples (Table 2). MOR-18 exhibited higher concentration of Brønsted acid sites compared with MOR-40, which may explain high selectivity to dodecene isomers over MOR-40. However, diffusion of bulky reactants and products could be easier for MOR with less active sites [11,40]. With increasing Si/Al ratio in MOR zeolite, the concentration of Lewis acid sites increased resulting in the sharp decrease in the selectivity to LAB isomers for MOR-180 compared

Table 3
Catalytic performance of parent zeolites for benzene alkylation at 140 °C, 20 bar, WHSV = 4 h^{-1}, benzene: 1-dodecene molar ratio = 6, 1 h T-O-S.

Parameter	Beta			Mordenite		
	USY	BEA-24	BEA-40	MOR-18	MOR-40	MOR-180
1-Dodecene conversion (%)	96.6	72.6	81.8	92.0	77.4	96.8
Product selectivity (%)						
Dodecene isomers	2.0	39.2	25.4	5.7	37.9	1.6
LAB isomers	96.7	59.7	74.6	93.4	58.5	19.2
>C_{12} HC	1.3	1.1	0.0	0.9	3.6	28.0
LAB isomer selectivity (%)						
2-LAB	25.7	23.6	30.8	68.1	33.8	53.7
3–6 LAB	71.1	36.1	43.8	25.3	24.7	16.7
2-LAB/3–6 LAB	0.4	0.7	0.7	2.7	1.4	3.2

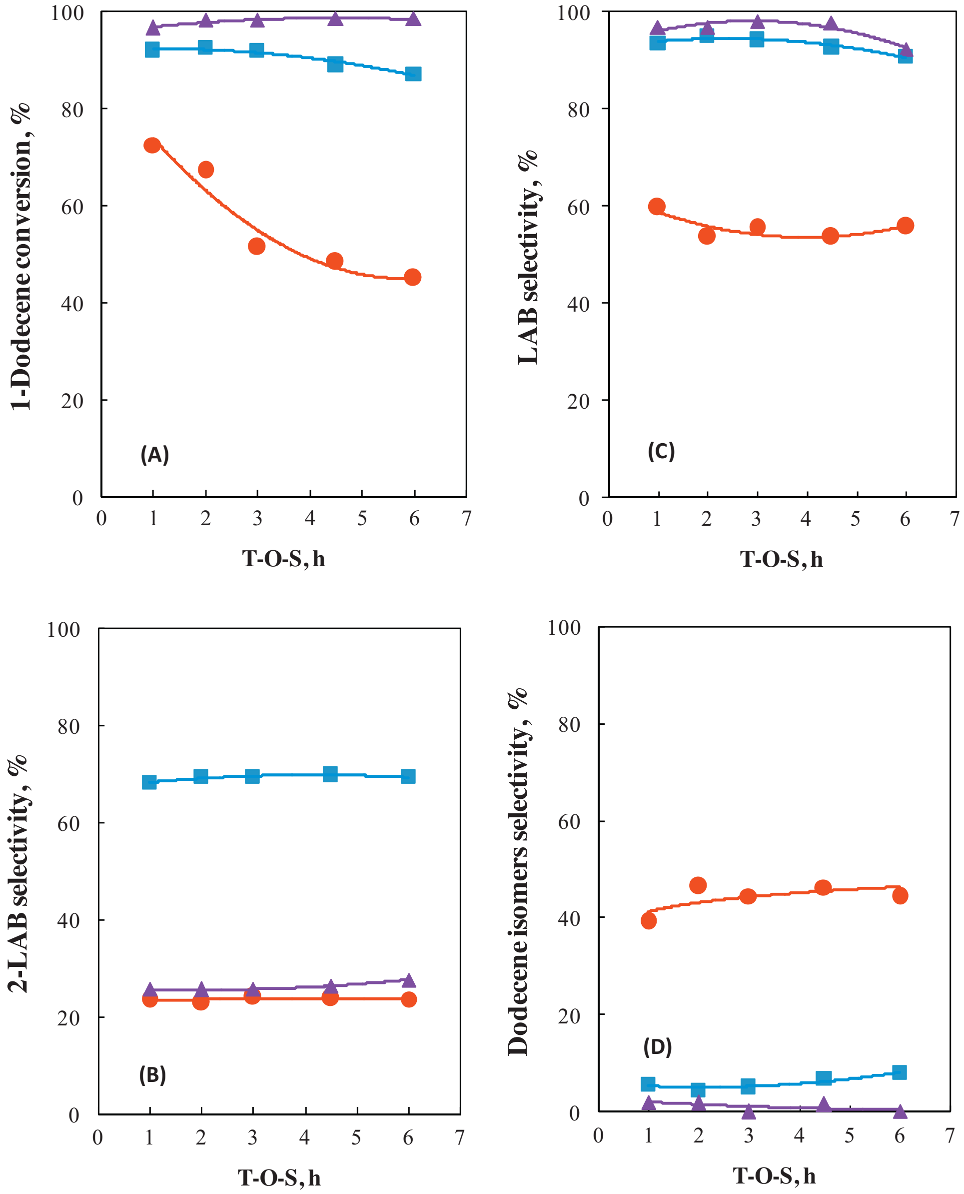

Fig. 6. Catalytic performance of parent zeolites (▲ FAU, ● BEA-24, ■ MOR-18) for 1-dodecene conversion and selectivities to LAB, 2-LAB and dodecene isomers at 140 °C, 20 bar, WHSV = 4 h^{-1}, benzene: 1-dodecene molar ratio = 6.

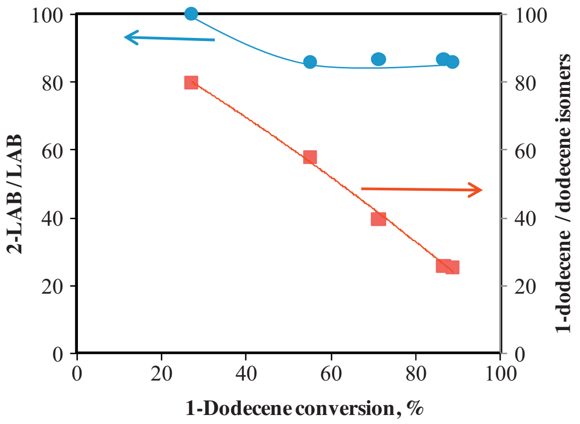

Fig. 7. Selectivity to 2-LAB and 1-dodecene versus 1-dodecene conversion for MOR-18 at 100 °C, 20 bar, WHSV = 5–40 h^{-1}, benzene: 1-dodecene molar ratio = 6, 1 h T-O-S.

with the other zeolite catalysts (Table 3). This was associated with increased amount of heavier hydrocarbons (>C_{12} HC) due to the dimerization–polymerization reaction [19].

The effect of Si/Al ratio on the benzene alkylation was studied using zeolites BEA-24, BEA-40, MOR-18, MOR-40, and MOR-180 as a function of T-O-S (Table 3 and Fig. 8). The conversion of 1-dodecene and the selectivities to LAB and 2-LAB for both BEA catalysts (BEA-24, BEA-40) decreased sharply with T-O-S. After 1.0 h of T-O-S, 1-dodecene conversion was 73% for BEA-24 compared with 82% for BEA-40. The selectivity to LAB was 60% over BEA-24 compared with 75% over BEA-40 and the selectivity to 2-LAB was 24% and 31%, respectively. The selectivity to undesired dodecene isomers decreased from 39.2% over BEA-24 to 25.4% over BEA-40. Although BEA-40 possesses a lower concentration of Brønsted acid sites compared with BEA-24 (Table 2), the number of its Lewis acid sites was higher than for BEA-24. As such, the selectivity to dodecene isomers over BEA-40 was lower (25.4%) compared with BEA-24 (39.2%) resulting in higher selectivity to LAB isomers over BEA-40.

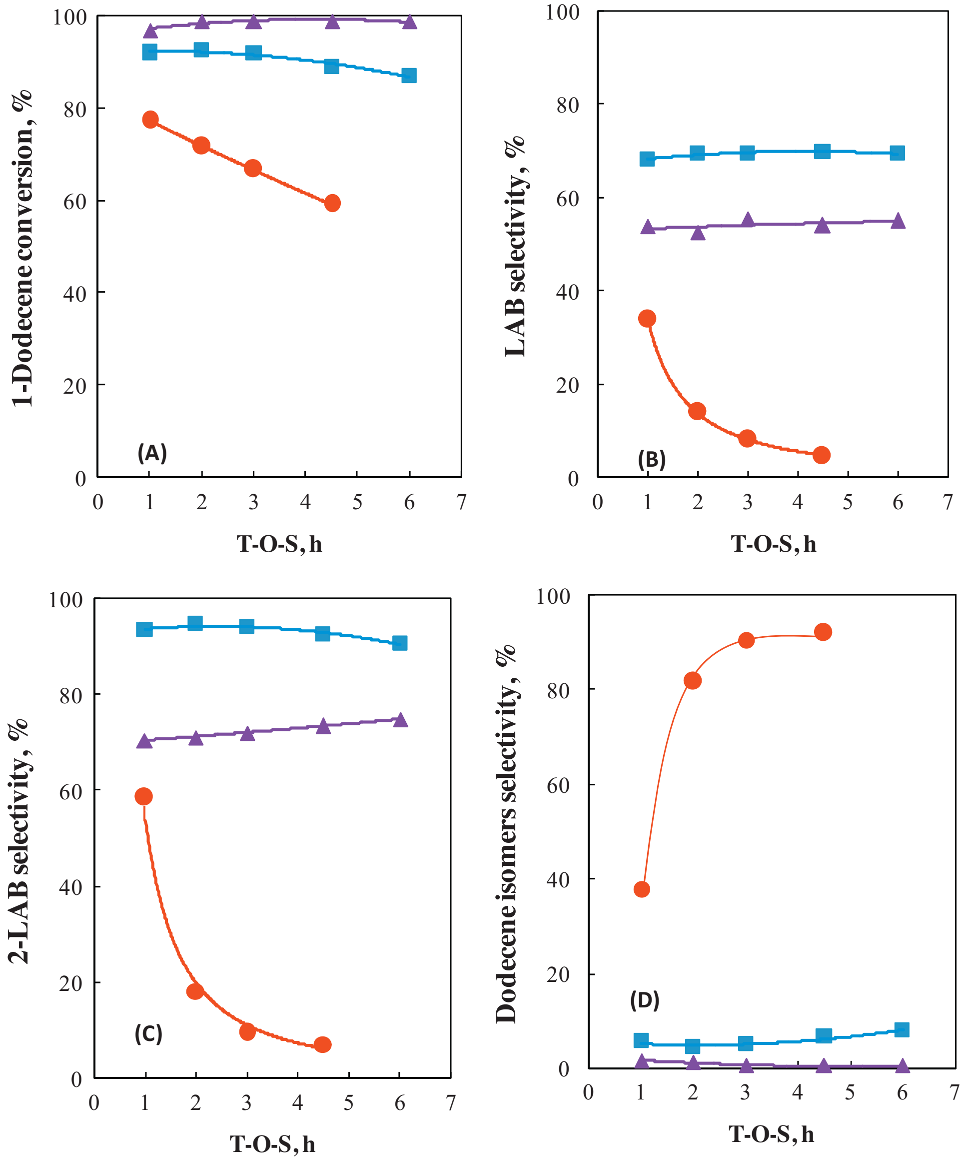

Fig. 8. Catalytic performance of parent MOR with different Si/Al ratios (■ MOR-18; ● MOR-40; ▲ MOR-180) for 1-dodecene conversion and selectivities to LAB, 2-LAB and dodecene isomers at 140 °C, 20 bar, WHSV = 4 h^{-1}, benzene: 1-dodecene molar ratio = 6.

3.4. *Effect of zeolite desilication*

The conversion of 1-dodecene and product selectivity characteristics of parent and desilicated BEA (BEA-24, BEA-40, DBEA-24, DBEA-40) and MOR (MOR-18, MOR-40, DMOR-18, DMOR-40) as a function of T-O-S are presented in Figs. 9 and 10 and Table 4. As discussed earlier, alkali-treatment increased the concentration of Lewis acid sites whereas the concentration of Brønsted acid sites decreased (Table 2).

As alkylation is catalyzed by moderate acid sites, higher LAB selectivity in desilicated BEA and MOR zeolites may be attributed to the inhibition of 1-dodecene isomerization. Table 2 shows that the desilication of BEA zeolites resulted in an increase in the concentration of Lewis acid sites and mesopore volume with a corresponding decrease in both the amount of Brønsted acid sites and micropore volume [24]. The conversion of 1-dodecene over parent zeolite BEA-24 (73%) increased significantly to 98% after desilication to DBEA-24. Selectivity to LABs for BEA-24 increased from 60% to 97% for DBEA-24 while the selectivity to dodecene isomers decreased from 39% to 2% indicating a significant drop in isomerization activity. Desilicated DBEA-24 showed a remarkable increase in the selectivity to 2-LAB from 24% (parent BEA-24) to 35% associated with a sharp drop in the selectivity to dodecene isomers (from 39% to 2%). This increase in 1-dodecene conversion and decrease in the selectivity to dodecene isomers over desilicated DBEA-24 may be attributed to the presence of a higher amount of mesopores in DBEA-24. Similar trend of improved 1-dodecene conversion and selectivity to LAB was observed for BEA-40. The improvement of 1-dodecene conversion and LAB selectivity with T-O-S for desilicated DBEA-40 was more pronounced than the improvement of BEA-24 as shown in Fig. 9. This improvement may be attributed to the presence of mesopores decreasing the real contact time, suppressing as the result the formation of coke precursors and subsequent catalyst deactivation.

Desilication of MOR-18 and MOR-40 resulted in the increase in the 1-dodecene conversion and 2-LAB selectivity, accompanied by significant decrease in the deactivation of MOR-40. 1-Dodecene conversion for both DMOR-18 and DMOR-40 was around 99% after 6 h of T-O-S (Fig. 10). Desilicated DMOR-40 showed a significant increase in the selectivity to 2-LAB from 34% (parent

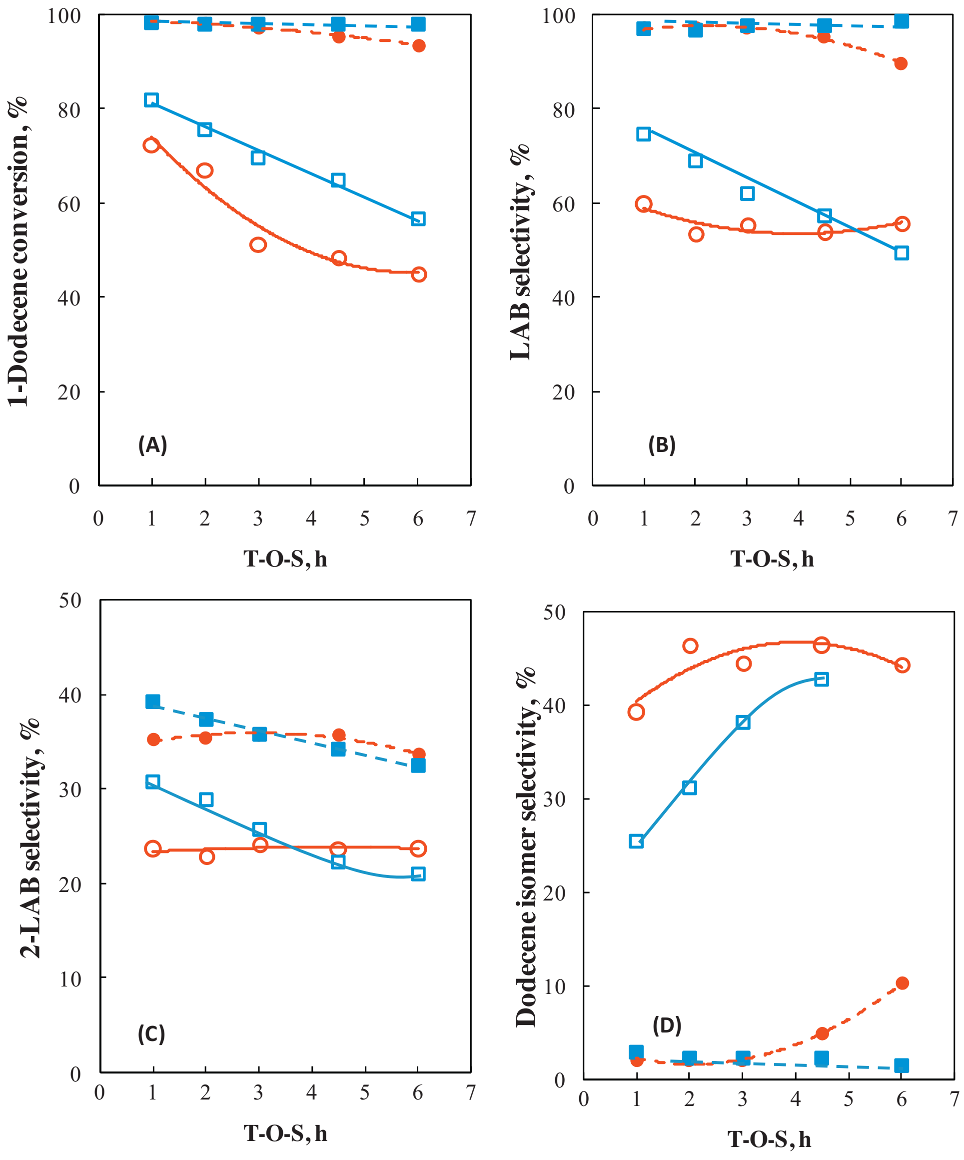

Fig. 9. Catalytic performance of parent and desilicated BEA (○ BEA-24; ● DBEA-24; □ BEA-40; ■ DBEA-40) for 1-dodecene conversion and selectivities to LAB, 2-LAB and dodecene isomers at 140 °C, 20 bar, WHSV = 4 h^{-1}, benzene: 1-dodecene molar ratio = 6.

MOR-40) to 60% associated with a drop in the selectivity to dodecene isomers (from 38% to <2%). The significant increase in 1-dodecene conversion and decrease in the selectivity to dodecene isomers over desilicated DMOR-40 may be attributed to a shortening of the real contact time due to desilication, which is related to higher mesopore volume of DMOR-40 being 0.29 cm^3/g) [15,16].

Positive effect of desilication over both BEA and MOR samples as for conversion and selectivity in benzene alkylation with 1-dodecene can be related to the changes of particularly textural properties of desilicated zeolites. The increase in both conversion and selectivity can be related to the increase in the mesopore volume and expectedly in the external surface area. We expect that alkylation can proceed at a higher

Table 4
Catalytic performance of parent and desilicated zeolites for benzene alkylation at 140 °C, 20 bar, WHSV = 4 h^{-1}, benzene: 1-dodecene molar ratio = 6, 1 h T-O-S.

Parameter	Beta				Mordenite			
	BEA-24	DBEA-24	BEA-40	DBEA-40	MOR-18	DMOR-18	MOR-40	DMOR-40
1-Dodecene conversion (%)	72.6	98.4	81.8	98.3	92.0	98.9	77.4	98.8
Product selectivity (%)								
Dodecene isomers	39.2	2.1	25.4	2.9	5.7	0.0	37.9	1.8
LAB isomers	59.7	97.1	74.6	97.1	93.4	97.8	58.5	88.2
>C_{12} HC	1.1	0.8	0.0	0.0	0.9	2.2	3.6	10.0
LAB isomer selectivity (%)								
2-LAB	23.6	35.2	30.8	39.3	68.1	70.0	33.8	59.6
3–6 LAB	36.1	61.9	43.8	57.8	25.3	27.8	24.7	28.6
2-LAB/3–6 LAB	0.7	0.6	0.7	0.7	2.7	2.5	1.4	2.1

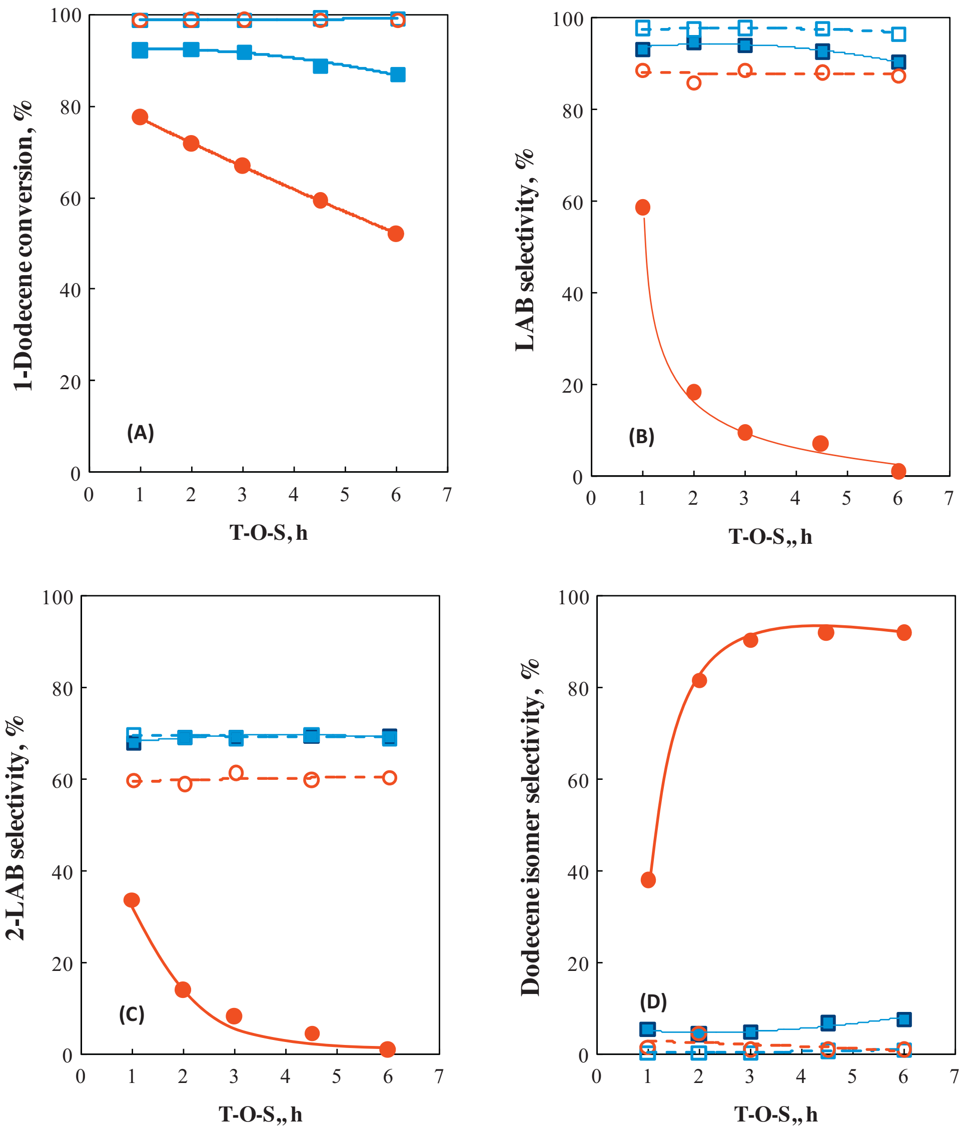

Fig. 10. Catalytic performance of parent and desilicated MOR (■ MOR-18; □ DMOR-18; ● MOR-40; ○ DMOR-40) for 1-dodecene conversion and selectivities to LAB, 2-LAB and dodecene isomers at 140 °C, 20 bar, WHSV = 4 h^{-1}, benzene: 1-dodecene molar ratio = 6.

reaction rate on the external surface of desilicated zeolites, increasing thus the rate of the reaction. With respect to the selectivity to 2-dodecyl benzene, the real contact time is decreased, as a result the primary alkylation product is not transformed to other isomers. In addition, the alkylation reactions proceeds now mainly on the external surface, limiting the accessibility of 1-dodecene to be adsorbed and isomerized (note that benzene to 1-dodecene ratio = 6:1).

4. Conclusions

The main conclusions of the study can be summarized as follows:

1. Conversion of 1-dodecene and the selectivities to 2-LAB over zeolites FAU, BEA, MOR and their desilicated analogs are controlled by zeolite pore structure. FAU zeolite exhibited the highest conversion, simultaneously with the lowest selectivity to 2-LAB due to its three-dimensional channel system with large cavities. Zeolite BEA showed the highest selectivity to dodecene isomers and MOR favored the formation of 2-LAB.
2. The effect of varying Si/Al ratio revealed that catalytic performance is improved (higher 1-dodecene conversion and selectivity to LAB) with increasing Si/Al ratios for BEA-40 while for MOR, a better performance was observed with decreasing Si/Al ratio (MOR-18).
3. The desilication of BEA and MOR zeolites by alkali treatment improved activity and selectivity to 2-LAB due higher concentration of Lewis acid centers and diffusion behavior in the micro-meso hierarchical structure. The selectivity to dodecene isomers significantly dropped down in all desilicated zeolites indicating a lower isomerization activity. Desilicated DMOR-18 exhibited the highest 1-dodecene conversion compared with the other desilicated zeolites. Selectivity to LAB was almost 100%, and the selectivity to 2-LAB was 70% at 99% 1-dodecene conversion. However, the enhancement in the catalytic performance of desilicated BEA was higher than that of desilicated MOR in terms of 1-dodecene conversion and 2-LAB selectivity. This may be attributed to the difference in mesoporosity between these zeolites.

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