Mesopore modification of beta zeolites by sequential alkali and acid treatments: composition-dependent T-atoms removal behavior back donating to hierarchical structure and catalytic activity in benzene alkylation

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Abstract: Acidic zeolites beta with wider Si/Al ratios were desilicated and dealuminated using the alkali–acid treatment approach involving hydrothermal alkali pre–etching. Zeolites beta subjected to mesopore modification were characterized by the techniques of XRD, N₂ physisorption, SEM, TEM, EDX, ICP–AES, NH₃–TPD, pyridine FTIR adsorption, and immersion porosimetry to examine changes of structural/textural and acidic properties with initial Si/Al ratio. Benzene alkylation with 1-dodecene was used as a model reaction to elucidate the influence of mediated acidity and texturally mesoporous structure on bulky hydrocarbon transformations. The resulting zeolites beta were shown to have hierarchical porous structures and regular mesoporous size distributions. Initial Si/Al ratios appeared to dominate significant mesoporosity development though no clear threshold of initial Si/Al ratio was

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identified to be more instrumental in forming mesopores. A volumetric fraction of intraparticle to total BJH mesopores proved to reduce with increasing initial Si/Al ratio. The modified zeolites showed more than 95% desilication selectivity whereas less than 5.0% dealumination selectivity upon overall treating processes. T-atoms removal efficiencies relative to areal, volumetric and diametrical factors revealed the coherent characteristics to T-atoms removal selectivities. Moreover, the dependency of benzene alkylation activity on mesopore size distribution was observed from changes of 1-dodecene conversion and LAB selectivity, both of which were promoted by the hierarchical zeolites. Despite both with comparable acidic properties, the typical sample subjected to the combined alkali–acid treatments was shown to have narrowing mesopore size distribution and hence to exhibit the enhanced catalytic performance for selective production of linear alkylbenzenes compared with the purely desilicated sample with broadening mesopore size distribution.

Keywords: Zeolite modification; Hierarchical BEA materials; Desilication selectivity; T-atoms removal efficiency; Benzene alkylation

1. Introduction

Zeolites are crystalline aluminosilicates built of tetrahedral Si and Al atoms connected by bridged O atoms, forming the well-defined microporous structures comprising periodic channels and cavities where possible [1]. Zeolites, in their acid form, are probably the most important heterogeneous catalysts used in the petrochemical and fine chemical industries [2–4]. The advent of new families of synthetic zeolites and zeotypes has considerably broadened the scope of zeolitic catalysis from strong/weak acid promoted hydrocarbon conversions, aromatic alkylation with olefins to special olefin epoxidation [5–7].

However, their small pore size often brings diffusion limitations encountered in zeolite catalysis [8],

rendering low utilization of the zeolite active sites, especially when large molecules are involved [9]. Considerable effort has been directed into hierarchical porous zeolite synthesis in order to enhance the accessibility to intrinsic framework acid sites [10–12]. As noted recently, due to the enhanced accessibility of active sites to bulky reactants the successful application of hierarchical zeolites leads to significant improvements in catalytic performance for hydrocarbon transformations that could be either difficult or impossible to take place on microporous zeolite materials [13–15].

As an alternative route of hierarchical zeolite synthesis, the post-synthetic treatments are considered as a sort of the potential methodology to investigate to mesoporous modification of known microporous zeolites [16]. The post-synthetic strategies able to construct intracrystalline mesopores involve the selective removals of framework T-atoms via steaming [17], acid and/or alkaline treatments [18, 19] in terms of the difference in zeolitic structure and composition [20]. Similar studies in this area are proceeding almost over the zeolite spectrum of industrial interest [21–23], giving rise to substantial improvements in the mesoporous structure and acid site accessibility of modified zeolites [24]. As one can expected, with the vast outreach of technologies crossing disciplinary fields such versatile approaches of surface and structural modification are most likely to continue to feature prominently in the future, but also ultimately extend the studies on secondary porosity engineering of zeolite-based materials.

Founding on relevant investigations on this subject [25–27], selective desilication upon alkaline treatment is the essential method to introduce additional mesopores into zeolite crystals [28, 29]. However, the structurally more significant is only a few zeolites representative of ZSM-5 [30] and mordenite [31], which is possibly due to many restrictive factors such as framework composition, channel low-dimension, crystal orientation, and crystal morphology [32]. In fact, it has now begun to be realized that zeolite

desilication in alkaline media proceeds preferentially from the out side to the inside of crystals [33], which seems reasonable when considering the mass transport mechanism between solid and liquid phases. Therefore, mention should be made of at least two potential issues relevant to both the role of varying framework compositions in selective desilication and the applicability of conventional desilication for diverse zeolite structures. Nonetheless, the selective desilication for textural mesopore formation has proven to be controlled by zeolite compositions [34]. In fact, an optimum Si/Al window of 25–50, for example, was observed for a variety of ZSM-5 zeolites [35]. Qualitative explanation for this is the repulsion of negative charges on lattice Al to the attack of OH^- ions in liquid phase, thereby preventing the extraction of neighboring framework Si atoms [36]. From the perspective of zeolite dissolution kinetics, the reaction rate constant of high silica ZSM-5 dissolving in caustic alkali solution is a linear function of the initial framework Si/Al ratios [37]. However, the radial gradient of aluminum distributions in ZSM-5 crystals has been shown to have a great impact on the mesoporosity development [38], albeit stressing less dependence of mesoporosity on a wide Si/Al range of 12–200 [39].

Principally, the desilication process of zeolitic framework should probably follow the same pattern as the dealumination, i.e., in the same type of lattice defects and mesopore formation. The main difference in this method compared to the dealumination lies in the leaching method by alkaline solutions [40]. However, no completely new materials produced by this method could be persuaded to behave similarly to the mesoporous zeolites synthesized using meso-templating approaches [41]. With regard to the achieved structures, the bulk alkaline leaching toward most microporous zeolites would seem to have encountered difficult to enforce the structurally controlled evolution of both mesopore size distribution and pore geometry [42], except for inevitable losses of crystallinity and microporosity. On the alkaline

treatments of differently structural zeolites, Verboekend et al. [43] investigated the desilication efficiency by correlating the mesopore area generated to the mass of zeolite dissolved, categorizing the latent tendency of mesopore formation in ZSM-5, ITQ-4, ferrierite, and ZSM-22 crystals. Very recently, Liu et al. [44] were also searching for the pore-inducing effect of hydrothermal alkali pre-etching on mesopore formation of zeolites beta and mordenite, demonstrating that the combined alkali-acid treatments allow upgrading the mesoporosity and pore size distribution of the modified zeolites after sequential desilication and dealumination.

In the present work, we further investigate the controllable dimensional effect of mesostructures based on the integrated alkali-acid treatment of zeolites beta with different Si/Al ratios. In zeolite chemistry aspects, the compositional, structural/textural and acidic properties are correlated with framework compositions of the initial zeolites beta. Finally, benzene alkylation with 1-dodecene was used to elucidate the effect of mediated acidity and texturally mesoporous structure on catalytic performance of hierarchical zeolites for bulky molecular reactions.

2. Experimental

2.1. Synthesis and ion-exchange of zeolites beta

Zeolites with BEA structure were synthesized by a seed-mediated growth method, following the procedure described elsewhere [45]. Briefly, Sodium and aluminate (NaAlO_2 , $\text{Al}_2\text{O}_3 > 41.0\%$) was dissolved in an aqueous solution of NaCl, NaOH, and tetraethylammonium hydroxide (TEAOH, 25%). The basic aqueous solution containing NaAlO_2 and TEAOH was added into a diluted silica sol under a vigorous stirring until a homogenized gel phase was formed. Commercial zeolite beta seed crystals (3.0 wt.%, Si/Al = 11.0) were well mixed with the resulting primary gel, followed by a room temperature

aging (pH 12.8). By the same procedure above, a series of starting mixtures were obtained with molar compositions of $1.27 \text{ Na}_2\text{O} : x \text{ SiO}_2 : 1.0 \text{ Al}_2\text{O}_3 : 11.57 \text{ TEAOH} : 730 \text{ H}_2\text{O} : 4.41 \text{ NaCl}$ ($x = 16\text{--}145$). Finally, the synthetic gels that differed in silica to alumina ratio were crystallized in Teflon-lined stainless steel autoclaves at 413 K for 240 h. The resulting solids were filtered, washed, and dried overnight at 383 K. The dried solids were calcined at temperature up to 813 K for 6 h. The zeolites synthesized were transformed into proton form by routine ammonium exchange, followed by calcinations at 823 K for 6 h. The calcined samples **with increasing initial Si/Al ratios** were designated to the first series of parent HB-*n* **zeolites in H-form ($n = 1, 2, \dots, 6$)**.

2.2. Alkaline and acid treatments of H-Beta zeolites

Acidic zeolites beta with different Si/Al ratios were sequentially desilicated and dealuminated in alkaline and acid media according to the following modification scheme. Typically, the initial H-Beta zeolite was wetted using a measured volume of 0.2 M NaOH solution at room temperature. After an incipient wetness impregnation, the wetted solid was then treated in an autoclave (120 ml) under the autogenous pressure at 358 K for 2 h. During the hydrothermal treatment above, a low volume of 0.2 M NaOH solution separated from the solid sample was used for steaming a quasi-equilibrium between the alkaline solution charged below and the liquid phase adsorbed by zeolite powders. Secondly, the hydrothermally alkali-etched sample was exposed to a 0.2 M NaOH solution (33 ml solution per gram zeolite) at 338 K for 0.5 h. The solid undergone the two-step alkaline treatments was filtered and washed until a pH close to 8.0. Finally, the solid obtained above was treated with a buffer solution (pH 2.5) of 1.0 M NH_4Cl and 0.2 M HCl at 353 K for 2 h, and this process was repeated for three times. The resulting sample was transformed into proton form using the identical condition to ammonium exchange. All of the

alkali–acid treated samples with increasing Si/Al ratios were designated to the second series of modified MHB-*n* zeolites in H-form (*n* =1, 2, ..., 6), including the relevant treatment conditions. For a comparison of acidity and catalytic performance with MHB-3, DHB-3 was prepared from HB-3 by conventional alkaline leaching under the identical treatment condition.

2.3. Physicochemical characterization

The structural characterization of various beta parents and their modified samples was performed on a Rigaku D/max–2400 diffractometer with CuK α radiation and a graphite monochromator. Diffraction patterns were obtained by continuous scanning in the angle range of 5–50 °(2 θ), with a step size of 0.02 °(2 θ) and a time per step of 0.4 s. The relative crystallinity for any parent HB(p) is derived from characteristic peak summation between 2 θ_i = 7.63° and 22.2°, namely $I_{\text{re,XRD}} = \sum I_i(\text{p}) / \sum I_i(\text{p})_{\text{max}} (\%)$, while the crystallinity preservation of each treated HB(t) is calculated from the formula: $f_{\text{XRD}} = \sum I_i(\text{t}) / \sum I_i(\text{p}) (\%)$. Nitrogen adsorption measurements were carried out at 77 K in an automatic apparatus Micromeritics ASAP 2420. Before the isotherms acquisition the samples were outgassed for 4 h at 573 K, under vacuum close to $\sim 10^{-4}$ Pa.

Scanning electron microscopy (SEM) images were obtained on a JSM–7500F with an accelerating voltage of 20 kV, while which allowed an energy–dispersive X–ray (EDX) analysis of a selected area scan focalizing on zeolite crystals to leave from amorphous phases. Transmission electron microscopy (TEM) analysis proceeded with a JEOL2000 electron microscope. Samples were diluted in ethanol and were then injected the solution onto a carbon coated copper grid.

Chemical compositions of solid samples and collected filtrates after sequential alkaline and acid treatments were determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES) on

a Perkin–Elmer Optima 3100RL. Before analysis, the alkali–acid treated zeolites were treated by strong caustic fusion at 723 K, followed by dilution with HCl. In addition, the filtrates obtained only by two–step alkaline treatments were analyzed without further acid dilution.

Temperature–programmed desorption of ammonia (NH₃–TPD) was conducted in a Dupont–2000 thermogravimetric analyzer equipped with a thermal conductivity detector. In the adsorption step, the sample (0.25 g) was activated under helium flow at 723 K for 1 h, and then was exposed to He/NH₃ mixture (95/5 vol%) at 423 K for 30 min, followed by a helium purge at the same temperature for 60 min. In the subsequent TPD steps, the temperature of ammonia desorptions was raised from 423 K to 823 K at a ramp rate of 5 K/min. The Brønsted and Lewis acidities of the samples were measured by pyridine FTIR adsorption in Thermo Scientific Nicolet 6700 FT-IR Spectrometer equipped with a high–temperature vacuum chamber. The sample (50 mg) of pre–treatment at 823 K for 1 h was used for pyridine adsorption at 423 K. After the adsorption, the physisorbed pyridine was removed at 423 K under vacuum (10^{−5} kPa) for 40 min. IR spectrum was recorded at room temperature.

2.4. Intraparticle mesoporosity measurement

The compacted grain densities ($\rho_{0,p}$ and $\rho_{0,t}$) of parent (p) and treated (t) samples were determined by water immersion porosimetry (WIP) technique reported previously [46], but substituting anhydrous ethanol for water. Prior to measurements, the self–supporting wafers of samples were ground to fine powders more than 200 meshes and dehydrated at 473 K. The intraparticle mesoporosity ($V'_{\text{meso},t}$) was estimated by the following model established elsewhere [45], where more details have been described.

$$V'_{\text{meso},t} = (1/\rho_{0,t} - 1/\rho_{0,p}) - (1/\rho_{F,t} - 1/\rho_{F,p}) \quad (1)$$

$$\rho_{F,t} = f_{\text{XRD}} \times \rho_{F,t} \quad (2)$$

2.5. Catalytic testing on benzene alkylation with 1-dodecene

Benzene (AR grade) and 1-dodecene (Fluka, GC grade) were used without further purification. Liquid phase alkylation of benzene with 1-dodecene were performed in a continuous flow fixed-bed reactor ($\Phi 10\text{ mm} \times 300\text{ mm}$) equipped with a preheater and a pressurized gas-liquid separator. The extruded catalysts were prepared from the starting materials consisting of NH_4^+ -typed zeolite powder (65 wt. %) and pseudoboehmite binder (35 wt. %). The resulting extrudates were then dried and calcined at 823 K to remove ammonia and water. For each run, the catalyst (1.0 g, equivalent to 16–20 mesh) was charged in the stainless steel reactor, in which the catalyst bars were gradually diluted with identically granular quartz. After activation at 673 K under a N_2 flow, the reactor was fed with a mixture of benzene and 1-dodecene (benzene to 1-dodecene ratio = 9:1 mol/mol) at reaction temperature 413 K, pressure 2.5 MPa, and WHSV = 3.5–5.5 h^{-1} . The liquid samples separated were analyzed on a HP-4890 GC equipped with a standard OV-101 capillary column connected to a flame ionization detector. Conversion of 1-dodecene and selectivity to linear alkylbenzenes (LAB) were determined according to the method reported previously [47].

3. Results and discussion

3.1. Physicochemical characterization

3.1.1. XRD phase and composition

Fig. 1 shows XRD patterns of various beta parents and their alkali-acid treated samples. As can be seen from the Fig. 1a, typical Bragg reflections of the series of HB-*n* samples indicate that the untreated zeolite crystals grew well with microporous BEA structure, though the relative crystallinity ($I_{\text{re, XRD}}$) for high silica HB-5 and HB-6 appears relatively low to those of the coordinate others. The XRD patterns in

Fig. 1b exhibit that the alkali–acid treatments under the identically processing condition led to a dramatic loss of crystallinity throughout the series of treated MHB-*n* samples, which should partially depend on the initial beta crystal perfectibility (reliability $R^2 = 0.81$), as evidenced by the lower crystallinity preservation (f_{XRD}) relative to individual parents. Moreover, for most of the modified samples the minor reflections, typically around 22.58° and 43.68° (2θ) in relation to respective (3 1 1) and (6 0 0) lattice planes, were attenuated or eliminated by this modification procedure.

Fig. 2 illustrates the variations of modified samples in crystallinity preservation (f_{XRD}), Si/Al (t) ratio and weight yield as a function of initial Si/Al (p) ratio. The Si/Al (t) ratio monotonously increased with a descending gradient but remained running over the given reference line. The fact that the combined alkali–acid treatments conducted to an increase in Si/Al (t) ratio is substantially owing to acid extraction to the zeolites already subjected to alkaline treatments. The curves of preservation and yield represent dissimilarly declining trends in the initial Si/Al (p) range, where both of the higher values occur at a lower molar Si/Al (p) ratio around 20. The severe reduction in crystallinity and yield can be explained by the lower concentration of framework aluminum species, since these negatively charged aluminum atoms are able to shield the silicon atoms from extraction during the alkaline treatment [48]. Moreover, the framework aluminum in BEA structure has been known to be less stable than in e.g. MFI and MOR structures [49] due to beta crystal growth with intrinsic stacking faults [50].

3.1.2. Adsorption behavior of hierarchical zeolites beta

Fig. 3 displays N_2 adsorption–desorption isotherms and corresponding BJH pore size distributions of the representative H-Beta parents (HB-1 and HB-2) and alkali–acid treated samples. As displayed in Fig. 3a, the isotherms of HB-1 and HB-2 belong to the type I in BDDT classification, according with the

microporous structure of the two starting samples. Only for relative pressures close to saturation, there is an appreciably enhanced uptake because of H-Beta crystallites aggregation. However, the isotherms obtained for the alkali–acid treated samples exhibit a dual character of transformation from an approximate type I into a typical type IV, since an upwards deviating pseudo–plateau occurs at lower relative pressures but a pronounced type–H4 hysteresis loop suddenly springs up from a middle relative pressure. The N₂ physisorbed differences at high relative pressures were ascribed to crystallites aggregation and large textural pores (see Fig. 4). Evidently, the adsorption behavior observed on the treated samples reveals the degenerative microporosity [51] and considerably developed mesoporosity in contrast to those on the intact microporous zeolites beta. The BJH pore size distribution curves presented in Fig. 3b indicate that the textural mesoporous structures were provided with the most probable mesopore diameters favorably centering at mean 5.57 ± 0.36 nm, and that the curves almost showed the feature of narrower normal distributions.

Structural/textural properties of intact zeolites beta and corresponding alkali–acid treated samples are summarized in Table 1. H-Beta zeolites used as parents differ slightly in the microporosity due to varying crystallinity with silica to alumina ratios of synthetic gels (Fig. 1). By correlating the formed mesoporosity with the initial Si/Al ratio from 9.4 to 64.0, one can conclude that, for the series of treated samples, the data on mesoporous surface area and mesopore volume were reduced gradually by increasing Si/Al ratios, albeit having an appreciably increased mesopore diameter. On the other hand, the microporosity was found fallen upon the alkali–acid treatments, confirmed by only the lower preservation of 52–63 % in microporous surface area and of 48–81 % in micropore volume. However, no further continuous decreases can be observed remarkably in the range of initial Si/Al ratios. The specific surface

area (S_{BET}) and total porosity ($V_{\text{micro}} + V_{\text{meso}}$) individually presented maximum values (i.e. $611 \text{ m}^2 \text{ g}^{-1}$ and $0.743 \text{ cm}^3 \text{ g}^{-1}$) at the lower Si/Al ratios. No clear threshold of initial Si/Al ratios was identified as a significantly optimal window in the wider examined range. The results obtained by XRD and N_2 physisorption indicate that alkali–acid treated H-Beta zeolites were hierarchical zeolite materials with most notable feature of narrowing mesopore size distribution.

In conclusion, these results imply that the H-Beta framework composition plays a predominant role in the controlled desilication, which facilitates the formation of significant mesoporous structures. Moreover, these also bring us to consider that the changing framework Al composition is fearfully likely to impose two different effects on controlled desilication. One involves the extent to which framework aluminum shields silicon from alkaline extraction. The other is the immediate consequence of less stable BEA structures resulting from increasing framework aluminum concentrations. The interplay of positive and negative aspects is responsible for the hierarchical structure, crystallinity and yield, thus possibly leading to the introduction of high proportionally crystalline mesoporosity, for example, in the case of MHB-2 and MHB-3.

3.1.3. Textural mesopore properties upon SEM, TEM and model

The SEM images in Fig. 4 demonstrated the morphological change of various treated samples with an increased initial Si/Al ratio ranging from 9.4 to 64.0. The hierarchically porous materials, as identified by N_2 adsorption, occurred in an aggregation state of beta crystallites [52] and the ovate-like aggregates possessed different particle sizes in spite of the increased Si/Al ratio in the precursor zeolites. The defect-rich domains occurring on particle surface seemed to penetrate into the particle entities due to Al-directed dissolution or etching along defects and boundaries. It was evident that, despite larger losses

of crystallinity and yields, the defect-based strategy taken for fabricating mesoporous structures is more effective for BEA structure than for MFI and MOR structures [53]. Further TEM observation focusing on disaggregate beta crystallites (Fig. 5) elucidated that most of the textural mesopores formed in zeolite beta crystals with normally polycrystalline morphologies were possibly crystalline and thoroughly disordered. Despite the occurrence of intercrystalline mesopores, the major mesoporosity development tended to lie in the extent to which the bulk crystals destructed as a function of parental Si/Al ratio as proposed to play an induced role in intracrystalline mesopore formation, thus coinciding with the XRD characteristics and N₂ adsorption behavior stressed previously.

Just as the observation above by SEM and TEM, the modified zeolites beta represented the complicated crystal morphologies of obviously differing from other zeolites undergone alkaline treatments. Therefore, a volumetric fraction of intraparticle to total N₂-adsorbed mesopores was estimated by drawing upon the model equations (Eq. 1 and Eq. 2) [46, 50] and the relevant parameters in Table 2. This survey is principally concerned with the locations and crystalline constructions of these mesopores. Fig. 6 illustrates the results of intraparticle mesopore volume ($V'_{\text{meso}, t}$) and its fraction in total BJH mesopore volume ($V_{\text{meso}, t}$). Evidently, the curves of $V_{\text{meso}, t}$ and $V'_{\text{meso}, t}$ values synchronously shift over their high peak regions in accordance with the Si/Al range of ca. 10–35. It is reasonable that the intraparticle mesopore volume obtained by the model maintains less than the corresponding BJH mesopore volume throughout the Si/Al ratios. The volumetric fraction of $V'_{\text{meso}, t}$ to $V_{\text{meso}, t}$ tends to a progressive change from 95.3% down to 86.6% when the initial Si/Al ratio changes from 9.4 to 64.0. The results indicates that the majority of textural mesopores identified by BJH method were preferentially located in crystalline environments, and high framework Al concentrations facilitated the formation of

intraparticle mesopores partially due to the hydrothermally alkaline pre-etching enough to occur in zeolite crystals and aggregated particles.

3.2. T-atoms removal selectivities

Al-directed selective desilication relative to dealumination has been currently appreciated in the realm of zeolitic mesoporous modification, but it is unclear about the zeolitic desilication behavior even in alkaline media. In this respect, full experimental investigations on Si and Al compositions of remained and dissolved zeolite phases may be the best access to such foundational realizations of T-atoms removals to impact on mesopore formation. In the case of any H-Beta sample undergone a process of alkali–acid treatment, it seems plausible to express an overall reaction of framework T-atoms removals as following:

In light of this reaction, there exist the Si and Al atom balances respectively available for desilication and dealumination, namely equations:

$$x_0 = x_1 + x_2; y_0 = y_1 + y_2 \quad (4)$$

The Si and Al compositions of the alkali–acid treated samples and their two–step alkaline filtrates are presented in [Table 1](#) and [Fig. 7](#), respectively. With a view to T-atoms balances between the generated solids and corresponding alkaline solution phases, the Si/Al (l) ratio of overall dissolved phases is calculated on the premise that H-Beta exposed to alkaline and acid solutions could have been completely converted into the solid product and dissolving species ([Appendix A](#)). Consequently, selectivities of desilication and dealumination of H-Beta, i.e. the atomic percentages of Si/(Si+Al) and Al/(Si+Al), are derived from the Si/Al (l) ratio of overall dissolved zeolite phases in relation to alkali–acid treatments.

As illustrated in [Fig. 7](#), the Si/Al ratios both in overall dissolved phases and in alkaline filtrates

increased rapidly with the initial Si/Al (p) ratio. The filtrates appeared to have larger Si/Al (f) ratios than the overall dissolved phases, despite exceptionally high Al concentrations in alkaline filtrates, in comparison with the previous observations by Groen et al. [54]. The processes of alkali–acid treatments could reduce the Si/Al ratios of extraction solutions to 0.50–0.65 times over the processes of previous two–step alkaline treatments. The increasing deviation of Si/Al (l) ratios from Si/Al (f) ratios indicated the presence of a decided dealumination effect of acid leaching (coupling with ammonium exchange) on the alkaline–treated zeolites. On T-atoms removal selectivities of H-Beta crystals after alkali–acid treatments, the desilication selectivity was shown to be considerably high (95.2–98.6%) but the dealumination selectivity remained under 4.8% in the initial Si/Al (p) range of 9.4–64.0. Moreover, by the analogous method, extremely high desilication selectivity towards the whole process of two–step alkaline treatments could be obtained from the Si/Al (f) ratio of combined alkaline filtrates, if it was appreciated (omitted in Fig. 7). These results on selective desilication of wide Si/Al H-Beta crystals demonstrated that, even for combined alkali–acid treated processes, framework Si atoms indeed far outperform framework Al atoms in dissolution reactivity, qualitatively coinciding with the previous results of H-Beta alkaline treatments [36, 37, 55].

3.3. T-atoms removal efficiencies

Desilication efficiency has been introduced to relate the mesoporous surface area generated with the mass of zeolite dissolved, viz. $Sm_{\text{meso,t}}/d(\text{weight loss})$, $\text{weight loss} = (1 - \text{yield})$ (wt%), in order to rationalize the optimal post–treatments of hierarchical zeolites [56]. In the present work, this method was extended to T-atoms removal efficiencies (T = Si + Al), viz. $f_{\text{T,S}} = dS_{\text{meso,t}}/d(\text{weight loss})$ and $f_{\text{T,V}} = dV_{\text{meso,t}}/d(\text{weight loss})$, respectively. By drawing upon the BJH algorithm (i.e. $D_{\text{meso,t}} \text{ (nm)} = 4V_{\text{meso,t}}/S_{\text{meso,t}}$), the

one-dimensional factor ($f_{T,D}$) is described as $f_{T,D}(\text{nm}) = 4f_{T,V}/f_{T,S}$, characterizing a diametrical efficiency of T-atoms removals connected with yielding mesopore sizes. Furthermore, the desilication selectivity obtained above enables us to differentiate Si and Al extraction contributions to additional mesoporosity, by which the areal factor $f_{T,S}$ can be separated into $f_{Si,S}$ and $f_{Al,S}$, and analogously, the volumetric $f_{T,V}$ is in relation to $f_{Si,V}$ and $f_{Al,V}$.

As shown in Fig. 8 (a and b), the decrease of framework Al concentration diminishes overall T-atoms removal efficiencies ($f_{T,S}$ and $f_{T,V}$) in respect that Al prevents Si extraction and limited mesopore formation. Analogously, the two desilicated efficiencies ($f_{Si,S}$ and $f_{Si,V}$) were related to net mesoporous surface area and net mesopore volume. However, the changes observed on dealumination efficiencies ($f_{Al,S}$ and $f_{Al,V}$) demonstrate only a minor influence of Si extraction on mesoporous surface area and mesopore volume. For the cases of high-silica zeolites beta, overmuch desilication induced ordinarily by preferentially etching from the external surface of crystals was confirmed to cause notable weight loss [57], resulting in an inefficient mesoporosity development. Thus, the major contribution to mesopore formation originates from extraction of silicon instead of aluminum and that these efficiency factors of T-atoms removals have specific attributes to point out zeolite modification directions to which larger mesoporous surface area or larger mesopore volume will be required.

One-dimensional factors ($f_{T,D}$ and $f_{Si,D}$) statistically represent the diametrical efficiencies, and it should be stressed that they are independent of weight loss founding on their defined expressions above. As shown in Fig. 8c, both of the diametrical efficiencies conformed to the uptrend of mesoporous diameter ($D_{\text{meso},t}$) changes when the Si/Al (p) ratio was increased. Dissimilar to those areal and volumetric factors discussed, these relatively high diametrical factors take place predominantly in the Si/Al (p)

region of more than 40. This is partly because high-silica zeolites beta contain sufficient defect domains of crystalline structure to form the basis of exteriorly strong alkaline etching and partly to ascribe the weakening effect of Al-directed desilication to mesoporous spatial distribution once reducing framework Al concentrations. In conclusion, the T-atoms removal efficiencies represent the coherent characteristics to T-atoms removal selectivities and may play an important role in providing the options both of zeolite compositions and of modification conditions. In addition, the results on structure property, T-atoms removal selectivity and mesoporous formation efficiencies increased our understanding of the zeolitic post-modification chemistry.

3.4. Effect of modification on acidity and catalytic performance

It is generally accepted that aromatic alkylation reactions conform to the acid-catalyzed consecutive reaction mechanism dealing with electrophilic substitution of benzene ring with resulting alkylcarbenium and [58] the Brønsted and Lewis acid sites accessible for larger carbon chains are considered as active species in the cascade catalytic reactions [59]. Alkylation of benzene with 1-dodecene was carried out over the intact and modified zeolites beta. The catalytic performance for this model reaction was examined in order to understand the interplay between the acidity and porous structure of the distinct catalysts since both of which behaved dissimilarly in alkylation reactions involving bulky molecules [60].

Acidic properties of typical H-Beta parents and modified samples are given in Table 3. As expected, there were explicit differences in variation of Si/Al ratios between the approaches of desilication whether followed by dealumination. Combination of desilication and dealumination was instrumental in increasing Si/Al ratios of modified samples (for example, MHB-3 vs. DHB-3), which imposed on zeolitic acidity by removing amorphous Al-rich debris from alkaline pretreated samples. In more details, for each

couple of different Si/Al zeolites the combined treatment procedure led to a decrease in acid sites by ammonia or pyridine adsorption and in the mediate strong acid distribution in 673–773 K. In contrast to those of individual beat parents, total losses of acid amounts of modified zeolites beta were ascribed to the reduction in crystallinity and framework Al concentration, suggested by dropping crystallinity preservations (Fig. 1b) and by increasing Si/Al ratios (Table 1). Meanwhile, the mediate strong acid distribution by NH₃-TPD and the B/L ratio by pyridine chemisorption were more clearly seen to heighten along with an increased initial Si/Al ratio, this may be attributed to the reducing and more isolated Al sites in BEA framework after subsequent dealumination [61].

Table 4 displays the results of liquid phase alkylation of benzene with 1-dodecene over the beta parents and modified zeolite catalysts. The higher WHSV at 4.5 h⁻¹ [62] and shorter time-on-stream (1 h, T-O-S) was adopted in an attempt to differentiate the initial catalytic activity for LAB synthesis among these diversely structural and acidic zeolites. In contrast to the modified zeolites beta, each of intact zeolites represented a lower 1-dodecene conversion accompanied by higher selectivity to LAB isomers, though their acid concentration and acid strength proved relatively high to individual modified samples. Evidently, the unmodified zeolites usually possessed relatively high initial activities of 1-dodecene isomerization promoted by stronger acidity whereas showed poor initial activities of dodecenes converting to LAB isomers due to inevitably diffusion limitations. However, 1-dodecene reacted to LAB isomers more actively over the modified zeolites than over the conventional zeolites beta, while the ratio of 2-LAB to 3–6 LAB isomers was seen to decrease to some extent. Moreover, 1-dodecene conversion for the modified beta catalysts reduced with both decreasing acid concentrations resulting from increased in Si/Al ratios, and that the selectivity to heavy alkylbenzenes were decreased to about one eighth of which

achieved on their parent zeolite catalysts. Combining the effects in slightly weak acidity but regularly hierarchical structure [63], one can thus conclude that mesoporous modification of conventionally microporous BEA zeolites facilitates selective conversion of 1-dodecene to LAB isomers in virtue of enhancing molecular diffusivity through coexisting mesopores, rather than the negative acidic effect that followed. Of trivial reduction in 2-LAB to LAB ratio should be the cause of enlarging mesopores.

Fig. 9 (a and b) illustrates the alkylation results at 6 h T-O-S using the catalysts of unmodified and modified zeolites beta, both of which vary with Si/Al ratio. The results demonstrate that the hierarchical zeolites held desired catalytic performance for benzene alkylation as compared to the microporous zeolites, whether the decrease in 1-dodecene conversion or the increase in LAB selectivity with increasing Si/Al ratios. In addition to LAB isomers, the selectivity to 2-LAB isomers identified as the most favorable precursors for yielding biodegradable surfactants [64] was observed significantly increasing with Si/Al ratio. Also, the results of alkylation reactions over catalysts MHB-1, MHB-3 and MHB-6 were approximately correlated with the mesopore sizes, regardless of relative BET surface area (0.94–1.0) and relative mesopore volume (0.75–1.0) (Fig. 9c). Similar trend of enhanced selectivities to 2-LAB and LAB isomers was observed over these catalysts, where this proved not to be the case for the change of 1-dodecene conversion with Si/Al (p) ratio.

To deliberate on catalyst stability the alkylation reactions proceeded with WHSV at 4.0 h^{-1} over DHB-3 and MHB-3 catalysts. In the first instance, there was not remarkably acidic diversity found in DHB-3 and MHB-3 (Table 8). Of greater difference between the two catalysts was the mesopore size distribution (Fig. A1) arose from the single desilication for DHB-3 and the sequential desilication and dealumination for MHB-3. As illustrated in Fig. 10, the change in 1-dodecene conversion and LAB

selectivity with the operating time was related closely to the different mesoporous structures between DHB-3 and MHB-3. The results suggest that the active sites within MHB-3 were more accessible to bulky molecules than those present in DHB-3 according to previous studies in zeolite modification and catalytic applications [2–5].

It is noticeable that in alkylation performance the MHB-3 characteristic of convergent mesopore size distribution held some advantages over its analog DHB-3 with poor broad pore size distribution, considering the difference in active stability and LAB selectivity, especially in 2-LAB selectivity increasing with time-on-stream. As an analogously structural effect demonstrated by Corma et al. [65], the results observed on MHB-3 substantiated the role of favorably hierarchical porous structures in alleviating intraparticle diffusion resistance to mass transfer. Therefore, the significant improvement in alkylation performance over MHB-3 should be attributed to an improved accessibility and molecular transport to and from the active sites in view of hierarchical porous structures. Moreover, the acidities of modified zeolites were moderated by desilication and dealumination and hence were likely able to suppress coke deposition deactivation of catalysts [66] besides the effect of introducing mesopores.

In short, the results concerning both of alkylation and acidity implicated that the catalytic activity and stability depended not simply on the improved porous structures. The synergistic interaction of regular mesopore structure and relatively mild acidity is essentially the key of modified zeolites beta being able to promote the alkylation reactions.

4. Conclusions

Acidic zeolites with wider Si/Al ratios were modified by alkali–acid treatments, i.e. the sequential combination of alkaline pre-etching, bulk alkaline and acid leaching. H-Beta zeolites that have undergone

desilication and dealumination revealed hierarchical porous structures with regular mesopore size distributions, characteristic of pore sizes centering on 4.6–6.1 nm range, specific surface areas expanding to $611 \text{ m}^2\text{g}^{-1}$ and mesopore volumes up to $0.64 \text{ cm}^3\text{g}^{-1}$. The increase in framework Al concentration appeared to play a predominant role of controlling desilication, leading to the formation of significant mesoporosity with regular mesopore size distribution. No clear threshold of initial Si/Al ratio was identified preferable for mesopore modification under the same treatment condition. The combined treatments to zeolites beta conducted to a moderately increase in Si/Al ratio which proved to impose on zeolitic acidity, and the larger losses of zeolite yields and relative crystallinity were observed to arise from excessive dissolution of parent zeolites.

Besides textural properties of mesopores observed by SEM and TEM, the volumetric fraction of intraparticle to total BJH mesopores decreased from 95.3% to 86.6% as the initial Si/Al ratio increased from 9.4 to 64.0. T-atoms removal selectivities were associated with the Si/Al ratio of dissolved phases. H-BEA zeolites presented selectivities more than 95% for desilication but fewer than 5.0% for dealumination. T-atoms removal efficiencies dealing with the areal, volumetric and diametrical factors reflected the coherent characteristics to T-atoms removal selectivities.

On alkylation of benzene with 1-dodecene, the catalytic performance of hierarchical zeolites beta was shown to be correlated with the accessible mesoporosity and regular mesopore size distribution in the light of 1-dodecene conversion and LAB selectivity both of which were improved with varying time-on-stream. Despite both with comparable acidic properties, the typical modified sample was shown to have narrowing mesopore size distribution and hence to exhibit the enhanced catalytic performance for selective production of linear alkylbenzenes compared with the purely desilicated sample with broadening

mesopore size distribution. Correlation between acidity and hierarchical structure indicated that the synergistic interaction of regular mesopore structure and relatively mild acidity is the key of modified zeolites beta being able to promote the alkylation reactions.

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Appendix A. Deduction on selectivities of T-atoms removals.

Fig. A1. BJH pore size distribution of desilicated DHB-3 and both desilicated and dealuminated MHB-3.

Table A1. Symbols and abbreviations

H-Beta	any parent zeolite beta in proton-form
LAB	linear alkylbenzenes
Si/Al (p)	Si/Al ratio of parent (mol/mol)
Si/Al (t)	Si/Al ratio of treated sample (mol/mol)
Si/Al (l)	Si/Al ratio of overall dissolved zeolite phases (mol/mol)
Si/Al (f)	Si/Al ratio of filtrates from two-step alkaline treatments (mol/mol)
$I_{\text{re, XRD}}(\text{p})$	relative crystallinity of parent H-Beta (%)
$I_{\text{re, XRD}}(\text{t})$	relative crystallinity of treated H-Beta (%)
f_{XRD}	relative crystallinity preservation (%)
S_{BET}	specific surface area by BET model ($\text{m}^2 \text{g}^{-1}$)
S_{micro}	microporous surface area by t -plot method ($\text{m}^2 \text{g}^{-1}$)

S_{meso}	mesoporous surface area by BJH model ($\text{m}^2 \text{g}^{-1}$)
$S_{\text{meso, t}}$	net mesoporous surface area of treated sample by BJH model ($\text{m}^2 \text{g}^{-1}$)
V_{micro}	micropore volume by t -plot method ($\text{cm}^3 \text{g}^{-1}$)
V_{meso}	mesopore volume of any sample by BJH model ($\text{cm}^3 \text{g}^{-1}$)
$V_{\text{meso, t}}$	net mesopore volume of treated sample by BJH model ($\text{cm}^3 \text{g}^{-1}$)
$V'_{\text{meso, t}}$	intraparticle mesopore volume by calculation model ($\text{cm}^3 \text{g}^{-1}$)
D_{meso}	most probable mesopore diameter by BJH model (nm)
$D_{\text{meso, t}}$	most probable mesopore diameter of treated sample by BJH model (nm)
FD_{BEA}	BEA framework density (T-atom number / $1000 \text{\AA}^3$)
$\rho_{F, p}$	framework mass density of parent H-Beta (g cm^{-3})
$\rho_{F, t}$	framework mass density of treated H-Beta (g cm^{-3})
$\rho_{0, p}$	anhydrous grain density of parent H-Beta (g cm^{-3})
$\rho_{0, t}$	anhydrous grain density of treated H-Beta (g cm^{-3})
$f_{\text{T,S}}$	T-atoms removal efficiency related to net mesoporous surface area ($\text{m}^2 \text{g}^{-1} \%^{-1}$)
$f_{\text{T,V}}$	T-atoms removal efficiency related to net mesopore volume ($\text{cm}^3 \text{g}^{-1} \%^{-1}$)
$f_{\text{Si,S}}$	desilicated efficiency related to net mesoporous surface area ($\text{m}^2 \text{g}^{-1} \%^{-1}$)
$f_{\text{Si,V}}$	desilicated efficiency related to net mesopore volume ($\text{cm}^3 \text{g}^{-1} \%^{-1}$)
$f_{\text{Al,S}}$	dealuminated efficiency related to net mesoporous surface area ($\text{m}^2 \text{g}^{-1} \%^{-1}$)
$f_{\text{Al,V}}$	dealuminated efficiency related to net mesopore volume ($\text{cm}^3 \text{g}^{-1} \%^{-1}$)
$f_{\text{T,D}}$	one-dimensional factor of T-atoms removals related to pore diameter (nm)
$f_{\text{Si,D}}$	one-dimensional factor of desilication related to pore diameter (nm)

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Figure 1

Fig. 1. XRD patterns of (a) parent H-Beta zeolites (HB-*n*) with various Si/Al ratios and (b) their modified samples (MHB-*n*) upon the same alkali–acid treatment.

Figure 2

Fig. 2. Crystallinity preservation (f_{XRD}), weight yield or atomic Si/Al (t) ratio of modified zeolites beta as a function of the initial Si/Al (p) ratio of H-Beta zeolites.

Figure 3

Fig. 3. N₂ adsorption–desorption isotherms (a) and BJH pore size distributions (b) of H-Beta parents (solid symbols) and modified zeolite samples.

Figure 4

Fig. 4 SEM images of hierarchical zeolites beta (MHB-*n*) obtained from H-Beta parents with Si/Al (p) ratios of 9.4, 16.3, 27.0, 35.4, 48.7, and 64.0 in sequence.

Figure 5

Fig. 5 TEM micrographs of hierarchical zeolites beta (MHB-*n*) obtained from H-Beta parents with different Si/Al ratios.

Figure 6

Fig. 6. Correlation of intracrystalline mesopore volume ($V'_{\text{meso},t}$) with BJH mesopore volume ($V_{\text{meso},t}$) and

the fraction of $V'_{\text{meso},t}$ to $V_{\text{meso},t}$ as a function of initial Si/Al(p) ratio.

Figure 7

Fig. 7. T-atoms removal selectivities derived from Si/Al (l) ratios of overall dissolved phases upon combined alkali–acid treatments, where Si/Al (f) ratios were obtained from the filtrates of only two–step alkaline treatments.

Figure 8

Fig. 8. T-atoms removal efficiencies of various Si/Al H-Beta zeolites varying with initial Si/Al (p) ratio, where the factors were related (a) to mesoporous surface area, (b) to mesopore volume, and (c) to mesopore diameter.

Figure 9

Fig. 9. Catalytic performance of (a) H-Beta parents and (b, c) modified samples for benzene alkylation with 1-dodecene as a function of Si/Al ratio and mesopore size (reaction temperature 413 K, pressure 2.5 MPa, WHSV= 4.5 h⁻¹, molar benzene/1-dodecene = 9/1, and 6 h T-O-S).

Figure 10

Fig. 10. (a) 1-Dodecene conversion and (b) selectivities to 2-LAB and total LAB isomers over DHB-3 and MHB-3 along with time-on-stream (reaction temperature 413 K, pressure 2.5 MPa, WHSV= 4.0 h⁻¹, and feed benzene to 1-dodecene molar ratio = 9/1).

Table 1

Chemical compositions and textural properties of parent H-Beta zeolites (HB-*n*) and corresponding modified samples (MHB-*n*) by sequential alkali and acid treatments.

Sample	Si/Al ^a	S _{BET} ^b	S _{micro} ^c	V _{micro} ^c	S _{meso} ^d	V _{meso} ^d	D _{meso} ^d
	/molar ratio	/m ² g ⁻¹	/m ² g ⁻¹	/cm ³ g ⁻¹	/m ² g ⁻¹	/cm ³ g ⁻¹	/nm
HB-1	9.4	522.7	463.2	0.203	14.0	0.019	< 1.7
MHB-1	19.6	598.2	238.5	0.115	354.7	0.578	4.56
HB-2	16.3	515.5	385.1	0.221	28.2	0.098	< 1.7
MHB-2	32.4	647.9	245.5	0.107	365.5	0.636	5.51
HB-3	27.0	515.7	436.9	0.207	17.2	0.071	< 1.7
MHB-3	43.2	629.6	240.3	0.114	343.2	0.622	5.67
HB-4	35.4	518.1	439.1	0.195	13.9	0.026	< 1.7
MHB-4	46.8	592.3	231.2	0.127	320.5	0.543	5.76
HB-5	48.7	536.4	454.7	0.191	38.1	0.026	< 1.7
MHB-5	56.9	623.8	250.6	0.136	317.4	0.524	5.82
HB-6	64.0	502.5	428.6	0.188	23.6	0.029	3.08
MHB-6	68.5	591.4	244.2	0.152	282.4	0.466	6.12
DHB-3	24.5	578.5	225.4	0.108	298.6	0.587	6.8 (48 ^e)

^a Chemical composition by ICP–AES.

^b Specific surface area (S_{BET}) by BET method.

^c Microporous surface area (S_{micro}) and micropore volume (V_{micro}) by *t*–plot method.

^d Mesoporous surface area (S_{meso}), mesopore volume (V_{meso}) and mesopore diameter (D_{meso}) by BJH model.

^e Only desilicated DHB-3 provided with dispersively distributed secondary pores (see [Fig. A1](#)).

Table 2

Parameters of the model equation established for estimating the fraction of intracrystalline mesoporosity of modified zeolites beta in proton form.

Sample	Yield /wt. %	f_{XRD} /%	$\rho_{\text{F}, \text{p}}$ ^a /g cm ⁻³	$\rho_{\text{F}, \text{t}}$ ^b /g cm ⁻³	$\rho_{0, \text{p}}$ ^c /g cm ⁻³	$\rho_{0, \text{t}}$ ^d /g cm ⁻³
MHB-1	56.6	60.5	1.526407	0.924	0.791±0.013	0.446±0.013
MHB-2	61.7	72.9	1.526407	1.113	0.795±0.012	0.475±0.012
MHB-3	45.7	69.7	1.526407	1.063	0.798±0.012	0.469±0.012
MHB-4	47.8	55.7	1.526407	0.849	0.811±0.013	0.442±0.014
MHB-5	43.7	51.8	1.526407	0.791	0.813±0.013	0.432±0.015
MHB-6	42.8	48.5	1.526407	0.740	0.816±0.013	0.430±0.015

^a Framework mass density ($\rho_{\text{F}, \text{p}}$) of parent H-Beta zeolite is derived from BEA framework density ($FD_{\text{BEA}} = 13.5 \text{ (T)/1000\AA}^3$ [50]), which is considered as a constant independent of framework Si/Al ratios since M ([SiO₄]) is equivalent to M ([AlO₄]⁻ conjugated with H⁺) on framework irrespective of the effect of extra-framework Al species.

^b Framework mass density ($\rho_{\text{F}, \text{t}}$) is correlated with the crystallographic degeneration factor (f_{XRD}), i.e. $\rho_{\text{F}, \text{t}} = f_{\text{XRD}} \times \rho_{\text{F}, \text{p}}$, wherein $f_{\text{XRD}} = I_{\text{re}, \text{XRD}}(\text{t}) / I_{\text{re}, \text{XRD}}(\text{p})$.

^c Anhydrous grain density of parent H-Beta zeolite.

^d Anhydrous grain density of treated H-Beta zeolite.

Table 3

Acidic properties determined by NH₃-TPD and pyridine FTIR adsorption for H-Beta parents and their modified samples.

Sample	TPD NH ₃ /mmol g ⁻¹	Acid distribution (NH ₃ mol %)			Acidity (pyridine mmol g ⁻¹)		
		423–673 K	673–773 K	>773 K	B acid	L acid	B/L ratio ^a
HB-1	0.57	55.5	40.2	4.3	0.36	0.20	1.80
MHB-1	0.45	57.6	39.3	3.1	0.31	0.13	2.38
HB-3	0.41	51.7	41.8	6.5	0.26	0.14	1.86
MHB-3	0.38	55.3	40.2	4.5	0.25	0.12	2.08
HB-6	0.32	48.6	43.5	7.9	0.22	0.10	2.20
MHB-6	0.29	50.8	45.1	4.1	0.19	0.09	2.11
DHB-3	0.40	58.7	37.7	3.6	0.24	0.16	1.50

^a Molar ratio of Brønsted (B) to Lewis (L) acid sites measured by pyridine FTIR adsorption.

Table 4

Results of benzene alkylation with 1-dodecene over H-Beta parents and their modified samples at 413 K, 2.5 MPa, WHSV = 4.5 h⁻¹, benzene to 1-dodecene molar ratio = 9/1, and 1 h T–O–S.

Zeolite catalyst ^a	HB-1	MHB-1	HB-3	MHB-3	HB-6	MHB-6
Pore size by BJH (nm)	< 1.7	4.6	< 1.7	5.7	3.1 ^b	6.1
1-Dodecene conversion (C%)	78.0	98.3	75.0	95.6	69.8	87.4
Product selectivity (C%)						
Dodecene isomers	38.6	3.1	24.7	3.3	21.8	3.8
LAB isomers ^c	60.2	96.8	74.5	96.6	77.4	96.2
Heavy hydrocarbons (>C ₁₂)	1.2	0.1	0.8	0.1	0.8	0.0
LAB isomer selectivity (C%)						
2-LAB	24.8	36.1	31.1	39.7	34.1	39.8
3–6 LAB	35.4	60.7	43.4	56.9	43.3	56.4
2-LAB/3–6 LAB (mol/mol)	0.70	0.59	0.72	0.70	0.79	0.71

^a Be composed of ca. 70 wt.% protonic zeolite and ca. 30 wt.% γ–Al₂O₃.

^b Minor secondary mesopores resulting from crystallite agglomeration.

^c Term LAB denotes linear alkylbenzenes.

Graphical abstract