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Toward industrial catalysis of zeolite for linear alkylbenzene synthesis: A mini review

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ABSTRACT

In this min-review, we discuss the potential of zeolite for industrial linear alkylbenzene (LAB) synthesis with special focus on 2-LAB isomer selectivity control and catalytic stability improvement. Some viable post treatment methods, including general dealumination and desilication modification, as well as delamination and pillaring methods, have been demonstrated for mesoporosity generation and catalytic property improvement particularly LAB isomer selectivity and catalytic stability.

1. Pursuing environmental friendly LAB process

Alkylbenzene sulfonate is employed in a wide variety of applications ranging from human daily life to industrial wetting and detergency. As one of the main classes of anionic surfactants, everything in alkylbenzene sulfonate industry ranging from detergent applications to technology advancement is associated strongly with environmental concerns. Linear alkylbenzene sulphonate (LAS) is a group of skeletal isomers with a general chemical formula represented as $C_6H_5C_xH_{2x+1}$, where x is between 8 and 16. The position of phenyl group and the alkyl chain length of LAS are crucial to biodegradability and solvency [1]. There are many skeletal isomers named according to the number of carbon attached to benzene ring. For example, the molecular structures of six dodecyl-benzene skeletal isomers are shown in Sketch 1 . Among LAS isomers, sodium 2-phenylalkane sulfonate (Na-2-LAS) has the greatest biodegradability [2] but the lowest solvency. Therefore, optimum composition of Na-2-LAB is a compromise of biodegradability and solvency.

Fig. 1 depicts the industrial production scheme of linear alkylbenzene (LAB) and LAS comprising production of LAB precursor and sulfonation of LAB. LAB is produced from alkylation of benzene and linear mono-olefin. The linear mono-olefin could be produced from either n-paraffin dehydrogenation; or ethylene oligomerization via SHOP method, Ziegler method, and peaked Ziegler method. Compositions of linear mono-olefin vary with the production process in terms of linear/branched olefin composition, carbon number in the range of C_8–C_{18}, paraffin and aromatics contents, di-olefin impurity, etc.

LAB synthesis by alkylation of benzene with long chain olefin is an acid catalyzed reaction [3]. Many acid catalysts have been reported for LAB catalysis, such as zeolite [4–6], sulfated metal oxides [7], ionic liquid [8], ion exchange resin [9], etc. The early alkylation catalyst $AlCl_3$ of the industrial process was replaced by HF catalyst at the end of the 60s; and immediately it became the preferred technology worldwide for LAB production. Until 1995 UOP commercialized the first solid acid catalyzed LAB technology using fixed-bed reactor, under the trade name of Detal. The new Detal technology offers considerable advantages over the existing HF process particularly improving process safety by elimination of HF acid handling and disposal; and process simplification. Zeolite as one family of acidic solid material can be useful for the catalysis of LAB synthesis. Many zeolites have been studied in searching for their catalytic potentials for LAB synthesis [4–6]. Nevertheless, several major issues should be addressed particularly optimum isomer distribution and catalytic stability in dealing with stringent feed specifications for successful industrialization of zeolite catalysis for LAB process. The present mini-review will discuss the development of zeolite catalyst for LAB synthesis particularly from industrial process perspective in terms of porosity effect and feed specification.

2. Controlling LAB isomer distribution

Fig. 2 depicts LAB isomer selectivity by catalysis of various catalysts. In terms of 2-LAB selectivity, all the catalysts could be classified into three categories, homogeneous catalysis, non-zeolite catalyst and zeolite. Among all the catalysts, HF exhibits the greatest

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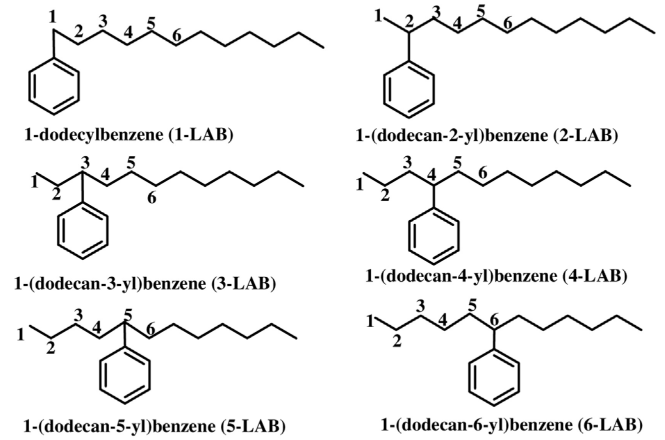


Sketch 1. Molecular structures of linear alkylbenzene skeletal isomers 1-dodecylebenzene (1-LAB); 1-(dodecan-2-yl)benzene (2-LAB); 1-(dodecan-3-yl)benzene (3-LAB); 1-(dodecan-4-yl)benzene (4-LAB); 1-(dodecan-5-yl)benzene (5-LAB); 1-(dodecan-6-yl) benzene (6-LAB).

2-LAB isomer selectivity less than 20%. All the heterogeneous catalysts exhibit increasing 2-LAB selectivity in the compensation of 5- and 6-LAB ones. The non-zeolite catalysts, such as $AlCl_3$, amorphous aluminosilicate, activated clay [10], supported metal oxide, and non-porous resin catalyst, all produce around 35% 2-LAB, 30% 5- and 6- LAB selectivity. When zeolite catalyst is used, 2-LAB selectivity increases in general with decreasing micropore opening [6]. In extreme case, MOR and MTW catalyze exclusively 2- and 3- LAB isomers with 2-LAB selectivity of 76% and 92%, respectively [11]. MOR and MTW both possess one-dimensional channel with a 12-oxygen membered ring (12-MR) pore opening size of 6.5 × 7.0 Å and 5.6 × 6.0 Å, respectively (Table 1). Another one-dimensional zeolite LTL with pore opening size of 7.0 Å catalyzed a lower 2-LAB selectivity of 40%. On the other hand, both FAU with cubic topology and EMT with hexagonal topology possess three-directional channel and cavity systems with pore opening size of 7.4 and 7.1 Å, respectively. The subtle difference in the pore structure results in a dramatic increase of 2-LAB isomer selectivity from 28% for FAU to 42% for EMT [12].

MWW zeolite is a family of layer zeolite including MCM-22, ITQ-2 and MCM-36 zeolite. They have hierarchical pore structure in common consisting of two independent two-dimensional pore systems and external isolated 12-MR cage (so-called "half cup", denoted as EC-12) located on the inter-crystalline surface. One sinusoidal channel contained in layers has 10-oxygen membered ring (10-MR) pore opening, and the other channel located between layers is constructed with 12-MR supercage (0.71 × 0.71 × 1.81 nm) having 10-MR windows (denoted as C10-12) [13]. Both C10-12 and EC-12 are catalytic active sites during LAB synthesis. The delaminated ITQ-2 zeolite possesses extraordinary mesoporous surface area [14] and thus increasing EC-12 sites. The pillared MCM-36 zeolite has more open supercage (the enlarged C10-12) with enlarged 10-MR window [15]. The pillared MCM-36 zeolite has more open supercage with enlarged window [16]. As shown in Fig. 1, MWW zeolite family bearing active sites located at EC-12 and C10-12 site catalyzes a 2-LAB isomer selectivity comparable to that over BTW zeolite. Among the MWW zeolite, ITQ-2 catalyzes the lowest 2-

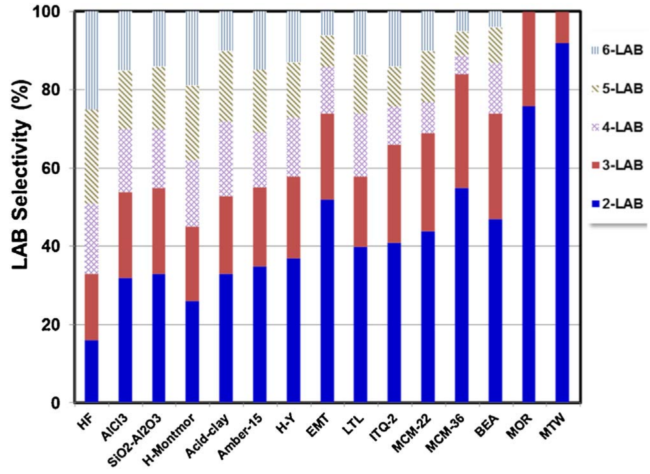


Fig. 2. LAB isomer selectivity generated from zeolite catalysis during LAB synthesis.

Table 1
Representative zeolite structures for the catalysis of LAB synthesis.

Catalyst	IZA code[a]	Micropore Structure[b]
H-Y	FAU	(12MR) 7.4 Å
EMT	EMT	(12MR) 7.4 × 6.5 Å
L	LTL	(12MR) 7.1 Å
H-β	BEA	(12MR) 6.6 × 6.7; 5.6 × 5.6 Å
H-M	MOR	(12MR) 6.5 × 7.0 Å
ZSM-12	MTW	(12MR) 5.6 × 6.0 Å
H-β	BEA	(12MR) 6.6 × 6.7; 5.6 × 5.6 Å
MCM-22, ITQ-2, MCM-36	MWW	(10MR) 4.0 × 5.5 Å; (10–12MR) 7.1 × 7.1 × 18.2 Å with 4.1 × 5.1 Å opening (12MR) 7.1 × 7.1 Å

[a] IZC Code in parenthesis.

[b] 12MR: 12-oxygen membered ring; 10MR: 10-oxygen membered ring.

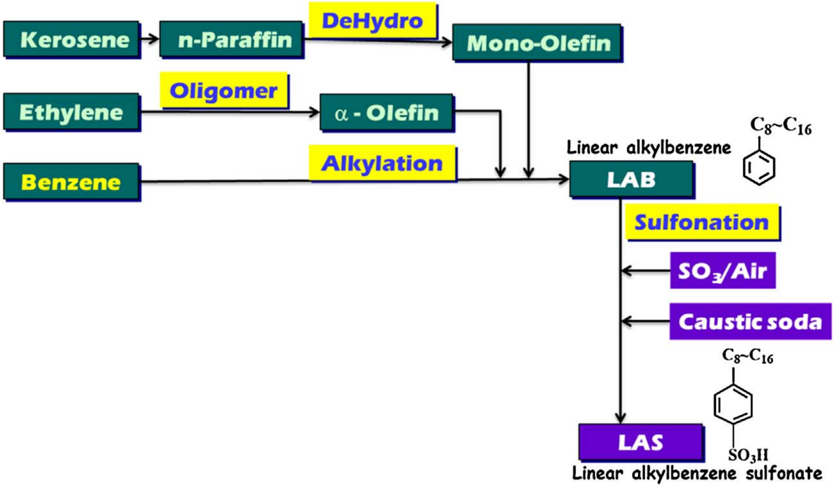


Fig. 1. Industrial LAB (linear alkylbenzene) and LAS (Linear alkylbenzene sulphonate) process scheme.

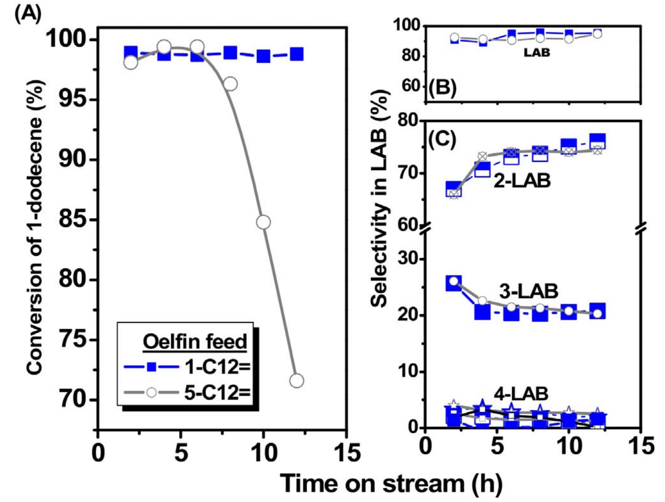


Fig. 3. (A) 1-Dodecene conversion, (B) LAB product selectivity, and (C) LAB isomer selectivity during LAB synthesis from 1- or 5- dodecene over CM21 (MOR zeolite) along with time-on-stream (reaction temperature 433 K; pressure 2068 kPa; WHSV 4 h^{-1}; H_2/total HC ratio 3.0 mol/mol; feed composition: benzene/n-decane/dodecene = 8: 0.5: 1 mol).

LAB but high 6-LAB isomer selectivity, and the pillared MCM-36 with the enlarged C10-12 site produces the greatest 2-LAB isomer selectivity.

In referring to the LAB synthesis from 1-dodecene by using MOR catalyst, alkylation with 5-dodecene had a faster deactivation rate but about the same LAB product selectivity and LAB isomer product distribution (Fig. 3). Clearly, there is no olefin molecular structure effect on the LAB isomer product selectivity. Presumably, 1- and 5-dodecene both isomerized into other olefin isomers quickly to thermodynamic equilibrium composition, therefore same LAB isomer product distribution was obtained. However, referring to Scheme 1, dodecene oligomerization competed with benzene alkylation. As a result of bulkier oligomer dimension, 5-dodecene oligomerization empowered severer deactivation effect than 1-dodecene oligomer, leading to faster deactivation in using 5-dodecene feed.

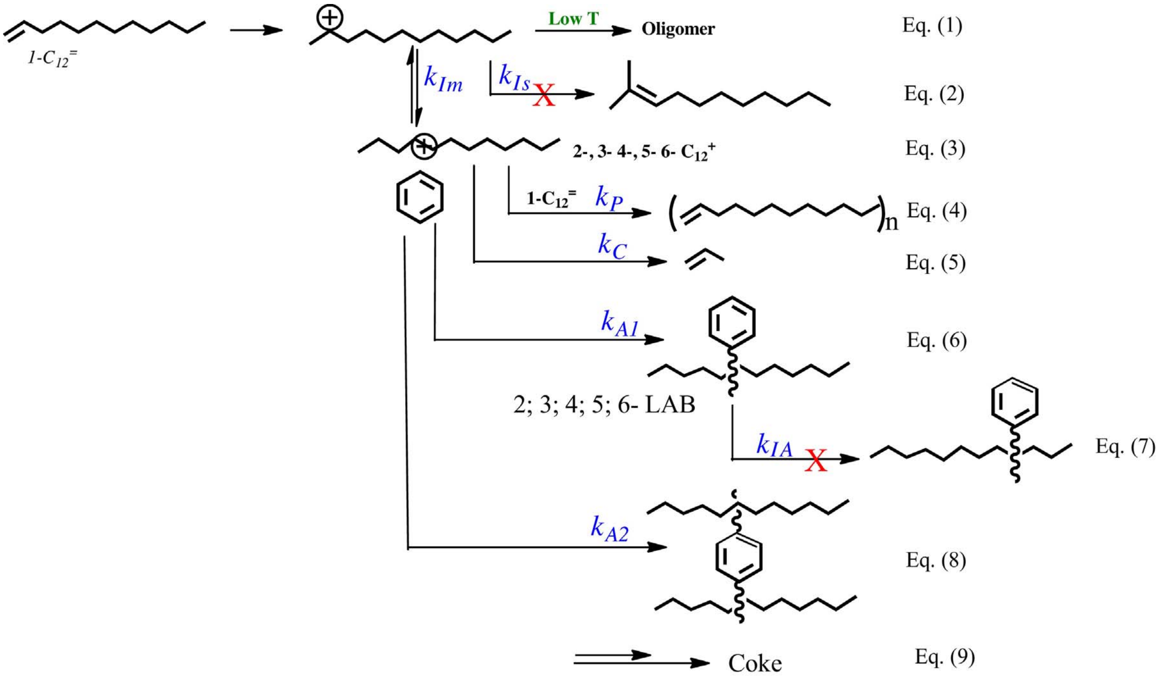
Scheme 1 proposes a possible reaction network during LAB synthesis over solid acid catalysts. Olefin protonation is believed to be the initialization reaction, following with double bond migration (Eq. (2)) by limiting skeletal isomerization (Eq. (1)) and also skeletal isomerization of LAB (Eq. (7)). Some side reactions would take place in accompany with the main mono-alkylation (Eq. (6)), including olefin oligomerization (Eq. (4)), cracking (Eq. (5)), multi-alkylation (Eq. (8)) and alkylbenzene coking (Eq. (9)).

Assuming that the entire LAB isomers are formed as primary products from alkylation reaction, the product selectivity of LAB isomer would depend on the relative rate constants of double bond migration versus alkylation as well as the relative diffusion rate of LAB isomer in the porous catalyst. As shown in Fig. 2, alkylation of 1-dodecene and 5-dodecene produced all the same LAB isomer selectivity, suggesting fast isomerization of internal olefin and alkylation inside zeolite pore. Thus, 2-LAB isomer selectivity depends strongly on the diffusivity of LAB isomer. As shown in Fig. 1, LAB isomer selectivity could be correlated with the pore opening size of zeolite.

3. Improving catalytic stability

3.1. Effect of zeolite textural property

Fig. 4 depicts the catalytic performances of MOR and MCM-22 samples at reaction temperature of 433 K using a benzene − olefin mixture feed at benzene/olefin (B/O) ratio of 10 (denoted as R10). In case of MOR, one commercial MOR catalyst ZM10 showed severe deactivation with extending time-on-stream (TOS). The deactivation is arisen from sensible plugging of the one dimensional pore channel by coke deposition. However, other commercial MOR samples CM21 and CM30 catalyzed a much more stable activity, at dodecene conversion of 100%. All three MOR catalysts produced similarly high LAB product selectivity of 97% at low multi-alkylation side-product selectivity (Fig. 4B), as well as high 2- and 3- LAB isomer selectivity of 64% and 35%, respectively (Fig. 4C) [17,18]. As shown in Table 2, MOR sample CM21, CM30 and ZM10 possessed mesopores of 9, 11 and 5 nm, respectively. Coke precursor is supposedly to be heavy alkylates such as dialkylbenzene. The improved catalytic stability of CM21 and CM30 could be attributed to the enhanced diffusivity of coke precursors from the mordenite surface through enlarged mesopores [18].



Scheme 1. LAB reaction network (Modified from [5]).

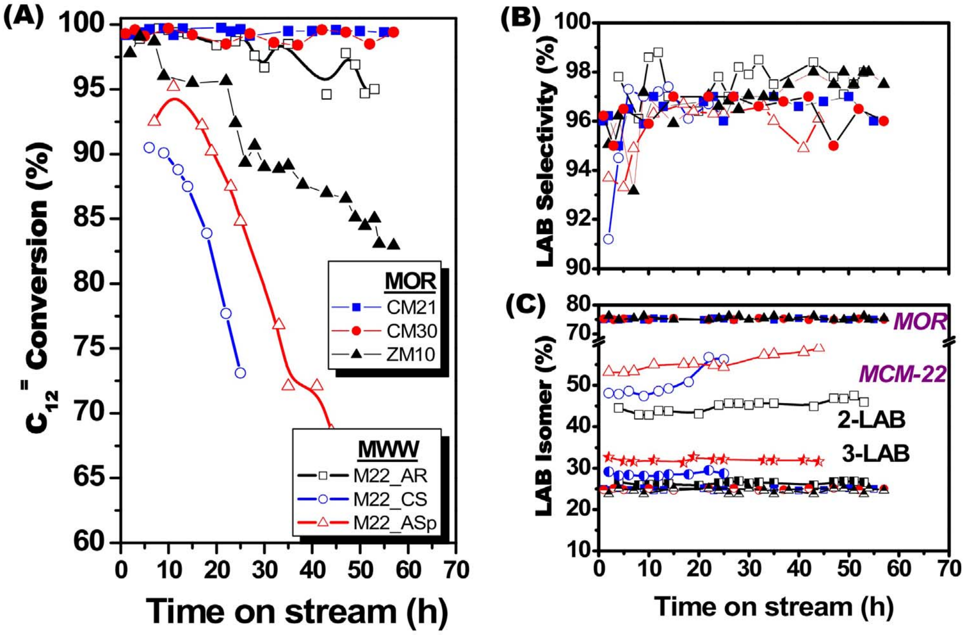


Fig. 4. (A) 1-Dodecene conversion, (B) LAB product selectivity, and (C) LAB isomer selectivity during LAB synthesis over different MOR and MCM-22 zeolite samples along with time-on-stream (reaction temperature 433 K; pressure 2068 kPa; WHSV 4 h^{-1}; H_2/total HC ratio 3.0 mol/mol; feed composition: benzene/n-decane/1-dodecene = 10: 0.5: 1 mol).

Table 2
Textural properties of various mordenite samples.

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{meso} (m^2/g)	Mesopore V_{meso} (cm^3/g)	Mesopore Pore Size (nm)
Parent mordenite					
ZM10	434	400	34	0.03	5.1
CM21	443	389	54	0.10	8.5
CM30	429	378	60	0.12	11.1
Dealuminated mordenite					
S-ZM10	419	336	83	0.07	3.9
A-ZM10	525	325	201	0.17	4.3
SA-ZM10	373	237	136	0.23	5.6
Desilicated mordenite					
02d30*1ZM10	454	391	64	0.08	6.9
Parent MCM-22					
M22_AR	461.5	166.9	294.6	0.36	9.5
M22_ASp	429.7	328.8	100.9	0.12	6.9
M22_CS	467.9	388.6	79.3	0.07	4.9
MWW zeolite					
IQ2_CS-90	772.9	116.6	656.3	0.73	7.8
M36_CS	606.3	169.2	437.1	0.40	4.0

On the other hand, three MCM-22 samples denoted as M22_CS, M22_AR and M22_ASp were prepared from colloidal silica, aerosol and alumina-silicate microsphere, respectively [19]. Among the three samples, M22_AR possessed the greatest external surface area, the largest pore volume and mesopore size (Table 2). While M22_AR was catalytic stable reaching a dodecene conversion nearly 100%, M22_CS and M22_ASp both deactivated along with increasing TOS (Fig. 4A). All the three MCM-22 samples catalyzed around 97% LAB product selectivity with slightly different 2-LAB isomer selectivity in the range of 45% (M22_AR) − 58% (M22_ASp). The difference in LAB isomer selectivity could be resulted from different external surface area associated with supercage.

3.2. Zeolite modification

Most of zeolites were reported not stable during LAB synthesis. As discussed above, textural property and mesopore structure have strong effect on the catalytic stability of zeolite in LAB synthesis. The LAB synthesis reaction is under mass transport control inside the micropores of zeolites. Zeolite mesoporosity could be generated from direct synthesis through removal of hard template or from leaching of framework T atoms during post treatment. In a recent review, Valtchev et al. [20] noted the unattended modification in mesoporosity from structural defects during general post-treatments such as thermal activation (drying and calcination), chemical activation (template removal processes), functionalization (surface modification), metal incorporation (ion exchange and impregnation). Skeletal aluminum or silicon could be selectively removed from zeolite framework by means of acid or base post treatment, namely dealumination or desilication, respectively.

The textural property of MOR sample ZM10 was modified by dealumination using high temperature steam, low temperature HNO_3 treatment or sequential steam-acid treatment (namely S-ZM10, A-ZM10 and SA-ZM10) [18,21]. Alternatively, ZM10 was post-treated with NaOH solution for desilication (denoted 02d30*1ZM10, a desilicated mordenite sample prepared from parent MOR sample ZM10 by NaOH treatment for 30 min for one cycle [18]). Multiple cycle post-treatment has been demonstrated [22]. The mesopore size of ZM-10 at original 5.1 nm was reduced down to 4 nm after dealumination post-treatment; but was enlarged greater than 8 nm. As shown in Fig. 5, the dealuminated MOR, such as S-ZM10, A-ZM10 and SA-ZM10, exhibited deteriorated catalytic stability (Fig. 5A) keeping the original LAB product (Fig. 5B) and product isomer selectivity (Fig. 5C). In contrast, the silicate 02d30*1ZM10 sample exhibited significantly improved catalytic stability (Fig. 5A) with the same product selectivity (Fig. 5B and C). The improved stability of the alkaline-treated mordenite can be attributed to the enhanced diffusivities of oligomers and coke precursors due to the enlarged mesopore size, ca. 7 nm.

The layered zeolite MWW family has MCM-22, ITQ-2 and MCM-36 zeolite members. The as-synthesized MCM-22 precursor (MCM-22(p)) could be converted by calcination to form three-dimensional MCM-22 zeolite. On the other hand, MCM-22(p) could be delaminated into ITQ-2

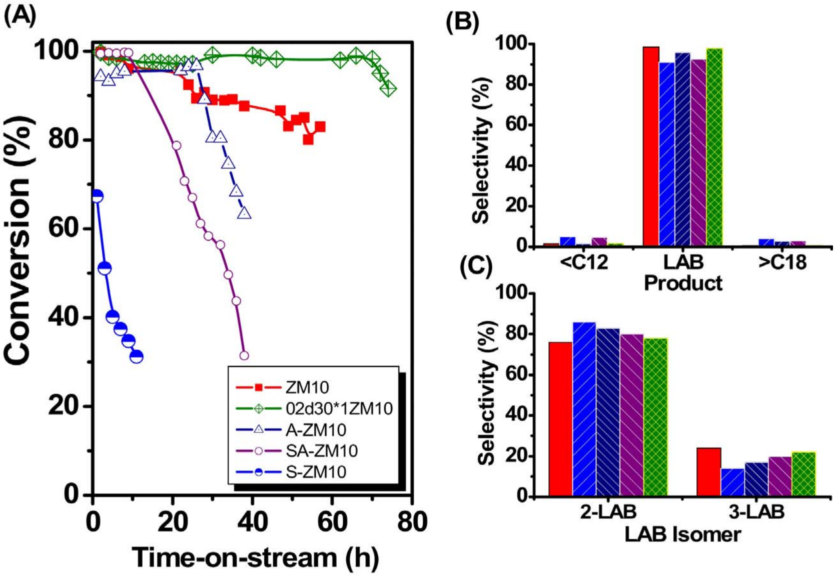


Fig. 5. 1-Dodecene conversion over various modified ZM10 (MOR zeolite) along with time-on-stream (reaction temperature 433 K; pressure 2170 kPa; WHSV 4 h^{-1}; H_2/total HC ratio 3.0 mol/mol; feed composition: benzene/n-decane/1-dodecene = 10: 0.5: 1 mol).

zeolite, or pillared to form MCM-36 zeolite. The active sites of MWW zeolite are located in three different pores, namely C10-10 in the two-dimensional pore channel, C10-12 site in the 12-MR supercage with 10-MR window, and EC-12 site in the external "half cup". In reference to MCM-22, the delaminated ITQ-2 zeolite possesses increasing EC-12 sites in compensation of C10-12 site number, and the pillared MCM-36 zeolite has more open supercage (the C10-12 site) with enlarged window.

As shown in Fig. 6, during the benzene alkylation at low B/O ratio of 10 and reaction temperature of 433 K, while M22_CS was not catalytic stable, IQ2_CS90 and M36_CS90 both exhibited much improved catalytic stability maintaining extreme high conversion (Fig. 4). The pillared M36_CS exhibited increasing di-alkylate by-products formation and a higher 2-LAB isomer selectivity. The improved catalytic stability of IQ2_CS90 and M36_CS in reference to M22_CS is due to increasing mesoporosity which is associated with increasing EC-12 site and enlarged C10-12 site, respectively, for increasing diffusivity of LAB product and suppressing LAB accumulation (Eq. (6), Eq. (9)). As for M36_CS, the enlarged C10-12 site could catalyze more favorably multi-alkylation (Eq. (8)) for increasing dialkylate yield.

4. Engineering approach for improving catalytic stability

4.1. Effect of operating condition

The reactant feed for LAB synthesis is benzene − olefin mixture. Tsai et al. reported that catalytic stability of zeolite in LAB synthesis could be improved at reasonable high reaction temperatures [17]. The intriguing property could be attributed to inhibition of olefin oligomerization (Eq. (4)) at elevated reaction temperature. On the other hand, increasing d ratio could inhibit olefin oligomerization and multi-alkylation (Eq. (8)), and wash away coke precursors. Therefore the

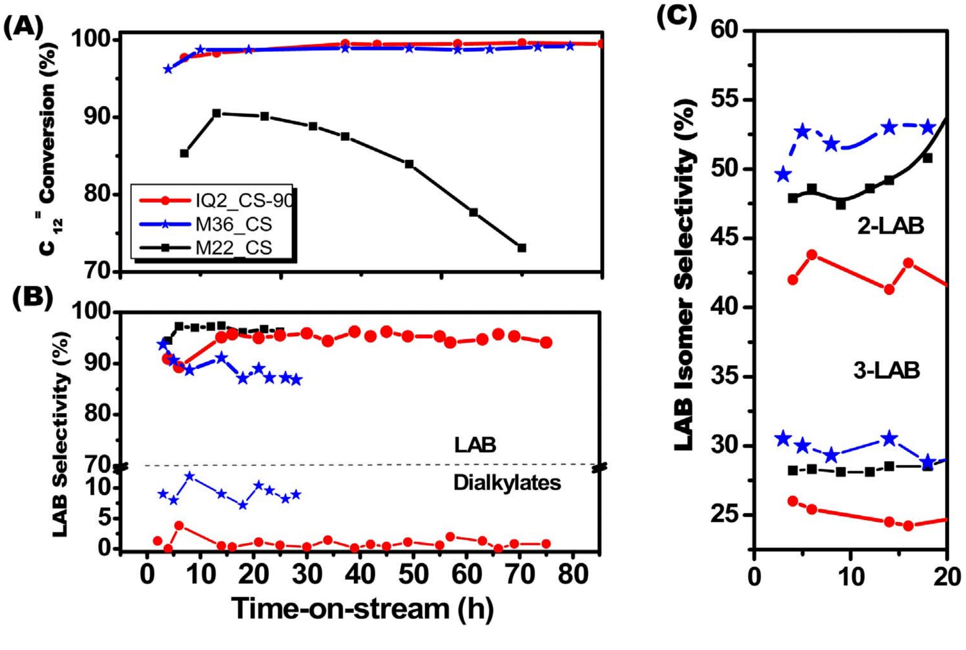


Fig. 6. (A) 1-Dodecene conversion, (B) LAB product selectivity, and (C) LAB isomer selectivity during LAB synthesis using R10 feed over different MWW zeolites along with time-on-stream (Reaction temperature 433 K; pressure 2068 kPa; WHSV 4 h^{-1}; H_2/total HC ratio 3.0 mol/mol).

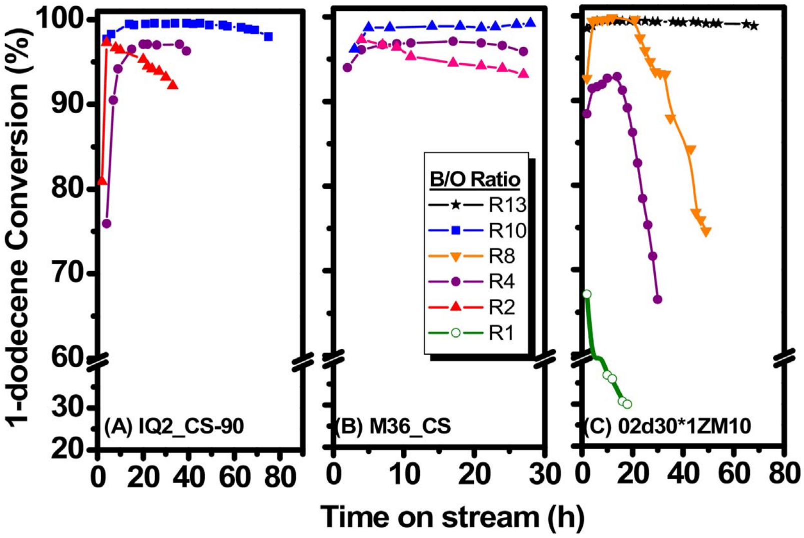


Fig. 7. 1-Dodecene conversion over (A) IQ2_CS-90; (b) M36_CS; and (C) 02d30*1ZM10 (desilicated mordenite) catalyst along with time-on-stream in using various benzene/olefin ratio feeds (reaction temperature 433 K; pressure 2170 kPa; WHSV 4 h^{-1}; H_2/total HC 3.0 mol/mol; feed composition: benzene/n-decane/1-dodecene = 1- 13: 0.5: 1; with R*x* notation where *x* represents benzene/1-dodecene molar ratio).

formation rate of coke precursor and catalyst deactivation rate could be greatly reduced by increasing B/O feed ratio.

As shown in Fig. 7, all the zeolites have improved catalytic stability at increasing B/O ratio. The desilicated mordenite sample 02d30*1ZM10 had improved catalytic stability over the parent MOR sample ZM10. Its activity was stable at B/O ratio greater than 10. On the other hand, the MWW family IQ2_CS-90 (one ITQ-2 sample) and M36_CS (one MCM-36 sample) after delamination or pillaring were more stable than the M22_CS (one MCM-22 sample). Both zeolite samples were very stable even in case of B/O ratio of 4.

Raising B/O feed ratio is an effective but costive engineering approach for reducing catalyst deactivation rate. According to UOP, Detal process applying an improved catalyst ZDA-2 could be operated at a less B/O ratio by 67% than the previous fluoride-based catalyst DA-114 [23], leading to significant reduction of energy consumption by 20%. Therefore, capital cost of benzene tower and operating cost could be greatly reduced. The current industrial HF process normally applies benzene/olefin (B/O) ratio of 4–10. Zeolite catalyst under development should be capable for long-term stable activity at B/O ratio not greater than 10, and preferably less than 4.

4.2. *Feed impurity*

Referring to Fig. 1, linear mono-olefin is commercially supplied as *n*-paraffin dehydrogenation (so-called "Pacol feed"); or ethylene oligomerization (so-called synthetic α-olefin). The "Pacol feed" contains higher impurities particularly di-olefin and aromatics than α-olefin. The composition and impurity of LAB feed, such as di-olefin and water, would affect strongly the deactivation rate of zeolite catalyst. From process development perspective, zeolite catalyst should be competitive to the current commercial HF process by using the same Pacol feed specification and B/O ratio corresponding to other process parameters such as reaction temperature and pressure (Fig. 8).

In dealing with deactivation problem from diene containing feed, one should either develop a more resistant zeolite catalyst or set stringent specification with low diene content. The latter approach is an easier but costly solution. Octadiene was used as a model compound for impurity test in LAB synthesis. As shown in Fig. 9, the desilicated mordenite sample 02d30*1ZM10 and the delaminated MWW zeolite sample IQ2_CS-90 could be catalytic stable in using R10 feed containing 0.05% octadiene having B/O molar ratio of 10. Both catalysts exhibited better tolerances to octadiene deactivation than their parent zeolite catalysts by desilication or delamination treatment. The IQ2_CS-90 exhibited stronger octadiene tolerance than the 02d30*1ZM10 in 0.1% octadiene containing feed. Those enhanced diene resistances of the zeolite catalysts could be attributed to their mesoporous structures or more open micropore structures [18,19]. On the other hand, according to Lin et al., the general practice by incorporation of metal function for the stabilization of zeolite activity does not work for LAB synthesis. For example, metal/mordenite catalyst showed even worse catalytic stability and LAB selectivity than H-mordenite catalyst [18].

4.3. *Catalyst regenerability*

Regenerability of MOR zeolite was tested in dealing with its deactivation problem. As shown in Fig. 9, the MOR sample ZM10 deactivated after on-stream of 45 h. After the deactivated catalyst was burned with air stream at 540 °C for 6 h by applying conventional calcination method, in case of "air regeneration", the deactivated catalyst was fully regenerated with exact the same catalytic performance with the original ZM10 sample. Alternatively, in "benzene extract" case, by flowing pure benzene feed (zero dodecene content) through the catalyst bed at the reaction temperature (180 °C) for 30 min, the activity of the deactivated ZM10 was partially recovered showing elevated dodecene conversion. The "benzene extracted" catalyst followed similar deactivation curvature with the original ZM10 catalyst. The "benzene extract" method could be periodically applied during normal operation to extend cycle length.

5. Perspectives

Zeolite catalyst has been successfully industrialized in many hydrocarbon conversion processes in the replacement of traditional homogeneous catalyst with much improved environmental impact with upgrading process safety, reduced waste production and hazardous material, as well as enhanced product safety. In aromatics alkylation area, variety of zeolite catalyst has already been industrialized for short chain alkylation, namely synthesis of ethylbenzene, cumene, n-propylbenzene, etc. Zeolite catalysis for long-chain linear alkylbenzene (LAB) synthesis LAB catalysis has been studied for over 40 years started from 1960s. Nevertheless, today industrial LAB synthesis is still catalyzed with HF. From the perspective of process industrialization, several major issues particularly optimum LAB isomer distribution and catalytic stability in dealing with stringent feed specification should be

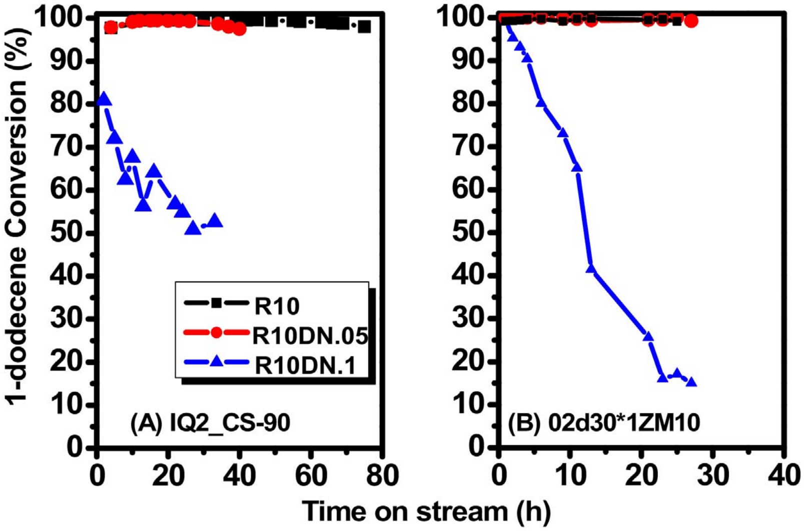


Fig. 8. 1-Dodecene conversion over (A) IQ2_CS-90 (delaminated MWW); and (B) 02d30*1ZM10 (desilicated mordenite) catalyst along with time-on-stream in using 0–0.1% octadiene containing feed (reaction temperature 433 K; pressure 2170 kPa; WHSV 4 h^{-1}; H_2/total HC 3.0 mol/mol; feed composition: benzene/n-decane/1-dodecene/octadiene = 10: 0.5: 1: 0 (R10 feed), 0.05% (R05DN feed), 0.1% (R10DN.1 feed)).

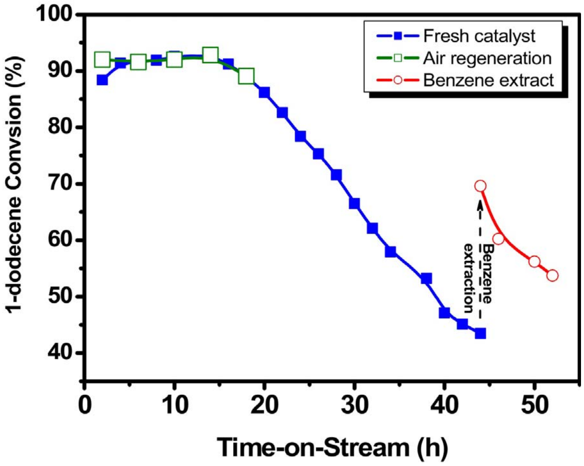


Fig. 9. 1-Dodecene conversion over ZM10 (MOR zeolite) subjected to air regeneration, or benzene extraction treatment along with time-on-stream (reaction temperature 433 K; pressure 2170 kPa; WHSV 4 h^{-1}; H_2/total HC 3.0 mol/mol; feed composition: benzene/n-decane/1-dodecene = 10: 0.5: 1 mol).

addressed. The present mini-review discusses the potential application of mesoporous zeolite for LAB synthesis with respect to porosity effect on LAB isomer selectivity and catalytic stability.

Among LAS isomers, sodium 2-phenylalkane sulfonate has the greatest biodegradability but the lowest solvency. Current HF process produces thermodynamic equilibrium LAB compositions with low 2-LAB isomer selectivity of 10% at much higher 5- and 6- LAB isomer composition. Most of zeolite catalyzes much higher 2-LAB isomer selectivity than HF process highlighting the potential for producing a more environmental benign detergent. As the current detergent market is used to the 5- and 6- LAB isomer rich product generated by HF process, development of new LAB process needs to compromise LAB isomer selectivity to enhance its market acceptability. Marinangeli and Lawson have developed a binary catalyst system comprising MOR and amorphous silica-alumina, by which 2-LAB could be isomerized over the latter catalyst into other LAB skeletal isomers [24]. Alternatively, it is concluded that LAB isomer selectivity from zeolite catalyst is mainly controlled by the structure and pore opening of zeolite microporosity. The industrial viable solution should revitalize the application of an appropriate zeolite framework structure.

Zeolite stability could be enhanced by engineering approach and catalyst approach. Engineering approach are raising B/O ratio and reaction temperature, periodical regeneration by extraction (for example, benzene washing), and stringent feed specification. Catalyst approach is more economic viable than engineering approach. As a rule of thumb, mesoporosity of zeolite could stabilize its catalytic stability [25] even for diene containing olefinic feed. Zeolite mesoporosity could be introduced by tuning the textural property of zeolite sample through hydrothermal synthesis, post-treatment, and post modification. The current mini-review presents a working strategy for manipulating the catalytic property of MWW zeolite family. While the crystal size of MCM-22 could be reduced through fine tune of hydrothermal synthesis condition to increase mesoporosity associated with population of EC-12 cage, the delaminated ITQ-2 zeolite through optimum delamination procedure and the pillared MCM-36 through controlling pillaring could further enhance EC-12 site and enlarge C10-12 site. All those practices have led to enhancement of catalytic stability and fine tuning LAB isomer selectivity.

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References

[1] J.G. Ma, B.J. Boyd, C.J. Drummond, Langmuir 22 (2006) 8646–8654.
[2] J.C.P. Penteado, O. El Seoud, L.R.F. Carvalho, Quim. Nova 29 (2006) 1038.
[3] I. Craciun, M.F. Reyniers, Guy B. Marin, J. Mol. Catal. A: Chem. 277 (2007) 1–14.
[4] J. Kocal, B. Vora, T. Imai, Appl. Catal. A: Gen. 221 (2001) 295.
[5] A. Aitani, J.B. Wang, I. Wang, S. Al-Khattaf, T.C. Tsai, Catal. Surv. Asia 18 (2014) 1.
[6] W.H. Chen, J.J. Wang, K.J. Du, H.T. Yen, S.B. Liu, I. Wang, T.C. Tsai, Curr. Organ. Chem. 18 (2014) 1322–1333.
[7] G.D. Yadav, N.S. Doshi, Organ. Proc. Res. Dev 6 (2002) 263.
[8] R. Sheldon, Chem. Commun. (2001) 2399–2407.
[9] M.A. Harmer, Q. Sun, Appl. Catal. A: Gen. 221 (2001) 45–62.
[10] M.H. Faghihian, C.R. Mohammadi, Chimie 15 (2012) 962–968.
[11] L.B. Young, U.S. Patent, 4 301 317 (1981) (to Mobil Oil Corp.).
[12] Y. Cao, R. Kessas, C. Naccache, Y.B. Taarit, Appl. Catal. A: Gen. 184 (1999) 231.
[13] M.E. Leonowicz, J.A. Lawton, S.L. Lawton, M.K. Rubin, Science 264 (1994) 1910.
[14] A. Corma, V. Fornes, S. Pergher, T.L. Maesen, J. Buglass, Nature 396 (1998) 353.
[15] W.J. Roth, C.T. Kresge, J.C. Vartuli, M.E. Leonowicz, A.S. Fung, S.B. Mccullen, Stud. Surf. Sci. Catal. 94 (1995) 301.
[16] W.J. Roth, C.T. Kresge, J.C. Vartuli, M.E. Leonowicz, A.S. Fung, S.B. Mccullen, Stud. Surf. Sci. Catal. 94 (1995) 301.
[17] T.C. Tsai, I. Wang, S.J. Li, J.Y. Liu, Green Chem. 5 (2003) 404–409.
[18] J.S. Lin, J.J. Wang, J.S. Wang, I. Wang, R.J. Balasamy, A.v. Aitani, S. Al-Khattaf,

T.C. Tsai, J. Catal. 300 (2013) 81–90.
[19] H.T. Yen, J.J. Wang, S.H. Siao, S.H. Cha, S.B. Hong, S.S. Al-Khattaf, I. Wang, T.C. Tsai, Catal. Sci. Technol. 6 (2016) 2715–2724.
[20] V. Valtchev, G. Majano, S. Mintova, J. Pérez-Ramírez, Chem. Soc. Rev. 42 (2013) 263–290.
[21] S.T. Tsai, C.H. Chen, T.C. Tsai, Green Chem. 11 (2009) 1349–1356.
[22] S.T. Tsai, P.Y. Chao, P.H. Chao, K.J. Du, M.J. Fang, S.B. Liu, T.C. Tsai, Catal. Today 259 (2016) 423–429.
[23] J.A. Kocal, U.S. Patent, 5 196 574 (1993) (to UOP Inc.).
[24] R.E. Marinangeli, R.J. Lawson, US Patent, 6 521 804 (2003) (to UOP LLC.).
[25] T.V. Harris, C.B. Campbell, P. Tequi, and J-L. Le Coent, US Patent, 7 071 370 (2006) (to Chevron Oronite Company).