



## 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.

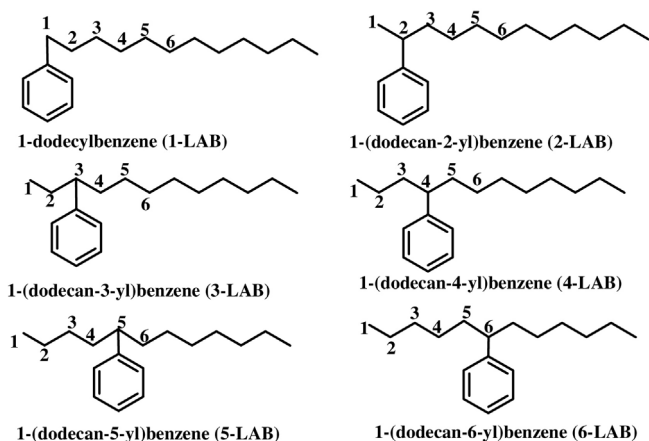
LAB synthesis by alkylation of benzene with long chain olefin is an acid catalyzed reaction [3]. Many acid catalysts have been reported for LAB catalysis, such as zeolite [4–6], sulfated metal oxides [7], ionic liquid [8], ion exchange resin [9], etc. The early alkylation catalyst  $AlCl_3$  of the industrial 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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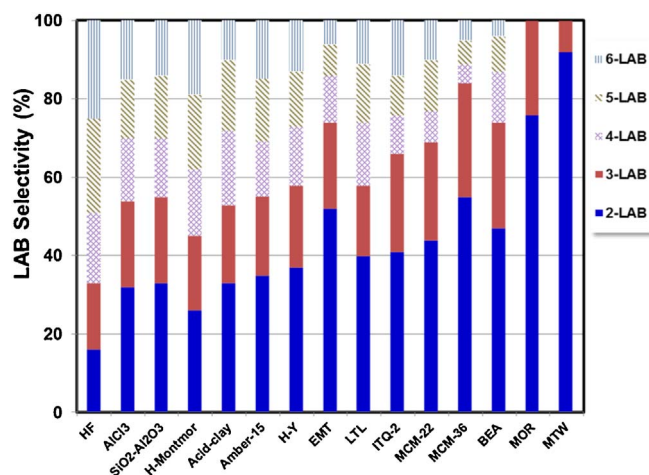
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**Sketch 1.** Molecular structures of linear alkylbenzene skeletal isomers 1-dodecylbenzene (1-LAB); 1-(dodecan-2-yl)benzene (2-LAB); 1-(dodecan-3-yl)benzene (3-LAB); 1-(dodecan-4-yl)benzene (4-LAB); 1-(dodecan-5-yl)benzene (5-LAB); 1-(dodecan-6-yl)benzene (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  $\text{AlCl}_3$ , 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  $6.5 \times 7.0 \text{ \AA}$  and  $5.6 \times 6.0 \text{ \AA}$ , respectively (Table 1). Another one-dimensional zeolite LTL with pore opening size of  $7.0 \text{ \AA}$  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  $7.1 \text{ \AA}$ , 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-



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

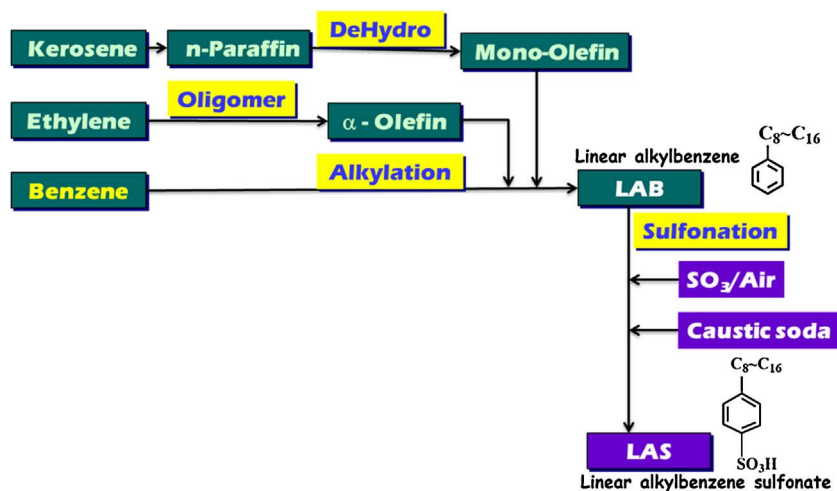
**Table 1**  
Representative zeolite structures for the catalysis of LAB synthesis.

Catalyst	IZA code <sup>a</sup>	Micropore Structure <sup>b</sup>
H-Y	FAU	(12MR) $7.4 \text{ \AA}$
EMT	EMT	(12MR) $7.4 \times 6.5 \text{ \AA}$
L	LTL	(12MR) $7.1 \text{ \AA}$
H- $\beta$	BEA	(12MR) $6.6 \times 6.7; 5.6 \times 5.6 \text{ \AA}$
H-M	MOR	(12MR) $6.5 \times 7.0 \text{ \AA}$
ZSM-12	MTW	(12MR) $5.6 \times 6.0 \text{ \AA}$
H- $\beta$	BEA	(12MR) $6.6 \times 6.7; 5.6 \times 5.6 \text{ \AA}$
MCM-22, ITQ-2,	MWW	(10MR) $4.0 \times 5.5 \text{ \AA}$ ;
MCM-36		(10–12MR) $7.1 \times 7.1 \times 18.2 \text{ \AA}$ with $4.1 \times 5.1 \text{ \AA}$ opening (12MR) $7.1 \times 7.1 \text{ \AA}$

<sup>a</sup> IZC Code in parenthesis.

<sup>b</sup> 12MR: 12-oxygen membered ring; 10MR: 10-oxygen membered ring.

MR supercage ( $0.71 \times 0.71 \times 1.81 \text{ nm}$ ) 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. 1.** Industrial LAB (linear alkylbenzene) and LAS (Linear alkylbenzene sulphonate) process scheme.

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