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Recent advances in the industrial alkylation of aromatics: new catalysts and new processes

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Abstract

Huge improvements towards the development of environmentally friendly processes have been achieved in the alkylations of aromatics with olefins, since the last four or five decades. Particularly, much efforts have been devoted to the research of solid catalysts adequate to substitute mineral or Lewis acids and free bases traditionally employed as catalysts in the acid or base catalyzed alkylations. Here we review the options industrially worthy of note in the alkylations of benzene and toluene for the production of ethylbenzene (EB), cumene, linear alkyl benzene and cymene. We also discuss features of different zeolites as a function of their activity and selectivity in the reactions considered. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical industry [1]. Consider that about 70% of the 29.3 million tonnes accounting the world benzene demand in 1999, were expected to be consumed by acid catalyzed alkylation with ethylene and propylene, 53 and 17%, respectively for the production of ethylbenzene (EB) and cumene. Analogously, *p*-diisopropylbenzene, C10–C14 linear alkylbenzenes (LABs), cymene, *p*-ethyltoluene and 4-*t*-butyltoluene are also important chemical intermediates obtained by acid alkylation of benzene or toluene aromatic ring. Finally, other chemical intermediates, such as 5-(*o*-tolyl)-pentene-2, isobutylbenzene and *t*-amylbenzene, are produced by side-chain alkylation of aromatics, catalyzed by base [2].

In many industrial processes these alkylations are still performed with catalysts showing drawbacks. Often such catalysts are strong mineral acids or Lewis acids (e.g. HF, H_2SO_4, and $AlCl_3$), which are highly toxic and corrosive. They are dangerous to handle and to transport as they corrode storage and disposal containers. Often, the products need to be separated from the acid with a difficult and energy consuming process. Finally, it occurs frequently that these acids are neutralized at the end of the reaction and, therefore, the correspondent salts have to be disposed. Similar problems arise when free bases are used as catalysts.

In order to avoid these problems many efforts have been devoted to the search of solid acid and base catalysts more selective, safe, environmentally friendly, regenerable, reusable and which have not to be destroyed after reaction. The aim of this contribution is to summarize some examples of new industrial processes based on the aforementioned solid catalysts.

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Only the alkylations accounting for the largest capacity will be discussed.

2. Alkylation of benzene to produce ethylbenzene and cumene

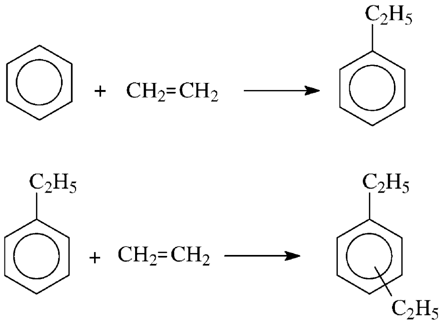
2.1. Ethylbenzene

EB is the key intermediate in the manufacture of styrene, which is one of the most important industrial monomer. Almost all EB is synthesized from benzene and ethylene, the worldwide capacity amounting to around 20 million tonnes per year.

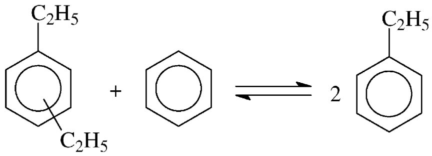
2.1.1. Traditional processes

In the traditional process, developed in the 1930s, the alkylation is performed reacting benzene and ethylene in the presence of a Friedel–Crafts catalyst (i.e. $AlCl_3$–HCl) at mild conditions ($T = 160\,^{\circ}C$). The EB produced by benzene alkylation, may undergo polyalkylation to di- and other polyethylbenzenes, according to the reactions depicted in Scheme 1.

After the product separation, the polyethylbenzenes are recycled back to the alkylation reactor. Here, polyethylbenzenes transalkylation takes place till the thermodynamic equilibrium is reached (Scheme 2). The final composition depends on the overall ethylene/benzene molar ratio (Fig. 1) [3].



Scheme 1.



Scheme 2.

The reaction is performed in the liquid-phase and, because of the corrosive effect of the catalyst, the

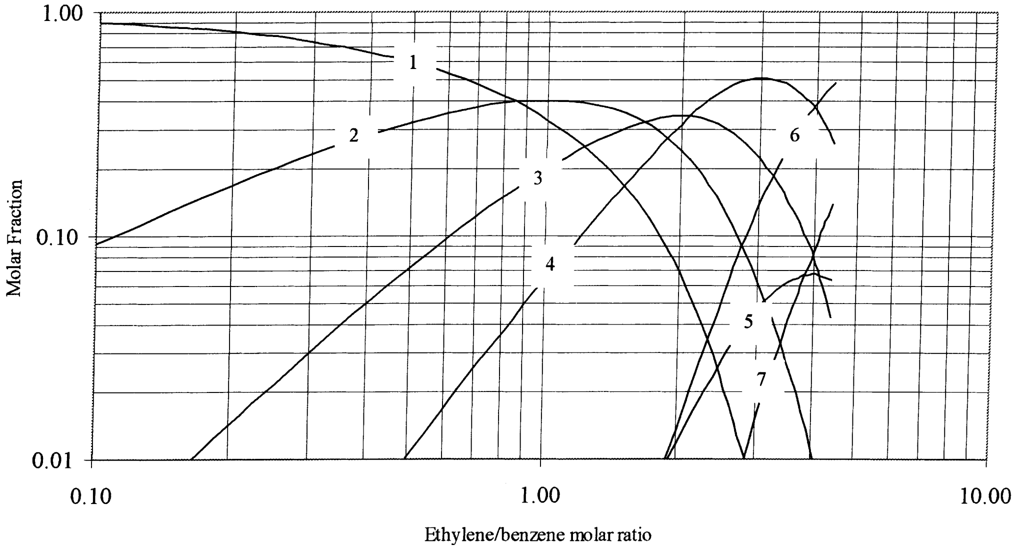


Fig. 1. Thermodynamic equilibrium of EB. 1: benzene; 2: EB; 3: DEBs; 4: triethylbenzenes; 5: tetraethylbenzenes; 6: pentaethylbenzene; 7: hexaethylbenzene.

process is carried out in enameled or glass lined reactors.

As a possible solution to the corrosion problems, supported catalysts have been proposed in the 1960s by UOP for liquid-phase (BF_3/Al_2O_3 in the Alkar^{TM} process) and gas-phase (Kieselguhr supported phosphoric acid (SPA)) operations. However, due to partial release of the acids, corrosion problems were not completely avoided. Besides, these catalysts are not active in the polyethylbenzenes transalkylation and cannot be regenerated. For these reasons such processes did not obtain large industrial interest.

2.1.2. *Solid acid catalysts*

The first solid acid catalysts for benzene alkylation with ethylene (and propylene) were used in the vapor-phase in the 1940s. They were based on amorphous silica-alumina gel, as those employed in commercial catalytic cracking processes [4].

Starting from the mid-1960s, different zeolite-based catalysts were extensively evaluated in benzene alkylation with ethylene and, in 1966, Venuto et al. [5] reported that large pore zeolites (e.g. REX, HY and REY) are more effective catalysts than amorphous silica-alumina gels. Besides, as far as REX is concerned, it was found that catalyst life is better operating in liquid-phase than in gas-phase, both in alkylation and transalkylation.

Despite the huge amount of research activity, the first industrial application of a zeolite catalyst occurred in 1976 by Mobil–Badger. This new process was commercialized in 1980 as “second generation Mobil–Badger process”. The alkylation of benzene is performed in a gas-phase fixed-bed reactor (e.g. $T = 390$–$450\,^{\circ}C$), using a ZSM-5, a medium pore zeolite. Analogously to the “$AlCl_3$–HCl process”, the polyethylbenzenes are recycled back to the reactor to undergo transalkylation [6]. ZSM-5 has a low coke-forming tendency and, therefore, life cycles between regenerations up to 40–60 days are possible [7]. With the third generation process, commercialized in 1990s, a second reactor was added, primarily for transalkylation, significantly improving the performance (Table 1).

2.1.3. *Liquid-phase alkylation with zeolite catalysts*

Lummus/Unocal/UOP [6] first introduced the liquid-phase EB process, using a zeolite catalyst, in 1989 and the first commercial plant was started up in 1990. The liquid-phase operation has the advantage of a better thermal control and a longer catalyst life (Table 1). The catalyst is based on an Y type zeolite, developed for the alkylation by Unocal since 1979 [8].

Other large pore zeolites, which are the most adequate in order to overcome the diffusion constraints observed in liquid-phase operation, were considered as catalyst for EB production (e.g. L, Omega, mordenite, ZSM-12, Beta). As a result of these investigations, in the early 1990s [9,10], zeolite Beta was demonstrated to give better performance than Y (Table 2). According to Bellussi et al. [11], zeolite Beta is more selective than zeolite Y due to different features in the channel systems. In the case of Beta zeolite the channel openings ($0.57\,nm \times 0.75\,nm$ and $0.65\,nm \times 0.5\,nm$) are only slightly larger than the size of benzene molecule and do not permit the formation of those molecules whose critical diameters are significantly larger. On the other hand, in the case of Y zeolite, supercages ($\text{diameter} = 1.2\,nm$) are present which allow bulky by-products formation. Zeolite Beta was also proved to be a good catalyst for the liquid-phase transalkylation of *m*-diethylbenzene. Though less active than USY, zeolite Beta shows better selectivity, producing less diphenylethanes and xylenes [12].

Recently, zeolite MCM-22 was demonstrated to give good performance in the liquid-phase alkylation of benzene with ethylene [13]. In particular, MCM-22 shows a catalytic activity which is comparable (with lower deactivation rate) to USY and around 2.4 times less than zeolite Beta. On the other hand, MCM-22 is much more selective than USY and Beta, producing diethylbenzenes (DEBs) in significantly lower quantities (Fig. 2) [13].

A new catalyst based on MCM-22 was recently used in a new EB technology, called EBMax^{TM} by Mobil–Raytheon [14]. In this new technology the alkylation is performed in liquid-phase, while the transalkylation is still operated in gas-phase with a ZSM-5 based catalyst. The first industrial application was realized in 1997 (Table 1). More recently, a new zeolite catalyst (trade name TRANS-4) was developed so that the transalkylation is carried out in the liquid-phase too. The nature of the zeolite was not disclosed.

Since 1989, also Lummus/UOP have been improving their liquid-phase process. Currently, the

Table 1
EB production processes

	Process (year)						
	Monsanto–Lummus (<1975)	Mobil–Badger second generation (1980)	Lummus/Unocal/ UOP (1989)	Mobil–Badger third generation (1990)	CDTECH EB[a] (1994)	Mobil–Raytheon EBMax[b] (1995)	Lummus/UOP EBOne[c] (1996)
Alkylation							
T (°C)	160	390–440	240–270	390–440			
Catalyst	$AlCl_3$	ZSM-5	Y	ZSM-5	Y	MCM-22	EBZ-500
Phase	Liquid	Vapor	Liquid	Vapor	–	Liquid	Liquid
Feed ratio	2.5	7.6	7.2	7.6	–	4	4–6
Life (year)	–	0.25	1	1	5	3	2
Transalkylation							
	No	No	Yes	Yes	Yes	Yes	Yes
Catalyst	–	–	Y	ZSM-5	Y	ZSM-5	EBZ-100
Phase	–	–	Liquid	Vapor	Liquid	Vapor	Liquid
Yield (%)	99.7	98.1	98.2	99.2	99.7	99.5	99.6

[a] From [56].
[b] From [55].
[c] From [57].

Table 2
Zeolite performances in benzene alkylation with ethylene[a]

Catalyst	Conversion (%)	Selectivity			
		Ethylbenzene (%)	Diethylbenzene (%)	Triethylbenzene (%)	Other (%)
Zeolite Y	100	82.0	8.4	0.7	8.8
Zeolite Beta	100	91.1	7.9	0.3	0.7

[a] Operation conditions: $P = 3.10\,\mathrm{MPa}$; benzene/olefin $= 7$; $T = 160\,^{\circ}\mathrm{C}$; WHSV $= 4.6\,\mathrm{h}^{-1}$.

commercialized process is named EBOne. Two different zeolite catalysts are used in alkylation and transalkylation (UOP trade names EBZ-500 and EBZ-100, respectively). No details were disclosed about the zeolite used for the preparation of these catalysts but, according to the patent literature, it is supposed to be a modified zeolite Beta [15]. The performance of this new process are comparable to those reported for EBMax$^{\mathrm{TM}}$ (Table 1).

CDTech, a partnership between ABB Lummus and Chemical Research & Licensing, developed an improved technology for EB production based on a catalytic distillation process. In the catalytic distillation, reaction and distillation occur simultaneously in a single column, with the catalyst contained in bales and stacked in the distillation column-reactor. As a result of the distillation, the reaction products are continuously removed from the catalytic zone and a low production of polyethylbenzenes is obtained. Nevertheless, a transalkylation reactor is required (Table 1). According to the earlier patent [16], the catalyst is supposed to be based on an Y type zeolite. However, in analogy with EBOne process, the catalyst now in use should be based on zeolite Beta.

Several industrial units were recently revamped or realized with these new liquid-phase technologies. Accordingly, only 24% of the worldwide production are still based on $AlCl_3$–HCl technology. The balance is almost based on zeolite catalysts: 40% in the gas-phase and 36% in the liquid-phase.

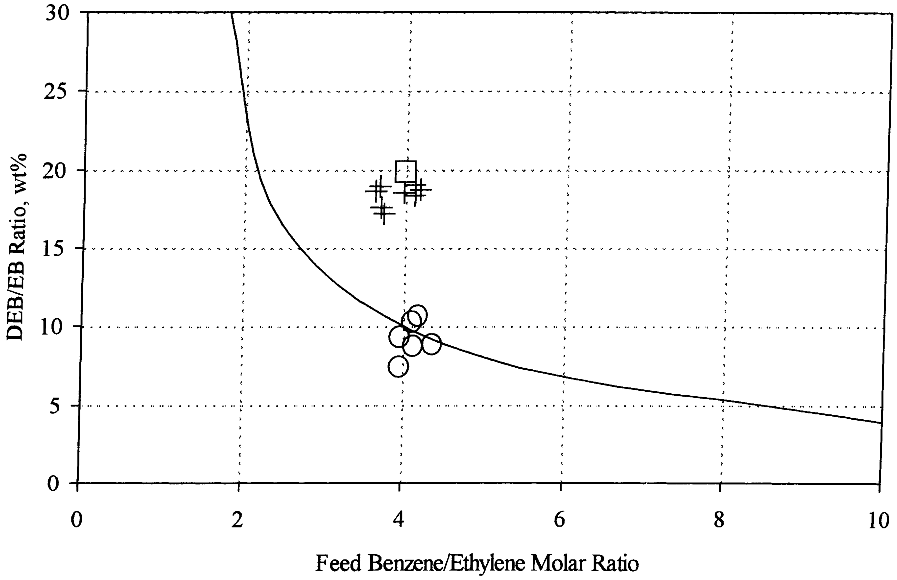


Fig. 2. Comparison of DEB/EB ratio (220 °C; 3.44 MPa). Equilibrium DEB/EB ratio; (○) MCM-22; (+) Beta; (□) USY-1.

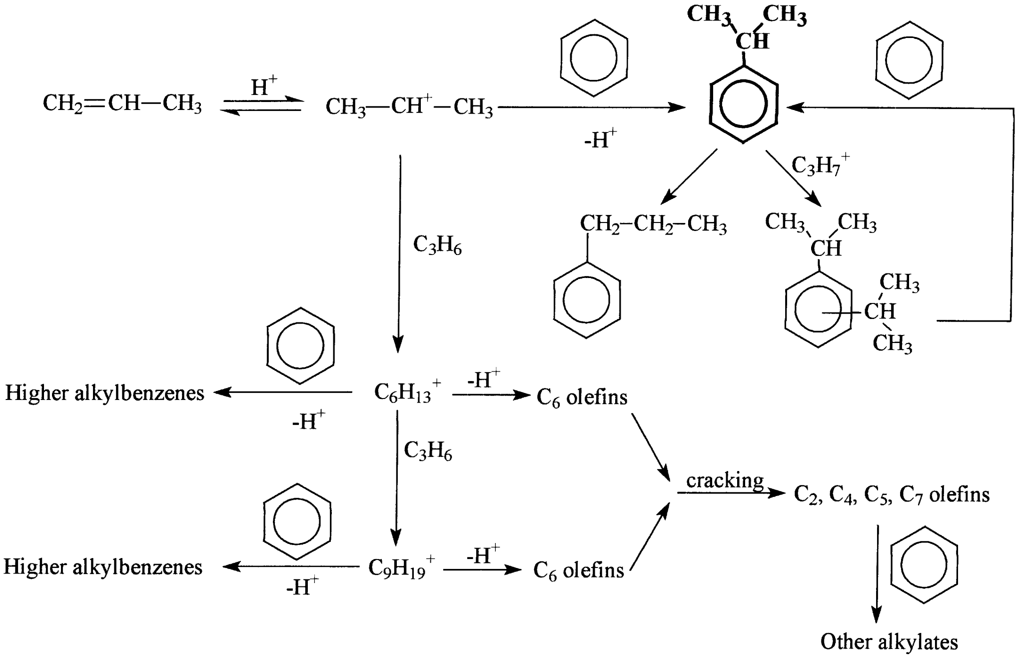


Fig. 3. Acid catalyzed alkylation of benzene with propylene.

2.2. Cumene

The manufacture of cumene as a blending agent for high-octane gasoline was carried during the Second World War on a very large scale. Nowadays cumene is the intermediate for the production of phenol and acetone and its worldwide capacity is around 8 million tonnes per year, distributed over around 40 plants.

2.2.1. Traditional processes

The mechanism of the acid catalyzed alkylation of benzene involves the propylene protonation by way of the acid sites (Fig. 3). The protonated species can react with benzene producing cumene which, subsequently, can undergo further reactions mainly to di- and tri-isopropylbenzenes. *n*-Propylbenzene is also produced from cumene by secondary isomerization. Di- and tri-isopropylbenzenes can transalkylate with benzene to give cumene. Alternatively, the protonated species can react with a second propylene molecule producing a C6 species which can be further transformed through oligomerization, cracking, isomerization and alkylation, to olefins and other alkylbenzenes.

The first industrial process technology used for cumene production was based on free sulfuric acid as catalyst, but due to the problem related with the use of a free acid, such technology was abandoned in favor of a new one based on SPA. Such a technology, developed by UOP in the late 1940s, is still the most diffused in the cumene production. The alkylation is carried out in the liquid-phase in a fixed bed reactor at 180–240 °C. The formation of polyalkylated compounds, which cannot be transalkylated by SPA, and propylene oligomers is minimized operating with high benzene/propylene ratio. Typically this condition is realized by dividing the catalyst over several beds and by splitting the propylene feeding over each of the beds (i.e. splitted feed) [17].

In the 1970s, Monsanto–Lummus introduced a technology, aimed to improve cumene yield by polyisopropylbenzenes transalkylation, based on $AlCl_3$–HCl. However, only few plants were realized by this technology [18]. SPA and $AlCl_3$ processes offer different feature (Table 3), but both suffer from a variety of drawbacks such as high environmental impact, corrosive catalysts and formation of oligomers and other

Table 3
Cumene traditional production processes

	SPA process	$AlCl_3$ process
T (°C)	180/240	110
Feed ratio (benzene/propylene)	5/10	2/5
Pressure (MPa)	3/4	10
Phase	Liquid	Liquid
Yield on benzene (%)	94.6	98.8
Yield on propylene (%)	91.2	98.5
Life (year)	1	–

impurities. These were the reasons, which drove many efforts toward the development of new technologies based on solid catalysts.

2.2.2. *Solid acid catalysts*

The evolution of the catalytic systems for cumene production is somehow similar to that described for EB. As for EB, after early attempts with amorphous silica-alumina [4], acidic zeolites were extensively evaluated also for cumene synthesis. An early report on the gas-phase alkylation of benzene with propylene catalyzed by X and Y zeolites dated back to 1965 [19]. However, differently from EB, the research efforts took longer time to reach an industrial application. This time lag probably depended on the inability of ZSM-5, the first catalyst of EB Mobil–Badger process, to satisfactorily catalyze the cumene synthesis in gas-phase. ZSM-5, in fact, produces an elevated cumene isomerization to *n*-propylbenzenes, possibly due to the high temperature necessary to overcome the diffusion constraints in its 10-membered ring (10MR) pores [20]. Besides a quite rapid decay was observed due to the higher tendency of propylene to produce oligomers with respect to ethylene. On the other side, ZSM-5 shows poor catalytic activity in liquid-phase alkylation, probably because of diffusion constraints [11].

As a matter of fact, the important steps towards applicable results were (a) the move to the liquid-phase operation and (b) the use of zeolites with 12MR pore openings (e.g. Y, mordenite, ZSM-12, Omega, Beta and MCM-22[1]). Based on these zeolites, new commercial processes or industrial test runs were announced in the 1990s by Dow–Kellogg, Mobil–Raytheon, CDTech, EniChem and UOP.

2.2.3. *Liquid-phase alkylation with zeolite catalysts*

Five are the commercial cumene processes based on zeolite catalyst (Table 4). Dow–Kellogg claimed the development of a new process, named 3-DDM cumene process, which uses a highly dealuminated mordenite as catalyst. While being referred to as “one-dimensional” zeolite (i.e. containing non-intersecting 12MR pores), mordenite was converted by dealumination into a novel catalyst with a pseudo three-dimensional structure, providing optimal performance and stability [18]. The Mobil–Raytheon cumene process operates in a fixed bed reactor system. The nature of the catalyst was not disclosed, however, according to the patent [21], the zeolite is supposed to be MCM-22. The CDTech technology is based on a catalytic distillation column-reactor and operates as above reported for EB. In a recent paper by ABB Lummus researchers [22], good performance in terms of catalytic activity were reported for catalyst based on zeolite Y. Very little was published about the catalyst used in the UOP cumene process, called Q-max [23]. However, according to the patent literature, it should be based on zeolite Beta [15]. EniChem also developed an industrial alkylation technology based on a Beta zeolite catalyst [24]. According to the published literature, all the zeolite-based processes commercially offered have comparable functioning (cumene yield above 99.5%, product purity as high as 99.95%).

Dow demonstrated for the first time the 3-DDM catalyst in 1992, in an add-on transalkylation reactor of the SPA cumene plant in Terneuzen (The Netherlands). The first industrial plants for cumene production based on zeolite technologies were started-up in 1996 by Mobil–Raytheon, EniChem and UOP, independently. By the end of 1998, 11 cumene units were operating with zeolite catalysts [25].

2.3. *Catalysts comparison in cumene and ethylbenzene productions*

Reviewing the new alkylation technologies for both EB and cumene synthesis, four different zeolites resulted to be successfully used for the catalyst formulation, i.e. Y, Beta, MCM-22 and mordenite, having

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[1] MCM-22, while being a medium pore zeolite, in this reaction behaves like a large pore zeolite (see Section 2.3.1).

Table 4
Zeolite-based technologies for cumene production

	Process				
	3-DDM/Dow–Kellogg	Mobil–Raytheon	CDTech	Q-max/UOP	EniChem
Zeolite	Mordenite	MCM-22	Y	Beta	Beta
Reactor	Fixed bed	Recycled fixed bed	Catalytic distillation column	Fixed bed	Fixed bed

zeolite structures identified with the codes FAU, *BEA, MWW and MOR, respectively. According to the patent literature each catalyst based on the zeolites reported show excellent catalytic performance in EB and/or cumene synthesis. An inevitable question arises at this stage: which zeolite is the best choice for EB and/or cumene synthesis? Many investigations were performed on this important topic and some of the results reported in the literature may offer clues for the solution of the question.

2.3.1. Zeolite selection

Beside the zeolites employed in the commercial processes discussed, other structures were investigated in the liquid-phase alkylation of benzene (e.g. ZSM-12, ZSM-5 and Omega). A comparison among large pore zeolites (e.g. ZSM-12, Beta, Y and mordenite) in the liquid-phase alkylation of benzene with propylene ($T = 230\,^{\circ}$C; benzene/propylene = 6.5) was reported by Rao et al. [26] (Fig. 4a and b). According to the authors, ZSM-12 exhibits relatively stable behavior in the selectivity to cumene, only slightly better than Beta, but much better than mordenite and Y. The formation of diisopropylbenzenes (DIPBs) decreases in the order Y > mordenite > Beta > ZSM-12. Unfortunately no details about the formation of the unrecoverable by-products (i.e. oligomers and *n*-propylbenzene) were described. On the other hand, as far as the DIPBs transalkylation to cumene is concerned, Pradhan and Rao reported that, among large pore zeolites, Beta zeolite is the best catalyst in terms of activity and stability [27], followed by LaY and by mordenite (Fig. 5).

Analogously, but more recently, molecular mechanics calculations and experimental investigations on several nanoporous structures, also including MWW (i.e. MCM-22) structure, were performed. Molecular mechanics calculations were expected to provide information about the catalytic properties characterizing different zeolites in benzene alkylation with propylene [28]. The minimum energy pathway (MEP) for diffusion of cumene through the pore systems (Table 5) indicates that, a part from MWW structure, cumene diffuses substantially unhindered through the large pore zeolites (energy barriers <6 kcal/mol), which, in fact, are considered the most active.

Table 5
Energy barriers for alkylation products diffusion (kcal/mol)

	Cumene	*o*-DIPB	*m*-DIPB	*p*-DIPB
*BEA	5.0	53.4	13.7	3.4
MOR	3.3	22.7	12.4	2.8
FAU	6.3	17.0	4.0	2.4
MTW	5.1	66.0	15.3	4.6
MWW[a]	55.7	No diffusion	148	79.2

[a] Pore system containing the supercages, running at $z = 0$. The energy barriers for diffusion of cumene in the sinusoidal channel system running at $z = 1/2$ are 90 kcal/mol.

The high-energy barriers obtained for cumene diffusion through MWW pores are in contrast with its catalytic behavior, which is very alike to that of the large pore zeolites having 12-membered ring (12MR) openings. However, MWW can be classified as a medium pore zeolite. In fact, it is characterized by a complex porous structure, formed by two non-interconnected pore systems, both having 10MR openings. One pore system is constituted by large supercages (a sort of cylinder 18 Å long and 7.1 Å wide) interconnected by slightly elliptical openings, the other by sinusoidal channels also with a slightly elliptical section. To account for the unexpected performances of MWW in cumene synthesis it is assumed that a significant number of the large cavities that characterize the MWW structure are opened to the exterior at the termination of crystallites. Following this model, it is assumed that on the [0 0 1] surface of the platelet-like crystallites are present emisupercages, having a free diameter of ca. 0.71 nm (Fig. 6). Therefore,

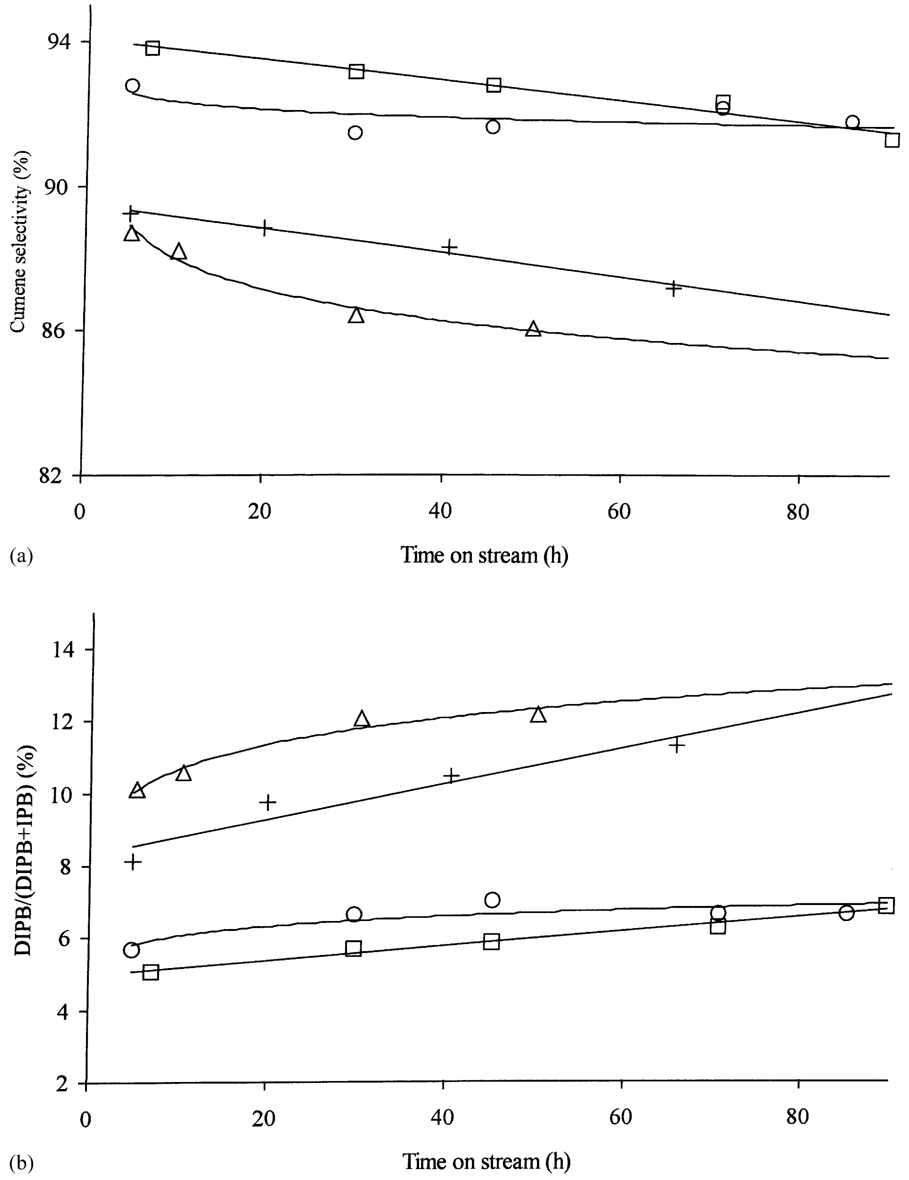


Fig. 4. (a) Large pore zeolites in benzene alkylation with propylene—cumene selectivity. Reaction conditions: 230 °C; 2.6 MPa; WHSV: 3.5 h^{-1}; benzene/propylene: 6.5. (□) ZSM-12; (○) Beta; (+) mordenite; (△) Y. (b) Large pore zeolites in benzene alkylation with propylene—diisopropylbenzene selectivity. Reaction conditions: 230 °C; 26 bar; WHSV: 3.5 h^{-1}; benzene/propylene: 6.5. (□) ZSM-12; (○) Beta; (+) mordenite; (△) Y.

cumene formation should occur in these cavities, almost without diffusion barriers. This hypothesis is further confirmed by observing that MCM-22 catalytic activity is significantly depressed by deactivating, with 2,6-di-*t*-butylpyridine, the acid sites in the large "half cavities" opened at the crystallites exterior [29].

The MEPs for diffusion of DIPBs were also calculated [28]. In this case significantly different energies characterize the diffusion of *o*-DIPB, *m*-DIPB and

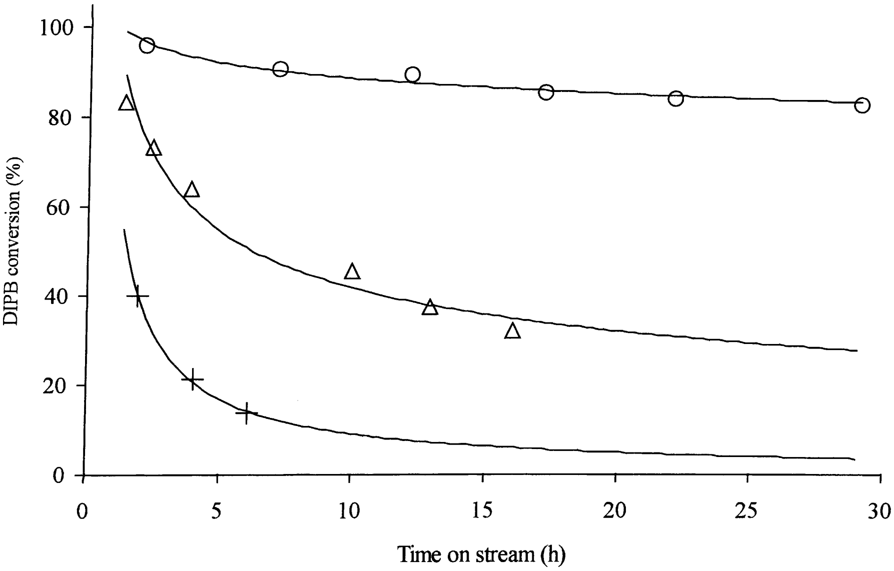


Fig. 5. Large pore zeolites in DIPBs transalkylation. Reaction conditions: 170 °C; atmospheric pressure; WHSV: 3.5 h^{-1}; benzene/DIPB: 17. (○) Beta; (△) Y; (+) mordenite.

p-DIPB through the pore systems of the structures considered (Table 5) and a product shape selectivity in the order MWW > MTW >* BEA > MOR > FAU should be expected.

In the molecular mechanics calculations, binding energies (BE) were also evaluated [28], which allow to understand the selectivity properties of different zeolites. Assuming that the formation of the by-products (DIPBs and *n*-propylbenzene) is a successive reaction of cumene, it was hypothesized that the by-products formation is favored in the zeolites that retain strongly the product, showing high BEs (Table 6). Accordingly, the tendency towards the by-products formation should increase in the order FAU ≪ *BEA < MWW ≃ MOR ≃ MTW. Indeed, the overall cumene selectivity experimentally obtained (liquid-phase; $T = 150\,°C$; benzene/propylene = 7) decreases in the order *BEA > MWW ≃ MOR ≃ FAU > MTW (Table 7). The trend described differs from the theoretical data only for FAU, whose selectivity is probably governed by the large supercages.

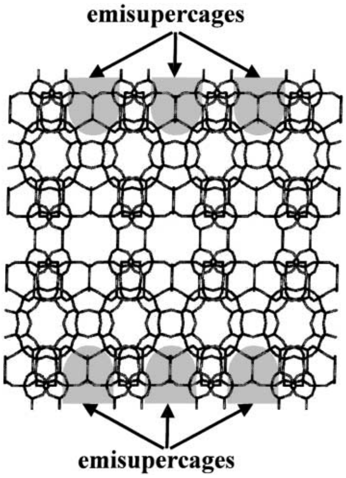


Fig. 6. MWW structure, large cavities opened to the exterior at the termination of the crystal (emisupercages).

Table 6
Calculated BE (kcal/mol) for cumene in the zeolites

*BEA	MOR	FAU	MTW	MWW[a]
−12.1	−18.2	−2.0	−19.4	−17.1

[a] In the emisurpercages on the crystal surface.

*BEA showed to be the most efficient catalyst also by examining the by-products distribution, DIPBs, oligomers and *n*-propylbenzene, experimentally produced in the reaction (Fig. 7) [28]. MWW is generally worse than *BEA, which produces any

Table 7
Selectivity obtained with different zeolite catalysts

	*BEA	MOR	MWW	FAU	MTW
Overall selectivity on propylene (%)	99.87	98.61	98.74	98.30	97.32

by-product in lower amounts. On the other hand, the lowest quantity of DIPBs is obtained in the presence of MTW. However, in this case the amounts of *n*-propylbenzene and propylene oligomers are significantly higher than in the case of *BEA. Finally, MOR and FAU produce less *n*-propylbenzene than *BEA but almost twice and three times the amount of DIPBs, which give rise further amount of *n*-propylbenzene during transalkylation. Therefore, the lowest overall amount of *n*-propylbenzene is expected for *BEA. Hence, it was concluded that among the zeolite structures studied, zeolite Beta should be the best choice for liquid-phase alkylation of benzene with propylene.

Slightly different conclusions were reached by Corma et al. [29] who showed that MCM-22 is better than Beta mainly because of its stability. Particularly, performing the reaction in a wide range of temperature (180–220 °C) and benzene to propylene ratio (3.5–7.2), the selectivities obtained on Beta and MCM-22 were very similar, Beta behaving better at 180 °C and MCM-22 at 220 °C. On the contrary, zeolite Beta showed an initial activity slightly higher with a deactivation faster than MCM-22.

In the case of benzene alkylation with ethylene, the BEs were also evaluated in MWW, *BEA and FAU by Cheng et al. [13] (Table 8). As in the case

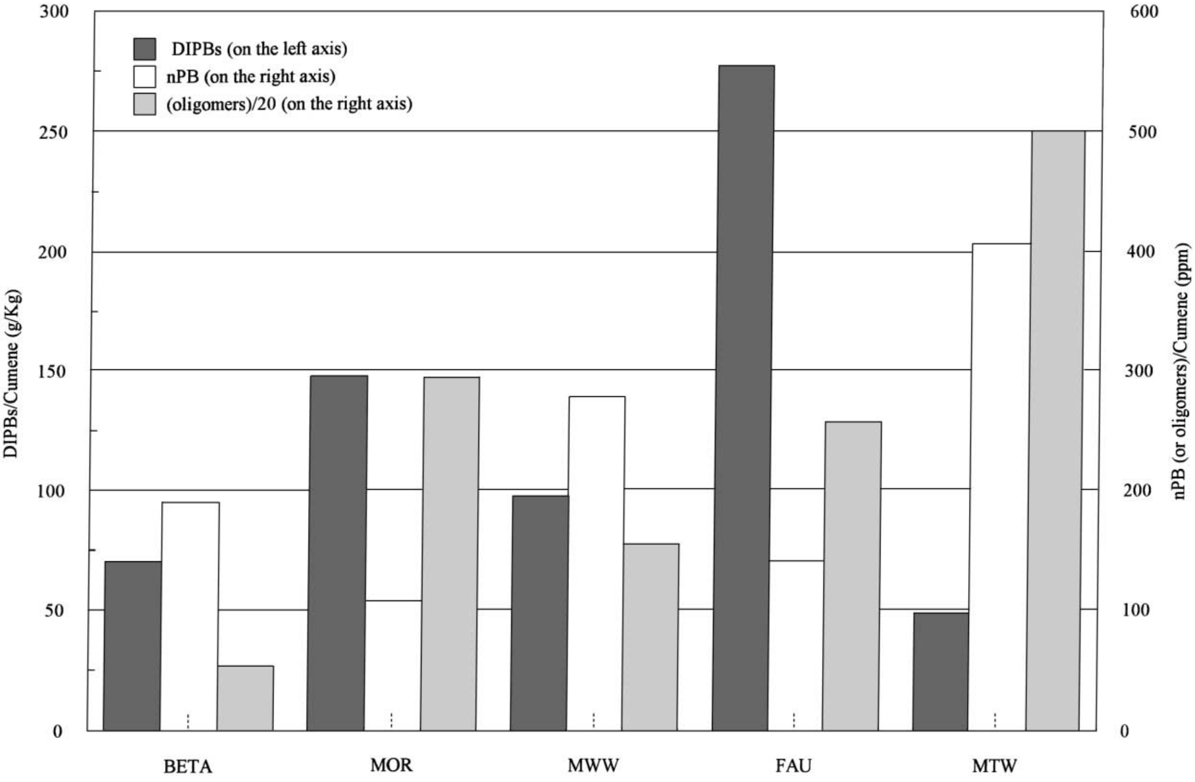


Fig. 7. Large pore zeolites in benzene alkylation with propylene. By-product selectivities. Reaction conditions: 150 °C; 3.8 MPa; benzene/propylene: 7.

Table 8
Calculated BE (kcal/mol) for EB in the zeolites

*BEA	FAU	MWW
−27.9	−15.4	−24.4

of cumene [28], the authors concluded that to higher BEs should correspond higher selectivity to polyalkylbenzenes and, therefore, that MCM-22 would behave better than Beta. This was in agreement with the experimental data obtained using catalyst pellets, prepared from zeolites (e.g. MCM-22, Beta and USY) and alumina, in the liquid-phase alkylation of benzene with ethylene ($T = 220\,^{\circ}\mathrm{C}$, benzene/ethylene = 4) (Fig. 2). Instead, no correspondence was found in the case of USY, probably because of similar reasons to those reported for cumene [28]. With the same approach used for cumene [29], Cheng et al. [13] proved that the alkylation reactions take place primarily within the 12MR emisupercages and that the 10MR system contributes little to EB synthesis.

Comparing MCM-22, Beta and ZSM-5 in the same reaction (liquid-phase, $T = 200–240\,^{\circ}\mathrm{C}$, benzene/ethylene = 3–9), Corma et al. [29] came to similar conclusions. Beta is more active than MCM-22, while ZSM-5 appears to be a poor catalyst, mainly because of a fast deactivation. However, differently from Cheng et al. [13], Corma et al. [29] reported a higher selectivity to DEBs for MCM-22 than for Beta.

The data reported do not allow a straightforward conclusion. Beta is certainly a catalyst better than Y and mordenite in cumene synthesis; analogously Beta is unquestionably better than Y in EB synthesis. Besides, according to the molecular mechanics estimation of the BEs (i.e. limiting the evaluation to the zeolite structures) it seems that the structure *BEA is the most suitable for cumene synthesis, while MWW is the most suitable for EB synthesis.

On the other hand, some of the evidences obtained from different experimental data showed to be contradictory. These apparent discrepancies may be due to important features of the catalysts, other than the zeolite structure, such as zeolite composition, particle size and shape. As a matter of fact, decreasing the framework aluminum content of zeolite Beta by direct synthesis or by isomorphous substitution with boron, a decrease of catalytic activity and selectivity was reported for both cumene and EB synthesis [11]. Besides, a significant decrease of catalytic activity was observed by increasing the particle size (i.e. size of crystal conglomerates) from 0.2 to 1 mm. Such a behavior was attributed to the influence of intraparticle diffusion [11]. Therefore, the worse performance of *BEA than MWW in EB synthesis reported by Cheng et al. [13] could be due to its lower aluminum content (i.e. Si/Al = 21.5) with respect to the one used by Corma et al. [29] (i.e. Si/Al = 13). Similarly, the better performance of *BEA than MWW in cumene synthesis could be due to the large aluminum content (i.e. Si/Al = 10 versus 15) [28].

2.3.2. *Zeolite catalyst formulation*

The alkylation catalyst is usually shaped into pellets or beads, by mixing the selected zeolite with a binder (e.g. γ-alumina). A typical shaping procedure is the extrusion of dough obtained by mulling the zeolite powder with the binder. The porosity and the crushing strength of the final pellets are influenced by several parameters, e.g. dough composition and aging, use of peptizers, plastifying agents and pore formers, die size and shape. Hence, starting from the same zeolite it is possible to obtain catalysts with different textural properties (i.e. pore volume, pore size distribution, specific surface area). According to Girotti et al. [30] an important feature of a catalyst pellet is the extrazeolite porosity that can be tailored by a proper extrusion procedure. Starting from the same zeolite powder (e.g. Beta), three catalysts having the same composition but a different extrazeolite pore volume (0.40, 0.58 and 0.81 ml/g) were tested in the alkylation of benzene with propylene. Increasing the pore volume resulted in an increase of the catalyst life (Fig. 8). Therefore, the different behavior of catalyst pellets may be due to both the zeolite component and the formulation procedure.

Innes et al. [9] reported the activity and stability for zeolite extrudates in the cumene production under liquid-phase decreases in the order Beta > USY > REY > Omega > ZSM-5. For the same reaction Ercan et al. reported a better activity for zeolite Y extrudates than zeolite Beta extrudates [22]. These evidences could be due to different texture properties of the extrudates.

Ercan et al. stated the mass transfer effects in the alkylation with catalyst of different shape (i.e.

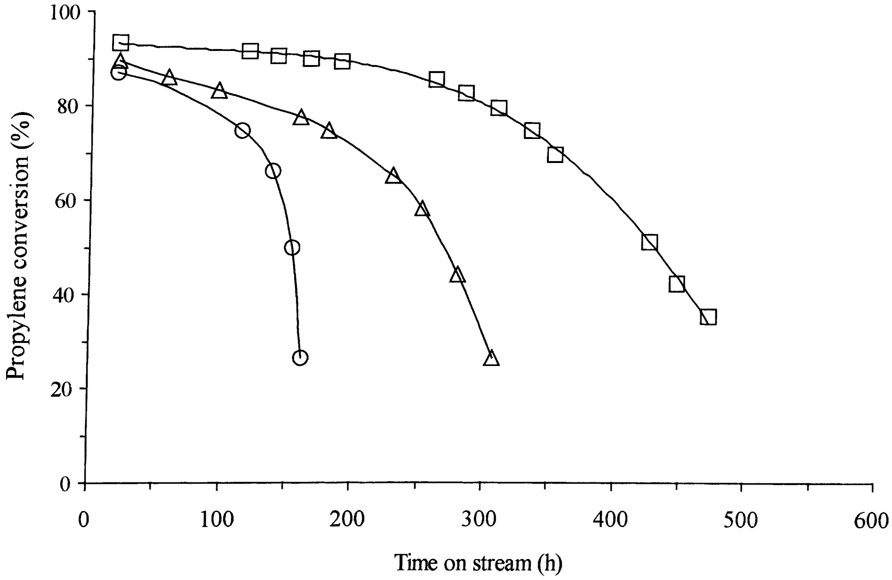


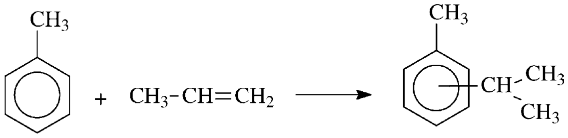
Fig. 8. Benzene alkylation with propylene. Effect of the catalyst extra-zeolite pore. (□) 0.81 ml/g; (△) 0.58 ml/g; (○) 0.40 ml/g.

extrudates and granules) and size. As the cumene synthesis is relatively fast, the external mass transfer resulted rate limiting. Therefore, the cumene process can benefit from catalyst size reduction. To overcome the mass transfer limitations, a different formulation approach was proposed by Jansen et al. [31]. This new approach is based on the coatings of shaped support with zeolites. The advantages of these structured catalysts are to increase the activity per weight of zeolite, to reduce the pressure drop and to improve the heat transfer. Coatings of α-alumina supports (i.e. extrudates and spheres) with zeolite Beta were prepared and tested for the transalkylation of DEBs and for the EB synthesis. These catalysts may be usefully applied in catalytic distillation units.

3. Alkylation of toluene with propylene to produce cymene

3.1. Introduction and traditional process

Cymene (methylisopropylbenzene) production is commercially carried out by alkylation of toluene with propylene (Scheme 3).



Scheme 3.

m-Cymene and *p*-cymene are intermediates for the production of *m*- and *p*-cresol, by oxidation and acid cleavage. Although the demand for cymene is much lower than for cumene, some commercial units are operating with an installed capacity of around 40 kilo tonnes per year. The alkylation produces a mixture of cymene isomers (i.e. *o*-, *m*- and *p*-). The most preferred isomer distribution requires a low *o*-cymene content, since *o*-cymene is difficult to oxidize and inhibits the oxidation of the other isomers. The lowest *o*-cymene content is obtained from an isomer mixture at the thermodynamic equilibrium (Fig. 9a).

The isopropylation of toluene is an electrophilic substitution on the aromatic ring, activated on the *o*- and the *p*-positions by the presence of the methyl group. The *p*-position is favored because of steric hindrance of the methyl group. The *m*-cymene is thermodynamically more stable (Fig. 9a) [32] and can be obtained by either direct isopropylation or isomerization. Isomerization is the most important route to *m*-cymene, while the amount formed by

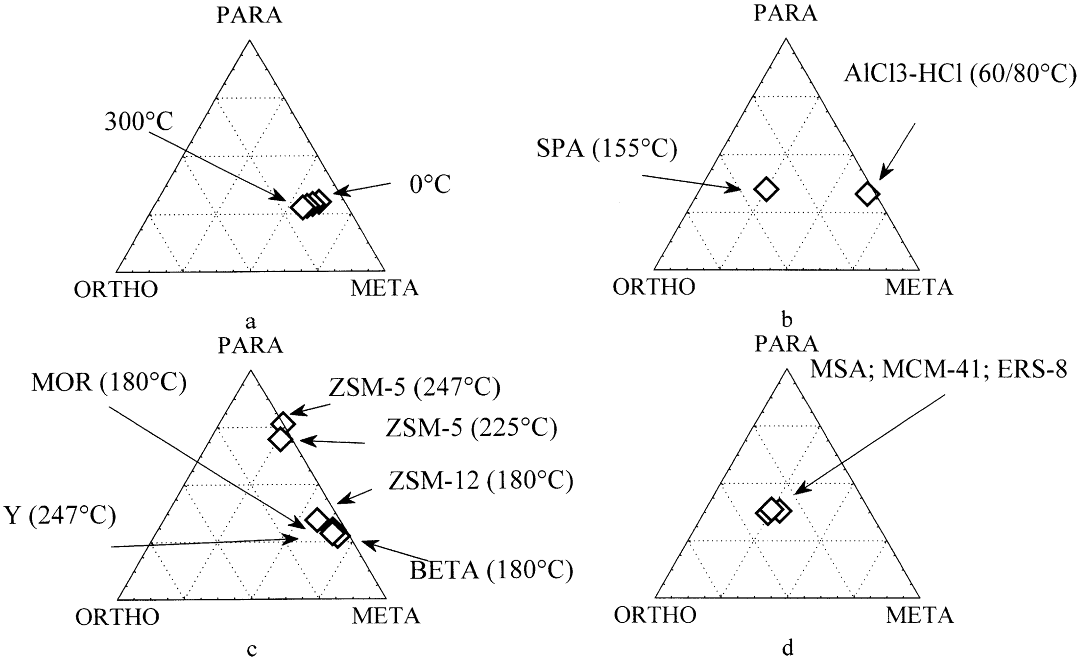


Fig. 9. Cymenes distribution: (a) equilibrium composition; (b) composition obtained by traditional processes; (c) composition obtained by zeolite catalysis; (d) composition obtained by silica-alumina catalysis.

direct isopropylation is less significant for the mechanistic reasons mentioned above. Hence, the final isomer distribution depends on the combination of alkylation–isomerization rates.

As for cumene, two catalytic technologies are applied for the production of cymene, based on AlCl$_3$–HCl and on SPA (Fig. 9b). Using AlCl$_3$–HCl (liquid-phase, $T = 60$–$80\,^{\circ}\mathrm{C}$), an isomer ratio close to the equilibrium one is obtained (i.e. 3% *o*-cymene, 64% *m*-cymene, and 33% *p*-cymene) [1]. After oxidation to cymene hydroperoxide, the excess of cymene, containing more *o*-cymene than the feed, is recycled to the alkylation step, so that the *o*-cymene content can again be lowered through isomerization on AlCl$_3$.

SPA process differs from AlCl$_3$ process for the isomer distribution obtainable, which is far from the equilibrium one (40% *o*-cymene, 25% *m*-cymene, and 35% *p*-cymene). The process has a separation unit (Cymex), based on a 13X molecular sieve, for the separation of *m*- and *p*-isomers, which allows the production of the pure corresponding cresols [33]. The *o*-isomer is then transferred to an isomerization unit.

3.2. New solid acid catalysts

The use of solid acid catalysts for this alkylation was explored too, in order to meet the aforementioned environmental and economic requirements. The isopropylation of toluene with propylene or isopropanol was largely studied using different zeolite catalysts. Fraenkel and Levy [34] reported that, in the gas-phase alkylation of toluene with isopropanol ($T = 250\,^{\circ}\mathrm{C}$), ZSM-5 is more *p*-selective than large pore zeolites like mordenite and Y (97.2% versus 46.0 and 37.6%, respectively). On the other hand, ZSM-5 catalyzes the production of *n*-propyltoluene in non-negligible amounts (9.9 wt.%), while mordenite and Y produce only cymene. The mechanism of *n*-propyltoluene formation was elucidated by Wichterlova and Cejka [35]. It was shown that cymene formed in the first alkylation step, undergoes to bimolecular reaction with toluene leading to *n*-propyltoluene. The ability to produce *n*-propyltoluene in the gas-phase alkylation of toluene with isopropanol increases in the order mordenite $<$ Y $<$ ZSM-5. The relative concentration

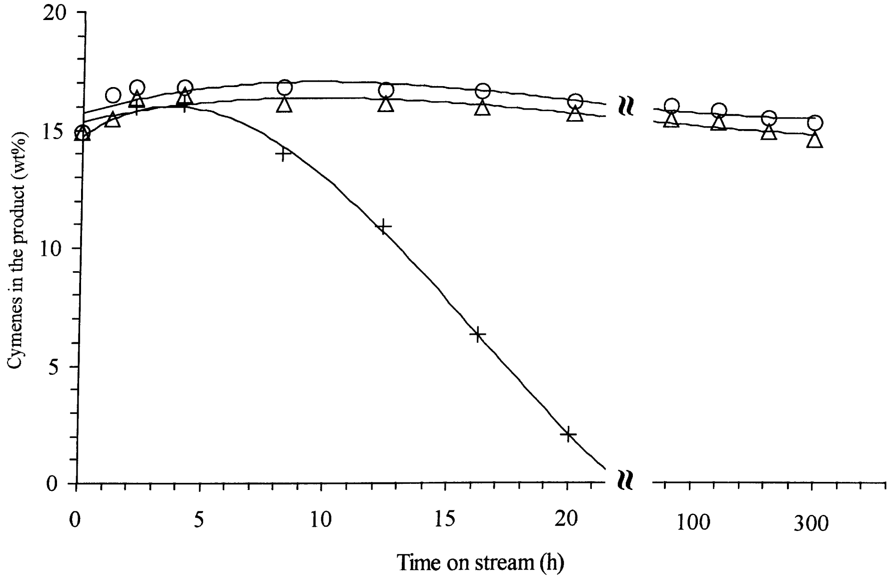


Fig. 10. Toluene alkylation with propylene. Activity and stability of large pore zeolites. Reaction conditions: 180 °C; WHSV: 4 h^{-1}; toluene/isopropanol: 8. (○) Beta; (☐) ZSM-12; (+) mordenite.

of *n*-propyltoluene to cymene increased substantially increasing the temperature ($T = 247–347\,°C$).

An increased selectivity to cymene in the gas-phase alkylation of toluene with isopropanol, was reported using different large pore zeolites (i.e. Beta, mordenite and ZSM-12) at a lower temperature (180 °C) [36]. In these conditions, ZSM-12 and Beta showed a larger stability (Fig. 10). Moreover, Beta was more selective to cymene, producing less diisopropyltoluenes and xylenes. Finally, Beta was demonstrated to give higher performances than ZSM-5 by Halgeri and Das [37] (Table 9).

In the liquid-phase alkylation of toluene with propylene ($T = 180\,°C$, $P = 3.9\,MPa$) [32], zeolite Beta produces a low concentration of *o*-cymene and a high *m*/*p* ratio, that approaches the thermodynamic equilibrium upon increasing the residence time (Fig. 9c). Also amorphous silica-alumina with controlled porosity (i.e. the mesoporous MCM-41 and MSA, the microporous ERS-8) were considered for the liquid-phase alkylation of toluene with propylene [32] (Table 10). Mesoporous MSA and MCM-41 show alkylation activities larger than the microporous ERS-8 and comparable with zeolite Beta at 180 °C. However, MSA and MCM-41 give a lower cymenes selectivity than zeolite Beta, because of the larger formation of polyalkylates. This can be due to both the presence of large pores and the low transalkylation

Table 9
Toluene alkylation with isopropanol

	ZSM-5	Beta
Toluene conversion (wt.%)	10.05	22.4
Cymene selectivity (wt.%)	62	98
n-Propyltoluene selectivity (wt.%)	14	0

Reaction conditions: $T = 225\,°C$; WHSV $= 5.5\,h^{-1}$; toluene/isopropanol = 4.

Table 10
Comparison of MSA, MCM-41, ERS-8 and Beta zeolite in toluene alkylation with propylene

	MSA	MCM-41	ERS-8	Beta
Propylene conversion (%)	99.5	99.5	98.6	99.2
Cymenes/C3 selectivity (%)	82.4	79.5	79.4	94.8
Cymenes/C7 selectivity (%)	89.7	88.7	88.6	96.3
Polyalkylates (wt.%)	11.9	14.1	14.3	2.5

Reaction conditions: $T = 180\,°C$; $P = 3.9\,MPa$; toluene/propylene = 7; WHSV $= 2\,h^{-1}$.

activity, in agreement with the low Brønsted acidity of this amorphous silica-alumina.

In conclusion, all large pore zeolites produce compositions close to the equilibrium ones. The medium pore ZSM-5 behaves differently, according to its *p*-selectivity (Fig. 9c).

The distribution of cymene isomers obtained with MCM-41, MSA and ERS-8 is far from the equilibrium (Fig. 9d) and much more similar to the one reported for SPA [38]. Such a behavior indicates the low isomerization activity of amorphous silica-alumina.

In conclusion, zeolite Beta is the best candidate to substitute $AlCl_3$–HCl for the liquid-phase alkylation of toluene with propene. However, MSA and MCM-41 can be considered as a possible alternative to SPA catalyst.

An alternative route to produce cymene was proposed by Bandyopadhyay et al. [39]. Accordingly cymene was produced by transalkylation of toluene with cumene and 1,4-DIPB. Among the large pore zeolites considered, Beta was more active and selective than Y and ZSM-12.

Finally, the dehydrogenation of α-pinene, although beyond the aims of this review, has to be mentioned as a very interesting route to produce *p*-cymene selectively. Thereby up to 98% yield of *p*-cymene can be achieved [40,41].

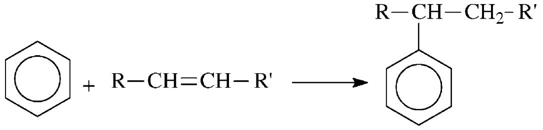
4. Linear alkyl benzene

4.1. Introduction and traditional processes

Linear alkylbenzene (LAB) is the primary raw material used to produce LAB sulfonate (LAS), a surfactant detergent intermediate. LAB global demand is about 2.7 million metric tonnes per year, its growth being mainly expected in the less developed areas of the world [42].

Traditional processes [43] for LAB production all include an alkylation unit with liquid catalysts, which depending on the process, may implies the following.

1. Alkylation of benzene with olefins C10–C14 in the presence of HF.
2. Alkylation of benzene with chloroparaffins C10–C14, in the presence of $AlCl_3$.



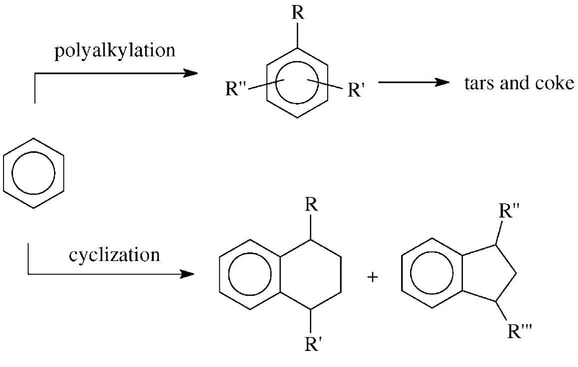
Scheme 4.

3. Alkylation of benzene with olefins C10–C14, in the presence of $AlCl_3$.

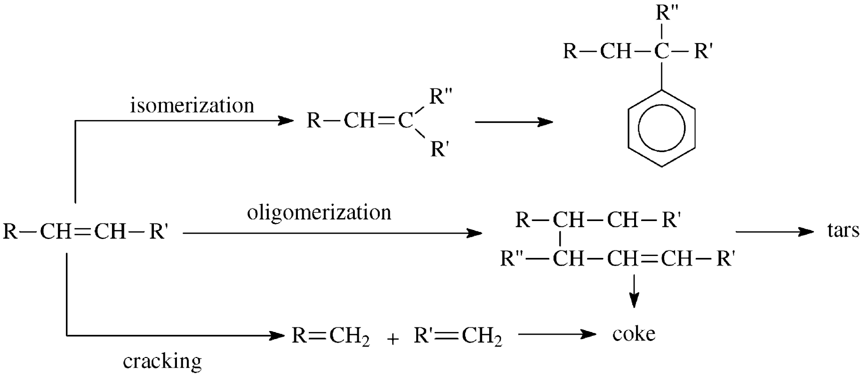
Nowadays, most of the LAB is produced from linear internal olefins and the majority of commercial applications worldwide are based on HF catalyst (process 1). The main reaction (Scheme 4) is usually accompanied by benzene (Scheme 5) and olefin (Scheme 6) side reactions, with co-production of undesired compounds.

Polyalkyl benzenes, indanes and tetralines are the typical compounds produced by benzene side reactions, while branched alkyl benzenes and oligomers, which are precursors of tars and coke, are usually produced by olefin side reactions. Polyalkylation and oligomerization reactions are depressed by increasing the benzene to olefin ratio in the feed, which in commercial processes is set at 8 (Table 11). In addition, as a general feature, the processes are designed, by controlling the reaction temperature, to minimize skeletal isomerization of the olefins, since high linearity is necessary to yield a product that biodegrades at high rates.

Each of the LAB processes creates slightly different LAB products (Table 11), the chloroparaffins/$AlCl_3$



Scheme 5.



Scheme 6.

Table 11
Commercial processes for the production of LAB

	Alkylation with chloroparaffins	Olefin/ $AlCl_3$	UOP/HF alkylation
Catalyst	$AlCl_3$	$AlCl_3$	HF
Temperature (°C)	65–70	60–75	40–60
Feed ratio	8/1	8/1	8/1
Lab linearity (%)	<90	98	92–94
Tetralins (%)	3–4	<1.0	<0.3

alkylation gives the poorest product with the lowest linearity (88 wt.%) and the highest tetralins content (6–10 wt.%). On the other hand, the two processes based on olefin alkylation are comparable as far as the tetralins production is concerned (<1 wt.%), the olefin/$AlCl_3$ process being better as far as the linearity is concerned (98 wt.% versus 93 wt.%).

The critical drawbacks related with the use of liquid catalysts as HF and $AlCl_3$, represented a great driving force towards the development of a new solid catalytic system, able to substitute the traditional catalysts and to keep the high standards of the product quality already reached.

4.2. *Alkylation with solid acid catalyst*

Among the solid acids considered as catalysts for benzene alkylation, various zeolites [44], clays [45], heteropolyacids [46], sulfated zirconia [47] and immobilized ionic liquids [48] were tested. However,

Table 12
Benzene alkylation with C10–C13 olefins[a]

Catalyst	*T* (°C)	Olefins conversion (%)	LAB linearity (%)	Life (h)
Zeolite				
Y	155	99	91.7	140
Beta	155	99.5	78.5	120
ERB-1	155	98.7	88.45	<40
L	155	92.8	72.92	<20
CaY	155	99.8	41.8	>160
ReY	155	99.8	91.61	120
LaY	155	99.8	94.89	160
Pillared clay				
Al–PILC	155	93.1	98.5	16
AlCe–PILC	155	100	93.8	140
AlGaCeMg–PILC	155	100	94.2	240

[a] Benzene/olefin = 15.

they gave results, which have not industrially exploited so far.

In the case of zeolites, for instance, all the materials evaluated in the reaction with a real olefin stream showed a high activity at low time on stream (Table 12 [49]). Even so, some of them are not stable: ERB-1 and L zeolites deactivated just after 40 and 20 h time on stream, respectively. On the other hand, Y and Beta zeolites, which are characterized by large pores structures and showed high activity for 140 and 120 h time on stream, respectively allow poor selectivities to linear alkyl benzene, which, never exceed 93 and 74 wt.%, respectively. Better results were found in the case of catalysts based on clays. In particular, a catalyst based on a montmorillonite pillared with aluminum, gallium, cerium and magnesium (AlGaCeMg–PILC) allowed total conversion with 94.2% selectivity to linear LAB for over 240 h (Table 12 [50]).

An important breakthrough was achieved by UOP in 1992, which jointly with CEPSA developed the new Detal^{TM} process, based on a fixed bed of acidic, non-corrosive catalyst to replace the liquid HF acid used in the UOP former process [51]. According to the published literature, the catalyst, a fluorided silica-alumina, was discovered and patented by UOP [52,53]. The researchers found that selectivity of the fluorided silica-alumina increases with increasing silica content. However, the best overall performance comes from those catalysts with silica to alumina ratio of from 65/35 to 85/15. The catalyst is prepared by impregnating the silica-alumina with HF and the finished catalyst contains 1–6% fluorine. The Detal^{TM} process proved to yield a superior product compared to that from HF acid technology (Table 13), the product linearity is higher (95%) and total tetralins are lower (<0.5%).

As far as the stability is concerned, the Detal^{TM} catalyst is satisfactorily active with periodic mild rejuvenation: it was demonstrated that during the commercial test, in 14 months of operation, the catalyst temperature was within 5 °C of the start of run temperature [23].

Table 13
LAB by Detal^{TM} process

n-Alkylbenzene (wt.%)	Tetraline (wt.%)
95	<0.5

Finally, as a proof of the improvement achieved with the use of a solid acid catalyst, the process economics [54] turned to be favorable. The estimated erected cost for Detal^{TM} process is about 7% lower than the HF process. The difference is due to the lower cost of Detal^{TM} unit, which does not require costly materials or equipment for safety and effluent treating. Another additional savings in operating costs are expected because Detal^{TM} process does not require scrubbing and inorganic salts waste disposal.

The Detal^{TM} catalyst and process was successfully demonstrated at Petresa's demonstration unit in Spain in 1992, and today three LAB complexes use this technology [55].

5. Conclusions

For the aromatic alkylations accounting the largest productions, new solid catalysts and new processes conforming the environmental and safety concerns are currently available. Various solid catalysts based on different zeolites have been developed for the production of EB and cumene up to the industrial scale. The data available do not allow to easily ascertaining which the best catalyst is. However, to our knowledge and according to molecular mechanics calculations, it seems that the structure *BEA is the most suitable for cumene synthesis, while MWW is the most suitable for EB synthesis. Besides it has been demonstrated that, although zeolite structure is very important, zeolite composition and morphology are very critical and cannot be ignored in the alkylation catalyst formulation. The new technologies operate in the liquid-phase and showed to be very rewarding as far as the productivity and stability are concerned, so that a complete substitution of $AlCl_3$, HF and H_3PO_4 with solid acid catalysts is expected by 2010.

As far as cymene is concerned, a "green solution" based on a solid acid catalyst is also available, although the industrial stage has not been demonstrated so far. Beta zeolite and mesoporous alumina oxides are in this case the best catalysts ever tested, depending on the isomer composition desired.

Finally, the most recent achievement in the field of aromatic alkylations catalyzed by solid acids has been accomplished in LAB production. In this case also the technology has been industrially demonstrated and is now commercially available.

The new deal towards processes environmentally benign, which has just been inaugurated with the recognition of the qualities of some solid catalysts, is expected to be further reinforced by the validation of other tools now available. Structured catalysts that leads to smaller, cleaner and more energy efficient technology (i.e. process intensification), the use of ionic solvents, the exploitation of new substrates, are only some of the new directions that should be performed in order to improve the sustainability of the alkylation processes.

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