ALKYLATION OF HYDROCARBONS WITH ZEOLITE CATALYSTS - COMMERCIAL APPLICATIONS AND MECHANISTIC ASPECTS

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ABSTRACT

HZSM-5 zeolite is now used commercially in the Mobil-Badger process for alkylation of benzene with ethylene. Due to the relatively high temperature (ca. 400 °C) and the shape selective catalyst, the chemistry and the by-products differ substantially from those in conventional ethylbenzene processes. The shape selective alkylation of toluene with ethylene in modified HZSM-5 gives para-ethyltoluene which is a raw material for poly-para-methylstyrene, a competitor for polystyrene which waits for its acceptance in the polymer industry. Selective side chain alkylation of toluene with methanol on basic faujasites, especially CsX, leads to a mixture of styrene and ethylbenzene. Brönsted acid faujasites in a fresh state are able to catalyze the alkylation of i-butane with light olefins. However, side reactions inevitably lead to carbonaceous deposits which bring about a deterioration of the catalytic performance: After a relatively short time on stream, the zeolite no longer alkylates i-butane; instead, it oligomerizes the olefins.

INTRODUCTION

Alkylation is best defined as the generation of an alkyl group, usually at a C, O, N, or S atom, in an arbitrary substrate. Typical alkylating agents are alkenes, alcohols, alkyl halides, and esters. The new bond may be formed by an addition, insertion, or substitution type of reaction. It is evident that such a definition covers a vast number of organic reactions, the mechanisms of which may differ substantially from each other. Indeed, alkylations may proceed via carbocations, via carbanions, via radicals or via transition metal complexes.

In practice, alkylations via carbocations play by far the most important role. They are catalyzed by acids: In petroleum refining, alkylation of i-butane with light olefins is widely used to produce

high octane gasoline. Since many decades, the commercial processes have been relying on liquid catalyst systems, viz. H_2SO_4 or HF. In petrochemistry, various aromatic raw materials are upgraded by alkylation. In particular, benzene is alkylated with ethylene, propene or a mixture of C_{10} to C_{20} alkenes to manufacture ethylbenzene, cumene, and linear alkylbenzenes, respectively. In almost all these processes, either so-called Friedel-Crafts type catalysts, e.g., $AlCl_3/HCl$, or one of the above-mentioned liquid acids are traditionally employed [1]. However, some years ago, HZSM-5 zeolite has been introduced on a commercial scale as a catalyst for benzene/ethylene alkylation.

Without any doubt, there is additional commercial potential for *acid* zeolite catalysts. Among their principal advantages over conventional acids are (i) the easy recovery of products, (ii) the regenerability, (iii) the lack of corrosiveness, (iv) the absence of noxious or environmentally hazardous streams, and (v) the possibility of shape selective alkylation. Furthermore, *basic* zeolites are attractive catalysts because they enable selective side chain alkylation in alkylaromatics.

In the present article, the industrial use of zeolites as alkylation catalysts will be reviewed. Moreover, mechanistic aspects of alkylation will be discussed with emphasis on zeolites as catalysts. For space reasons, the discussion will be confined to alkylation of hydrocarbons.

ALKYLATION OF AROMATICS

Ethylbenzene, the Mobil-Badger process. Ethylbenzene is the key intermediate in the manufacture of styrene which is one of the most important industrial monomers. Almost all ethylbenzene is synthesized from benzene and ethylene, the worldwide capacity amounting to ca. $10 \cdot 10^6$ t/a.

In the conventional ethylbenzene technology, liquid phase and gas phase processes are usually distinguished. In the liquid phase processes, $AlCl_3/HCl$ is the most widely used catalyst. The temperatures and pressures are 90 to 150 °C and 1 to 10 bar, respectively. In the gas phase processes, solid catalysts such as $SiO_2-Al_2O_3$ (Koppers), H_3PO_4/SiO_2 (UOP), or BF_3/Al_2O_3 (UOP, Alkar process) are employed. The temperatures are around 300 °C and the pressures above 50 bar.

In 1976, the Mobil-Badger ethylbenzene process was announced [2]. It is based on HZSM-5 zeolite [3] modified, perhaps, by phosphorus [4]. The first commercial unit with a capacity of 500000 t/a went on stream in 1980 at the American Hoechst Corp., Bayport, Tex. Somewhat earlier

the process was implemented at Cosden Oil & Chemical Co., Big Spring, Tex., by revamping an idle Alkar unit [5]. A simplified flow sheet of the Mobil-Badger process is depicted in Fig. 1.

Alkylation is carried out in the gas phase at ca. 400 °C and 20 bar. The molar benzene/ethylene ratio in the feed is 6 to 7. The heat of reaction (ca. 100 kJ/mol) is removed by injection of cold reactants between the catalyst beds. The conversion of ethylene is 100 %. During alkylation, coke deposits slowly onto the catalyst. For regeneration, the deposits are burnt periodically, hence at least two reactors are required for a continuous operation of the plant. The cycle length bet- ween successive regenerations is in the order of one to several weeks. In the separation section, excess benzene is first recovered for recyc- le. Ethylbenzene is then separated from the heavier by-products. In the final column, a diethylbenzene cut is removed from the heavy ends. Upon recycling, the diethylbenzenes undergo transalkylation with ben- zene, whereby additional ethylbenzene is formed.

Compared to conventional liquid phase processes, the Mobil-Badger process offers all the aforementioned advantages. It is, moreover, ener- gy efficient since the heat of reaction is recovered at a high tempera- ture level. Although hardly any yield data have been published by the licensors, it is known [3] that the nature and concentrations of by- products differ substantially from those encountered in conventional ethylbenzene processes. In the latter, polyethylbenzenes (up to hexa- ethylbenzene) are typically formed by multiple alkylation. It is very unlikely that, inside the shape selective ZSM-5 catalyst, the bulky
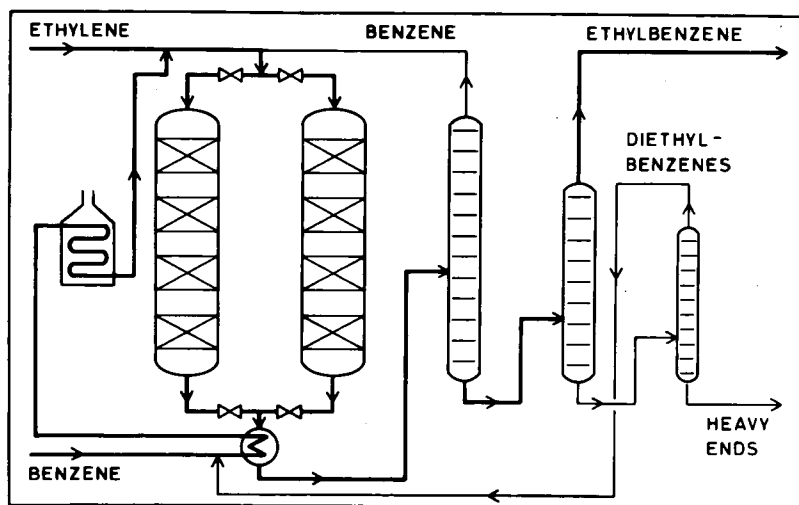

Fig. 1. The Mobil-Badger ethylbenzene process.

polyethylbenzenes with three or more ethyl groups form. Nor could such bulky products diffuse out of the pentasil pore system. On the other hand, certain by-products do occur in the Mobil-Badger process which do not normally play a significant role in the conventional processes, viz. alkylaromatics with side chains other than ethyl groups. Even toluene and xylenes are formed, especially at elevated temperatures [4]. Possible reaction paths which lead to such by-products will be discussed below.

Of utmost importance for the commercial success of HZSM-5 zeolite was its low tendency to build up coke deposits. Probably, the rapid coking of acid faujasites and mordenites, especially when in contact with olefins, prevented such large pore zeolites from attaining commercial acceptance as catalysts in alkylation of aromatics.

Para-ethyltoluene. Toluene is a less expensive raw material than benzene, and the price gap between the two aromatics has been steadily widening over the past decade. Hence, there is an increasing incentive for replacing benzene by toluene. In principle, the whole chemistry from benzene to polystyrene (alkylation with ethylene, dehydrogenation, polymerization) can be based on toluene as well. However, the acid cata lyzed alkylation of toluene with ethylene gives a mixture of ortho-, meta-, and para-ethyltoluene. During the subsequent dehydrogenation, part of the ortho isomer undergoes cyclization to indane and indene. These impurities are difficult to remove from the vinyltoluene monomer and deteriorate the final polymer.

All these problems can be avoided by alkylating toluene in a shap selective catalyst which prevents the formation of the bulky ortho-ethyltoluene. Unmodified HZSM-5 zeolite still gives the three isomers, essentially in their equilibrium distribution [6]. However, by modifying HZSM-5 with certain reagents, para-ethyltoluene is formed almost exclusively, together with minor amounts of the meta isomer. Suitable modifyers contain P, Ca/P, Mn/P, B/P, B/Mg, or Si [6]. It has been proposed [7] that they bring about subtle changes in the effective pore width of the zeolite.

Pure para-ethyltoluene can be readily dehydrogenated to para-methylstyrene [8]. Polymerization of the latter gives poly-para-methyl-styrene which has been claimed to be superior to conventional polysty-rene [8-10], at least for some applications.

In 1982, an idle styrene facility at American Hoechst Corp., Baton Rouge, La., was reactivated for the manufacture of para-methylsty-rene [10,11]. Its capacity is low (16000 t/a). It remains to be seen whether poly-para-methylstyrene and, hence, shape selective alkylation
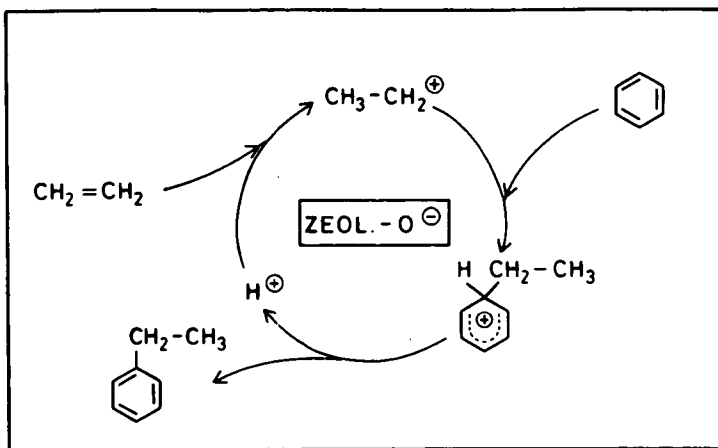
Fig. 2. Mechanism of acid catalyzed alkylation of an aromatic hydro-
carbon with an alkene.

of toluene with ethylene will be accepted on a large scale by the poly-
mer industry.

Mechanistic aspects of acid catalyzed alkylation of aromatics.
It has been repeatedly demonstrated, e.g. in ref. [12], and re-emphasi-
zed recently [13] that Brönsted OH groups are the active sites for hy-
drocarbon conversion in acid zeolites. The generally accepted mechanism
of benzene/ethylene alkylation is shown in Fig. 2. Protonation of the
alkene at the acid site gives an alkylcarbenium ion. Its electrophilic
attack on the aromatic Π-electrons results in a benzenium cation which
re-aromatizes by loss of a proton. While the Brönsted sites is restored,
the alkylated hydrocarbon desorbs.

It is clear that, in any ethylbenzene process the monoalkylated
product can again enter the catalytic cycle. This way, polyethylbenzenes
are formed at high olefin conversions. An alternative pathway for their
formation is the acid catalyzed transalkylation, e.g., of ethylbenzene
into diethylbenzenes and benzene. In HZSM-5 this reaction has been shown
[14] to proceed readily above 250 °C, probably by a pure Streitwieser-
Reif mechanism [15] via diphenylmethane type carbocations. This same me-
chanism then accounts for the reverse reaction, i.e., transalkylation of
diethylbenzenes (which are recycled in the Mobil-Badger process, cf. Fig.
1) with benzene into the desired ethylbenzene. Due to steric constraints,
very little, if any, polyethylbenzenes with three or more ethyl groups
will be formed inside the ZSM channel system.

As pointed out earlier, alkylaromatics can be formed in the Mobil-
Badger process, which contain C_3, C_4 or even higher side chains. A good
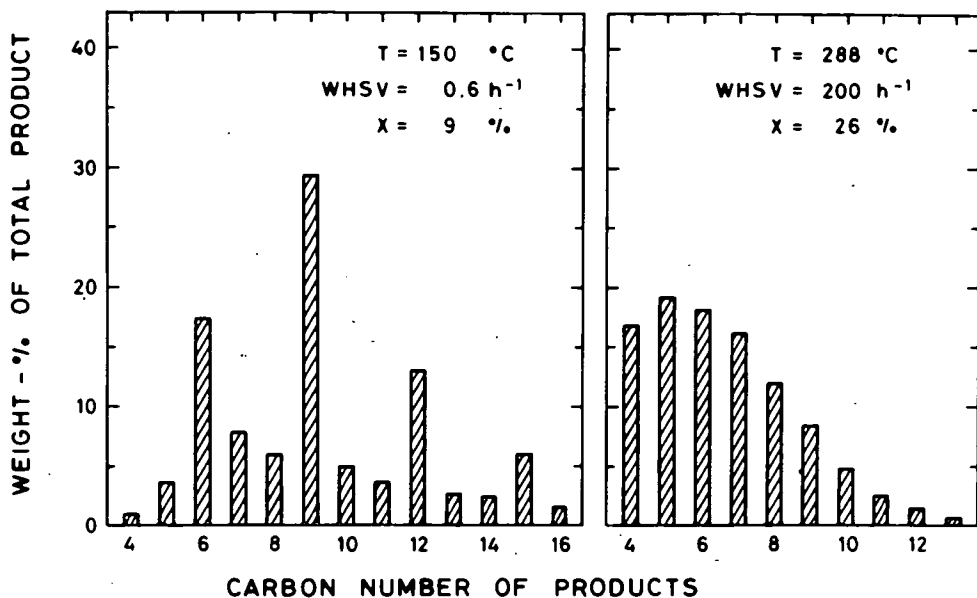
Fig. 3. Products from the conversion of propene in HZSM-5, after [18].

explanation for their occurrence emerged recently from model studies on the conversion of olefins in HZSM-5 [16-18]. Haag [18] published product distributions obtained from propene at different temperatures but comparable conversions (Fig. 3). At 150 °C, true oligomers (C_6H_{12}, C_9H_{18}, $C_{12}H_{24}$, $C_{15}H_{30}$) predominate. At 288 °C, by contrast, there is no indication at all for a common C_3 source. Rather, a pool of olefins is formed with a carbon number distribution governed by a temperature and pressure dependent pseudo-equilibrium [18]. The olefins are inter-converted by ionic oligomerization and cracking. Ethylene, though less reactive than propene, gave essentially the same result [17]. Hence, some propene, butenes and, perhaps, even higher alkenes will form in the Mobil-Badger process and eventually take part in the alkylation of aromatics. It appears that the existence of a pool of olefins with different carbon numbers also provides a key to the mechanism of the methanol-to-hydrocarbons conversion in HZSM-5 [18] and related materia [19].

Still other mechanisms must be invoked to account for the formati of *methyl*aromatics in the Mobil-Badger process. It is likely that the methyl groups arise from cracking of C_2, C_3, C_4, or other alkyl chains at elevated temperatures. One possible mechanism is acid catalyzed cra ing via non-classical carbonium ions. For paraffinic substrates, it has recently been claimed [20] that such a mechanism is favored both b

the steric constraints in pentasils and by high temperatures. Alternatively, thermal cracking via free radicals might occur at the zeolite surface [21].

Coke is inevitably formed as a by-product in almost all hydrocarbon reactions on acid catalysts. The low rate of coke formation in HZSM-5 is nowadays interpreted in terms of restricted transition state shape selectivity [22,23]. For a detailed discussion of coke formation and its inhibition in medium pore zeolites, the reader is referred to the excellent reviews by Csicsery [24] and Derouane [25].

Beside olefins, various alcohols have been used in numerous investigations to alkylate aromatic hydrocarbons on acidic zeolites. Methanol as an alkylating agent enables the introduction of a *methyl* group (no olefin is available for this purpose). As with olefins (Fig. 2), the reaction is envisaged [26,27] to proceed via protonation of the alkylating agent followed by electrophilic attack of the resulting cation on the aromatic ring. By use of suitable zeolites, alkylation with alcohols can be conducted in a shape selective manner. For instance, more than 90 mol-% of p-xylene (as compared to ca. 25 mol-% in equilibrium) were obtained from toluene and methanol in HZSM-5 modified with P or B [27,28].

Base catalyzed side chain alkylation of toluene with methanol. On acid catalysts, alkylation inevitably occurs at the aromatic ring which is easily understood in terms of the high electron density at this location (cf. Fig. 2). By contrast, alkylation in the side chain of alkylaromatics can be attained on basic catalysts. In recent years, particular attention has been paid to the side chain alkylation of toluene with methanol which leads to styrene and ethylbenzene (in a rigorous sense, only the formation of ethylbenzene represents a true alkylation). The commercial incentive stems from using toluene, instead of the more expensive benzene, as a raw material for the production of styrene.

Faujasite type zeolites exchanged with large alkali cations, especially RbX and CsX, were found to be the most effective catalysts for toluene/methanol side chain alkylation [29-33]. Special care must be taken during their preparation to eliminate acid sites, otherwise ring alkylation interferes [33]. Boron oxide acts as a promoter [30,32,34] which enhances the selectivity for styrene/ethylbenzene. Typically, the reaction temperatures are around 400 °C.

The precise nature of the basic sites in CsX is not clear. It has been suggested [35] that they consist of Cs_2O and metallic Cs formed by reduction of Cs_2O with carbonaceous residues. Interaction of toluene

with a free basic site gives a carbanion. The new carbon-carbon bond is then generated by addition of this carbanion to formaldehyde which results from dehydrogenation of methanol. The 2-phenylethanol type intermediate is dehydrated to styrene which is either desorbed or hydr genated to ethylbenzene. An undesirable side reaction is the decompo- sition of formaldehyde into $CO + H_2$.

It has been argued [30,32] that the role of the large alkali cat ions in the supercages of zeolite X is twofold: They strongly interact with the Π electron system of toluene. Moreover, due to their bulkiness and relatively high concentration, they occupy a considerable portion of the free space within the faujasite supercage. In such an environ- ment, toluene is envisaged to be adsorbed with the ring residing bet- ween two or more cesium cations. This way, the aromatic portion of the molecule is shielded and the attack of formaldehyde on the side chain is favored. If this picture is correct, then the toluene/methanol reac- tion in CsX represents a unique example for shape selectivity in fauja- sites. The boron oxide promoter inhibits the undesired decomposition of formaldehyde.

ALKYLATION OF ISOBUTANE

Its place in petroleum refining, stoichiometry of the reaction. Fluid catalytic cracking (FCC) is used in many refineries to produce gasoline from vacuum distillates. With modern zeolite catalysts, the gasoline yields in FCC are slightly above 50 wt.-%. Besides, some 15 wt.-% of C_3 and C_4 hydrocarbons are formed. The main constituents of this side stream are i-butane, butenes, and propene. Additional high octane gasoline can be manufactured by alkylation of i-butane with the mixed butenes and/or propene. Today, the worldwide capacity for alkyl tion gasoline amounts to nearly $50 \cdot 10^6$ t/a.

Isobutane/olefin alkylation cannot be described adequately by a simple stoichiometric equation. Alkylate *always* consists of a comple mixture of i-alkanes ranging from C_5 to ca. C_{12}. Typical carbon number distributions are listed in Table 1. It will be shown later that all possible i-alkanes with at least one tertiary carbon atom are usually formed.

The conventional liquid phase processes. In the commercial proces ses, liquid acids, viz. concentrated H_2SO_4 or anhydrous HF, are used exclusively. Today, the installed capacities of the H_2SO_4 and HF pro- cesses are roughly equal, with a trend towards HF alkylation [36].

The reaction is carried out at low temperatures (5 to 10 °C in H_2SO_4, 25 to 40 °C in HF) and moderate pressures, such as to keep the

Table 1

Alkylation of i-butane with butenes. Typical product distributions in wt.-%, after [36].

		H_2SO_4-process	HF-process
"Light ends":	$i-C_5H_{12}$	8	5
	$i-C_6H_{14}$	7	4
	$i-C_7H_{16}$	6	4
	$i-C_8H_{18}$	64	74
"Heavy ends":	$i-C_9H_{20}$ and higher	15	13

hydrocarbons liquid. The i-butane/olefin ratio in the feed is very high (10 to 20) in order to suppress undesirable side reactions of the olefins. An efficient removal of the heat of reaction is essential. Even under optimum process conditions, some tarry by-products are formed, especially in the H_2SO_4 processes. Propane and n-butane are completely inert.

Although the liquid phase processes have been operated successfully for decades, they are not free from drawbacks and shortcomings. Among these are the corrosiveness and toxicity of HF and the large amounts of tarry by-products formed in H_2SO_4 which are difficult to dispose of in an environmentally acceptable way. A viable and clean process based on a solid catalyst remains highly desirable.

Attempts to use zeolite catalysts. The principal feasibility of i-butane/olefin alkylation on acid faujasites was demonstrated as early as 1968 in the open literature: Mobil researchers published a note on i-butane/ethylene alkylation over deammoniated ammonium/rare earth X zeolite [37]. Much more detailed information was released by the group at Sun Oil Co. [38-42]. They alkylated i-butane with a variety of olefins, mostly on deammoniated ammonium/rare earth Y zeolite. In subsequent years, the fundamentals of the reaction were investigated by a relatively small number of academic groups [43-53]. The contributions of Schöllner et al. [43-46] and the recent papers by Daage and Fajula [52,53] deserve particular attention.

It emerges from all these studies that faujasites in a Brönsted acid form indeed give product distributions with all features of alkylate produced in H_2SO_4 or HF. Typical carbon number distributions of i-butane/n-butene alkylation (1-butene, cis-2-butene, and trans-2-
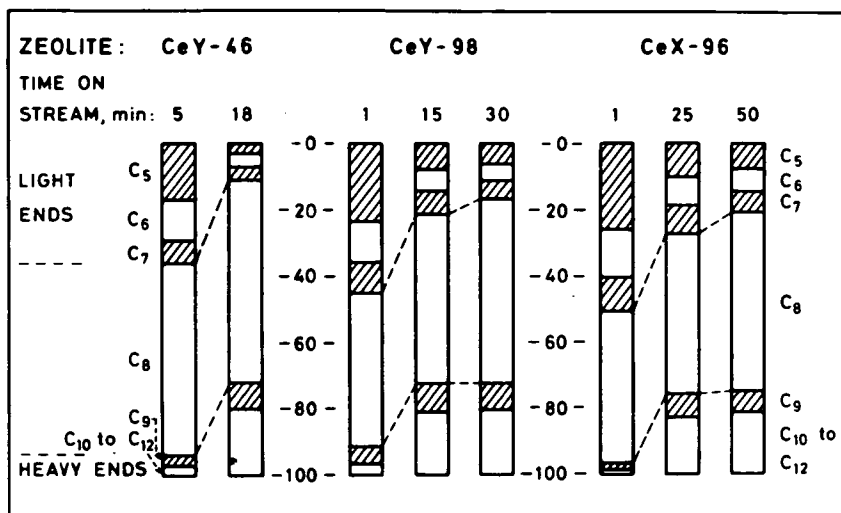
Fig. 4. Alkylation of i-butane with n-butenes on cerium exchanged faujasites ($\dot{n}_{\text{i-butane}} : \dot{n}_{\text{butene}}$ = 11 : 1, fixed bed reactor, $m_{\text{CeY-46}}$ = 1.1 g, $m_{\text{CeY-98}}$ = 1.4 g, $m_{\text{CeX-96}}$ = 1.5 g, T = 80 °C, P = 3.1 MPa, liquid feed rate = 7.5 cm³/h, [50,51]). Carbon number distributions in wt.-%.

butene give identical results) over cerium exchanged faujasites are shown in Fig. 4. The degree of cerium exchange is given in equiv.-%. All products are i-alkanes. As in H_2SO_4 or HF (cf. Table 1), a complex mixture of i-alkanes with 5 to 12 carbon atoms is formed. In all cases, i-octanes predominate. It is, moreover, seen that the carbon number distributions depend upon the time on stream: As the reaction proceeds, more heavy ends are produced at the expense of the light end (C_5H_{12} to C_7H_{16}).

Distributions of individual isomers in various alkylates are giv in Table 2. The data are limited to the C_5 through C_8 fractions becaus an individual analysis of the C_9 to C_{12} i-alkanes is not feasible, eve with the most powerful GC techniques. The data for the zeolite catalys are considered to be more reliable than those for the liquid acids. As a whole, it is evident that the same hydrocarbons form in H_2SO_4, HF, and acid faujasites: All i-alkanes with at least one tertiary carb atom are present (although sometimes in traces only). Conversely, all alkanes lacking tertiary carbon atoms (e.g., n-alkanes, 2,2-dimethylbu tane, 3-ethyl-3-methylpentane, or 2,2,3,3-tetramethylbutane) are absent Some apparent violations of this rule are probably due to n-pentane im- purities in the feed and analytical difficulties in the experiments with the liquid acids.

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Table 2

Alkylation of i-butane with butenes (technical C_4 cut for H_2SO_4 and HF, pure n-butenes for zeolite catalysts). Isomer distributions in mol-%, after [36,50,51].

Catalyst	H_2SO_4	HF	CeY-46	CeY-98			CeX-96
Time on stream, min	–	–	8	1	15	30	25
n-Pn	3	0	0	0	0	0	0
2-M-Bu	97	100	100	100	100	100	100
2,2-DM-Pr	0	0	0	0	0	0	0
n-Hx	0	0	0	0	0	0	0
2-M-Pn	17	25	12	15	19	17	19
3-M-Pn	9	11	45	22	23	27	20
2,2-DM-Bu	0	0	0	0	0	0	0
2,3-DM-Bu	74	64	43	63	58	56	61
n-Hp	0	0	0	0	0	0	0
2-M-Hx	3	6	6	6	8	6	9
3-M-Hx	2	3	15	7	11	11	12
3-E-Pn	0	0	3	1	1	2	1
2,2-DM-Pn	4	4	0	0	0	0	0
2,3-DM-Pn	34	35	60	29	39	42	39
2,4-DM-Pn	57	52	13	51	38	35	36
3,3-DM-Pn	0	0	0	0	0	0	0
2,2,3-TM-Bu	0	0	3	6	3	4	3
n-Oc	0	0	0	0	0	0	0
2-M-Hp	0.1	0.1	0.1	0.2	0.3	0.2	0.5
3-M-Hp $\}$ 3-E-Hx	0.4	0.3	0.3	0.4	0.8	0.8	1.1
4-M-Hp	0	0	0.2	0.1	0.2	0.1	0.3
2,2-DM-Hx	0	0	0	0	0	0	0
2,3-DM-Hx	6	7	10	5	13	12	14
2,4-DM-Hx	5	6	4	6	7	5	8
2,5-DM-Hx	8	5	0.3	3	4	2	5
3,3-DM-Hx	0	0	0	0	0	0	0
3,4-DM-Hx*)	0 4	0.8	45	7	14	24	10
3-E-2-M-Pn	0	0	2	1	1	2	1
3-E-3-M-Pn	0	0	0	0	0	0	0
2,2,3-TM-Pn	2	2	4	4	3	3	3
2,2,4-TM-Pn	39	53	4	22	18	12	22
2,3,3-TM-Pn	18	12	16	28	21	20	20
2,3,4-TM-Pn	21	14	14	23	18	19	15
2,2,3,3-TtM-Bu	0	0	0	0	0	0	0

*) both diastereomers

The main constituents of the i-octane fraction are trimethylpen-
tanes (except 2,2,3-trimethylpentane). From a technical point of view,
these highly branched isomers are the most desirable products since
their octane numbers are very high (around 100). In addition, consi-
derable amounts of dimethylhexanes always occur. Note that the content
of 3,4-dimethylhexane may vary over a broad range: In the liquid acids,
it is formed in negligible amounts. On CeY-46 (with a low density and,
presumably, a low strength of acid sites), by contrast, 3,4-dimethylhexa-
ne is by far the most abundant i-octane. The data for CeY-98 further
reveal that the content of 3,4-dimethylhexane increases significantly
with time on stream. All these results suggest that 3,4-dimethylhexane
is a key isomer with a mechanism of formation which deviates from the
desirable pathway of alkylate production.

Up to this point, the discussion was restricted to the catalytic
behavior of zeolites *in a fresh state*. At low times on stream, alkyla-
tion is extremely selective, no olefins, naphthenes or aromatics are
formed, even not in traces. During this initial *alkylation stage* the
conversion of the feed olefin is always 100 %, regardless of the reac-
tion conditions.

After a certain time on stream, the alkylation stage ends. At
this point, butenes begin to appear (Fig. 5), i.e., the olefin conver-
sion drops. Concomitantly, more and more alkenes occur in the C_5 to
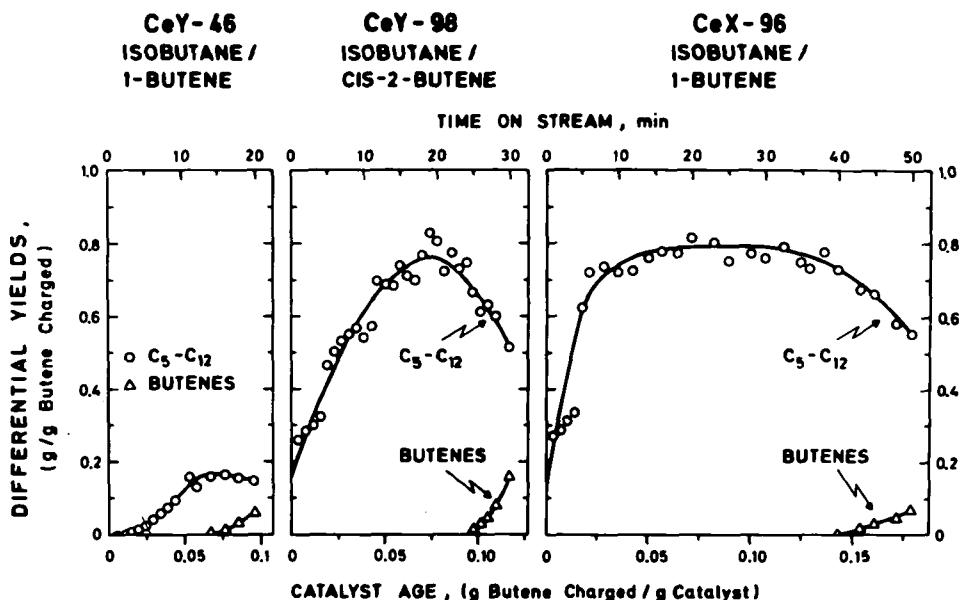

Fig. 5. Differential yields in alkylation of i-butane with n-butenes
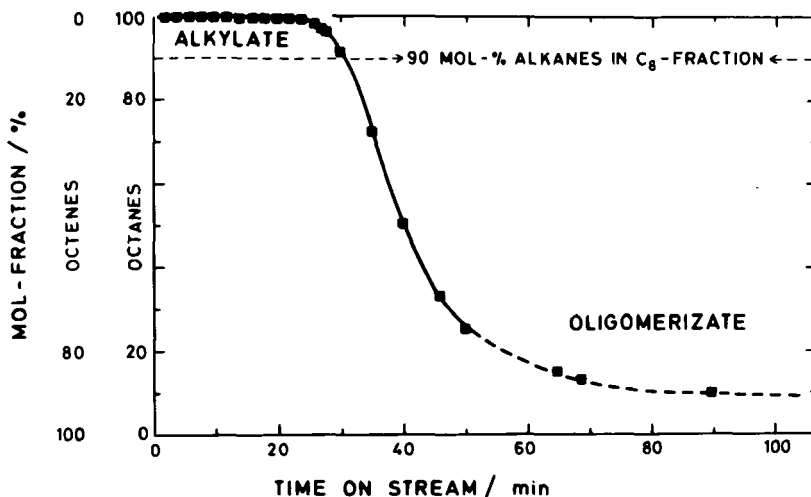on Ce faujasites at 80 °C, after [51].

Fig. 6. Isobutane/cis-2-butene conversion on CeY-98. Composition of the C_8 products, after [51].

C_{12} products. This is shown quantitatively in Fig. 6 for the C_8 fraction produced on CeY-98. It can be seen that, late in the run, the C_8 fraction mostly consists of octenes (in this section, the curve is dashed which is to indicate that the analytical accuracy is relatively low). In other words, the reaction is now better described in terms of butene dimerization or oligomerization. The dramatic shift in selectivity is due to catalyst aging. It is convenient to use the composition of the C_8 fraction [51] as a quantitative measure for the duration of the alkylation stage. Arbitrarily, we define the end of the alkylation stage as the particular time on stream at which the content of alkanes in the C_8 fraction has dropped to 90 mol-% (30 min on CeY-98, according to Fig. 6).

A stationary state is never attained in i-alkane/alkene alkylation on faujasite catalysts, at least not in a fixed bed reactor. An adequate investigation of this reaction requires experimental techniques which cope with the simultaneous occurrence of complex product distributions and rapid catalyst decay. One appropriate technique has been described [49-51]. It combines differential (or instantaneous) sampling in glass ampules with high resolution capillary GLC. If, moreover, an internal standard (such as propane or 2,2-dimethylbutane) is added to the feed mixture in a known concentration, then the analysis of each differential sample can be evaluated for the olefin conversion, the yields of individual products, and other quantities. Differential yields obtained in this manner are plotted in Fig. 5 and Fig. 7 versus
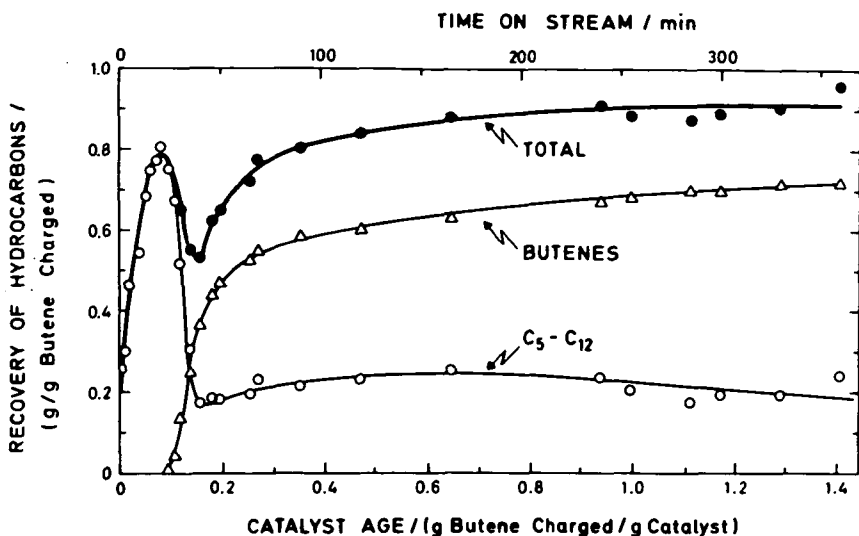
Fig. 7. Isobutane/cis-2-butene conversion on CeY-98. Differential yields of butenes and C_5 to C_{12} hydrocarbons, after [51].

time on stream. In both Figures, a second abscissa referred to as catalyst age [40] is used. It is defined as the cumulative mass of butene fed to the reactor per unit mass of catalyst. Catalyst age is proportional to time on stream. It is seen that the differential yield of C_5 to C_{12} hydrocarbons passes through a maximum. Late in the run, the total yield approaches 1 g/g butene charged.

In Fig. 5, the differential yield curves end at the respective time on stream, at which the content of i-octanes in the C_8 fraction has dropped to 90 mol-%. Integration of the C_5–C_{12} curves gives the following *integrated yields of alkylate*: 9, 70, and 125 mg alkylate/g catalyst for CeY-46, CeY-98, and CeX-96, respectively. For deammoniated ammonium/rare earth Y, the Sun Oil group [40] reported values which are better by one or two orders of magnitude (a continuous stirred tank reactor was employed and a different quality criterion for alkylate was chosen, so a direct comparison of the figures cannot be made). For a commercial process, such yields of alkylate are unacceptably low. The development of acid zeolites with much higher lifetimes in i-butane/ olefin alkylation remains a challenge in the field of catalysis.

Mechanistic aspects. Almost always, the mechanism of i-butane/olefin alkylation is interpreted in terms of a chain reaction which is delineated in Fig. 8 for linear butenes. Protonation of the olefin gives the secondary butyl cation. Hydride transfer from i-butane then leads to n-butane and the tertiary butyl cation. These steps are considered
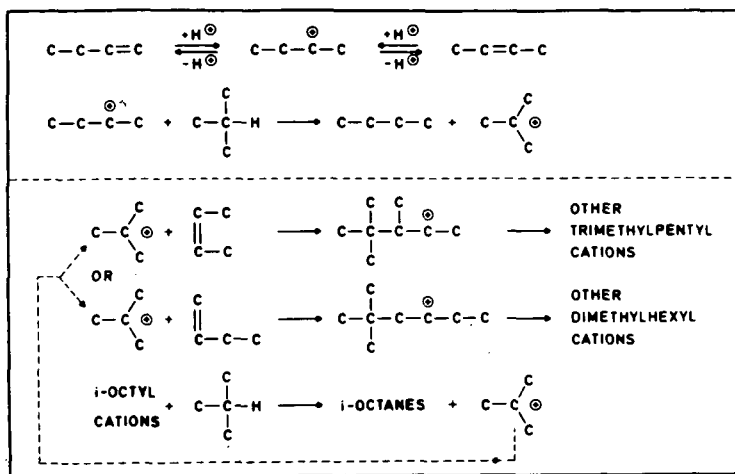
Fig. 8. Classical mechanism of i-butane/n-butene alkylation.

to initiate the kinetic chain only, hence the fact that virtually no n-butane occurs in the product is not a contradiction. Double bond shift in the alkene is considered to be rapid, therefore the tertiary butyl cation can add either 1-butene or 2-butene (which is much more abundant in equilibrium), regardless of which n-butene isomer is used in the feed. The original octyl cations formed in the addition step can rearrange whereby a variety of dimethylhexyl and trimethylpentyl cations are generated. Hydride transfer between the i-octyl cations and i-butane yields a mixture of i-octanes and the tertiary butyl cation which propagates the chain.

One important difference between the alkylation of aromatics and i-butane becomes evident from a comparison of Fig. 2 and Fig. 8: In alkylation of aromatics, the intermediate carbocation stabilizes by *loss of a proton*. By contrast, *transfer of a hydride ion* is required to produce the desired i-alkanes from alkylcarbenium ions. Of course, the latter can also stabilize by loss of a proton, but then olefins are formed, i.e., the overall reaction is olefin oligomerization instead of alkylation. It is likely that, at the relatively low temperatures around 100 °C, strong acid sites are needed to catalyze hydride transfer. These sites are soon deactivated by carbonaceous deposits.

While the classical mechanism (Fig. 8) provides a straightforward interpretation of the events which might lead to i-octanes, it suffers from severe shortcomings. For example, it does not give any explanation for the fact that alkylate always contains i-alkanes with carbon numbers other than the sum of the i-alkane and the olefin used in the feed.

Moreover, the skeletal isomerization steps postulated at the level of trimethylpentyl and dimethylhexyl cations (cf. Fig. 8) are in poor agreement with the knowledge collected in the field of catalytic iso- merization of long-chain alkanes. In the first place, it is doubtful whether such isomerization steps are catalyzed at all by zeolites *at the low temperatures* employed. In addition, it is difficult to under- stand why so little 2,2,3-trimethylpentane is formed from i-butane and n-butanes (cf. Table 2) whereas this particular isomer is predic- ted to be the primary i-octane (cf. Fig. 8). Compilations of thermody- namic data [54] do not give any indication for an unfavorable equili- brium. To account for these and other inconsistencies, a variety of side reactions have been invoked [55-57]. Among these are the so-called destructive alkylation and self-alkylation of i-butane. Another side reaction which leads from n-butenes to 3,4-dimethylhexane seems to be important in faujasites: If the secondary butyl cation adds 2-butene, then a 3,4-dimethylhexyl cation results. Hydride transfer gives 3,4- dimethylhexane. According to Table 2, this pathway is important on CeY-46 and on CeY-98 at high times on stream.

New insight into the H_2SO_4 catalyzed i-butane/olefin alkylation was gained by Albright et al. in the 1970's. By using sophisticated ex- perimental techniques, these authors showed that the mechanism is ex- tremely complex. The most important ideas were summarized by Albright [58]. Many of these ideas are probably very useful for a better under- standing of alkylation in zeolites. In particular, Albright et al. suggest that high molecular weight carbocations and hydrocarbons play a much more important role in the mechanism than hitherto assumed. There is no clear borderline between such species and the carbonaceous resi- dues. The latter are envisaged by Schöllner et al. [43] to consist of highly unsaturated hydrocarbons with cyclic structures.

Daage and Fajula [52,53] introduced the ^{13}C tracer technique to investigate the mechanism of i-butane/propene alkylation on deammoni- ated ammonium/cerium Y. Either i-butane or the alkene were labelled. A wealth of novel insight into the reaction mechanism was achieved. Among the most interesting conclusions are: There is little, if any, isomerization of tertiary carbocations, because stabilization of a ter- tiary alkylcarbenium ion by hydride transfer is faster than skeletal rearrangement. The authors divide the constituents of alkylate into four classes. Different mechanisms of formation are sketched for each class. There is no doubt that further application of the ^{13}C tracer technique can contribute to a better understanding of the extremely complex chemistry of i-butane/olefin alkylation, both in liquid acids and in zeolites.

SYMBOLS AND ABBREVIATIONS

m	mass	kg
$\dot{m}$	mass flux	$kg \cdot h^{-1}$
$\dot{n}$	molar flux	$mol \cdot h^{-1}$
P	pressure	Pa
T	reaction temperature	°C
WHSV	weight hourly space velocity $(\dot{m}_{feed}/m_{catalyst})$	h^{-1}
X	conversion	

D	di	Pr	propane
T	tri	Bu	butane
Tt	tetra	Pn	pentane
		Hx	hexane
M	methyl	Hp	heptane
E	ethyl	Oc	octane

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