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Transformation of hydrocarbons on zeolite catalysts

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Catalytic processes on zeolites and catalytic characteristics of zeolites have been reviewed in the area of petrochemistry and refining.

Keywords: Zeolite catalysts; petrochemistry; oil refining

1. Introduction

The processing of crude oil and of oil derivatives as well as the efforts at the pollution abatement are the areas which consume most of the catalysts. The catalysts used for liquid fuel production are of growing importance because of the Clean Air Act, which imposed special requirements for the quality of gasolines and diesel fuels. The new legislation and the necessity of upgrading less valuable oil components force the refiners to adapt the already existing catalytic processes and catalysts and to design new ones.

Therefore, there is no doubt that zeolites and zeotype catalysts can help to solve those challenges because of their unique and useful characteristics: high concentration of active sites which properties can be finely tuned, high thermal and hydrothermal stability, and high selectivity of the molecular sieves.

Consider that more than 90% of the crude oil is processed into fuels, so any modification of the fuel policy would substantially affect the refining scheme. According to the future legislation expected in the USA in 1995 and 1997, and in Europe and Japan after 2000 the following actions have to be undertaken:

- a decrease in the RVP of the gasoline;
- a limitation of the benzene concentration to 1% maximum (in Europe it is authorized up to 5%);
- a limitation of the aromatics concentration to 25%;
- a limited use of olefins in the areas with ozone derived problems;
- an incorporation of the oxygenated products into gasolines up to 16% of volume;
- a shift to unleaded gasoline (also applied in Europe);
- limitations in sulfur content, especially in the diesel fuel (also to be approved soon in Europe).

Considering those premises and the usual gasoline composition (table 1) one may expect that in order to decrease the RVP butanes should be eliminated with the corresponding impact on the gasoline yield and the final octane number. The same would occur if the content of aromatics were to be limited. The required decrease in the olefins content could be achieved by the extraction of the C_5 olefins from the light FCC gasoline which would decrease the gasoline yield and the octane. However, the latter parameters can be improved by producing alkylation gasoline from *n*-pentenes, and isomerization of *n*-pentenes to isopentenes to produce TAME. TAME together with MTBE produced from isobutene will allow to accomplish the required amount of oxygenated products. Therefore the production of *i*-butene and *i*-pentenes has to be increased by changing conditions and catalysts in the FCC units, as well as by designing new isomerization units capable of converting *n*-butenes, *n*-pentenes or, even better, the corresponding alkanes into the desired iso-olefins.

Furthermore, considering the octane number of the light strait run (LSR) gasoline given in table 1 it turns out that the refiners will not be able to introduce this stream into the pool without a previous isomerization. Finally, one can forecast that alkylation gasoline quality and amount will increase in future, especially if solid catalysts would be developed which could be used instead of the actual HF and H_2SO_4 catalysts.

In the case of the diesel fuel, it is first of all necessary to reduce sulfur content below 0.05 wt%, while the cetane number should remain high.

The aim of the paper is to review the role of zeolitic catalysts in adapting the new refining scheme and in the associated petrochemistry industry.

2. Isomerization of light strait run gasoline (LSR)

This gasoline stream is mainly formed by *n*-pentane and *n*-hexane, both with a low octane number (table 2), which negatively affects the final octane number of the gasoline. However, it should be possible to increase the octane number of LSR

Table 1
Average composition of gasoline, considering the different streams

Streams	% Volume	Octane clear (R + M)/2
n-butane	7	83
reformate	34	90
FCC gasoline	34	86
LSR	13	68
gasoline from alkylation and/or polymerization	7	92
C_5 and C_6 isomer	2	88
others	3	103

Table 2
RON of C_5 and C_6 alkanes

Hydrocarbon	RON
n-pentane	61.7
n-hexane	24.8
i-pentane	92.3
2M-pentane	74.5
3M-pentane	73.4
2,3DM-butane	102
2,2DM-butane	91.8

by isomerization in order to produce mono-, and especially dimethyl-alkanes. The results from fig. 1 clearly indicate that this is a thermodynamically controlled process, and therefore a successful isomerization catalyst should be able to carry out the reaction at temperatures as low as possible. That is why Pt on chlorinated or fluorinated alumina is used at temperatures below 200°C. However, such catalysts have three major disadvantages: the irreversible deactivation by H_2O, low sulfur resistance and the necessity of continuous fluor supply along with the feed.

Then large pore zeolites such as X and Y, containing Pt as the hydrogenation–dehydrogenation function, were proposed as alternative catalysts [1–3]. However, their moderated acidity required relatively high reaction temperatures, which carried a loss in the octane content. Other zeolites and zeotypes such as L, Ω, ZSM-12, beta, mordenite, and SAPOS have been used as the acidic component of bifunctional LSR isomerization catalysts [4,10]. Among them, mordenite and beta seem to be the most convenient. In the case of mordenite, an acidity maximum is theoretically expected at a Si/Al ratio of 9 [11]. However, it has been shown on various zeolites that it is possible to increase the acidity if the appropriate extra-framework Al species (EFAL) are created by the dealumination, and if the adequate interac-

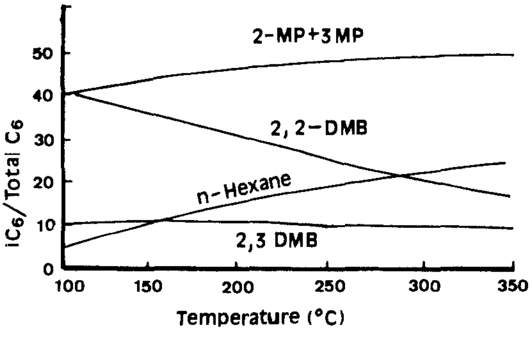

Fig. 1. Effects of temperature on the ratio of branched to unbranched C_6 alkanes.

tion occurs between the framework (FAL) and EFAL species [12,13]. In the case of mordenite, the results from fig. 2 do show that for the LSR isomerization the activity optimum corresponds to the FAL/EFAL ratio of ~ 3. Bearing this in mind it is possible to design an active catalyst based on considerably dealuminated mordenite ($Si/Al > 16$), being also highly resistant to the deactivation by coke and sulfur. With respect to the metal component, both Pt and Pd are adequate as far as they are highly dispersed [15], but Pt is more resistant to the sulfur poisoning than Pd.

Zeolite beta with its strong acidity [16] is active and selective for *n*-alkane isomerization [17], although the final activity depends on the synthesis conditions [18].

3. Catalytic reforming

By the naphtha reforming, the C_6–C_{10} *n*-alkanes are transformed into branched alkanes and aromatics, thus increasing the octane number of the stream processed. Industrial naphtha reforming is carried out on Pt-Re- and Pt-Re-Sn-Al_2O_3-Cl catalysts under hydrogen pressure, at temperatures in the range 360–500°C.

Fig. 3 shows that the selectivity to cyclic *n*-hexane is low, and if it comes out untransformed its effect on the octane number of the gasoline is negative. In order to avoid this, at first the 8-member ring zeolite, erionite was applied. This shape selective catalyst works in the postreforming, selectively cracking the *n*-paraffins and producing LPG, and thus increasing the octane number of the liquid products [20]. In order to slow down the catalyst deactivation Ni sulfur was deposited on erionite. Then erionite has been substituted by ZSM-5 in the "M-forming" process. The 10-member ring ZSM-5 zeolite does not only crack selectively *n*-paraffins but also alkylates benzene and toluene with the short chain olefins produced during the

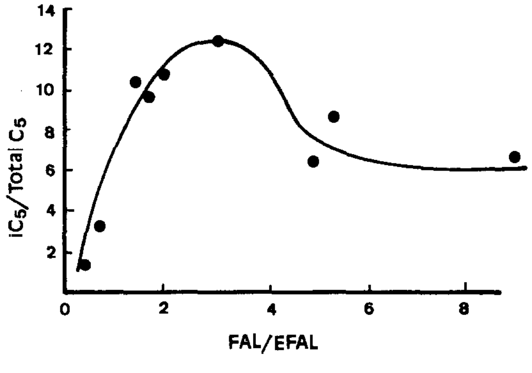

Fig. 2. Effect of the extraframework Al on the isomerization activity of dealuminated mordenite containing 0.3 wt% Pt.

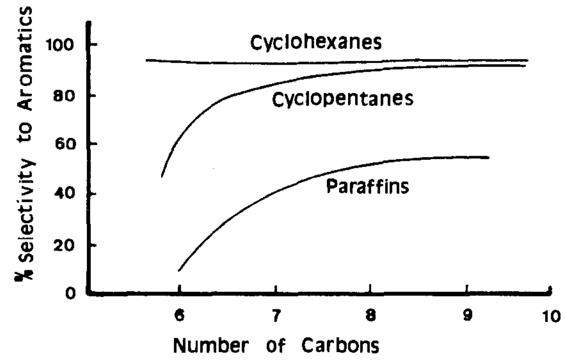

Fig. 3. Efficiency of the reformation at 480°C under 15 atm for different components of the feed.

cracking. This can be successfully applied for increasing the gasoline stream coming from the reformate and for the products of the reformulated gasoline, if the "M-forming" is coupled with a low severity reforming unit [21] (table 3).

A few years ago, when the limitation of aromatics in gasoline was not yet considered, a new reforming process was developed based on a large pore 12-member ring unidirectional zeolite such as L. This, when exchanged with K^+ or $K^+ + Ba^{2+}$ and containing Pt, worked well for the selective dehydrocyclization of *n*-alkanes, especially *n*-hexane and *n*-heptane, much more efficiently than the reforming catalysts based on Pt-Re-Sn-Al_2O_3-Cl [22,23] (fig. 4).

The major limitation of these catalysts is their short life and their low resistance to sulfur. Furthermore, since the reformulated gasolines are low in benzene, those catalysts will have limited application, unless the petrochemical demand of benzene and toluene will strongly increase.

4. FCC process

Together with reforming, FCC is the major gasoline producing unit. Nowa-

Table 3
Composition changes of the reformed gasoline caused by the application of M-forming

	Reforming	Reforming + M-forming
C_{5+} RON	84.5	89.6
aromatics		
B	18.5	16.9
T	23.4	22.5
X	0.6	1.1
C_9	0.2	2.9
C_{10}	0	2.0
C_{11}	0	0.3
total paraffins	44.0	35.9

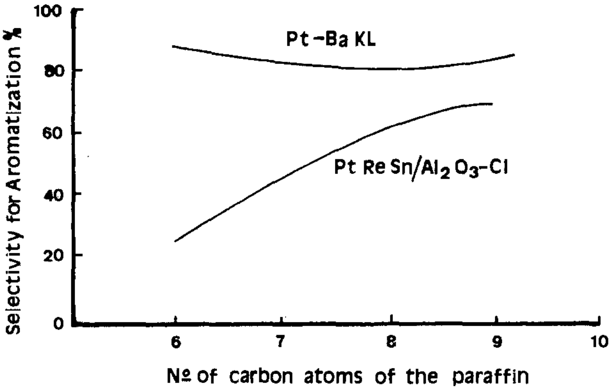

Fig. 4. Catalytic reforming on Pt/L zeolite.

days, the cracking catalysts are multifunctional and consist of crystalline and amorphous components with adequate acid, red–ox, adsorption, and pore size distribution properties. Such catalysts are also capable of cracking the heaviest components, while removing SO_x, NO_x, passivating Ni and V, and producing high octane gasolines. Nevertheless, the core of the catalyst is still based on zeolite Y. The variables which control the behavior of this zeolite within the FCC catalysts are:

- framework Si/Al ratio (unit cell size);
- crystal size–textural characteristics;
- Na_2O content;
- amount and type of EFAL.

A decrease in the unit cell size of zeolite, especially below 24.30 Å, indicating an increase in the framework Si/Al ratio, results in an increase of the octane (especially RON) of the gasoline produced. Meanwhile, more gasoline is recracked increasing the production of gas with a higher olefin to paraffin ratio, and decreasing the amount of coke [24].

However, the unit cell size is not the unique parameter controlling activity and selectivity and other factors are relevant as well. In the case of cracking catalyzed by acid sites, an important factor controlling the cracking activity is not the total number of zeolite acid sites, but the number of those accessible to bulky reactant molecules. Then, the textural properties such as presence of mesopores can be of great importance. Fig. 5 allows one to compare the gasoil cracking activity of two series of zeolites with varied Si/Al ratios, and dealuminated by two different procedures. It is clear that the one with the higher mesoporosity has the higher activity.

The same effect is achieved by changing the size of zeolite crystallites. Indeed, smaller crystallites have a higher external to internal surface ratio, and therefore the acid sites are more accessible for large gasoil molecules. Moreover, for small crystallites, the products can easier diffuse out of the zeolite surface thus precluding the consecutive reactions which lead to gases and coke, to saturation of olefins

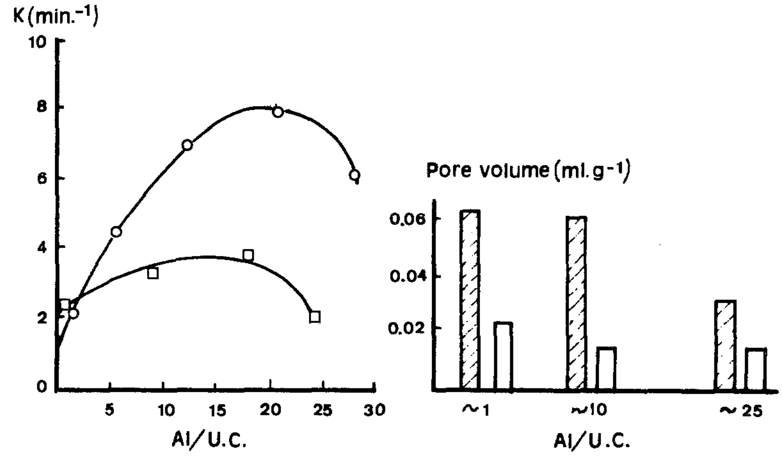

Fig. 5. (a) Activity of gasoil cracking on steam (○) and $SiCl_4$ (□) dealuminated zeolites Y; (b) mesopore volume for Y zeolites dealuminated by steam (▨); and $SiCl_4$ (□).

and to formation of aromatics by hydrogen transfer (cf. fig. 6). On top of that, smaller crystallites increase the gasoline quality by promoting the formation of isoolefins [25,26].

At present, many cracking units are being changed from purely conversion units producing liquid fuels only, to installations giving high octane gasoline together with high yields (as high as the gas compressor can allow) of propylene, *i*-butane, *i*-butene, *n*-butenes, and *i*-amylenes. In other words there is a tendency imposed by the new legislation on reformulation of gasoline by using FCC units not only to produce gasoline but also to produce raw materials for petrochemistry.

The amount of Na_2O in the catalyst is of significant importance especially in the case of zeolite USY. Too high Na_2O level (above 0.2 wt%) has a negative effect on the activity, gasoline RON, hydrothermal stability, and stability against vanadium.

During the zeolite Y activation, as well as in the FCC regeneration zone, the zeolite dealumination occurs with the concomitant formation of EFAL, which remains inside zeolite as tetrahedrally, octahedrally, and pentacoordinated species [27–29]. Some authors claim that EFAL has a negative effect on gasoil cracking behavior [30], while others postulate that is has both, a beneficial effect by converting bottoms, and a negative effect because it may produce more dry gas and coke [31]. Recently it has been shown [32] that it is possible to prepare more selective equilibrium FCC catalysts during the zeolite activation, if a part of the EFAL is removed by treatments with complexing agents [32], or with mineral acids [33].

Beside the modification of zeolite Y, one can change the product distribution in the FCC units by introducing other zeolites as additives. ZSM-5 in amounts of 1–3 wt% makes possible to recrack *n*-olefins and *n*-paraffins which increases the RON of the resulting gasoline and gives higher yields of olefins in LPG [34–36]. The

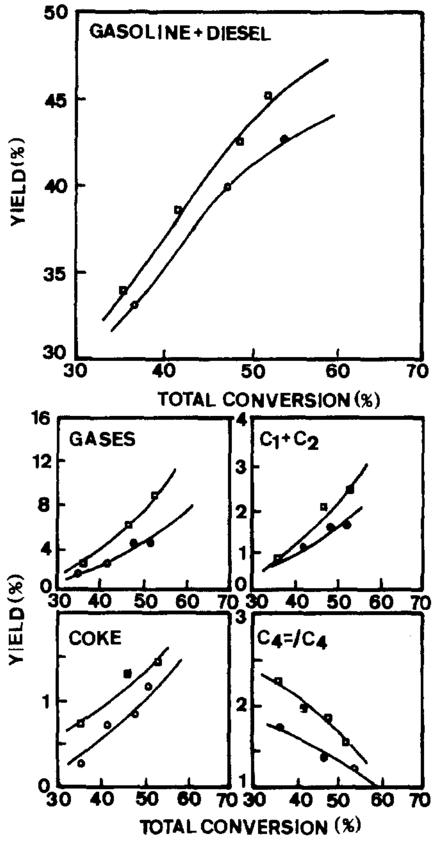

Fig. 6. Gasoil cracking selectivity on USY 0.3 m (Si/Al = 3.0) (○) and USY SK-40 (Si/Al = 2.4) (□) using 750°C, 5 h, 100% steam treatment.

effect of the ZSM-5 additive depends on the severity of the unit. Namely at high severities the additive concentrates aromatics, while at lower severities if predominantly affects the recracking of long chain *n*-olefins of gasoline [37]. It has to be stressed again, that the final behavior of ZSM-5 depends on the crystal size and the framework Si/Al ratio [38].

In order to improve the product distribution in the FCC units several molecular sieve materials have been studied. These are zeolites: L, omega, offretite, mordenite, beta, and silicoaluminophosphates: SAPOS-5, 11 and 37 [39–41]. Among them beta and SAPO-37 present most interesting features. Zeolite beta is especially adequate for production of *i*-butene, *n*-butene, and propylene, together with high octane gasoline [44]. In this case, even more than before, the cracking behavior of the beta zeolite depends on the synthesis and activation conditions [44]. SAPO-37 with a faujasite structure is highly active, giving gasoline of relatively good quality. However, there is a limitation for its industrial use and this is its high cost of synthesis.

At present new matrices with improved cracking activity and special pore size distribution are being developed, and it seems that the main progress will result from multifunctional zeolitic catalysts coupled with special active matrices.

5. Alkylation of isobutane with olefins on zeolites

Alkylation gasoline is especially suitable for the future needs because of the desirable properties: low RVP, practically no aromatics and olefins, a high octane number, and a low sensitivity factor. Unfortunately, the actual processes are based on the HF and H_2SO_4 acid catalysts and therefore the development of solid acid catalysts for alkylation is of much interest. Large pore zeolites can catalyze with high conversions and yields, the alkylation of *i*-butane/butenes to trimethylpentanes (TMP) [45–49]. The best are zeolites: Y, beta, ZSM-20 and MCM-22. From the mechanistic point of view, a high density of framework Al, and consequently high hydrogen transfer ability was required to keep high yields of TMP and to preserve the catalyst life [46]. Then, it has been shown that dealuminated USY and REUSY zeolites are poor alkylation catalysts [48]. However, the latter has to be reconsidered, since high Si/Al ratio beta zeolites, while being poor catalysts for hydrogen transfer reactions, are active and selective for alkylation (table 4).

As concerns the distribution of TMP isomers, it was suggested that the lower selectivity of zeolites Y with respect to HF and H_2SO_4 catalysts used for the 2,2,4-TMP production was due to geometrical restrictions [48]. This has to be revised in the light of our results (table 4), which prove that zeolite beta with smaller pore dimensions than zeolite Y, is more selective for the formation of 2,2,4-TMP.

Table 4
Isobutane/butene alkylation. Comparison of beta and Y zeolites. Initial product distribution (TOS = 1 min)

	Beta	USY (24,53)
Conv. $C_{4=}$ (wt%)	99.60	99.60
C_5/C_{5+}	13.58	15.03
C_6/C_{5+}	8.46	9.92
C_7/C_{5+}	9.00	9.04
C_8/C_{5+}	37.33	48.65
C_9/C_{5+}	31.63	17.36
TMC_5/C_8	68.51	77.69
DMC_6/C_8	30.85	20.62
2,2,4-/TMC_5	51.55	38.99
2,2,3-/TMC_5	6.19	7.44
2,3,4-/TMC_5	27.99	22.80
2,3,3-/TMC_5	14.28	30.77

However, the fast deactivation is a serious limitation of the zeolite catalysts for this reaction.

6. Production of middle distillates with low sulfur from vacuum gasoil

Vacuum gasoil and heavier fractions are hydroprocessed in order to remove contaminants such as S, N, and metals introduced with the feed. These fractions can also be hydrocracked to obtain gasoline and diesel fuel. The HDS and HDN processes are carried out on MoO_3, WO_3, CoO, and $NiO/\gamma\text{-}Al_2O_3$ catalysts. Zeolites, especially the ultrastable (USY) type, on the alumina matrix with Mo and Ni introduced, are hydrocracking and even desasphalting catalysts [50]. HDS catalysts containing zeolites are also available. However, they are relatively more expensive than those based on alumina. Therefore, unless the price difference is compensated by a much higher HDS, HDN and aromatics hydrogenation activity and by a longer catalyst life, their use will be limited.

7. Hydrocracking

The hydrocracking involves the C–C bond breaking to give gasoline, kerosene and diesel, starting from HCO from FCC units, gasoil from thermal cracking, vacuum gasoil, etc. The hydrocracking catalysts are bifunctional and are formed by an acidic support with a hydrogenation–dehydrogenation function added which can be either a noble metal or Wo-Mo-Ni-Co when the feed contains sulfur compounds. As the acidic component amorphous silica–alumina is still used [51] but zeolite catalysts are taking over. Large pore zeolites such as Y, mordenite, L, omega, etc., have also been studied. Mordenite, because of the geometrical restrictions, is not used for hydrocracking heavy fractions; however, it may be useful to produce LPG by the gasoline hydrocracking [52]. Preparation and activation inconveniences limited the use of L and omega [53]. Among the other zeolites studied, USY seems to be most suitable since it has a high activity with a good resistance to poisoning by coking, NH_3 and H_2O [54,56] (fig. 7).

High flexibility in the hydrocracking process is achieved by using USY based catalysts, since by controlling the Al content of the zeolite (unit cell size) it is possible to optimize the production of diesel, kerosene, or gasoline (fig. 8).

The kerosene and diesel obtained by hydrocracking are lower in aromatics than the corresponding products obtained by direct distillation, or produced in the FCC unit. Moreover, the former have better smoke point and cetane index properties. It follows that for a refinery with sufficient hydrogen and able to face the relatively high inversion required, hydrocracking seems to be the suitable process.

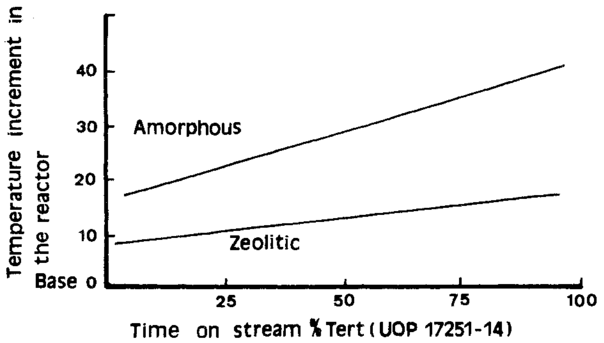

Fig. 7. Deactivation of hydrocracking catalysts based on amorphous and zeolitic acid components.

8. Improving diesel properties

In the case of diesel, besides the cetane index there are other desirable properties such as: viscosity, pour point, freezing point, etc. If diesel is used as the transportation fuel in a cold climate, the freezing point becomes the crucial parameter. This depends on the diesel composition, and fig. 9 [57] shows that the freezing point of diesel can be lowered by removing linear paraffins. This can be achieved either by the selective hydrocracking of the linear components (dewaxing), or by the isomerization converting linear paraffins to their branched isomers.

Pt/mordenite has been used to produce low pour point distillates from diesel as well as from partially dewaxed naphthenic and paraffinic distillates [58,59]. Medium pore zeolites such as ferrierite [60], and ZSM-5 [61] are capable of dewaxing atmospheric gasoil and producing diesel with the pour point at −25°C.

When highly paraffinic crudes are processed, the dewaxing can be combined with the FCC unit. Then two options are possible either to dewax LCO coming from the FCC unit or to separate the lighter fraction of the FCC feed and process it in the dewaxing unit. In the latter case FCC processes the heavier fraction only, so throughput and LCO yield are increased [62] (fig. 10).

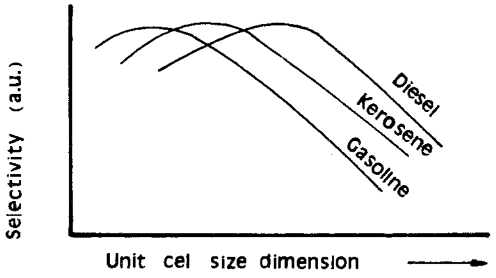

Fig. 8. Influence of the USY unit cell size on hydrocracking severity.

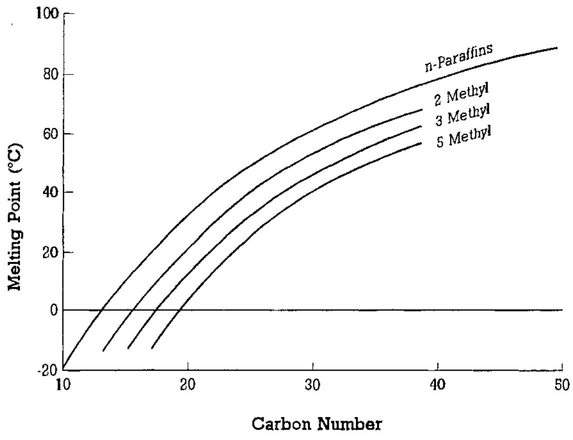

Fig. 9. Freezing point of branched and unbranched paraffins.

If dewaxing is the solution of choice for improving diesel quality, it is even better to isomerize linear paraffins in order to avoid diesel losses. This could be done on bifunctional catalysts consisting of a noble metal and a zeolite. In order to avoid cracking and hydrogenolysis, a good balance between the acid and the hydrogenation–dehydrogenation function has to be adjusted [63,64]. It has been reported that the optimum balance depends not only on the zeolite type, but also on the feed [63] (table 5).

The geometry factor in zeolites can be worked out to achieve selective hydroisomerization of a given set of hydrocarbons from a complex feed [65]. This makes possible to isomerize short-chain *n*-paraffins in the presence of long-chain ones and vice versa.

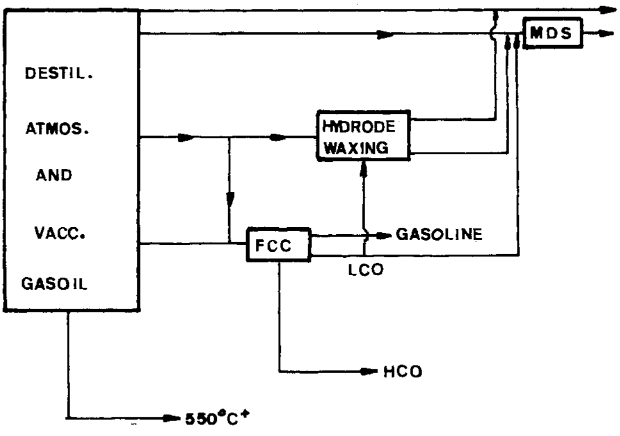

Fig. 10. Coupling of dewaxing and FCC units.

Table 5
Maximum isomerization yield (%) on several large pore zeolites

Catalyst	Feed nC_{10}	nC_{12}	nC_{15}	nC_{16}	nC_{17}
1% Pt USY	52	–	–	50	47
0.5% Pt HY	–	–	–	–	61
0.3% Pt HY	56	–	–	–	57
0.75% Pt ZSM-20	62	69	67	69	72
1% Pt ZSM-20	52	–	–	–	50
1% Pt beta	63	–	–	–	51

9. Production of fuels from CH_4 and LPG using zeolite catalysts

In search for less expensive raw materials let us consider C_1–C_4 alkanes. At present, much attention is devoted to the conversion of CH_4 to methanol and ethylene. Starting from *n*-butane, it is already possible to produce commercially maleic anhydride. Propane and butane can be converted to the corresponding olefins by using Cr–Al catalysts. C_2–C_4 olefins can be also obtained from methanol using 10-member-ring zeolite and zeotype catalysts. On the other hand, methanol can be produced from the synthesis gas obtained from methane, and perhaps in future methanol will be directly produced from methane. If olefins are available, they can be easily converted to aromatics, fuels or commodity products [66].

If the natural gas or coal are the substrates for the synthesis gas production, zeolite may be an alternative to the classical Fischer–Tropsch catalyst. Indeed, when ZSM-5 or SAPO-11 are admixed to the catalysts for the methanol synthesis, it is possible to produce aromatics-rich gasoline, in one step. The final product distribution depends on the framework Si/Al ratio of the zeolite, on the presence of reducing elements in the zeolite, and on the reaction temperature [67,68].

The LPG fraction can be converted, in a single step, in aromatics by means of the Cyclar process, which uses Ga_2O_3 on ZSM-5 as a catalyst [69]. With this process it is possible to obtain conversions higher than 65% with selectivity to aromatics higher than 50%. The catalyst is quickly deactivated and needs continuous regeneration. That is why a moving bed type process has been designed for Cyclar.

The Ga_2O_3/ZSM-5 catalyst behaves as a true bifunctional catalyst for the following reactions:

- dehydrogenation (mainly occurring on metal);
- oligomerization and cyclization (on zeolite);
- aromatization (mainly on metal)
- dealkylation, transalkylation and isomerization of alkylaromatics (on zeolite).

The reaction mechanism has been widely discussed and the different points of view are given in refs. [70–78]. Besides ZSM-5, other zeolites such as mordenite, omega, ZSM-12, beta, offretite, ferrierite, etc., have been used for this reaction [79–82].

This process must be reconsidered now since aromatics may not be a priori products, however H_2 is formed in appreciable amounts and this is, and will be, an important product in many refineries.

The different ways of processing C_1–C_4 fraction using zeolite catalysts are shown in fig. 11.

10. Zeolites in petrochemistry

The application of zeolites in petrochemistry has involved their use as catalysts for alkylation and isomerization of aromatics and alkylaromatics, and more specifically of the C_8 and C_9 fraction. The C_8 alkylaromatics are formed by ethylbenzene and *m*-, *o*-, and *p*-xylenes. Ethylbenzene is a raw material for the production of styrene. Para and ortho-xylenes are oxidized to phthalic and terephthalic acid and then used for the plastic production. Meta-xylene can be oxidized to isophthalic acid. Propylbenzene from C_9 fraction is transformed to cumene hydroperoxide, which then gives phenol and acetone. The high demand for the C_8 and C_9 alkylaromatics is satisfied by the reformate unit and by a possible Cyclar unit followed by other processes. Zeolites are important catalysts for transalkylation of toluene to give benzene and xylene. This process is carried out at relatively high temperature (450–500°C) on a ZSM-5 based catalyst.

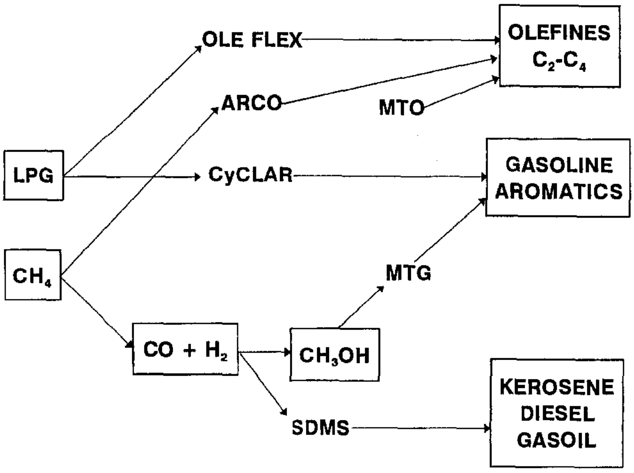

Fig. 11. Upgrading C_1–C_4 paraffins on zeolite catalysts.

The product distribution obtained in the toluene transalkylation process is shown in table 6.

It is possible to increase the selectivity to *p*-xylene by modifying the opening of the zeolite pores. Thus impregnation with phosphorous, exchange-impregnation with magnesium salts etc., increase the selectivity to para-xylene since the relative rate of toluene transalkylation, diffusion of xylenes and their isomerization are changed [83–86].

Among the three xylene isomers the highest commercial demand is for para, then for ortho, and finally for meta. This makes necessary to separate the equilibrium mixture ($\sim$ 50% meta, $\sim$ 25% para and $\sim$ 25% ortho), and to isomerize the resultant meta isomer. The shape selectivity associated especially with medium pore zeolites makes possible to obtain yields of para isomer above those expected from the thermodynamic equilibrium, while the losses because of transalkylation are very low. ZSM-5, SAPO-11, SAPO-5, mordenite, beta and omega are good isomerization catalysts [87–91], but ZSM-5 is the most convenient [92] for xylene isomerization. However, when high amounts of ethylbenzene are present in the feed, its dealkylation can be a problem.

11. Synthesis of alkylaromatics

As it has been said before, alkylaromatics are widely used to produce styrene (ethylbenzene), phenol (cumene), and surfactants for detergents (C_{10}–C_{20} alkylbenzenes). $AlCl_3$ and phosphoric acid on kieselguhr are used as catalyst to produce various alkylaromatics. However, corrosion problems, economics, and environmental reasons require a substitution of these catalysts by zeolites. Large pore zeolites are active at the laboratory scale, but deactivate too fast to be used in the industry [93]. The deactivation is strongly decreased for medium pore zeolites especially for ZSM-5, used as catalysts. Based on this zeolite the Mobil–Badger process allows to obtain ethylbenzene from benzene and ethylene at 370°C and 14–27 atm pressure. The most important subproduct, i.e., diethylbenzene, can be minimized by adjusting the

Table 6
Production of xylenes by transalkylation of toluene at 33 atm, H_2/to = 2.5 mol mol^{-1}, toluene conversion 42.6 wt%.

Products of distribution (wt%)	
C_5	1.5
benzene	17.9
toluene	57.4
p-xylene	4.7
m-xylene	11.5
o-xylene	5.2
ethylbenzene	0.2
C_{9+}	1.8

operating variables [94]. Quite recently, UNOCAL and ENI have announced an alkylation process on liquid phase, based on zeolites Y and beta respectively.

Styrene can be substituted, for some applications, by para-methylstyrene, which can be produced by alkylation of toluene with ethylene on a modified ZSM-5 zeolite [95]. In a similar way, benzene can be alkylated with propylene to produce cumene on acidic zeolites. However, if medium pore zeolites, especially ZSM-5, are used as catalysts the amount of polyalkylates formed is very low [96].

Long chain alkylbenzenes, which are used for detergents, have to be produced avoiding the branching isomerization in order to increase detergent biodegradability. The alkylation is properly catalyzed by HF but it is desirable because of environmental reasons to substitute this acid by solid catalysts. However, the use of zeolites is still limited because of the chain isomerization and the catalyst deactivation [97].

12. Zeolites as oxidation catalysts

The introduction of zeotypes containing framework Ti and V, has opened new possibilities for zeolites as oxidation catalysts. Thus, Ti containing silicalite in presence of H_2O_2, at moderated temperatures (20–150°C) and in an adequate solvent, is active for oxidizing alkanes into secondary alcohols and ketones [98,99]. The hydroxylation of phenol into hydroquinone and catechol on a titanium silicalite (TS-1) offers advantages over the processes in use [100–102]. Other oxidations involving monoolefins, diolefins, alcohols, cyclohexanone (ammoxidation) are carried out successfully on TS-1 catalysts [103–108].

In order to prepare a successful oxidation catalyst the formation of TiO_2 should be avoided, while isolated Ti must be in the framework positions.

The oxidation properties of zeolites TS-1 (MFI) and TS-2 (MEL) are limited to relatively small molecules which can penetrate the pores of the MFI and MEL structures. However, because of the unfavorable reaction conditions (low temperature and solid–liquid phase), the oxidation efficiency towards monobranched alkanes, cycloalkanes, and some alkene aromatics is relatively low. This, however, could be improved by synthesizing large pore Ti-zeolites. They have been prepared with $TiCl_4$ by isomorphous substitution [109]; however, such prepared samples show very poor catalytic performance. Ti-beta has been the first, large-pore Ti zeolite prepared by synthesis [110,111], and it shows a higher activity than Ti-silicalite for oxidizing bulkier cycloalkenes and olefines [112]. The impact of Ti and V zeotypes, as well as zeolites, as guest for oxidizing complexes will open new possibilities for the production of commodities and fine chemicals.

13. Conclusions

The acid–base characteristics, the possibility to be combined with other catalytic functions, the unique shape selective properties, and the high stability of zeolites make these materials extremely versatile catalysts. The new zeotypes with atoms other than Si and Al in the framework, open new possibilities limited only by our imagination.

From the point of view of oil refining and petrochemistry, everything indicates that soon polyfunctional catalysts such as multizeolites, metal-zeolites, oxide-zeolites, etc. will be used. Finally, extra and ultra large pore zeolites, if made active and stable, will be capable of processing larger molecules. This will find for them an immediate application for processing heavier fractions, as well as for the production of fine chemicals.

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