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The impact of catalytic materials on fuel reformulation

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Abstract

Fuel reformulation has been seeded by the growing consciousness of the potential damages mankind was causing to the ecosystem and to itself. Fuel reformulation means that fuels are defined on a chemical composition base with additional engine-technology related standards rather than on pure performance bases. These standards, which are getting more and more stringent, can be met by different leverages, mainly catalysts and processes operating conditions.

This survey reviews the contribution of catalytic materials to the production of cleaner fuel components through some significant examples selected from scientific and technical literature. Having described the trends in automotive fuels quality, production of gasoline and diesel pool components is discussed relating the required properties to the material active site configuration, i.e. acidity/basicity, structural parameters, physical constraints. While distinctions are made between pathways leading to gasoline and those leading to diesel, sulfur removal is faced on a more generalized approach.

Keywords: Catalytic materials; Fuel reformulation; Sulfur; Reformulated gasoline; Reformulated diesel

1. Introduction

As a consequence of the growing awareness of mankind to the potential damage to the earth's ecosystem, a fuel revolution is taking place: "reformulated fuels" are defined on a chemical composition base with additional performance standards rather than on a *behavior base*.

The energy history has experienced the introduction of fossil fuels in the last couple of centuries causing a continuously growing release of contaminants to the atmosphere. Their nature and effects are different and we can divide them into toxic and non-toxic to the human health and into "short range" and "long range" environmental effects. Table 1 gives rough and simplified indications, taking into account the major effect.

Many excellent papers have been published on how refinery technologies can contribute to meet the specifications for reformulated fuels [1]. Therefore this survey will focus on the specific contribution of catalytic materials, keeping in mind that the operating conditions of the main units (FCC, reformer) can significantly contribute to the goal.

2. Trends in automotive fuels quality

The challenge for the internal combustion engine is the reduction of pollutant exhaust coupled with a lower CO_2 emission. A higher quality of fuels can reduce the exhaust either directly through an improved combustion or indirectly by enabling the use improved exhaust abatement technologies. Several programs have contributed to the definition of fuels standards and some of them are still in progress: in Europe the European Auto-Oil Program I and II (EPEFE), "Clean Air

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Table 1
Main exhaust gases contaminants and their effects

Species	Toxic	Non-toxic	Short range	Long range	Effect
CO_2		X		X	Greenhouse
CO	X		X		Lethal effects
NO_x	X		X	X	O_3 depletion contribution
Olefins		X		X	O_3 depletion
SO_x	X		X		Acid rains
Benzene	X		X		Carcinogenic

For Europe" (CAFE) and "European Climate Change Program" (ECCP); in the US, the US Air Quality Improvement Research Program (AQIRP), Phase I and II.

The standards fixed by the European Union are reported in Table 2; the last column shows the baseline before 2000.

From January 1998, the requirements of the US reformulated gasoline are evaluated via a set of equations—Model I and its evolution, the Complex Model—which predict emissions from fuel characteristics. However, limits have been set for benzene (1%, max) and oxygen (2 wt.%, min). Recently, California banned methylterbutil ether (MTBE)—beginning in 2003, but then delayed to 2004—the main oxygen adductor, because of its poor biodegradability.

Table 2
Standards fixed by the European Union

		2000	2005	Before 2000
Gasoline				
Sulfur	ppm, max	150	50	500
Aromatics	vol.%, max	40[a]/42	35	n.r.[b]/40[a]
Olefins	vol.%, max	18	*18*[c]	n.r.
Benzene	vol.%, max	1	*1*	1[a]/5
RVP	kPa	60/70[d]	*60/70*[d]	70/90[d]
Diesel fuel				
Sulfur	ppm, max	350	50	500
Density	kg/m^3, max	845	*845*	860
Cetane no.	Min	51	*51*	49
T_{95}	°C, max	360	*360*	370
PAH	wt.%, max	11	*11*	n.r.

[a] National specification.
[b] Not restricted.
[c] The values given in italics are the standards to be confirmed.
[d] Arctic climates.

2.1. Ideal gasoline

In the previous paragraph the requirements of reformulated fuels have been reported. Briefly, if the focus is on the chemical nature, gasoline should:

- have a low content of double bonds, either aromatics and olefins; be almost free of heteroatoms;
- have some oxygen at least in the US with the exception of California.

If attention is switched to physical properties, the lighter part (C_4–C_5 cuts) of the gasoline should be reduced to fulfill the RVP requirements. The higher boiling fraction should be diminished (lower T_{90}[1]) as well: the overall result is a narrowing of the boiling point distribution.

The ideal gasoline molecule has a high H/C ratio (2.25 if we assume isooctane as reference) and no heteroatoms with some exception for oxygen, it has a low-volatility and a high octane number. Therefore highly branched paraffins with 8–10 carbon atoms would best fulfill all these requirements. Isooctane—which has an octane number equal to 100 by definition—is the reference structure and it can be assumed as a model: other molecules should come as close as possible. However, this is extremely ideal: in fact various cuts, whose physico-chemical properties have been improved accordingly, are pooled to fulfill the regulations.

2.2. Ideal diesel fuel

This fuel should be constituted of linear paraffins with a carbon atom ranging from 10 to 20. A limited number of branches are beneficial because of cold properties. Unfortunately (poly)aromatics rings are present because of the heavy cuts blended in the pool. The lightening of the diesel (lower density and a lower T_{95}) should contribute to have more hydrogenated species while eliminating the very high boiling components. These heavy molecules are precursors of the particulate matter (PM10) which is now a severe concern with respect to diesel-fuelled vehicles. The PM10 formation is favored by a high flame temperature (poor cetane) and the prevalence of C–C bonds

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[1] T_y indicates the temperature at which a percentage (y) of a given fraction distillates.

instead of C–H bonds in the molecular structure of components.

The standards for reformulated diesel are, however, less developed than those of gasoline because diesel is considered to be a less sophisticated product. The contributions of catalytic materials to fuel reformulation will be discussed first in terms of “components to be removed”, followed by a review of the options either to produce high value “premium” components or to add value to some orphan or low value streams.

3. Sulfur removal

It has been clearly known since the beginning of the fuel reformulation era that sulfur is the real evil. Many technologies are available on the market approaching the sulfur removal problem in different ways. Process options, referring to the fluid catalytic cracking (FCC) unit as the key unit in a refinery, range from feed pretreatment to product post-treatment passing through absorption solution via suitable materials like “gasoline sulfur reduction” FCC catalysts or specially developed solids as in Phillips 66’s ZSORB process. A survey of the commercially available processes is reported in Table 3 [2].

The traditional hydrodesulfurization (HDS) treats a given cut with H_2/H_2S in quite severe conditions (3–20 MPa, >350 °C). Traditional catalysts are cobalt–molybdenum (CoMo) or nickel–molybdenum (NiMo) mixed oxides supported on alumina. Under real conditions the active phase works in sulfidized form.

Table 3
HDS commercial technologies

Type	Process name	Vendor
Distillation	CD Hydro	CD Tech
FCC additive	Gasoline S reduction	Grace division
Adsorption	ZSORB	Phillips 66
Selective hydrotreating	CD HDS	CD Tech
	Octgain 220	Mobil
	Scanfining	Exxon
	Prime G	IFP
	FGTP	H. Topsøe AS
Non-selective hydrotreating	Octgain 125	Mobil
	ISAL	UOP

Table 4
HDS relative reaction rate of several molecules

Molecule	Relative desulfurization rate	Acronym
Thiophene	23	
Benzothiophene	13	BT
Dibenzothiophene	1	DBT
2,8-Dimethyl-dibenzothiophene	1, 2.5–3	2,8-DMDBT
3,7-Dimethyl-dibenzothiophene	1.5	3,7-DMDBT
3,6-Dimethyl-dibenzothiophene	0.2	3,6-DMDBT
4,6-Dimethyl-dibenzothiophene	0.1	4,6-DMDBT
Benzonaphthothiophene	3	

The various S-containing species have different reactivity with respect to the loss of the heteroatom: a typical reactivity scale is reported in Table 4 [3], where dibenzothiophene has been assumed as reference.

It appears that the more substituted the molecule in the positions close to the sulfur atom the less reactive the structure is. We may state that a steric factor is dictating this scale. However since a deep HDS is required to meet the very low standards fixed for the coming years (see Table 2), catalysts should be able to convert also the less reactive compounds at an acceptable rate. A nice example is given by van Looij et al. [4] in the paper where they compare the activity of $CoMo/Al_2O_3$ and $NiMoP/Al_2O_3$. They emphasize the use of close-to-industrial practice conditions to compare the catalysts, particularly the H_2/H_2S ratio that should be in the range 15–20 Nl/Nl for a once-through trickle bed. In some cases a too high H_2/H_2S levels off the differences.

The $CoMo/Al_2O_3$ shows superior HDS performances because a lower residual sulfur is obtainable at shorter residence time (Fig. 1a) but $NiMoP/Al_2O_3$ is more active at high HDS level (Fig. 1b). Since they used a real feed (Arabian Light Straight Run Gasoil), they pointed out the effect of contaminants and showed that NiMoP is more effective in the conversion of basic N-containing compounds (HDN catalyst). However using a nitrogen-free synthetic gasoil, they ruled this as the root cause of the higher desulfurization rate of $NiMoP/Al_2O_3$ at high desulfurization level.

The practical results was that a stacking of the two catalysts gave better performances in the HDS reaction then the single materials. The investigation of the reaction mechanism, specifically the effect of acidity on the HDS activity [5], can explain what happens.

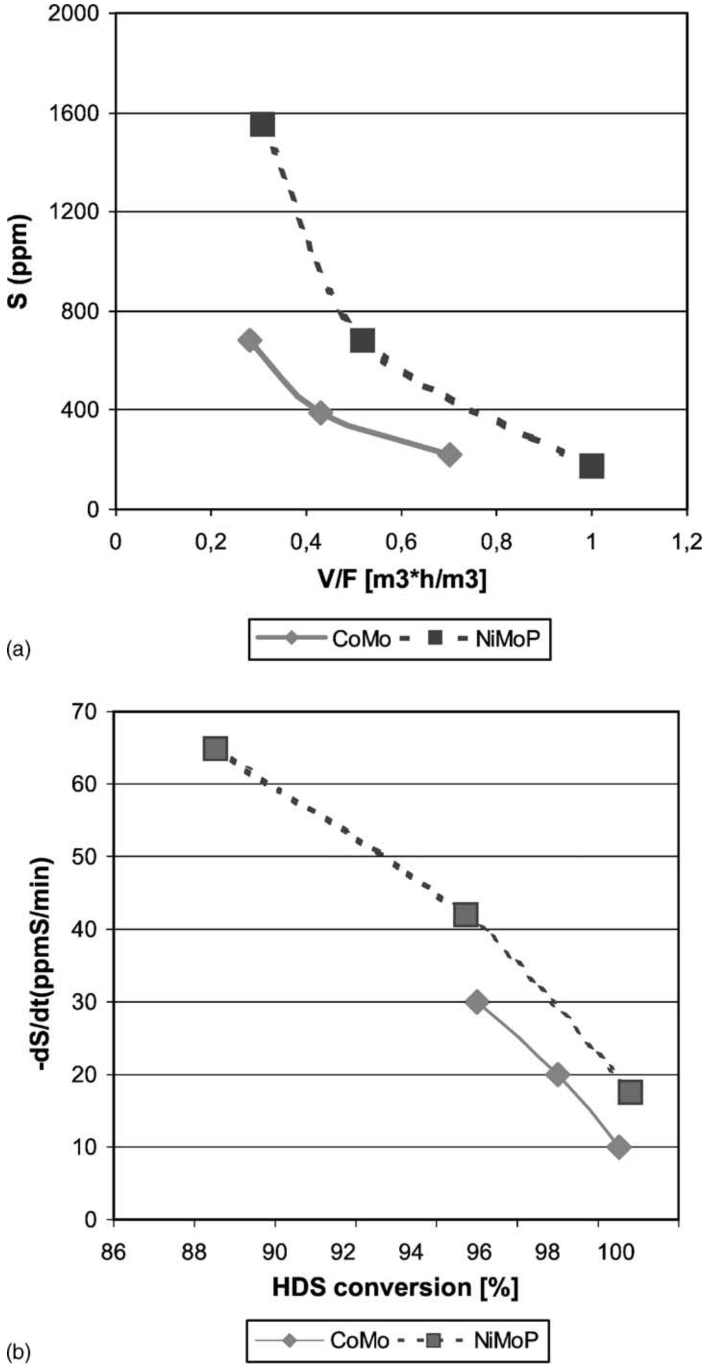
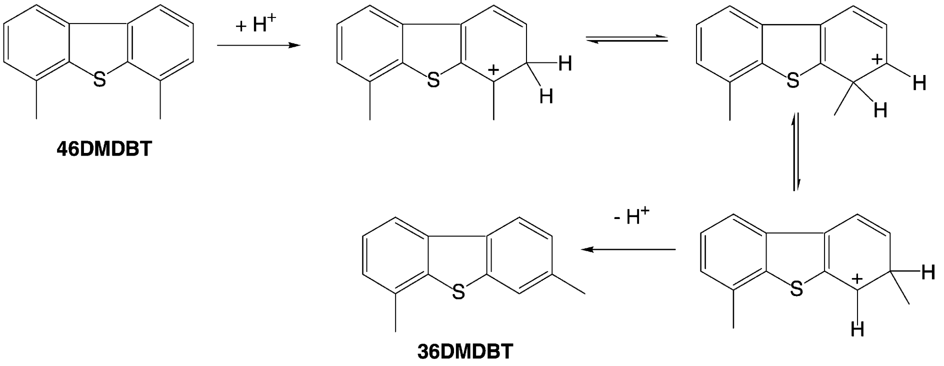


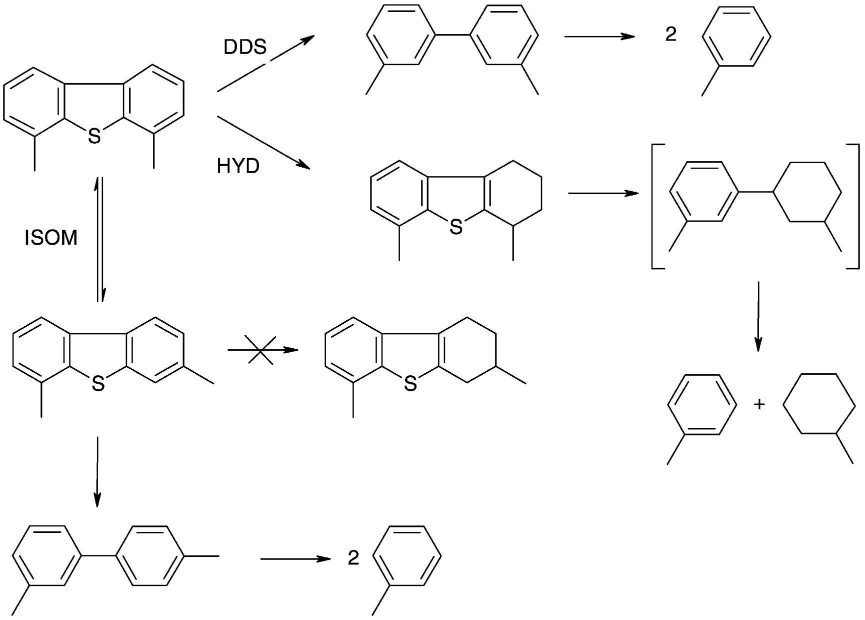
Fig. 1. (a) Sulfur content as a function of space time (feed SRGO); (b) desulfurization rate as a function of HDS level (feed SRGO).

Table 5
Activity of various supported NiMo catalysts in HDS reaction with two different molecules and splitting of the total HDS activity (A_T) of NiMo/A in DDS contribution (A_{DDS}) and hydrogenation (A_{HYD}) and their ratio R

	Total activity in HDS (A_T)			NiMo/A			
	NiMo/A	NiMo/A + SA	NiMo/Y	A_T	A_{DDS}	A_{HYD}	R
DBT	9.7	10.1	10.1	9.7	7.7	2	3.9
4,6-DMDBT	1.7	4.3	3.6	1.7	0.3	1.4	0.2



Scheme 1. Acid catalyzed isomerization of 4,6-DMDBT into 3,6-DMDBT.



Scheme 2. Hydrodesulfurization simplified mechanism with DDS, hydrogenation (HYD) and isomerization (ISOM) routes.

The HDS is thought to proceed through two main pathways that are said to take place on two different types of sites:

1. the direct cleavage of the C–S bond to give biphenyl: direct desulfurization (DDS);
2. hydrogenation of one benzenoic ring (HYD) followed by the removal of S leading to cyclohexylbenzene.

In the work of Michaud et al. [5], the NiMo active phase was supported on three different acid supports: alumina (NiMo/A), alumina mixed with silica/alumina (NiMo/A + SA), and a zeolite Y (NiMo/Y). The HDS activity of the three materials is reported in Table 5.

Comparing the activity of NiMo/A + SA and NiMo/Y with that of NiMo/A, it appears that the introduction of an acid component/function clearly improves the HDS reaction rate of the substituted 4,6-DMDBT while that of DBT remains almost unchanged. On the right-side of the table it is shown that the two S-containing molecules have different preferential pathways: DBT reacts according to DDS while 4,6-DMDBT undergoes mainly HYD.

It was noted that upon introduction of a stronger acid function in the catalyst, two new products—3,6-DMDBT and 3,4′-dimethylbiphenyl—appeared in the reaction mixture of 4,6-DMDBT. This strongly suggests an acid promoted isomerization of 4,6-DMDBT—via protonation at position 3 and methyl shift (see Scheme 1)—to 3,6-DMDBT which in turn reacts faster as shown in Table 4. From the product distribution, 3,6-DMDBT is said to react mainly via DDS, in this resembling DBT. The overall picture of the reaction mechanism turns out as shown in Scheme 2: the two initially postulated pathways (DSS and DHY) are added to a third pathway, the isomerization (ISOM).

The higher activity at high HDS level of the NiMoP/Al_2O_3 with respect to CoMo/Al_2O_3 can be now explained in terms of a higher acidity favoring the isomerization of the more resistant S-containing species. It is well-known [6] that a phosphorus modified alumina is more acidic than a simple alumina and indeed NiMoP/Al_2O_3 proved to be more acidic than CoMo/Al_2O_3 since it had a high HDN activity, i.e. an higher reactivity vs. basic compounds.

4. Gasoline reformulation

4.1. Benzene reduction

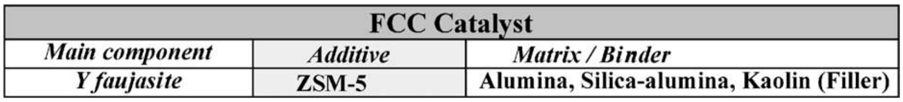
Benzene level is already very low in many gasolines. However its reduction passes through process solutions rather than catalytic manipulation. A lower severity in the reformer solves the problem giving also a higher yield in gasoline, but of poorer octanic quality. The feed to the reformer could be pretreated to remove C_5–C_6 naphthenic species, rapidly evolving to benzene under reactions conditions, to be processed in ring opening and skeletal isomerization to branched isomers.

4.2. Olefin reduction and valorization

4.2.1. FCC catalyst

FCC is a key unit in the today refinery. The great majority of US refineries are based on a FCC unit. FCC processes different feeds (LCO, VGO) with the purpose of reducing the chain length. A number of reactions take place: the basic mechanism involves the formation of carbenium ions that can lead to isomerization, β-scission, dealkylation and transalkylation, and hydrogen transfer. The reaction rates increase with the chain length and in moving from paraffins to olefins.

The simplified reaction mechanism demands an acid catalyst: actual catalysts are based on zeolites, either as main components and/or additives. The FCC catalyst is a very complex and highly sophisticated system in which some main roles can be envisaged (see Fig. 2). The active component, typically a Y zeolite is incorporated into an inorganic oxide (matrix), like alumina or silica–alumina, which plays a role both in reducing the dimension of larger molecules



FCC Catalyst		
Main component	*Additive*	*Matrix / Binder*
Y faujasite	ZSM-5	Alumina, Silica-alumina, Kaolin (Filler)

Fig. 2. Ingredients of a FCC catalyst.

Table 6
Qualitative product distribution from catalytic cracking using differently pretreated Y zeolite [7]

	USY	REUSY	REHY	REY
Dry gas yield	Low	Low	Low	Low
C_3/C_4 yield	High	Moderate	Moderate	Low
C_3/C_4 olefins	High	Moderate	Moderate	Low
Coke formation	Very low	Very low	Low	Moderate
Gasoline selectivity	Moderate	High	High	High
Octane potential	High	Moderate	Low	Low
Cracking activity				
383–482 °C cut	Moderate	Moderate	Low	Low
>482 °C	Moderate	Moderate	Low	Low

Table 7
Product distribution as a function of the zeolite Y UCS

UCS[a] (Å)	24.40	24.29	24.26
Conversion of feed (%)	62.6	66.2	70
Selectivity (%)			
Gasoline	56	56.4	59
LCO	21.2	21.2	19.2
MCB	16.2	12.6	10.8
$C_3^{=}$	5.7	6.4	6.9
$nC_4^{=}$	4.2	4.6	4.7
$iC_4^{=}$	1.3	1.8	2.3
S olefins	11.2	12.8	13.9
Coke (%)	4.1	4.1	4.1
Gasoline composition			
n-Paraffins	4.4	3.8	3.6
Iso-paraffins	32.5	29	25.8
Aromatics	25.4	24.7	23.6
Naphthenes	11.3	10.9	10.1
Olefins	27.3	31.6	36.9
Iso-amylene	4.5	5.4	6.5
FCC + Alky[b] + Ether[c]			
Total gasoline	74.8	81.4	86.5
Total aromatics	17.4	17.1	16.1

[a] Unit cell size.
[b] Alkylation produced from $C_3^{=}$ and $nC_4^{=}$.
[c] MTBE and TAME.

and in mitigating the effects of metals. A binder is also used to give mechanical resistance and act as a filler to densify the microspheres Enhanced performance is often due to additives: a classical one is ZSM-5.

The overall product spectrum can be influenced by modifying the zeolites. A dealumination procedure is a rather common treatment to improve thermal and hydrothermal stability and can be accomplished via different procedures. It leads to the expulsion of some aluminum atoms which can de identified as extra framework aluminum (EFAL) species. The dealuminated zeolite (USY: ultra stable Y) has a lower number of acid sites[2]—however of enhanced strength—and a reduced dimension of the unit cell with respect to the parent Y zeolite.

The stabilization of the Y zeolite can be obtained by exchanging the monovalent cation or the proton with a trivalent rare earth (REY) leading to an equilibrated REY with an acid site density and a total acidity higher than in USY, however of lower average strength. This leads to different catalytic performances as shown in Table 6.

Intermediates between USY and REY are REUSY zeolites obtained by exchanging USY with varying amounts of rare earths. Similar materials (REHY) are prepared from a partially rare earth exchanged NH_4Y followed by calcination. The rare earth content of REHY is usually higher than REUSY.

Table 6 drives the selection of the zeolite main component. When Y has been picked, the product spectrum can be tailored by changing the dimension of the unit cell size (UCS) as shown in Table 7 [8].

It appears that the smallest UCS reduces the aromatics formation while improving the gasoline yield, unfortunately at the expense of an augmented olefin content. A simple explanation of the different product distributions is proposed in footnote 2 on the basis of a lower number of acid centers.

The alkene formation is favored when the hydrogen transfer is reduced, i.e. the concentration of acid sites is diminished which pairs to the reduction of UCS. Therefore the composition and the isomer distribution within a given fraction could correlate with the dimension of the unit cell. Attention focuses on the C_4 cut because of the many downstream possible conversions; however similar results were obtained for C_5 fraction. It has been shown [9] that alkene concentration grows when the UCS decreases (Fig. 3a) leading mainly to isobutene because the

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[2] A lower number of acid centers reduces the bimolecular reaction (hydrogen transfer responsible of double bond saturation, hydride transfer responsible of chain transfer) in favor of the monomolecular ones (β-scission, isomerization). Reduction of the bimolecular reactions favors olefin yield and octane while reduces the yields of LPG and gasoline and the coke formation.

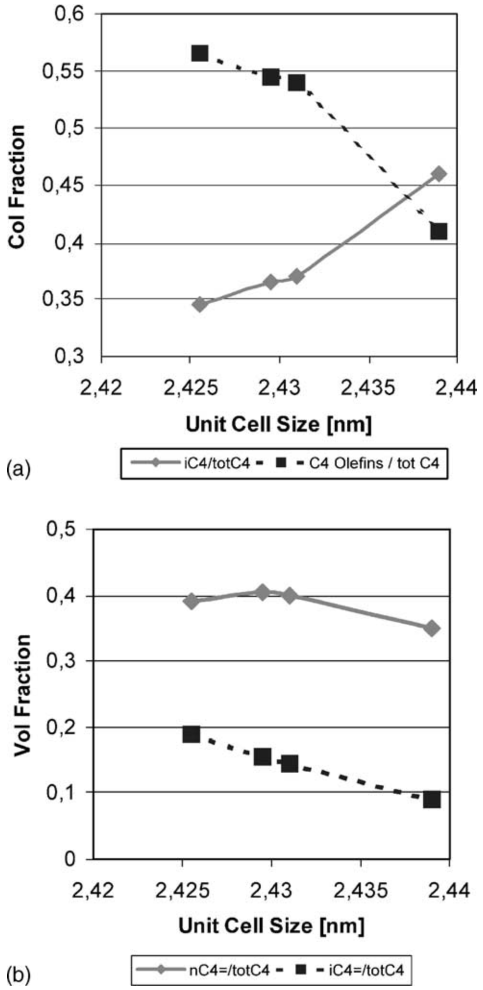

Fig. 3. (a) Effects of Unit Cell Size on total olefins and isobutane within the C_4 cut; (b) effects of Unit Cell Size on the distribution of olefin isomers within the C_4 cut.

linear isomers seem to level off someway (Fig. 3b). Below a certain value of the UCS, the site density is low enough to suppress the formation of the linear double bond via hydrogen transfer from a short-living secondary carbenium ion, whereas the long-living tertiary carbenium ion demands for even lower site densities.

Typically a FCC additive catalyst is ZSM-5 because of its acidity and shape selectivity. The dimension of the channel allows treating preferentially the straight chain low-octane structures converting them to branched chain. In fact it can be seen in Fig. 4 [10] that the ZSM addition increases the iso-to-normal ratio at various carbon atoms and independently of the base catalyst.

However it should be noted that ZSM-5 is more effective at low carbon atoms since the longer the chain the more difficult to penetrate the channel. It is expected moreover that the side chains are mainly methyl group since already an ethyl group makes the molecule too bulky to leave the narrow channels of the zeolite [11].

Attention should be paid to the effect of aging on ZSM-5 performance. The aging modifies the acidity of the materials and therefore the activity. The alkane cracking diminishes with time on stream due to the removal of stronger acid sites while alkene cracking persists until the residual acidity is so low that only alkene isomerization takes place (Fig. 5) [12].

The β-zeolite has been shown to offer advantages with respect to Y based FCC catalysts due to the higher acidity but the lower site density. In Table 8 [8] the use of a β-based catalysts seems to offer advantages in the production of reformulated gasoline assuming that the olefins—whose iso-to-normal ratio is approaching the equilibrium limits—are etherified (see below).

The improved quality can be ascribed to a lower site density (β can be synthesized at very low Si/Al ratio) which reduces hydrogen transfer and to the higher acidity which favors the skeletal rearrangement to branched isomers.

Data in Table 8 (USY vs. USY/ZSM-5) confirms that the presence of ZSM-5 favors the formation of branched structures and it is worth noting that it increases also the RON and MON. It has been shown [13] that such an effect extends up to four units for RON and two units for MON and it correlates almost linearly with the ZSM-5 amount (in the range 0–3 wt.%).

An industrial catalyst requires a matrix or a binder—sometimes the distinction is not so clear—which can be used to introduce further functionalities. In a FCC catalyst the matrix is usually an acid component—alumina or silica/alumina—with larger pores whose main role is to pre-crack large molecules of the bottom fraction so that they can diffuse in the narrow channel of the zeolites to be further processed.

In Table 9 the matrix is increasing the conversion of the feed while improving the yields to desired products.

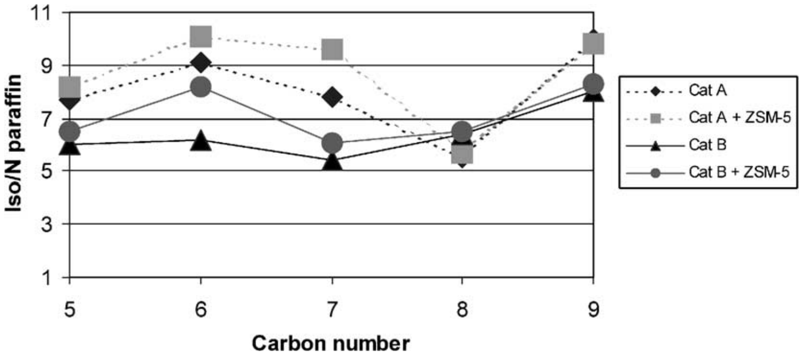

Fig. 4. Effect of ZSM-5 addition to iso-to-normal paraffin ratio.

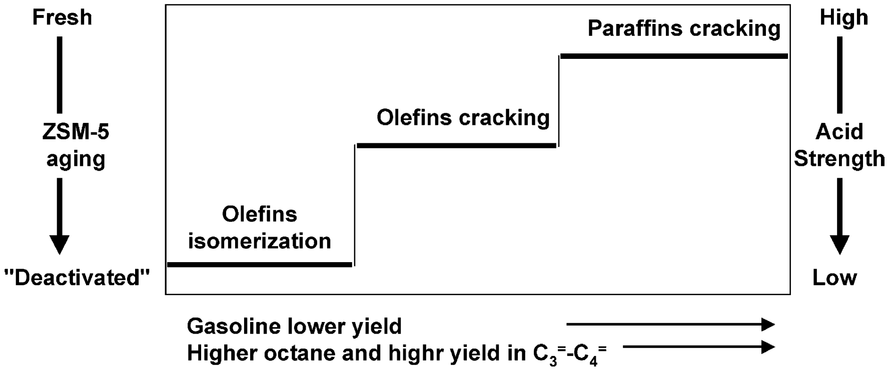

Fig. 5. Influence of ZSM aging on reaction network as a function of aging.

In some cases the matrix can perform further action as shown in Table 10 [15] to improve the isoolefins which in turn are to be converted to ethers or dimerized. To limit the hydrogen transfer, a fine tuning of the silica–alumina material—in terms of acidity (Lewis/Broensted > 1.5) with a concentration of Broensted acid sites $<30\,\mu$mol/g having a surface area higher than $50\,m^2/g$—has been achieved acting on the preparation procedure.

4.2.2. *High octane component*

In the previous paragraph, the trend in FCC catalysts was the increase of olefins. The key step is their downstream conversion to higher quality products, i.e.

Table 8
Gasoline composition RFG-1 is a proprietary W.R. Grace, β-based FCC catalysts

	USY	SiO_2–AlO_3	USY/ZSM-5	RFG-1 (β)	Equilibrium
Alkanes	35.1	32.5	31.4	26.4	
Alkenes	25.7	32	29.1	42.6	
Naphthenes	9.3	7.5	8.4	7.3	
Aromatics	29.9	28	31.1	23.7	
RON	91.2	92.6	93.4	93.6	
MON	80.2	80.7	81.5	80.2	
$iC_4^=/\mathrm{tot}C_4^=$	0.28	0.30	0.32	0.40	0.45
$iC_5^=/\mathrm{tot}\ C_5^=$	0.52	0.67	0.62	0.65	0.66

Table 9
Effect on matrix on production distribution [14]

	Commercial bottom up-grading catalyst	Syntec catalyst
Conversion (wt.%)	Base	+2.2
Yield (wt.%)		
Gas	Base	−0.2
LPG	Base	+1
Gasoline	Base	+1.3
LCO	Base	−1.6
Slurry	Base	−0.6
Coke	Base	+0.1

Table 10
AH (Engelhard proprietary material) = 20% Y + 80% SiO_2–Al_2O_3

	Engelhard material, AH	Commercial Y zeolite
UCS (Å)	24.27	24.23
Catalyst/oil ratio	9.9	5
Conversion (%)	66	66
C_4 yields (%)		
Isobutene	1.9	0.6
Straight butenes	3.7	1.6
Isobutane	4.1	4.2
n-Butane	0.6	0.7
Isobutene/total C_4 alkenes	0.34	0.27
C_4 alkenes/C_4 alkanes	1.2	0.45

the winning strategy turns out to be the up-grading of low value streams.

4.2.2.1. Etherification and dimerization.

A simple way to “eliminate” C_4 and C_5 olefins from the gasoline pool is their etherification with MeOH [16], leading either to the single ether (MTBE, TAME) or to their mixture, depending on the row material. This conversion is well established. However a gloomy future may be predicted as a result of the MTBE ban from California gasoline, dated January 2003,[3] due to poor biodegradability. The fate of MTBE in the USA might also influence the standard in other parts of the world.

Alternatives, however, should be available since the removal of oxygenated compounds from gasoline provokes a lack of octane. The selective dimerization of C_3–C_5 olefins, followed by hydrogenation producing sulfur-free, low-volatility branched paraffins is a quite valuable option. The major interest addresses C_4 in the attempt to directly convert a MTBE plant to produce isooctane (2,2,4-trimethylpentane (224-TMP)) via selective dimerization of isobutene since the 224-TMP has a 100 octane number by definition.

The dimerization is a typically acid catalyzed whose control is quite difficult because the exothermicity increases the temperature, kinetically favoring the formation of trimers (C_{12}, high octane, but in the upper range of boiling range for gasoline) and tetramers (C_{16}, poor octane, out of boiling range).

Snamprogetti has envisaged a strategy to moderate the acidity under working condition by controlled addition of MeOH. The acid group of sulfonic resins ($–SO_3H^+$) converts to $–SO_3MeOH_2{}^+$, which is less acidic and it allows a better control on selectivity to dimers and on heat release. The effect of adding substoichiometric MeOH to an isobutene-containing stream is reported in Fig. 6.

Developing such a principle, Snamprogetti [17] is now able to offer commercial processes (CD*Isoether*) that can produce mixtures of high octane C_8 compounds and MTBE in relative amounts, depending on the MeOH to isobutylene ratio, up to the extreme of pure isooctane (see Fig. 7). The quality of the product, proven from significant industrial runs is even superior to that of alkylate (see Table 11).

4.2.2.2. Skeletal isomerization of paraffins and olefins.

The conversion of linear hydrocarbons to their branched isomers fits well with the reformulation trend of gasoline since the octane number is greatly improved. The skeletal isomerization reaction suffers from severe competition with cracking. This competition is even worse for longer chain molecules. A distinction has to be made between paraffins and olefins: the former can go directly into the gasoline

Table 11
Typical values of some properties of CDIsoether dimers vs. alkylate

	CDIsoether dimers	Alkylate	
		HF	H_2SO_4
Clear octane			
RON	100.2	96	97
MON	100.3	94	94
Density (g/cm^3)	0.720	0.697	0.697
RVP (kPa)	12	31	31

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[3] The ban has been recently delayed to 2004.

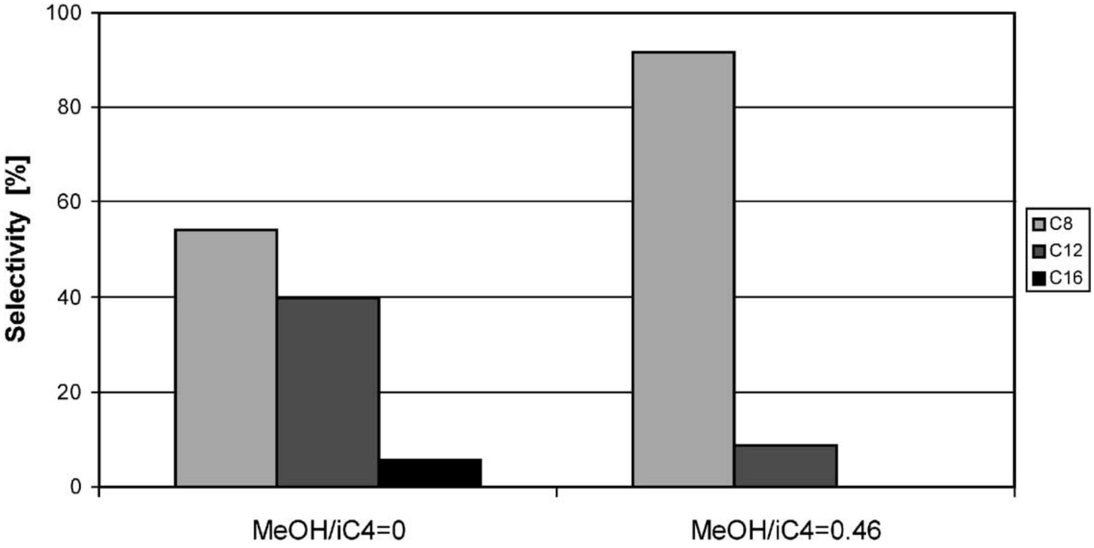

Fig. 6. Effect of MeOH on the distribution of isobutene oligomers on a MTBE catalyst sulfonic resin.

if of the proper chain length, while the latter should be further processed. Therefore the skeletal isomerization of C_4–C_5 olefins attracted interest in recent years because the conversion of linear isomers could increase the overall output of ether (MTBE or TAME, see Section 4.2.2.1) from a given stream.

Today this conversion is less appealing because the future of ethers is less clear, as described above, while

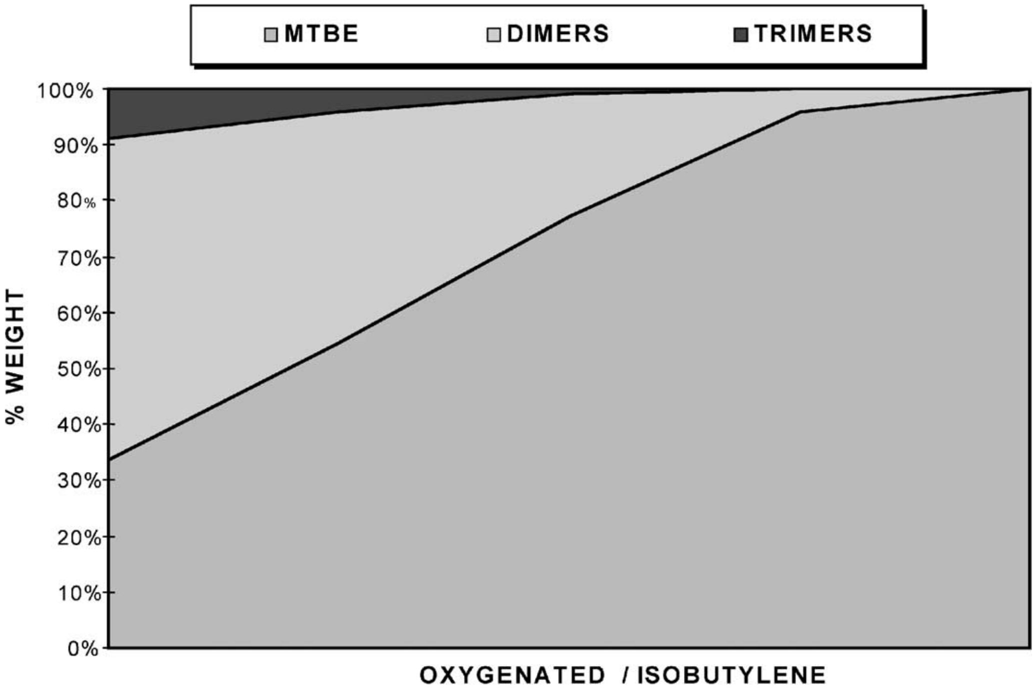

Fig. 7. Effect of oxygenated/isobutylene ratio on product distribution.

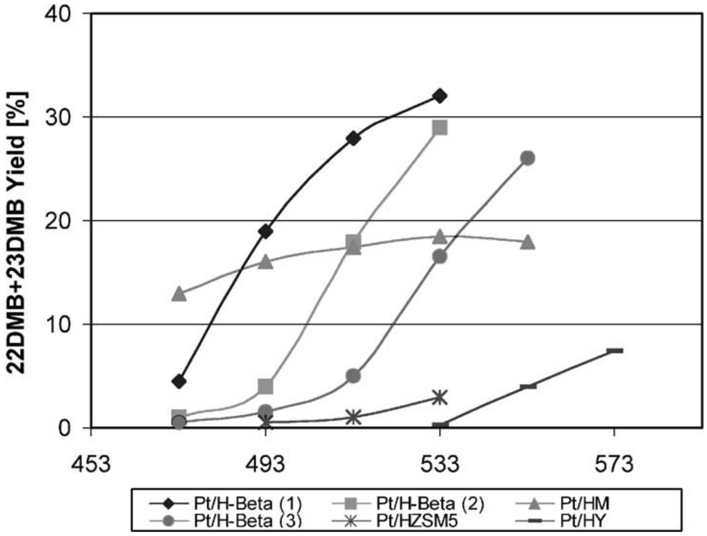

Fig. 8. Hexane isomerization activity of different zeolites modified with platinum.

that of paraffins is still of great interest. However, while the skeletal isomerization of C_5–C_6 paraffins is consolidated and commercially available, the challenge remains for the longer chain (C_7–C_8) paraffins.

Possible sources are the Light Straight Run (LSR) naphtha and the feed to the reformer when pretreated to remove these aromatics precursors. In the case of C_5–C_6 paraffins, a quite strong acidity is required to modify the carbon skeleton whereas it has to be milder in the case of higher paraffins to prevent cracking. In both cases a (de)hydrogenation function is required since the skeletal rearrangement takes place on the olefin. The overall mechanism is commonly agreed as DeHYD → ISOM → HYD. Also the relative steric hindrance of the isomers should be considered or used in the catalyst design.

Pt-mordenite has been one of the first materials to be developed since 1970s.[4] The noble metal provides (de)hydrogenation activity while the acidity of the unidimensional medium pore zeolite (6.7 Å × 7.0 Å) promotes the skeletal isomerization. The acidity of mordenite is typically increased via dealumination (steaming and or acid leaching) taking advantage of the improved isomerization activity induced by EFAL [18a]. It has been recently demonstrated [18b] that leaching reduces the diffusion resistance of the reactant hydrocarbon due to the formation of mesopores. However the zeolite channel dimension inhibits the formation of the more bulky 2,2-dimethylbutane. Therefore attention might be focused towards larger pore zeolites such as omega (mazzite), a unidimensional (7.4 Å × 7.4 Å) zeolite [19], which, behind a claimed higher acidity [20] can accommodate branched structures more easily. A higher acidity means a lower operating temperature and therefore a more favorable thermodynamic equilibrium. Also β-zeolite has been claimed to be active and selective in this reaction. Quite interesting is the comparison of the different zeolitic structure as done by Lue et al. [21] whose results are plotted in Fig. 8.

The small pores of ZSM-5 do not allow the formation of dimethylbutane (DMBs) whereas the moderate acidity of Y requires an higher temperature to run the reaction but the competitive cracking limits the DMB yield. Mordenite is even more acidic than β, given the low temperature at which the material is active, but the dimension of the channels does not allow a full exploitation of the potentiality. β couples available acidity and a suitable channel system and therefore it turns to be the best catalyst. However it seems there is an effect of the noble metal and its method of loading as can be deduced by the different activity of the three different Pt/H-β.

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[4] The Shell's Hysomer process for C_5–C_6, available since 1970s is based on a Pt/mordenite.

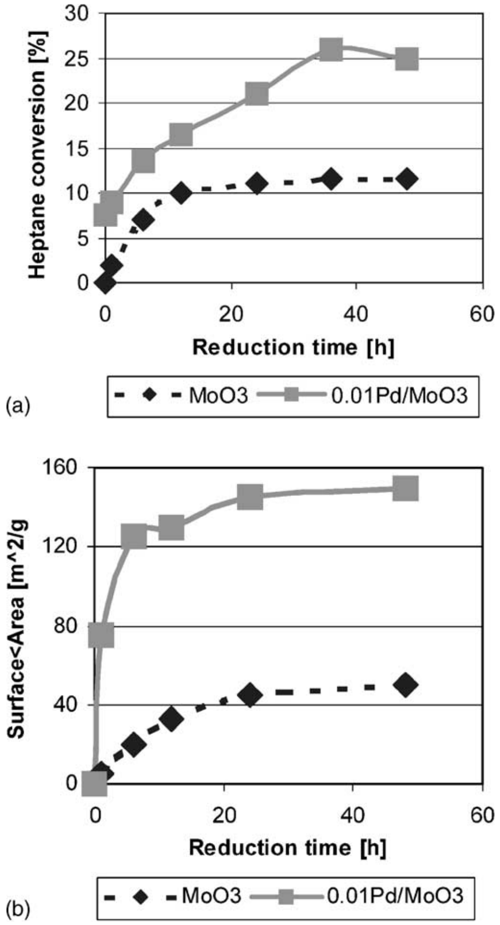


Fig. 9. (a) Effect of reduction time on activity expressed as heptane conversion; (b) effect of reduction time on surface area.

Other than zeolites, other interesting materials have been proposed. Oxygen treated tungsten carbide performs the isomerization and it was shown that a bifunctional mechanism holds, where the WC_x plays the role of the metal and WO_x has acidic properties. The oxycarbide phase was also claimed in case of Mo_2C whose selectivity did not match with those of Pt/β. However, MoO_3 properly reduced [22] was also active: in this case the formation of a small amount of metallic Mo would explain the activity. The surface addition (0.01 wt.%) of a noble metal (Pd) markedly increases the activity. Higher loading did not improve it any more. In both cases the relationship with the reduction time is reported in Fig. 9a. A similar plot for the surface area is reported in Fig. 9b, suggesting that the reaction rate is correlated with the surface area.

Two main classes of materials are used in C_4–C_5 olefins oligomerization: alumina modified materials (SISP process by Snamprogetti [23]) and zeolites, almost exclusively ferrierite, as such (Isomplus process by Shell–Lyondell–CD Tech [24]) and modified (Isotex process by Texaco process [25]), because of the channel dimensions and form. The main side reaction was the dimerization of the reagent, followed by cracking to light ends. Fine tuning of the acid center strength and shape selectivity were respectively used to oppose such an undesired path. Selectivities up to 85–95% were reached depending on the feed (C_5 linear olefins conversion is easier than that of C_4) and concentration (the more diluted the reagent the better) with a conversion ranging from 30 to 55%. An important factor was the content of oxygenates (water, alcohols, ethers) in the feed which was shown to increase the catalytic activity in the case of the alumina modified material while it appeared to be detrimental in the case of ferrierite [26]. If we refer to water for simplicity, this was very likely due to the creation of further OH surface groups—the active center—in the case of the alumina based materials. In the case of ferrierite based catalysts instead, water is likely to weaken the $SiO_xAlO^-H^+$ active center.

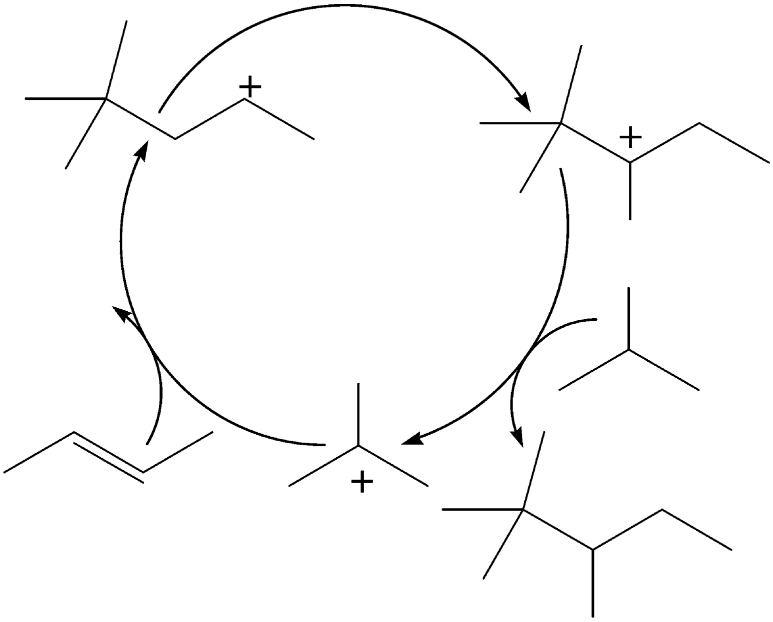
4.2.2.3. Alkylation. Alkylate defines a mixture of C_8 isomers, mainly trimethylpentane, with minor amounts of higher components obtained via acid catalyzed addition of isobutane to linear butenes. Although other feed compositions have been proposed, the standard $iC_4/n\text{-}C_4 =$ alkylation couples products of high quality with the minimum consumption of the acid. Today two families of alkylation technologies are available: the H_2SO_4 based and the HF-based, proposed by UOP and Phillips. A review of the commercial processes is given by Corma and Martinez [27].

Both of them suffer from a severe environmental impact. The H_2SO_4 process produces spent acid containing tar (the consumption can reach 70–100 kg of catalyst consumed per ton of alkylate)—which is difficult and costly to treat.

The HF process went through incremental improvements; however, HF still remains potentially highly corrosive and volatile and, in many industrialized countries approval for HF-based new units will not be given. Therefore the high potential for reformulated gasoline faces severe constraints in the production cycle which, in turn, generates a strong impulse to searching for solid alkylation catalysts. Many materials have been tested starting with zeolites in the late 1960s. However catalysts that have reached the stage of pilot unit are not based on zeolites, instead they are composites of mixed oxides. UOP (alkylene process) proposed $AlCl_3/Al_2O_3$ with a small amount of noble metal (Pt); Catalytica/Neste Oy/Conoco selected a boron trifluoride on Al_2O_3, while CD Tech/Chevron developed SbF_5/acid-washed silica. All of them are supported, strong Lewis acids. H. Topsøe AS proposed the most innovative approach: a supported or anchored trifluorsomethansulfonic acid (triflic acid F_3CSO_3H) on silica. The key feature is the switched-flow regime since the acid moves along the bed due to a chromatographic effect. The feed is top-fed for a certain time then the flow is reversed into a bottom-feed to ideally maintain the acid within the bed.

All the proposed technologies suffer from drawbacks that have up to now delayed their market penetration. The acids however are of high strength as indicated in terms of $-H_0$ (Hammet indicators) [28]. All of them contain halogens whose high electronegativity induces a net charge separation: this may be assumed as the cause of the strong acidity. However there are other strategies to get solid acid: both the already mentioned zeolites and the sulfated modified inorganic oxides like titania or zirconia. Many papers has been published on the alkylation activity of such acid materials sometimes in contradiction each other. Weitkamp, reviewing the large mass of information produced by Corma et al., concluded in an exhaustive paper [29] that the "in-depth studies by Corma et al. nicely demonstrate that the performance of an acid zeolite as catalyst in isobutane/butene alkylation depends on a complex and subtle manner on its history, i.e. the recipe of hydrothermal synthesis, the chemical composition, the post-synthesis treatments, the amount and nature of EFAL and the density and strength of Broensted acid sites".

Similar conclusions can be drawn in the case of sulfated material—mainly zirconia—where sulfating and activation conditions, together with the calcination procedure and sulfur source and concentration, strongly influence the anchoring of SO_4 group to the surface of the inorganic oxide and therefore the initial catalytic performance.



Scheme 3. Simplified cycle of alkylation *n*-butene/isobutane.

In general, all these materials have good initial activity, which is lost more or less rapidly. The regeneration—either via oxidative combustion of the surface heavy organic compounds (HOCs) or via noble metal promoted hydrogenation to facilitate their removal—rarely restores the initial activity. The understanding of deactivation is of great importance to synthesize more robust materials: Weitkamp and Traa [30] recently proposed the intermolecular hydrogen transfer as the crucial step to be improved.

The simplified mechanism (Scheme 3) moves from a terbutil carbenium ion, which undergoes addition to *n*-butene. The secondary octyl cation rapidly rearranges (intramolecular hydrogen shift) to get a more stable tertiary carbenium ion that should exchange hydrogen with an isobutane molecule to close the catalytic loop. This intermolecular hydrogen shift seems to be the weakness of many solid acids since this property is quite quickly lost under reaction conditions. If other olefins add[5] onto these surface C_8 carbocations, HOCs form which in turn generate light ends via β-scission or deactivate the catalyst "covering" the active site.

5. Diesel reformulation

Diesel is a less evolved fuel and a minor number of process options can be proposed to have a high quality cut. We select three different routes making use of different feedstocks: (i) up-grading of light cycle oil (LCO)—a refinery internal stream—via dehydrocyclization of polycondensated rings to reduce aromatic content while both improving the cetane number and reducing the density; (ii) oligomerization of light (C_4–C_5) olefins, a stream potentially available in refinery; (iii) conversion of natural gas via syngas and Fischer–Tropsch reaction, today know as the gas-to-liquids (GTL) route.

5.1. Up-grading of LCO

The bulky molecules—from 2 to 4 condensed aromatic rings with side chains-require adequate pore dimensions (order of mesopores) to let them reach the active site. Two functions are required: hydrogenating centers—like noble metals—and acid types to favor the rupture of C–C bonds. Both types have severe requirements. The hydrogenating centers must resist the sulfur poisoning action while the acid ones should not be too strong to avoid cracking to light ends. New materials[6] developed according to these guidelines show better performance than those of expected for an industrial type catalyst (Fig. 10).

Scheme 4 [31] shows the effect on cetane number and boiling point when double bonds are saturated and the ring is properly opened starting from 2-butil naphtalene as a model compound. Experimental results indicating the dependence of cetane improvement and density reduction on aromatic saturation [31] are clearly shown in Fig. 11.

5.2. Olefins oligomerization

The light olefins oligomerization route, catalyzed by acid sites is a promising way to obtain a premium quality diesel, free of sulfur and aromatics. The key factor is the chain growth control since the branching has to be limited to have a good cetane number. Two strategies can be envisaged: one related to the acid center—a fine tuning of the strength or modification of the environment—the other related to the dimension of the channel of the catalyst—thus an application of the well-known concept of "shape selectivity". A further topic to be addresses is the heavy organic materials formation that in general demands regeneration treatment: therefore the catalyst should also be tolerant of such a rejuvenating procedure. Many acid materials perform the desired C–C bond connection of a limited number of olefins (3–5 units) but they are lacking in maintaining the linearity of the chain (i.e. high cetane number). Recently proposed processes (Nesko [32], COD conversion of olefins to diesel [33]) very likely make use of a modified ZSM-5, which couples good shape selectivity to consolidated commercial availability, which means an extensive knowledge in controlling the acidity (strength and number, location) in scaling-up of the production and regeneration procedures. Cetane numbers of the order of 48–52 have been reported.

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[5] The kinetics of olefin addition has been modeled as a faster reaction compared with intermolecular hydride transfer. An high ratio of isobutane over olefins could limit this parallel path, but industrial feasibility poses however limits to the ratio.

[6] Results from a partnership project.

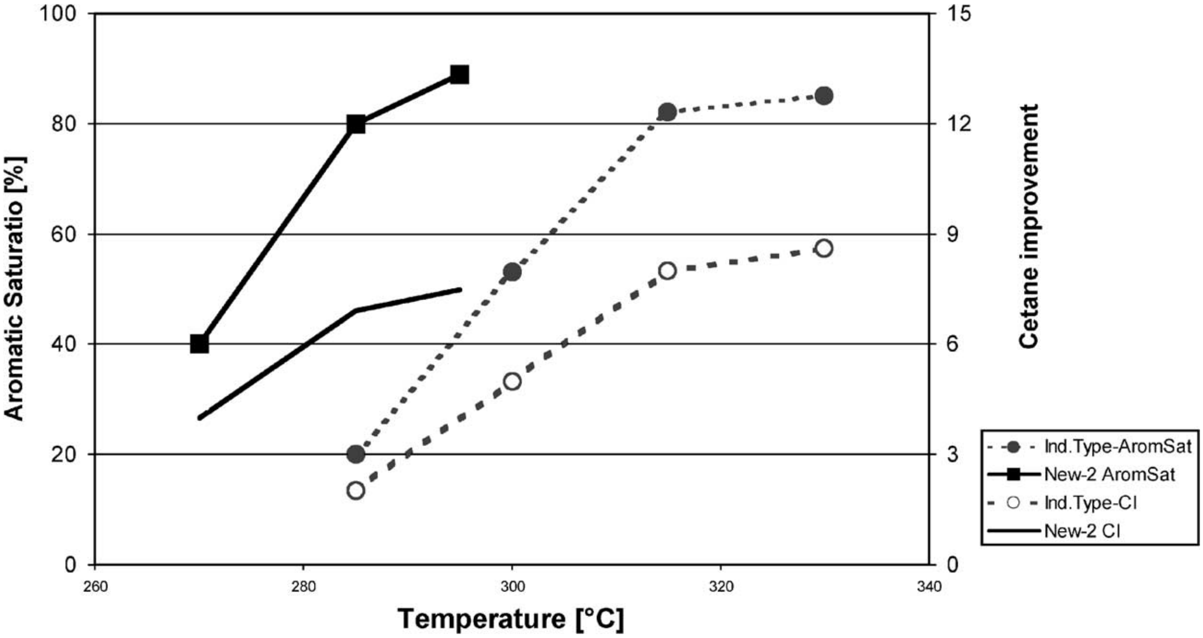
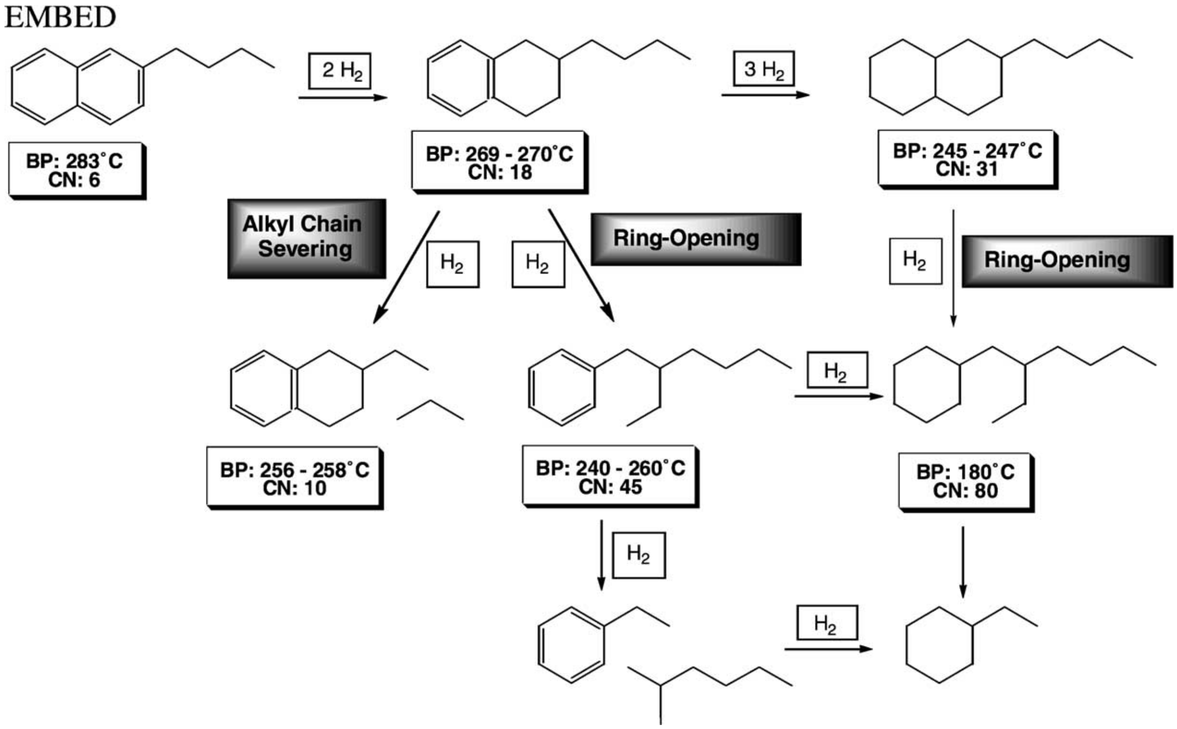


Fig. 10. Effect of temperature on aromatic saturation (filled square) and cetane improvement (circle) for two different catalysts: a reference industrial type catalyst (open symbols); a new one (filled symbols).



Scheme 4. LCO up-grading network and properties of model compounds.

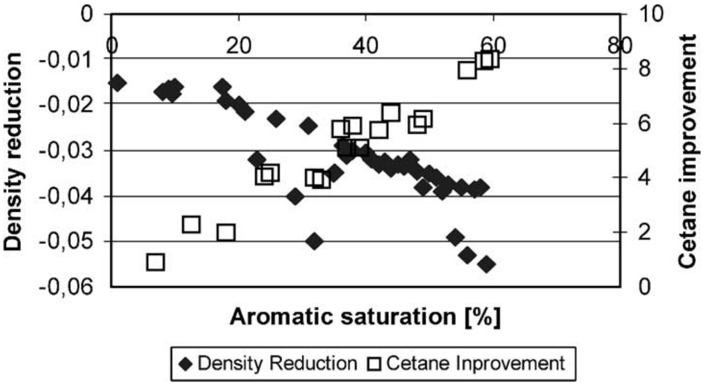


Fig. 11. Correlation of density reduction and cetane improvement of a LCO as a function of aromatics saturation level.

Although there is some potential, no (semi) industrial scale unit have been built up to now. Presumably also the limited feed availability and the limited demands of premium diesel components have determined such an impasse. The COD process has the peculiarity to deal with olefins from Fischer–Tropsch synthesis via syngas, developed within the MossGass project of South Africa. This is in someway bridging the oligomerization with the GTLs technologies aimed to produce high quality fuel from natural gas or, in a more imaginative perspective, to open the doors to a "methane-based refinery".

5.3. Fischer–Tropsch reaction: the GTLs route

The huge and continuously growing reserves of natural gas have stimulated its exploitation in term of liquid fuels because of its intrinsic characteristic: high energy content, absence of heteroatoms, high hydrogen-to-carbon ratio in the raw material, geographical availability, and growing cost of reinjection and flaring (when dealing with oil-associated gas).

The preferred route has been identified in the Fischer–Tropsch reaction [34] where syngas (CO and H_2) is converted to a mixture of linear hydrocarbons according to a distribution dictated by the so-called α parameter defined by Eq. (1)

$$\alpha = \frac{r_g}{r_g + r_t} \qquad (1)$$

where r_g is the rate of chain growth and r_t the rate of chain termination. This descends by the well-recognized mechanism of "polymerization" where the building block is $-CH_2$-derived from CO hydrogenation of the catalyst surface. Catalysts play a role in determining the α value although there is some influence of the operating conditions, pressure and temperature. Cobalt and iron are the almost exclusively used metals with a basic distinction: iron tends to produce shorter chain (low α) while cobalt allows α value close to 1. Since the interest lies in liquid fuels, cobalt is the preferred choice, assisted by low temperature and high pressure.

The GTL is nowadays targeted to diesel because of the linearity of chains in the product mixture, which leads to good cetane number. However all the three leading technologies—proposed by Sasol (South Africa) which relies upon the consolidated experience in coal derived liquids (10.000–20.000 bbl/day) via Fischer–Tropsch reaction; by Shell [35] which proved the technology in the 12.500 bbl/day plant in Bintulu (Malaysia); by ExxonMobil which reached the PDU scale—include a hydrotreating section downstream of the Fischer–Tropsch reactor in order to better tune the product structure (chain length and branching) to diesel requirements (cetane number, cold properties, flash point).

A syngas preparation section—that can or cannot make use of catalysts—is included in the industrial complex, making it a huge investment of the order of a billion US dollars with a significant influence of the location factor. The importance of these GTL technologies is the raw material: a liquid fuel is derived from natural gas instead of oil. It opens opportunities for natural resource exploitation, which will influence our future, but, given the many implications, technical and socio-economical involved, cannot be discussed in this paper.

6. Conclusions

The catalyst can play a significant role in the production of higher quality fuel as required by standards which step-by-step are going to be introduce all over the world due to growing consciousness of the damage to human health and environment from existing products.

In this paper I have deliberately focussed the attention on the role of catalytic materials, selecting significant examples even if they have not reached final industrial application. To reach this goal, however, a catalyst will have to be combined with the right reactor and run under the optimal operating conditions.

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