

Impact of Zeolites on the Petroleum and Petrochemical Industry

W. Vermeiren · J.-P. Gilson

Published online: 15 May 2009
© Springer Science+Business Media, LLC 2009

Abstract The general features of zeolites that led to their widespread use in oil refining and petrochemistry are highlighted as well as the details of their impact on selected processes. The analysis of the catalyst market and the position of zeolites therein is a good indication of their strategic importance. Zeolites have brought many *disruptive* changes to these fields (e.g. FCC). They impacted also these industries in an equally important way, although more subtle, by *incremental* improvement of processes. The new and vast challenges facing oil refining and petrochemistry as well as the managed transition to sustainable environmental benign transport fuel industries and chemical industries will require creative science and technologies. Zeolites offer the basis of many of these technological solutions provided efficient and balanced cooperations between industry and academia are further developed.

Keywords Zeolites · Molecular sieves · Oil refining · Petrochemistry · Emerging technologies · Emerging feedstock

1 Introduction and Scope

Zeolites have ceased to be minerals merely displayed in museums, and have become a commercial and scientific success-story since their large-scale utilization in industry. It all started with the use of synthetic zeolites in oil refining and petrochemicals. The rest is now part of industrial history: it is a case study of breakthrough and incremental innovation [1–3] and a model of interplay between science and technology, from very fundamental academic research and industrial curiosity to efficient large scale production of zeolites and their deployment in catalytic- or adsorbent-based processes.

This contribution is not another updated compilation of zeolite-based processes found in oil refining and petrochemistry; many reviews exist already [4–7] and point to further and more detailed studies. In particular, the two-volume contribution of Marcilly [7] is a compulsory reading for the serious beginner for the depth and the breadth of its coverage; moreover, it gives a unique perspective by a seasoned practitioner acquainted with both fundamental and applied aspects of zeolites and other acid-base catalytic processes.

This contribution aims to paint a broad picture of the subject, with a few close-ups on selected topics. It is followed by a general reflection on the future use of zeolites in industry and the need for collaboration between industrial and academic researcher. It is intended for newcomers in the world of zeolites science and technology and intends to enable them to deepen and broaden their insights to generate new ideas, processes and products for the benefit of society as a whole. Zeolites have so far been extensively used in the petroleum industry and could still play an important role in the major challenges ahead of us. These are the exploitation of non-conventional petroleum

W. Vermeiren (✉)
TOTAL Petrochemicals, Rue de l'Industrie, 52,
1040 Brussels, Belgium
e-mail: walter.vermeiren@total.com

J.-P. Gilson
Laboratoire Catalyse and Spectrochimie, ENSICAEN,
Université de Caen, CNRS, 6 Boulevard Maréchal Juin,
14050 Caen Cedex, France
e-mail: jean-pierre.gilson@ensicaen.fr

resources (tar sands, heavy crude oil and oil shales), non-petroleum resources like gas and coal and valorization of biomass for our petrochemicals production and fuel supply.

This review focuses mainly on zeolite applications in refining and petrochemistry. For details of zeolite applications in fine chemicals, the reader is referred to the specialized literature.

2 From the Pioneers to Today

Much of the pioneering work on zeolites, particularly the synthesis of new zeolites comes from the former Union Carbide and Mobil companies. Probably one of the most important paradigms is the launch of using quaternary ammonium hydroxides in the synthesis of zeolites [8]. This led to the discovery of zeolite ZSM-5 in 1963 by former Mobil [9]. Often in order to arrive to industrial applications and commercialization, external factors (market push) are required. Chen describes how the US government's decision to remove lead from gasoline, provided the needed economic incentive to commercialize the expensive ZSM-5 zeolite [9]. Even with such external stimuli, it takes often many years before delivering commercially viable applications. For instance, the MSTDP (Mobil Selective Toluene Disproportionation Process) was commercialized in 1988, seventeen years after the discovery of the ZSM-5 synthesis [9].

These discoveries of the early sixties have led to a new discipline in material science, catalysis, separation science and petrochemical or organic chemistry. These disciplines have since then progressed at a continuous pace. Figure 1 shows the number of zeolite related publications, between 1960 and 2008. It demonstrates that the rate of publications is ever increasing, highlighting the continuous scientific interest in these materials. The same can be seen in Fig. 2 for the number of US patents, indicating that many

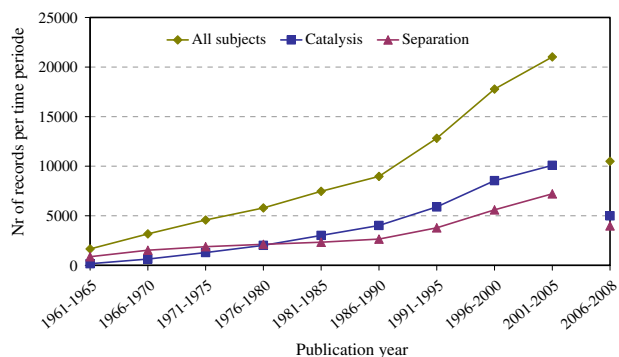


Fig. 1 Number of non-patent publications on zeolites and molecular sieves (non-carbon) (the search has been performed in the CAlus database using STN)

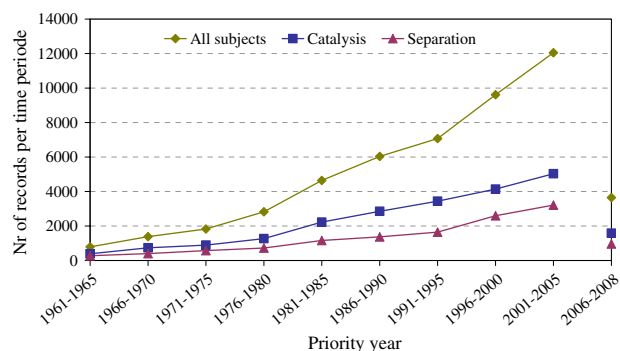


Fig. 2 Number of US patent publications on zeolites and molecular sieves (non-carbon), based on priority date (the search has been performed in the CAlus database using STN)

potential new innovations are still judged worth protecting by industry.

The International Zeolites Association (IZA) has registered 179 different zeolites structures (see Table 1, reproduced from [10]). Of these 179, only 18 are reported to be used in commercial operation. It is believed that some other zeolite structures might be employed industrially as a large proportion of the scientific and patent literature is devoted to them (ZSM-22, ZSM-23, ZSM-57) and it is also alleged that in the very near future the SAPO-34 will be commercially used in the Methanol-to-Olefins (MTO) process. Hence, for the extensively studied SAPO-34, it will have taken more than 25 year to reach commercialization. Although, it was identified in the late 1980s that this material exhibited the right structural and compositional features for the selective conversion of methanol into mainly ethylene and propylene, the economic viability rules the commercialization process. MTO represents a real paradigm shift as the whole process is new and the feedstock, methanol, is different from the conventional feedstocks directly available from fossil resources, namely naphtha, LPG (Liquid Pressurized Gas) or ethane. Moreover methanol is only another intermediate and is today produced in limited quantities through elaborate processes from fossil resources, like natural gas and coal.

Recently, UOP has introduced a new concept in zeolite synthesis by optimizing the way the typically well-known ingredients are put together, the so-called “*Charge Density Mismatch*” (CDM) approach [11, 12]. The aluminosilicate reaction mixture is characterized by the mismatch between the charge density on the organoammonium structure directing agent (SDA) and the charge density on the potential aluminosilicate network that is expected to form. These conditions can be accomplished by creating an aluminosilicate reaction mixture (typically a clear gel) using a large SDA (low charge density) and a low Si/Al ratio (high charge density). The crystallization of a zeolite from such a reaction mixture does not proceed spontaneously.

Table 1 Registered zeolite structures by the International Zeolites Association [10]: commercially used zeolites are highlighted

ABW	ACO	AEI	AEL	AEN	AEI	AFG	AFI	AFN	AFO	AFR	AFS
AFT	AFX	AFY	AHT	ANA	APC	APD	AST	ASV	ATN	ATO	ATS
ATT	ATV	AWO	AWW	BCT	*BEA	BEC	BIK	BOG	BPH	BRE	CAN
CAS	CDO	CFI	CGF	CGS	<i>CHA</i>	-CHI	-CLO	CON	CZP	DAC	DDR
DFO	DFT	DOH	DON	EAB	<i>EDI</i>	EMT	EON	EPI	ERI	ESV	ETR
EUO	EZT	FAR	FAU	FER	FRA	<i>GIS</i>	GIU	GME	GON	GOO	<i>HEU</i>
IFR	IHW	IMF	ISV	ITE	ITH	ITW	IWR	IWV	IWW	JBW	KFI
LAU	LEV	LIO	-LIT	LOS	LOV	LTA	LTL	LTN	MAR	MAZ	MEI
MEL	MEP	<i>MER</i>	MFI	MFS	MON	MOR	MOZ	MSE	MSO	MTF	MTN
MTT	MTW	MWW	NAB	NAT	NES	NON	NPO	NSI	OBW	OF	OSI
OSO	OWE	-PAR	PAU	PHI	PON	RHO	-RON	RRO	RSN	RTE	RTH
RUT	RWR	RWY	SAO	SAS	SAT	SAV	SBE	SBN	SBS	SBT	SFE
SFF	SFG	SFH	SFN	SFO	SGT	SIV	SOD	SOS	SSF	SSY	STF
STI	<i>*STO</i>	STT	SZR	TER	THO	TOL	TON	TSC	TUN	UEI	UFI
UOZ	USI	UTL	VET	VFI	VNI	VSV	WEI	-WEN	YUG	ZON	

Bold represent zeolite structures exhibiting typically catalytic applications and *italic* represents zeolite structure exhibiting typically separation/adsorption applications

Crystallization can be induced by the controlled addition of supplemental SDAs that have charge densities that more suitably match that of the desired low ratio aluminosilicate network. The advantages of this approach are greater control over the crystallization process and efficient cooperation of multiple templates. The approach is demonstrated for a new family of zeolites (UZM stands for UOP Zeolite Material), UZM-4, UZM-5, UZM-8, UZM-9, UZM-15 and UZM-17 [11, 12]. In particular, the UZM-8 with its unique layered structure has a large number of acid sites at or near the external surface of the zeolite crystals. In the alkylation of aromatics with ethylene or propylene with UZM-8, the mono-alkylated product can readily desorb from the zeolite surface and hence limits the formation of multi-alkylated products and di-aryl-alkanes [13]. It has been announced that this new UZM-8 zeolite has been, after only 6 years of development, offered for sale in late 2006 for the use in the liquid phase alkylation of benzene with ethylene [14]. Although, little scientific research has been published, it seems that this material could exhibit features similar to the MCM-22 and EU-1 zeolites, materials where the acidity and the molecular environment at the external surface of the zeolite crystals are believed to be essential for the improved performance in alkyl-aromatic reactions (alkylation, isomerisation and disproportionation) [15, 16]. These two zeolites possess non-interconnected channels accessible through 10-member ring apertures, but one of the channels exhibit supercages defined by 12-member rings. The outer surface of both zeolites is believed to be covered by open large side-pockets circumvented by 12-member rings.

Recently, other classes of molecular sieves have been synthesized: (i) the mesoporous silica-based materials of

the M41S family (MCM-41, MCM-48 and SBA-15 are the best known) and (ii) the crystalline microporous titanosilicates (ETS family developed by former the Engelhard) [17, 18] and the silicotitanates (co-developed by Sandia National laboratories and UOP) [19]. These new materials are claimed to be commercially used: MCM-41 probably as a low acidic support of metallic catalyst for applications like hydro-processing, including hydro-demetalation [20] and the microporous titanosilicates or silicotitanates are being used commercially in separation and ion exchange. Commercialization of MCM-41 required about 10 years and the major challenge was associated with the identification of an application where the performance incentive was high enough to justify risks and cost of industrialization.

Despite the continued rising availability of newer molecular sieves structures and the associated R&D activities in academic and industrial research institutes, only 18 have been commercialized. This discrepancy between availability and commercial use has several explanations related to the requirements of economically viable technologies:

- (i) Zeolites not-requiring organic template molecules have reached the largest volume applications: zeolite A, X, Y, high-alumina ZSM-5 and mordenite. Other high-alumina ferrierite, zeolite L, T and F do not require organic template, however their use is not widespread.
- (ii) Significant performance benefits over existing catalyst must be demonstrated when more exotic reagents, like complex organic templates (often not commercially available) or metal precursors or toxic or hazardous ingredients are employed [21].

- (iii) Seldom has the as-synthesized material provided the optimal catalytic or adsorptive performance. An excellent overview of different post-synthesis techniques is provided in volume 3 of Molecular Sieves [22].
- (iv) Last but not least, the active and selective molecular sieve material has to be formulated in a shape that can be used in industrial reactors. This requires the design of a composite blend of ingredients that provide mechanical strength to the shaped body and of processing aids required for the shaping process [23–25].

Moreover, the 179 known structures presently harvested are only a tiny fraction of the 2.5 million structures that are theoretically feasible [26]. Such a database could be the basis for “Designer Catalysts”. Powerful computational exploration will be required to screen such large database for the multitude of possible applications [27]. Also high-throughput techniques will contribute to the identification of the most efficient molecular sieves [28, 29].

3 Catalysts and Zeolite Market

By itself, the catalyst manufacturing business is already a sizeable and growing activity [30, 31]. It is generally segmented, Table 2, in Refining, Environmental, Polymer and Chemicals. While the environmental catalyst market is growing fast, refining and petrochemicals are presently stable or slightly declining in relative terms. Environmental catalysts constitute the largest catalyst market and its share will grow to over 30% in 2011. The market size of refinery catalysts is still rising and at a higher pace than the demand growth of refined products ($\sim 1.5\%$) due to the required additional hydro-treating capacity required to comply with the new sulfur specifications (now 50 and next 10 ppm in diesel and gasoline) and bottom of the barrel conversion to produce more light refined products (*whitening of the barrel*). The mergers of oil companies are a challenge for catalyst manufacturers as this consolidation reduces the market base. Negotiations on catalyst prices setting are more difficult with these large players.

However, it should be recalled that these catalysts have a large leverage effect, often more than 2 orders of magnitude and play a key role in the industries they serve (automotive, pollution abatement, refining and petrochemicals). Indeed, if in a refinery or petrochemical complex a major unit shuts down due to a catalyst failure, ripple effects are often felt on the market. Catalysts in general and zeolites in particular are performance chemicals, i.e. their value resides not only in their chemical composition but especially in their ability to promote much

desired changes (higher gasoline production, better fuel quality, low cost base chemicals for polymer manufacturing, highly selective processes...).

A focus on the refinery catalyst market, Table 3, highlights the importance of two zeolite based catalytic processes: fluid catalytic cracking (FCC), mainly a gasoline making process, and hydro-cracking (HDC), mainly a middle distillates making process [31, 32]. They underline that one of the main goal of refineries is to produce transportation fuels. While FCC represents the largest volume of catalyst used in a refinery, HDC catalysts are poised for the fastest grow.

A closer look at the worldwide zeolite consumption, Table 4, reveals the various and relative uses of zeolites. Natural zeolites have by far the largest use, but it is mostly as commodities for low value/large-scale applications [33–35]. The global synthetic zeolite market had a value of approximately 1.8 billion \$ in 2004, of which catalysts represent 27% on a value basis but only a 14% on a volume basis. It indicates that, on average, zeolite-based catalysts are used for higher value applications. Among the catalytic applications of zeolites, FCC accounts for over 95% of the synthetic zeolite consumption. This application as well as HDC is based on the Y type zeolite of the FAU family, the other zeolites of commercial importance in catalytic applications are the AEL, BEA, FER, LTL, MFI, MOR, MWW, TON structures [36–42]. Some, like CHA (SAPO version), hold promises if their application, in this case the Methanol-to-Olefins (MTO) process, are brought commercial [43]. It is sobering that so few zeolite structures have reached the commercial stage, but it is in part a tribute to their versatility. Indeed, many zeolites, like FAU and MFI, can be engineered either during or after their synthesis so that their properties can be finely tuned highlighting that each zeolite structure is the mother of a large family of catalytic materials, each member promoting a different reaction. The 241 kta of synthetic zeolites consumed in 2004 were marketed to the end-user as 665 kta of final zeolite-based catalyst, indicating that on average commercial zeolite-based catalyst contain 36 wt% of zeolite [32, 33]. This stresses the importance of the often-neglected operation of shaping of zeolite catalysts that allows its tailoring to the type of reactor used (fixed, moving or fluidized beds).

Many producers vie for the zeolite market, Table 5. Some are pure zeolite manufacturers for one or two applications, pure catalyst manufacturers, business units of large chemical or oil companies while others are either process licensors involved in the catalyst manufacturing or suppliers of finished catalysts through joint-venture [33]. New players (Sinopec in China for instance) are now venturing out of their local market and have global ambitions. In the important FCC market, only 3 major players have a global presence and in the smaller and niche

Table 2 Global catalyst manufacturing business [31], AAGR is Average Annual Grow Rate, constant 2005 \$

Market segment	2005		2008		2011		AAGR (%) 2005–2011
	10 ⁶ \$	Share (%)	10 ⁶ \$	Share (%)	10 ⁶ \$	Share (%)	
Refining	2693	19.4	2929	18.4	3242	18.5	3.4
Environmental	4404	31.7	5393	33.9	5871	33.5	5.6
Polymers	2959	21.3	3472	21.8	3938	22.5	5.5
Fine chemicals, intermediates	1350	9.7	1430	9.0	1515	8.6	2.0
Petrochemicals	2475	17.8	2701	17.0	2951	16.8	3.2
Total market [10 ⁶ \$]	13881		15925		17517		4.4

Table 3 Refinery catalyst market [31, 32]

Process	Year								AAGR (%) 2005–2011	Share (%)			
	2003		2005		2008		2011						
	10 ⁶ \$	kta	10 ⁶ \$	kta	10 ⁶ \$	kta	10 ⁶ \$	kta		Value 2003	Volume 2003	Value 2011	Volume 2011
FCC	826	551	855	565	919	594	998	627	2.8	25.9	15.2	25.2	15.3
Reforming	127	7	127	8	134	8	142	8	2	4.0	0.2	3.6	0.2
Hydro-cracking	170	7	173	7	189	8	208	8	3.4	5.3	0.2	5.3	0.2
Hydro-treating	811	123	913	131	1042	143	1219	160	5.6	25.4	3.4	30.8	3.9
Other ^a	611	–	625	–	645	–	674	–	1.3	19.2		17.0	
Alkylation	644	2947	644	2972	679	3139	715	3305		20.2	81.1	18.1	80.5
Total	3189	3635	3337	3683	3608	3892	3956	4108		100	100	100	100

^a Other includes hydrogen production, polymerisation, isomerisation, etherification, sulphur recovery, lubes, etc.

Table 4 Zeolite consumption and supply [33], on anhydrous basis

Zeolite consumption/supply (kta)	2001	2004	2004 share (%)		Growth (%)
			Volume	Value	
Synthetic zeolites consumption					
Detergent builder	1188	1325	78.2	56	11.5
Catalysts	184	241	14.2	27	30.9
Adsorbents/desiccants	92	126	7.4	17	36.9
Total	1464	1692			15.6
Synthetic zeolites capacity	1926	2029			5.3
Natural zeolites consumption	>3100	>2500			−19.3
Natural zeolites production	3293	2557			−22.3

specialties markets, many of the players try to find their place. It is quite likely that this market will evolve in the future. Finished zeolite based-catalysts represent about 6% on volume basis of all used catalysts, homogeneous and heterogeneous [32].

4 Zeolite Use in Industry

During the second half of the former century, the industrial applications of zeolites or in general molecular sieves have

emerged. The majority of the base chemicals that constitute our daily consumers goods and energy carriers like transportation fuels have passed through the micro- and mesopores of molecular sieves. Some zeolite structures, mainly MFI and FAU and to a minor extend also MOR are very versatile materials, i.e. their properties can be tuned to the specific requirements of very different industrial applications.

Tanabe and Hölderich gave an account of acid–base catalyzed processes that have been commercialized or have been proposed for commercialization. A total of 124 acid–

Table 5 Major synthetic zeolite producers, based on [33]

Major synthetic zeolite producers	Application			
	FCC	Detergent	Adsorbant/desiccant	Specialties
Albemarle, including former Akzo	X	X		X
BASF (former Engelhard)	X			X
Catalyst&Chemical Industries	X			
Ceca			X	X
ExxonMobil				X
Industrial Zeolites	X	X		
Instituto Mexicano Del Petroleo	X			
MAL			X	
Mizusawa Ind. Chem.		X	X	
OAO Salavanteorgsintez	X			
PQ/Zeolyst/Ineos Silica		X	X	X
Shandong Aluminium Corporation		X		
Sinopec (RIPP)	X			X
Süd-Chemie, including Tricat			X	X
Tosoh		X	X	X
Uetikon/Zeochem			X	
UOP			X	X
W. R. Grace & Co	X		X	X

Bold represents global players in the FCC catalyst market

base catalyzed processes were available, of which 74 were zeolite-based [44].

Although, only 18 zeolite structures are being used, more than 25 different types of commercial processes (chemical transformations) using zeolites, Table 6, are exploited. Moreover, each process type is being proposed by several licensors; these are often based on different catalyst formulations (with respect to zeolite structure, composition, crystal size, post-treatments, additional catalytic functions, like hydrogenation/dehydrogenation metals, oxides or sulphides and binder composition) and hence each time resulting in different catalytic performances. An illustration of this vast assortment is provided by the yearly OGI compilation, demonstrating that more than 150 commercial zeolite-containing refining catalysts are proposed for only a few refining processes (paraffins and aromatics isomerisation, FCC, hydro-cracking, hydro-treatment, aromatization) [45].

The potential of zeolites is probably best illustrated by their saga in FCC [1] where they led to a step change in the oil refining industry. Their high activity, increased selectivity towards the gasoline fraction and lower coke make relative to the previous generation of catalysts (amorphous silica–alumina's) allowed refiners to increase gasoline output while cutting the number of FCC units. This is a dramatic illustration of the leverage of zeolite catalysts (a new catalyst allows to drastically reduce the capital requirement of an industry). Since this breakthrough, many

incremental improvements in the FCC catalyst and process have made this zeolite based catalyst ever more efficient ... and hard to replace.

Some features of these crystalline inorganic porous materials are the keys to their success [46]:

- Their high acidity or mild basicity can be tuned easily
- Their structure resists or adjusts to high temperatures (>400–800 °C) allowing their use in the very harsh conditions (regeneration by air combustion of deposited coke for instance) of refinery and petrochemicals transformations
- Their pore system is either 1, 2 or 3 directional allowing an optimum management of the molecular traffic
- They are non-corrosive and non-toxic and have a “green” character
- Their shaping (extrudates, spheres, microspheres) make them easy to handle and to separate in various catalytic reactor configurations
- They have a wide range of composition (Si/Al ratio, presence of other T atoms such as Ti, Ga, Fe, B,...) and their properties can be tuned by ion-exchange
- A wide variety of structures (>179) are at the disposal of imaginative application scientists, although only a few have reached the commercial stage
- The crystal size of each structure can be tuned, although typical values are in the range of 0.1–5 μm. This allows a precise control of:

Table 6 Types of commercial processes using zeolite-based catalysts

Zeolite structure code	FAU	LTL	MOR	BEA	MWW	MCM-49	MTW	MFI	FER	AEL	RHO	EUO	Area
Zeolite name	Y, USY	L	Mordenite	Beta	MCM-22, MCM-49	ZSM-12	ZSM-5, TS-1	Ferrierite	SAPO-11	Rho	EU-1		
<i>Process</i>													
Naphtha isomerisation			B										Refining
Iso-dewaxing								B		B			
Dewaxing								M					
Hydro-cracking	B												
Hydro-dearomatization	B												
FCC	M							M					
Olefin oligomerisation					M			M					
Olefin isomerisation								M					
<i>Petrochemicals</i>													
Ethylbenzene				M				M					
Cumene	M		M	M									
C ₂ , C ₃ -transalkylation	M		M	M									
<i>p</i> -Ethyltoluene								M					
<i>p</i> -t-Butylethylbenzene						M							
Xylene isomerisation								M/B					
Ethylbenzene isomerisation			B									B	
Toluene disproportionation			B					B					
C ₉ + transalkylation			B										
Naphtha aromatisation		B											
LPG or olefin aromatisation								B					
<i>Chemicals</i>													
Amination			M					M			M		
Hydration								M					
Chlorination/isomerisation		M						M					
Beckmann rearrangement								M					
Oxidation								M					
Acylation	M			M									

M stands for monofunctional catalyst and B stands for bifunctional catalysts

Table 7 Examples of shapes and sizes of catalysts

Catalytic reactor type	Shape	Typical size	Typical applications
Moving bed	Spheres	1–3 mm	Cyclar: aromatisation of LPG
Fixed bed	Extrudates/spheres/pellets	1–5 mm	Hydro-cracking, aromatics isomerisation
Fluidized bed	Microspheres	40–100 μm	FCC, Beckmann rearrangement, MTO
Special reactors	Monoliths/membranes		Exhaust catalysts, ethanol dehydration

- Pore accessibility
- The diffusion path length (hence control of zeolite utilization and selectivity based on the matching between the shape/size of the zeolites and the molecules inside the pores)
- The ratio of external (typically equivalent to 10–40 m^2/g) to internal (typically equivalent to 300–700 m^2/g) surface to control shape selectivity, secondary product formation and deactivation

Typically, low-silica zeolites, exhibiting a high Cation Exchange Capacity and a rather low acid strength, are used for adsorption and ion exchange applications. On the other hand, high-silica zeolites, with a low Cation Exchange Capacity and hence a high acid strength, find application as catalysts or adsorbents of apolar molecules.

Zeolite catalyst shaping, often neglected by academic researchers, is a mandatory step in their large-scale deployment (including the addition of a binder such as aluminas, clays, silicas, silica–aluminas, that can be inert or active) and adds other desirable features to the zeolite-based materials (adsorbents, catalysts). Indeed the large scale of refinery and petrochemicals operations imposes often fixed-bed reactors where pressure drop has to be minimized and mechanical strength (crush strength and attrition) be high enough to sustain loading, heating (thermal expansion and shrinking) and unloading of the catalyst bed. In some applications, the binder used in the shaping process is welcome as a heat vector (FCC) or improves accessibility by providing mesoporosity. In addition to these “physical” effects, the binder can react with the zeolite [47, 48] and impart for instance further resistance to steaming [49, 50] to the neat zeolite. Depending on the characteristics of the reaction to be engineered [51, 52], fixed, moving or fluidized beds are used as well as structured reactors (monoliths for instance). Table 7 illustrates some types of shapes and dimensions encountered in typical refinery and petrochemicals operations.

The field of adsorbents benefited greatly from the pore size engineering afforded by ion-exchange in zeolites. This early and very simple example of nanotechnology, Table 8, shows it is possible to easily manipulate zeolites at a *sub-nanometer* level. The pore openings of the LTA structure can be tuned between 2.9 and 4.4 Å by simply performing a K^+ , Na^+ or Ca^{2+} exchange [40, 41]. This opens the

possibility to design adsorbents for drying applications, purification or separation of normal-paraffins from iso-paraffins. Likewise, the FAU structure can be tuned by changes in the Si/Al ratio (X or Y) or by ion-exchange to simultaneously dry and purify complex hydrocarbon streams, to be a selective adsorbent for *para*-xylene [53] or an efficient oxygen enrichment adsorbent. These adsorption processes can be combined with catalytic processes to improve the overall selectivity of reactions limited by thermodynamic equilibrium [54]. Recently, Engelhard discovered a new family of molecular sieves based on titanasilicates (ETS) of which the pore opening can be manipulated by controlled dehydration of the as-synthesized materials [17, 18].

5 Some Oil Refining Applications

Oil refining is a complex and huge industry. It is covered in great details in excellent monographs [55–58]. Only a partial and oversimplified view can be given here.

The major role of a modern refinery is to adjust the supply of reactants/feedstocks (crude oils) with the product demand (transportation fuels, specialties like lubricants, solvents, paraffins, bitumen...). The crude oils have a tendency of being heavier (higher molecular weight) and more difficult to convert chemically (H/C ratio moving to lower values due to the presence of aromatics) and highly loaded in metals, Sulfur, Nitrogen while ever stringent constraints (regulations, performances,...) are put on the products. These opposing trends are often summarized as the “*Whitening of the Barrel*” meaning that ever more dirty crudes are to be refined in ever more clean (white) products. In addition, the environmental constraints on the refinery (greenhouse gas emissions for instance) impose ever more efficient and clean processes. In a nutshell, a refinery has the challenge to [59–61]:

- Increase H/C of crude fractions to make on-spec products
- Remove pollutants (metals, S, N,...)
- Be efficient:
- Typical thermal efficiency (based on lower heating value) for a refinery operation is $\sim 90\%$ compared to

Table 8 Examples of zeolites or molecular sieves engineered and used as adsorbents [18, 40, 41]

Zeolite type	Pore opening (Å)	Adsorbed molecules	Excluded molecules	Applications
LTA 3A Si/Al = 1, K ⁺	2.9	H ₂ O, NH ₃	n-P, n-O	Drying of olefin containing streams (cracked gas in FCC and steamcracker)
LTA 4A Si/Al = 1, Na ⁺	3.8	H ₂ O, CO ₂ , C ₂ H ₆	n-P, n-O > C ₂	Drying and purification
LTA 5A Si/Al = 1, Ca ²⁺	4.4	n-P	i-P	i-P/n-P separation
FAU 13X Si/Al = 1.2–1.5, Na ⁺	7.4	P, N and aromatics	PNA	Simultaneous drying and purification: H ₂ O, H ₂ S, CO ₂ and oxygenates
FAU Ba(K)X	~7.4	Preference for <i>p</i> -xylene		<i>p</i> -Xylene separation from xylene–ethylbenzene mixtures
LiX	~7.4			Oxygen enrichment
ETS-4	~3.7	N ₂ , CO ₂	Methane	Inerts removal from natural gas

i iso, *n* normal, *P* paraffin, *O* olefin, *PNA* poly-nuclear-aromatic

67% for methanol synthesis and less than 60% for existing GTL (gas to liquid) processes

- Typical carbon efficiency for a refinery is about 93% (>70% transportation fuels, <25% specialties) while the remaining 7% is used for auto-consumption (steam, hydrogen manufacture). Such high carbon efficiency gives oil refining and petrochemistry the best E-Factors (ratio of mass unit by-product per mass unit of desired product) calculated by Sheldon for several industry segments [62]

Figure 3 shows the major operations of a refinery, a suite of physical separations (distillation, extraction, adsorption, crystallization) and chemical transformations (treatments, deep conversions, isomerizations, catalytic and thermal processes). The process steps partially or completely colored in green, use zeolite-based adsorbents or catalysts.

A matrix, Table 9, can be constructed where for each refinery cut (products collected in a specified boiling range), the desired products are highlighted, the required reactions and their specifications [40, 57]. For instance, in the case of gasoil, it is imperative to combine, among others, good cetane (cetane number >51), low sulfur (<10–50 ppm), minimum polyaromatics (<11%), adequate density (<0.845 g/mL) and cold flow properties. The choice of processing options is therefore strongly imposed by the product specifications. These requirements vary of course from country to country and the refinery diet is a function of its location and supply chain. Modern refineries are very complex and highly versatile industrial installations.

In order to better understand the general layout of a process, one needs to analyze it stepwise [63] and therefore:

- Lay down the stoichiometry
- Analyze the thermodynamics (thermicity, equilibrium composition)
- Get a grasp for the kinetics and the catalysts involved
- Evaluate the deactivation pattern and rate (will determine the reactor configuration)
- Integrate at the macro level using the rules of chemical engineering

The following three zeolite-based catalytic processes encountered in oil refining are briefly highlighted within this framework.

5.1 C_{5–6} Paraffins Hydro-Isomerization

The goal of this transformation is to increase the octane rating of the light naphtha fraction. It is done by skeletal isomerization of *n*-paraffin's as the octane numbers (both the Research Octane Number [RON] and Motor Octane Number [MON]) increase with the degree of branching of the molecules. It is a particularly attractive contribution to the gasoline pool [54, 60, 61, 64] since all other contributing processes have major drawbacks as far as process safety (H₂SO₄ or HF catalyzed Alkylation) and environmental regulations (Reformate, FCC Naphtha, Oxygenates, Polygasoline, Butanes) are concerned.

The thermodynamic analysis of the reaction indicates it is mildly exothermic (although the presence of aromatics in the feed will increase exothermicity by the contribution of their hydrogenation to the enthalpy of reaction), is independent of pressure (no change in the number of moles between reactants and products). The C_{5–6} isomer distribution at the thermodynamic equilibrium, Fig. 4, sets the scene for the catalytic strategy. The catalysts have to be

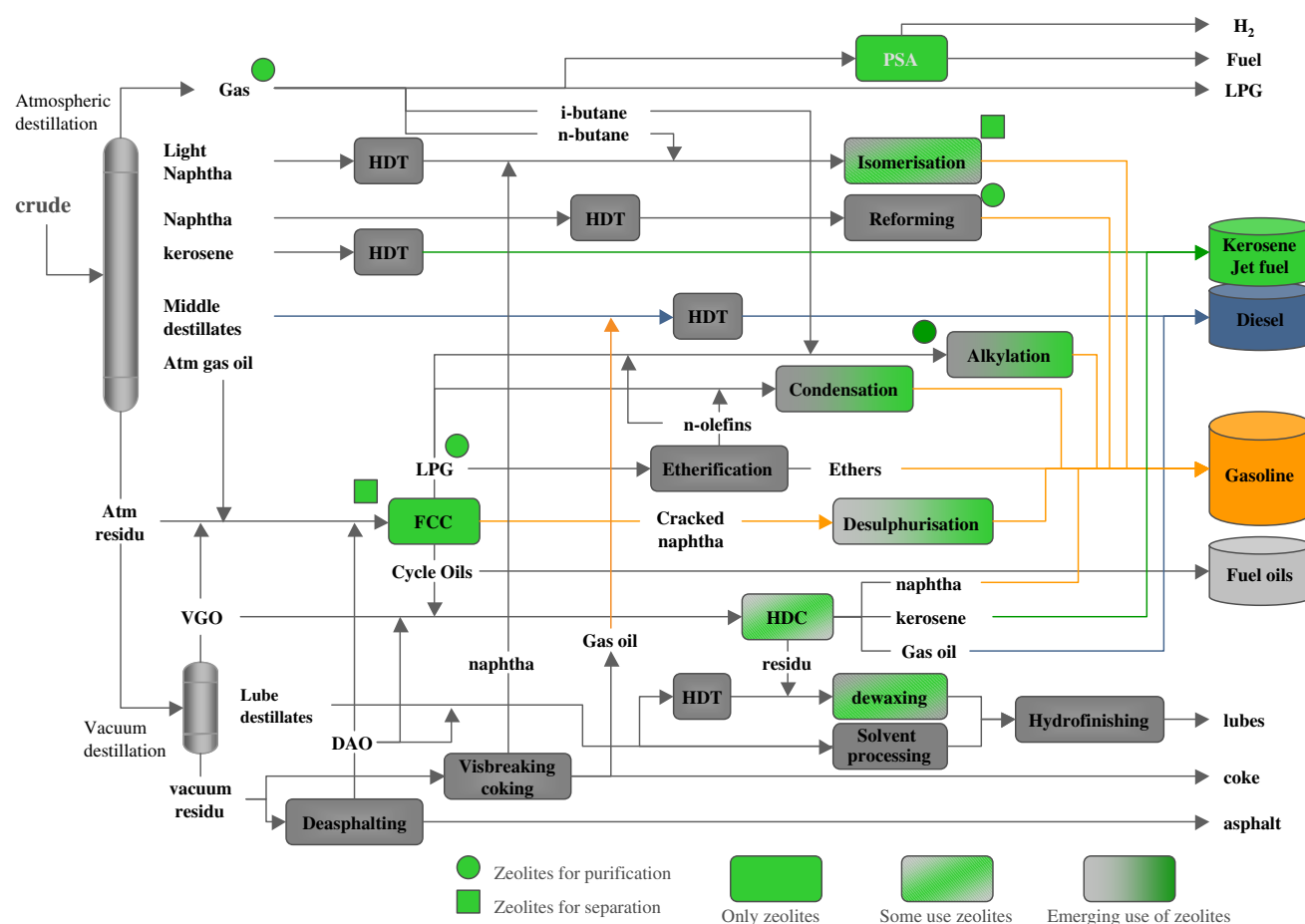


Fig. 3 Some of the major operations found in modern refineries

very active in order to maximize the yields of the branched isomers by working at the lowest temperature possible. The three technologies available today are highlighted in Table 10. They are all based on bi-functional catalysts consisting of a noble metal (Pt) dispersed on an acidic support and operate in the presence of hydrogen. In all technologies, the desired isomerization reaction is followed by the cracking of the branched isomers [54, 64]. The acidic support and the role of hydrogen differentiate their mode of action:

- Chlorinated alumina [65], also capable of hydro-isomerizing the more refractory *n*-butane
- Sulfated zirconia [66]
- Partially dealuminated MOR [64]

Since the isomerization of *n*-paraffin's is an equilibrium-limited reaction, it would appear that the zeolite catalyst should be the least desirable due to its relatively low activity and associated gain in Octane Numbers. However a closer look at the catalysts and their response to processing conditions, Table 10, shows that the MOR based catalyst is

the most "robust" and is relatively easy to regenerate. It is therefore a solid option for a refiner seeking a solution to its octane problem without the need for extensive purification of the feedstock. This illustrates that the selection of an industrial catalyst is a complex process of optimization and that, for instance, the most active catalyst is not automatically the most desired option.

In addition to this once-through mode of operation, it is possible to further increase the octane by a clever separation and recycling of the linear paraffin's [54]. The strategy is as follows: since the thermodynamic equilibrium sets a maximum to the conversion of *n*-paraffins, removing unconverted *n*-paraffins from the isomerized product and recycling them will result in an overall higher selectivity towards isomerized products. The separation between *n*- and iso-paraffin's is possible by selectively adsorbing *n*-paraffins on the molecular sieve 5A (LTA ion-exchanged with Ca^{2+}) described in Table 8. Depending on the temperature and pressure, the separation as well as the catalytic processes can take place in the gas or the liquid phase (the Isosiv[®] or Molex[®] adsorption processes are the most

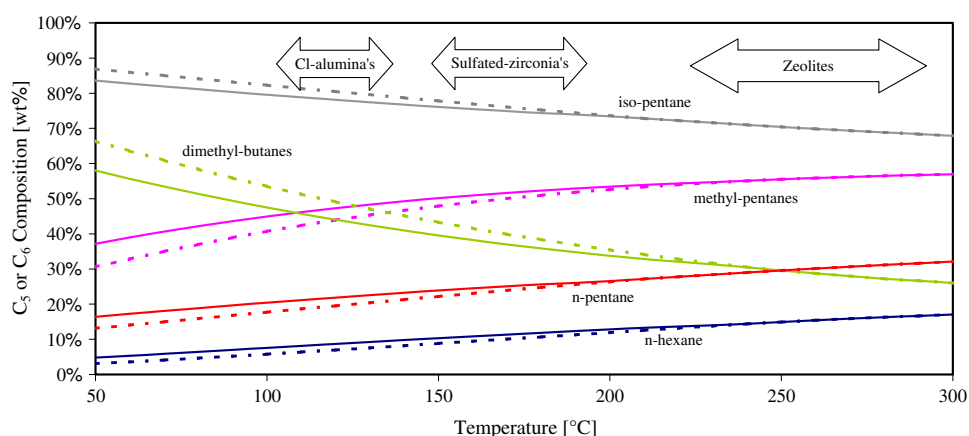
Table 9 Interplay between specifications, molecular characteristics of the products and reaction involved

Main product	European 2005 specifications	Performance characteristic	Preferred hydrocarbon structures								Reactions leading to these hydrocarbon structures		
			n-P	i-P	n-O	i-O	Alkyl-Naph	Poly-Naph	Alkyl-Aro	Poly-Aro	Crack	Hydro-crack	Hydro-isom
LPG		Olefinicity ¹	–	–	+++	+++					+++	–	–
		Branching ²	–	++	–	++					+++	++	++
Gasoline	<1% benzene <35% aromatics <50 ppm sulphur <18% olefins	Octane number	–	++	+	++	+ / ++		+++		++	+	++
Gasoil	>51 cetane number <50 ppm sulphur <0.845 gr/ml density <11% polyaromatics	Cetane number	+++	+ / ++	+++	+	+	–	+ / ++	–	–	+++	++
		Pour point	–	++	–	++	++	++	++		–	– / +	++
Lubes		Viscosity index	+++	+ / ++			+ / ++	–	+ / ++	–	–	+++	++
		Pour point	–	++			+ / ++	+ / ++	+ / ++	– / +	–	– / +	++

P paraffin, *O* olefin, *Naph* naphthene, *Aro* aromatic, *Crack* cracking, *Isom* isomerization

1: iso-butene for etherification and *i/n*-butenes for alkylation; 2: iso-butane for alkylation; –: negative effect; +: poor to medium; ++: good; +++: excellent; –/+ or +/+ indicates the dependence on chain length

Fig. 4 Thermodynamic equilibrium of pentanes/hexanes and temperature ranges of typical utilization of chlorided alumina, sulfated zirconia and MOR zeolite based isomerization catalysts. Solid line represents liquid phase and dashed line gas phase equilibrium



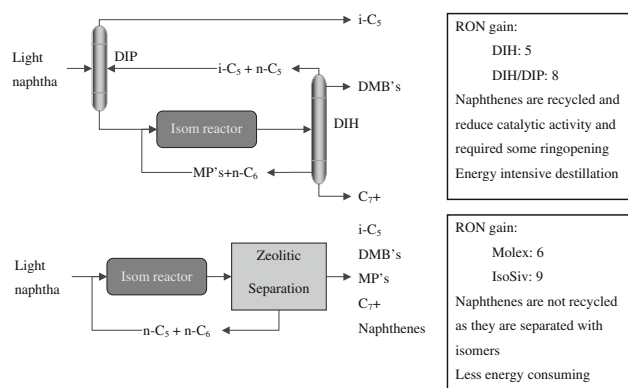
practiced of these technologies). The net result is, in addition to the obvious octane gain, a flatter response of selectivity to temperature and the disadvantage of zeolitic catalysts, needing a higher reaction temperature, largely disappears, albeit at the cost of an extra unit (increase in capital expenditure). Another degree of flexibility by this combination of reaction/adsorption is provided by the relative positions of these 2 operations. Indeed, depending on the feed composition, it will be advantageous to install the isomerization section either upstream (feedstocks with *high* *n*-paraffin's content) or downstream (feedstocks with *low* *n*-paraffin's content). Figure 5 illustrates a possible strategy for the position of an adsorptive zeolite-based separation unit and its advantages. It is clear that each case is to be studied in details and that only a full economic evaluation

will allow the refiner to decide which solution will be optimal given its refinery configuration and constraints.

Further improvements are still possible in this refinery operation. For instance the complete integration of the isomerization and the separation sections in a single (in situ adsorption or the use of membranes for in situ separation) reactor [64] and the co-processing of C_{5-6} hydrocarbons with C_7 (the latter challenge, based on the great activity difference between C_{5-6} and C_7 hydrocarbons is well illustrated in Fig. 4.1 of Ref. [7]) are highly desirable but very challenging improvements still waiting for a solution. Inherently, once the hydrocarbon contains 7 or more carbons the cracking through β -scission becomes favorable as intermediate secondary or tertiary carbocations crack into tertiary carbocations, which is thermodynamically a

Table 10 Main characteristics of the 3 families of C_{5–6} hydro-isomerization catalysts

Catalyst	Pt/chlorinated alumina	Pt/sulfated zirconia	Pt/mordenite
Activity	High	Medium	Low
RON gain	12–14	10–12	8–10
Sensitivity to contaminants	High Sulphur, nitrogen removal Drying needed to prevent chlorine loss Needs chlorine make up in feed!	Medium to low Less sensitive to water	Low Tolerates water and small amounts of sulphur
Regenerable	No	Yes (?)	Yes

**Fig. 5** Process configuration of hydro-isomerisation units. *Above*: Process line-up with a reaction section and no adsorption section (*DIP* DeIso-pentanizer, *DIH* DeIso-Hexanizer). *Below*: Process line-up with an isomerization section upstream an adsorptive zeolite-based separation process

favorable reaction [67, 68]. Isomerization of light naphtha, especially C₅'s, will probably be reduced in the near future because of the blending of bio-ethanol with gasoline. Addition of ethanol does increase the vapor pressure (RVP) of gasoline [69] and in order to keep the RVP according to specifications, less light isomerate can be blended into the gasoline pool. As far as zeolitic catalysts are concerned, modified MOR is presently the only zeolite in commercial use although another zeolite, MAZ, displays both a higher activity and selectivity towards branched products [70–72]. New and powerful computational tools, based on Monte-Carlo simulations, appear to be very useful [72] in rationalizing the selectivities of various pore structures; ultimately, they could prove of vital importance in the design of isomerization catalysts by matching the catalyst to the molecular composition of these (relatively) simple feeds.

A final word of caution on the laboratory evaluation of isomerization catalysts: it is important to report catalytic activity/selectivity on feedstocks containing mixtures of hydrocarbons (C_{5–6} paraffin's and C₆ naphthenes) as adsorption and transport phenomena can play an important role [73, 74]. It has also been observed [75] that the presence of naphthenes strongly inhibits C_{5–6} hydro-isomerization on

both Pt/MOR and Pt/Sulfated Zirconia catalysts, while some based on Pt/Tungstated Zirconia display a much smaller inhibition. Therefore, catalysts tested with pure feedstocks could wrongly be claimed to have superior performances and their application be restricted to very specific (and rare) cases.

5.2 Cracking and Hydro-Cracking of Heavy Feedstocks

While hydro-isomerization of C_{5–6} described in the paragraph above is a mild operation of rearrangement of the skeleton of paraffin's, the two zeolite-based processes outlined below are designed to fundamentally alter the chemical structures of their feedstock. As stated in the introduction, some important requirements of a refinery are:

- To adjust the feedstock characteristics to the products requirements; in that respect, it can be broadly stated that the role of a refinery is to increase the H/C ratio of the feedstock to match the requirements of the products (whitening of the barrel)
- To produce transportation fuels (gasoline, kerosene and diesel) in the right mix while meeting the latest specifications

The cracking (FCC) and hydro-cracking (HDC) operations meet these two important requirements. Both adjust the H/C ratio, but in different ways. FCC transforms, during the cracking of the feed over a mono-functional (acidic) catalyst, some of the feedstock in coke and is therefore a *Carbon-Rejection* process. In HDC, hydrogen is added to the feed with the help of a bi-functional catalyst (acid and metallic) and is therefore called a *Hydrogen-Addition* process. They both produce transportation fuels: while FCC is mostly a gasoline (and optionally a light olefins) producer, HC is mostly a middle distillates (kerosene + diesel) producer. These two complementary processes are key conversion technologies in a modern refinery. The FCC unit is in addition the only catalytic unit producing olefins (almost absent in crude oils), a key link

Table 11 Main features of FCC (fluid catalytic cracking) and HDC (hydro-cracking) processes

Cracking process	FCC	HDC
Principle	Carbon rejection	Hydrogen addition
Catalyst functionality	Monofunctional	Bifunctional
Operating pressure	Close to atmospheric pressure	>100 bars
Need for hydrogen	No hydrogen present	A lot of hydrogen present
LPG	Highly olefinic	Nearly no olefins
Naphtha (15–220 °C)		
Olefins (wt%)	>20	No olefins
Aromatics (wt%)	>20	Little aromatics
Octane number	High	Low
Use	Gasoline pool	Reformer or steamcracker feed
Kerosine (150–250 °C)		
H (wt%)	10.4	14.0
S (wppm)	>1000	20
Gasoil (250–370 °C)		
H (wt%)	9.4	13.6
S (wppm)	>5000	40
Cetane number	<30	>50

with the petrochemistry, the other being the aromatics produced in the catalytic reformer unit. Often the naphtha produced as a byproduct in the HDC is sent to the steam cracker, as its normal-to-iso paraffin ratio is too high to make a good gasoline blending components. Table 11 summarizes the main features of these two major processes.

5.2.1 Fluid Catalytic Cracking (FCC)

The early oil cracking processes and its modern version, FCC, are landmarks of the industrial history [76, 77]. The modern process is a complex interplay between catalyst, process engineering and the ever-changing needs of the market. General and in-depth reviews are available [78, 79] and the latest advances and challenges have been described recently [80, 81].

The cracking reaction is endothermic, not limited by thermodynamics and increases the number of moles. It is therefore favored at high temperature and low pressure. The catalyst cokes very rapidly (<sec) and needs to be regenerated frequently. This is done commercially by the use of a fast circulating bed (fluidized bed) transporting the deactivated catalyst to the regenerator where the coke is burnt and the catalyst recirculated to the reactor (called a riser). This rapid circulation of the catalyst imposes considerable constraints on the catalyst design and shaping. It is however a blessing since the heat generated during the exothermic regeneration (coke combustion) is returned to the riser section to balance the endothermic cracking reaction. The FCC unit is therefore a two-reactor unit: one, the reactor, operating in a reducing environment, the other,

the regenerator, operating in an oxidizing environment. The other important components are the stripping section (where the coked catalyst is steam-stripped from adsorbed hydrocarbons), the cyclone section (where the solid catalyst particles are separated from the hydrocarbon vapors), the slide valves regulating the flow rate of spent/regenerated catalysts and therefore the heat balance of the unit and the injection section (nozzles design).

A schematic unit is represented in Fig. 6. It shows that the preheated feed is atomized, mixed and injected with hot regenerated catalyst ($\sim 70 \mu\text{m}$ particles) at the bottom of the riser; the volume expansion further helps the catalyst and feed to move upwards for about 2 s while the endothermic cracking takes place. The catalyst is then (steam) stripped from much of the hydrocarbons still adsorbed in the catalyst pores and separated from the fluid phase in cyclones. The products are then sent to a separation section while the spent catalyst (loaded with strongly adsorbed coke molecules) is transferred to the regenerator. There, the coke is burned for about 15 min with air and returned hot to the bottom of the riser where it brings heat and a fresh activity.

It is an elegant and efficient way to manage a very unstable operation by allowing it to operate continuously and therefore supplying a constant contribution to the gasoline and light olefins pools.

In order to better apprehend the revolutionary contribution of zeolites (Y type of the FAU structure), one needs to examine the various reactions happening during the cracking process. Figure 7 summarizes these reactions by hydrocarbon types: paraffins, olefins, naphthenes and aromatics. In addition to cracking, coke deposition and

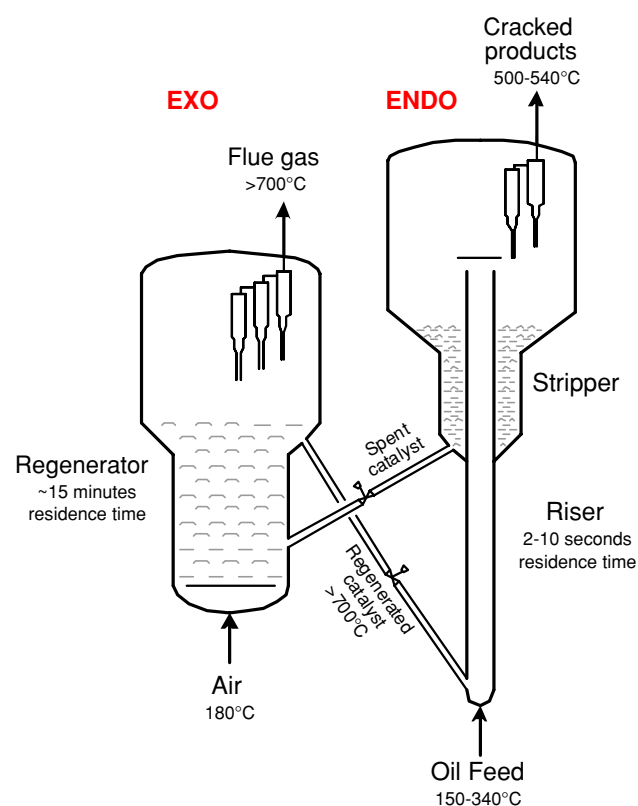
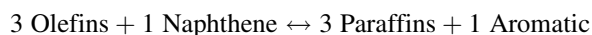


Fig. 6 Schematic representation of a modern FCC (fluid catalytic cracking) unit

secondary reactions (isomerization, dehydrogenation, transalkylation, side-chain cracking), a very important reaction takes place, i.e. hydrogen transfer [82].

It consists in the redistribution (via successive hydride and proton transfers) of hydrogen between a saturated or partially saturated hydrocarbon molecule and an unsaturated one; its net result can be written as [6]:



These are successions of bi-molecular transformations where the following events occur:

- *Olefin*: adsorbs on a protonic site as a carbocation
- *Naphthene*: adsorbs on a nearby site
- These two molecules being close by in the near spherical cavity of the zeolite (supercage), an hydride can be abstracted from the naphthene, the operation repeated to yield paraffins and aromatics

The acidic sites of the Y zeolites, located in a very confined environment (spherical cavity of about 13 Å), favor such bi-molecular events. Under FCC conditions, this reaction is displaced to the right hand side and the use of zeolite Y further accelerates the production of paraffins and aromatics. These two types of molecules are less reactive than olefins and naphthenes and the net result is a higher

gasoline yield, as represented by the reaction scheme of Fig. 8. FCC is a classical example of maximizing the yield of an intermediate complex product. The reactants (typically a gasoil fraction, i.e. C_{20+}) are transformed in the desired products (gasoline, i.e. C_{5-11}) that can further react by cracking (i.e. C_{1-4}) or polycondensation (i.e. “coke”). The crucial role of zeolites, compared to their amorphous silica–aluminas predecessors, is to maximize gasoline yield by selectively producing molecules less prone to further cracking and condensation. Of course, the coke make of zeolites is also lower.

This was the origin of the revolution brought by zeolites in FCC: upon their widespread introduction, the gasoline produced in the US increased substantially while at the same time the number of FCC unit decreased markedly [1]. Later on, the riser design was further improved to take advantage of the superior activity of the FAU zeolite based catalysts. The penalty of switching to zeolites was that the lower concentration of olefins in the gasoline decreased its octane rating. However, because it is possible to finely tune the acid site density of zeolites (Si/Al ratio), the hydrogen transfer properties of zeolite Y can be adjusted by ion-exchange, in particular with trivalent Rare-Earth (RE: La, Ce,...) ions. They stabilize the zeolite against steam dealumination (steam is present in the FCC unit at two stages: the stripping and especially the regenerator) and their concentration in the zeolite allows the refiner to pre-program the state of the equilibrium catalyst that will operate in the unit between two extremes:

1. *Octane making FCC catalysts*: their low RE (below about 3 wt% RE_2O_3) content allows the zeolite to dealuminate strongly, thus lowering its acid site density and consequently its hydrogen transfer capability. The olefin rich gasoline has a high octane rating
2. *Gasoline making catalysts*: their high RE (up to 15 wt% RE_2O_3) content prevents the zeolite from dealuminating strongly, thus maintaining a high site density and consequently its hydrogen transfer capability. The paraffin and aromatic rich gasoline is more stable and therefore produced in higher volume

The extra benefit of steaming the FAU zeolite (during the zeolite preparation process or the FCC operation itself) is that mesopores are generated; together with the matrix porosity, they provide an extra accessibility of bulky molecules to the zeolite crystal where the critical hydrogen transfer reaction can take place efficiently. All these features illustrate the exceptional adaptability of the FAU zeolite to the FCC requirements and explain its longevity: so far no other material, zeolitic or not, has been able to displace or even come close to displacing it.

The process (fluidized bed, heat shocks, mechanical resistance...) and catalytic (activity, selectivity, stability)

Fig. 7 Main reactions observed during the cracking of hydrocarbons molecules

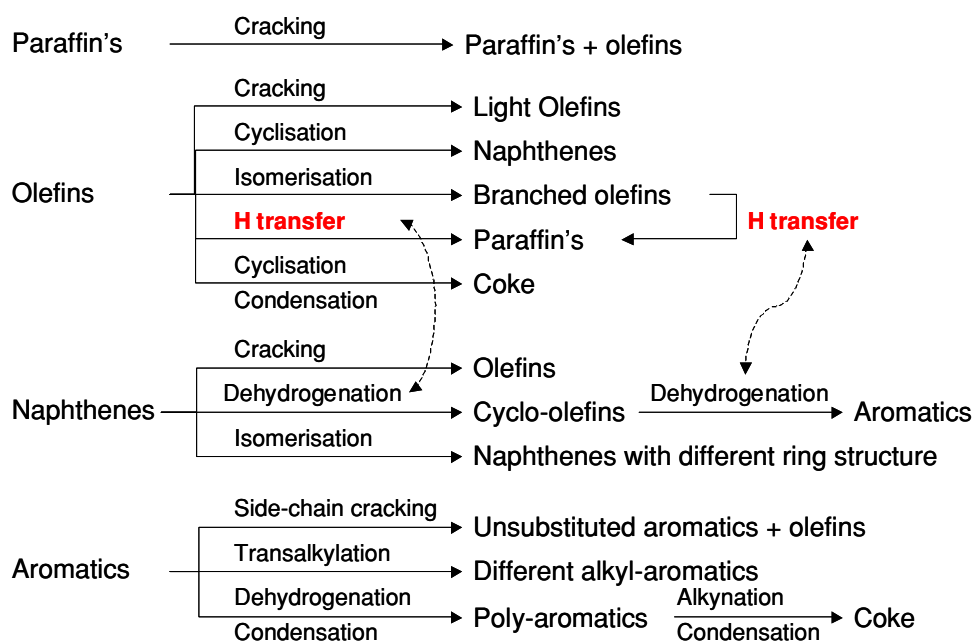
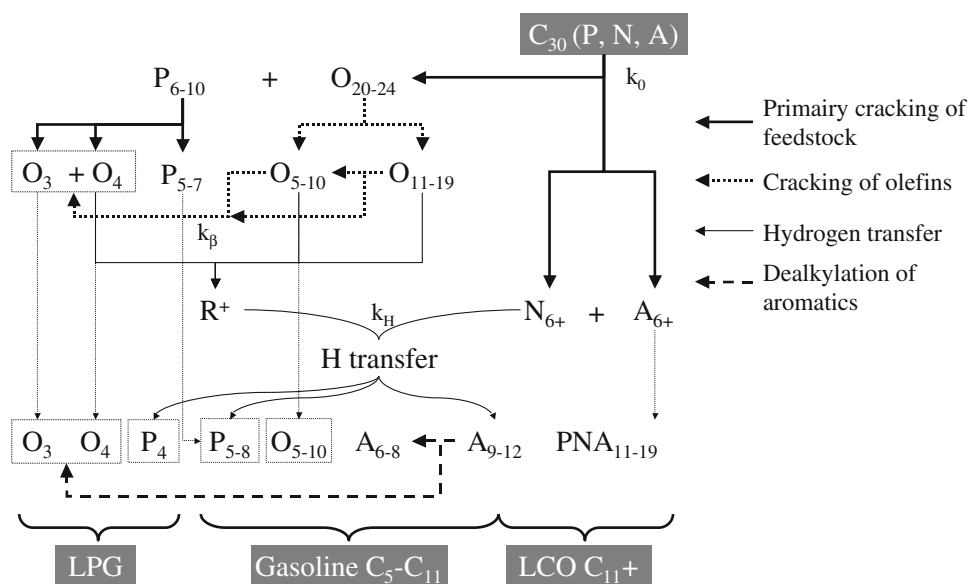


Fig. 8 Simplified reaction network for FCC (k 's represent rate constants for: primary cracking of gasoil in gasoline (k_0), cracking of gasoil in gases (k_1), hydrogen transfer (k_H) and cracking of gasoline by β -scission to gases (k_β) while $[R^+]$ and $[N]$ stand for carbocations and naphthene concentrations, respectively)



requirements make FCC catalysts very complex formulations [83]. In addition, their large consumption (inventory in the unit and addition rate) dictates a moderate price. By putting together these requirements, a typical FCC catalyst particle ($\sim 70 \mu\text{m}$ diameter particle), Fig. 9, comprises the following ingredients:

- The zeolite crystal, ion-exchanged with the desired level of rare-earth, to achieve the desired gasoline properties
- An active matrix designed (composition and porosity) to pre-crack large molecules
- A clay (kaolin) acting as a filler and an heat sink

- A binder to maintain the integrity of the spray-dried particles

FCC catalysts are now produced in very large-scale equipment with sophisticated process control equipment insuring their manufacturing under some very stringent quality control procedures.

In addition to the cracking catalyst, other particles (additives) of the same size and density can be introduced in the unit [3, 80] to promote some reactions (combustion promoters, SO_x transfer, bottoms cracking...). One very important additive is the so-called octane booster: it reduces the quantity of gasoline and increases its olefinicity

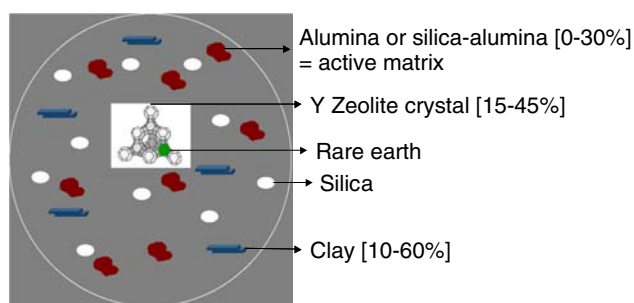


Fig. 9 Typical FCC catalyst particle ($\sim 70 \mu\text{m}$ diameter) and its composition

(hence its name) by promoting its cracking in lower olefins (mainly propylene). It is based on the smaller pore MFI zeolite. It is therefore a new supplier of olefins for the petrochemistry and further increases the link between an oil refining and a petrochemicals complex.

Such a complexity brings however an unusual degree of flexibility to the FCC unit and allows the catalyst manufacturer and its refinery client to customize FCC catalysts and additives to the specific and changing needs of the market. The high circulation rate of the catalyst and additives increases further this flexibility by providing options to change catalysts on very short notice. Table 12 presents a summary of the options available as a function of FCC catalyst composition (zeolite and matrix). The choice of an FCC catalyst and its cocktail of additives are therefore crucial for an efficient operation of the unit; the financial rewards of a proper choice illustrate nicely the leverage a catalyst can have on a manufacturing unit.

Many challenges still face the FCC units [80, 81, 84], such as:

- The heavier and dirtier crudes, difficult to process due to their metals (Ni affects the coke selectivity and V, Na, Fe,... destroy or severely reduce the zeolite activity), sulfur (SO_x emissions, the S content of the FCC gasoline requiring either to process the feed upstream, the products downstream in separate units or to find effective FCC additives), nitrogen (NO_x emissions) contents and their higher coke making tendency
- The present quality of co-products (the LCO, Light Cycle Oil, a middle distillate high in aromatics and sulfur needs further upgrading to be incorporated in higher quantities in the diesel pool)
- New regulations on particulate emissions and disposal of used (and contaminated by heavy metals) FCC catalysts
- The market demand, in particular European and Asian, for a lower ratio gasoline/diesel

FCC is still a good route to accomplish high conversion of heavy gasoils, but it is not the preferred route to produce

Table 12 Effect of the FCC catalyst composition (Zeolite and Matrix) on its activity, selectivity and stability [82]

Catalyst type	USY	REUSY	REHY	REY	Matrix
<i>Property</i>					
Dry gas make	Low				High
C_3/C_4 olefins	High	Moderate		Low	High
Coke/conversion	Very low		Low		Very high
Gasoline selectivity	Moderate	High			Low
Octane potential	High	Moderate	Low		High
<i>Cracking activity</i>					
Feedstock 340–480 °C	High				Moderate
Feedstock >480 °C	Moderate		Low		High
Steam/V/Na stability	Moderate		Low		High
Ni dehydrogenation	Low				High

USY ultra-stabilized Y zeolite, i.e. very low in RE, *REUSY* rare-earth exchanged USY zeolite, *REHY* rare-earth partially exchanged Y zeolite, *REY* fully rare-earth exchanged zeolite

low-aromatics and low sulphur transportation fuels. Subsequent hydro-processing is required to remove sulphur and to reduce aromatics, especially the polyaromatics in the Light Cycle Oil (LCO) fraction, consuming additional hydrogen and destroying some octane-value for the gasoline fraction. A major concern is the LCO, exhibiting a very low cetane value, a high content of polyaromatics and hence increasingly difficult to blend with advanced diesel. The challenge is to develop a new generation of FCC process and catalyst that provide good conversion of heavy fractions to low-aromatics transportation fuels with maximum production of light olefins (mainly propylene).

Because of the limited flexibility of processing heavier and dirtier feedstock and some lower quality features of the gasoline and diesel fractions, FCC faces tough competition from hydro-cracking and thermal cracking (visbreaking, coking) processes.

However, history tells us that researchers and engineers have so far always been up to the numerous challenges encountered in FCC.

5.2.2 Hydro-Cracking (HDC)

While FCC produces gasoline from heavier oil fractions by a carbon-rejection process based on a mono-functional acidic catalyst, HDC produces middle-distillates (mainly diesel and to a lesser extent kerosene) and optionally base oils by a hydrogen-addition process based on a bi-functional (acidic and metallic) catalyst [85, 86]. The feedstock of the HDC unit comes from the atmospheric and vacuum distillation towers, the FCC unit (LCO fraction), and various

thermal processes with a marked tendency to process ever heavier feed. The main reactions encompass hydro-treatment (hydro-desulfurization, -denitrogenation, -demetallation) and hydro-cracking. Other reactions taking place are:

- Hydrogenation of (poly)aromatics, olefins
- Hydro-dealkylation of alkyl aromatics
- Hydro-decyclization of naphtheno-aromatics and ring opening
- Isomerization of paraffins and naphthenes

These reactions are all exothermic and only the aromatics saturation is limited by thermodynamics (i.e. at high temperature and low hydrogen partial pressures, aromatics concentration will increase spontaneously thus defeating the transformation purpose). The relative high stability of the catalysts thanks to the high hydrogen partial pressure, preventing formation of coke precursors, allows the use of fixed bed reactors with the possibility to stage catalyst beds with different compositions. The presence of multiple catalyst beds per reactor is a consequence of the exothermicity of the reaction [87–89]: interstage cooling of the reactants/products mixture is necessary in order to maintain the temperature gradient within manageable values (about 20 °C).

There are basically three options for the processing scheme, Fig. 10; they are based on the connection between the hydro-treating and the hydro-cracking sections:

- *Single-Stage*: all catalysts are in the same (single) reactor and all the products (including H₂S and NH₃) emerging from one catalyst bed move to the following bed of the unique reactor
- *Series Flow*: the catalysts are distributed in two reactors, one dedicated to hydro-treating, the other specifically to hydro-cracking. As in the Single-Stage configuration, all products (including H₂S and NH₃) emerging from the first reactor move to the second one
- *Two-Stage*: the catalysts are distributed in two reactors, one dedicated to hydro-treating, the other specifically to hydro-cracking. The difference with the Series-Flow configuration resides in the removal of H₂S and NH₃ between the two reactors. Such a configuration sends an almost H₂S and NH₃ free feed to the second reactor where a so-called “well-balanced” hydro-cracking catalyst (i.e. the hydro-/dehydrogenating function is a noble metal) can operate near the “ideal” conditions (acid function being the rate determining step) and maximize the yields of the desired products [82, 90, 91]

These configurations make the process particularly flexible as it can produce LPG, Naphtha, middle distillates and lubricants base oils. In order to produce the latter, a fraction of the residue is not recirculated to the reactor and sent to the base oil plant. The catalysts are all bi-functional and shaped in the form of extrudates for fixed bed applications:

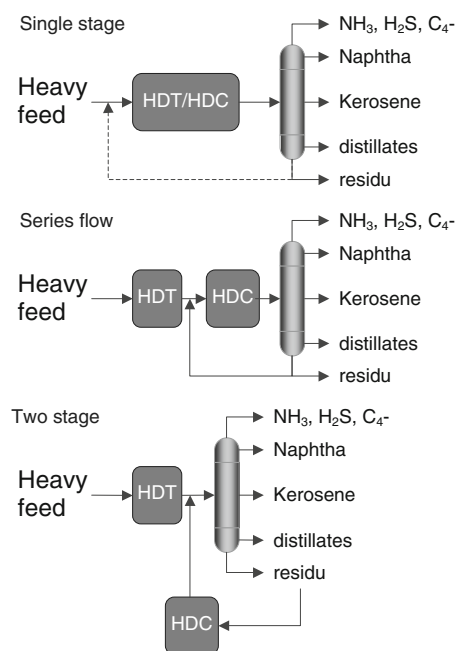


Fig. 10 Simplified process configurations used in hydro-cracking

- *Acidic function*: supplied by amorphous silica–aluminas (ASA), fluorided aluminas, zeolites or combinations of those
- *Metallic function*: supplied either by sulfided NiMo and/or NiW or a noble metal (Pt, Pd)

As in FCC, zeolites (Y type FAU) are present in HDC and play an important role alongside amorphous silica–aluminas (ASA). The zeolite Y used in HDC is dealuminated; it brings high activity (high acid site strength), stability (low coke make and resistance to nitrogen poisons compared to pure ASAs) together with a good accessibility due to the presence of mesopores generated during the steam dealumination process [92]. As in FCC, the zeolite Y brings a high degree of flexibility: the Si/Al ratio can be finely tuned by dealumination (steaming, leaching...) and regulates the selectivity (naphtha versus middle distillates) of the zeolite containing catalyst. As the Al content decreases (measurable by a shrinking of the unit cell size of the zeolite crystal), the kerosene (and diesel) selectivity increases as successive cracking reactions (towards naphtha and gases) are minimized. The operation in fixed bed reactors prevents however to achieve a degree of flexibility such as in FCC where the catalyst could enter the (fluidized) bed on very short notice.

The reactions taking place in HDC lead to very desirable products, for instance:

- *Diesel*: low in S, N and aromatics yielding high cetane and on spec fuel. HDC diesel is the best contributor to the diesel pool

- *Kerosene*: the same features apply and the smoke point (linked to soot formation during combustion and hence the aromatic content) is excellent

A summary of all the options offered to the refiner by modern HDC processes and catalysts illustrates its flexibility, Table 13 [57, 82]. So far, no zeolite other than Y has made any significant inroads in commercial operations; again, as in FCC, its extreme adaptability combined with a well-proven and economic manufacturing process is responsible for its commercial success.

Many challenges are facing HDC: the widespread use of heavier conventional feedstocks and the emerging extra-heavy unconventional crudes (tar sands, shale oils...). The intrinsic low coking tendency of zeolites makes them prime candidates, but their microporosity could be a potential drawback. While a solution may come from new mesoporous materials, it is likely that hybrid catalysts combining well controlled, interconnected and homogeneous micro- and meso-porosity could prove an interesting research avenue [92–94]. In addition, these new (nano) engineered materials could well have to operate in moving bed reactors (ebullating, slurry...), so that their shaping will require close collaboration between catalyst and process engineering. The field is thus gaining in interdisciplinarity and attractiveness for new researchers; it could prove very fertile in the coming years.

Another application of zeolite catalysts, closely related to HDC, is the production and upgrading of lube fractions (base oils) to design modern lubricants. While the volume of lubricants is dwarfed by the transportation fuel market, they have per volume a higher value and zeolites technologies have already contributed to very significant breakthroughs. The zeolite-based processes (production of lube bases by HDC and further upgrading on shape selective zeolites) are increasingly displacing the older extraction and crystallization processes [95] along the whole lube chain. The high value and tight specifications of lubricants provided refiners and process licensors the opportunity to introduce more expensive zeolites or molecular sieves (zeolites β , TON, MTT, AEL...). The chemistry involved is a combination of hydro-isomerization, hydro-cracking modulated by the shape-selectivity of the zeolites involved; its fundamentals have been extensively studied especially by the Belgian (P.A. Jacobs/J.A. Martens and co-workers, see for instance [96]) and German (J. Weitkamp and co-workers, see for instance [97]) schools. A recent review illustrates the beneficial effect of mono-dimensional zeolites or molecular sieves (ZSM-48, ZSM-22/23 and SAPO-11) for isomerisation whereas large-pore zeolites (Beta, USY, and ZSM-12) allow the formation of multibranched isoparaffins, which are susceptible to cracking [98]. The field of zeolites applied to

lube oil processing has been introduced and reviewed quite recently in excellent papers [99–101]. Most of these lube-producing catalysts perform dewaxing by isomerization and are bifunctional catalysts. Beside this hydro-isomerisation of long-chain molecules to improve their fluidity properties, also monofunctional dewaxing catalyst have been commercialized (so-called Cold Flow Improvement or CFI) [102]. These catalysts are typically placed at the backend of hydro-desulphurization catalysts in order to improve the cold flow properties of heavy gasoils.

A related new application of selective hydro-isomerization is the isomerization of the paraffinic hydrocarbons produced during the hydro-deoxygenation of natural oils [103–106]. In this new process of transforming natural triglycerides into diesel components, linear intermediate paraffin's are produced that have to be isomerized slightly to improve the cold flow properties. Hence highly selective isomerization catalysts, precluding cracking, are required in order to maximize the bio-diesel yield. SAPO-11 has been proposed in this respect [107].

Further advances in lube oils upgrading will probably be strongly influenced by the application of new experimental techniques (High Throughput Experimentation in the synthesis, characterization and testing of zeolite materials) and computer-based (in-silico) screening of potential (even yet to be synthesized) molecular sieves where the tailoring of the catalyst to the product specification will play an ever increasing role [72]. The feedstock supplied by the newly installed or announced GTL (gas to liquid) plants in countries with advanced natural gas feedstock, will be free of almost any impurity (olefins, aromatics, sulfur, nitrogen...) and the upgrading catalysts will be able to operate under quasi ideal conditions, thus maximizing the yields of high value products [108].

6 Petrochemical Applications

In volume of products processed, petrochemicals represent around 10% [109] of the oil refining industry. While in petroleum refining, the two major conversion units, FCC and HDC, are based on zeolites, this is not the case in petrochemistry. The petrochemicals building blocks, olefins, aromatics and syngas ($\text{CO} + \text{H}_2$ in various proportions) are produced by steam cracking of various oil fractions (a non-catalytic process), catalytic reforming of naphtha (Pt dispersed on a chlorided alumina as in oil refining) and steam reforming of natural gas, Fig. 11 [110]. Zeolite catalysts are found further downstream, especially in aromatics processing and olefins production. The FCC unit can be tuned to produce light olefins, mainly propylene (~30% of the worldwide propylene production is

Table 13 Guidelines for the selection of HDC catalysts highlighting the specific features of zeolite based catalysts [57, 82]

Desired product	No. stages	Hydrogenation function			Acidic function		
		Pd/Pt	NiW	NiMo	Zeolite	Silica–alumina	Doped alumina
Max naphtha	One	+++	++	++	+++		
	Two	+++			+++		
Max kerosene	One		++	+++	+++		
	Two	++	++	++	++	++	
Max middle distillate	One		++	++	++	++	
	Two		++	++		++	+
Max lube	One		++	++	++	++	+
Highest activity	Pd/Pt			Zeolite			
Features	Sulphur sensitive			Less NH ₃ sensitive → one stage applications			
	Higher activity and hence favours aromatics hydrogenation equilibrium and superior coke precursor hydrogenation			More active and hence lower temperature, less coke production Shape selectivity excludes large coke precursor to enter: less coke Microporosity results in consecutive cracking of primary products and hence lighter products			

produced on FCC's) but its contribution to the ethylene pool is still marginal.

6.1 Aromatics Production

Table 14 gathers the existing and some emerging technologies to produce aromatics. With the exception of a few units transforming light paraffin's or olefins [111–120] as well as naphtha, the bulk of the aromatics is produced by the catalytic reforming of naphtha [121] and as byproduct of the thermal cracking of naphtha. These two latter processes either do not use catalysts or use non-zeolitic catalysts. Benzene, for instance, is directly recovered from reformat (37%) and pyrolysis gasoline (36%) by extraction or produced in zeolite-based processes such as toluene disproportionation, toluene trans-alkylation or as a byproduct from *p*-xylene production (14%) [122]. Although, the majority of aromatics are still produced in the catalytic reformer or recovered as byproducts in steam cracking of liquid hydrocarbons, several zeolite-based processes have been proposed recently. These new processes upgrade low-value intermediate streams or refinery and steam cracker byproducts [123]. In general the zeolitic catalysts used in these processes contains a metallic function and a high acid density in order to maximize aromatization by dehydrogenation and hydrogen-transfer reactions. The relative ratios of the two catalytic functions depend on the nature of the feedstock. In the case of a paraffinic feed, the dehydrogenation function is rate limiting, compared to the oligomerisation/cyclisation [124] whereas in case of olefinic feed the hydrogen-transfer reaction needs to be optimized.

The result is on one hand, light saturates (LPG) and on the other hand, an aromatics rich liquid fraction, that can be treated in conventional aromatic recovery complexes. One process, using platinum on zeolite KBaL, shows a very high selectivity for the production of benzene or toluene from *n*-hexane or *n*-heptane. It is so far the only catalytic application of zeolites as a basic support for a metal phase; the zeolite support is essential for the high selectivity for aromatics [125].

6.2 Aromatics Processing

A breakdown of the aromatics supplied to a petrochemical complex is provided in Table 15 together with the thermodynamic equilibrium composition, the boiling and melting points of the C₈ aromatics cut. It illustrates that some much desired products, such as *para*-xylene and benzene, are in general produced in sufficient quantities but in diluted concentrations. Aromatics processing will therefore be required to squeeze out a maximum of valuable aromatics from the most available feedstock, namely reformat and pyrolysis gasoline. In 2007, the demand for benzene, toluene and xylenes was respectively 40.6, 20.9 and 40.7 million tons per year [126], illustrating the need for processing to balance the supply of aromatics with their market demand. Although ethylbenzene has large scale applications for the production of styrene monomer and the amounts of ethylbenzene in the mentioned feedstock can be considerable, it is rarely isolated as such from these complex mixtures. Due to the difficulty to separate ethylbenzene from xylenes, it has to be transformed into other aromatics in order to valorize the aromatic nucleus. This

role. Intramolecular isomerization will only occur when steric hindrance in the vicinity of the acid sites limit the formation of diphenyl-methane intermediates (as for medium-pore zeolites) or when acid properties result in fast coke deposition on the zeolite surface as to prevent further formation of bulky intermediates [15, 127, 128]. Figure 13 illustrates the type of transformation that should be practiced for a given methyl-to-phenyl ratio of the feedstock. It is obvious that when the feedstock contains only C₈-aromatics, disproportionation/transalkylation has to be avoided to prevent undesirable C₉-aromatics production. Disproportionation of toluene (TDP) streams can maximize the production of benzene and also produce *p*-xylene if the medium-pore zeolite has been additionally treated (minimize the catalytic activity of the external surface of the crystals and/or reduce the size of the pore-openings [9]). On the other hand, higher xylenes/benzene ratios can be produced when C₉-aromatics are added to toluene streams. Figure 14 shows a fully integrated “methyl”-phenyl complex, including zeolite-based TDP or transalkylation and xylene isomerization. Another zeolite, Ba(K)X is used more and more to isolate the *p*-xylene from the other C₈-aromatics in a simulated moving bed adsorptive separation. As the yield for the desired product, *p*-xylene is only partial, the recycle streams in such a “methyl”-aromatic complex can be very high which is reflected in the high capital investments involved. Table 16 summarizes the typical catalysts that are proposed for this aromatic processing [36]. It is believed that EU-1 (EUO) is a newcomer in the narrow group of commercially used zeolite structures [15, 129]. After an initial deposition of coke during which the disproportionation and dealkylation activity decreases, it becomes a very active catalyst for ethylbenzene isomerisation. It is believed that the ten-member channels are blocked with coke and the remaining desired activity is ensuing from the large side-pockets at the external surface of the zeolite crystals [15, 130].

The replacement of the conventional catalysts (AlCl₃, supported phosphoric acid and HF) started in the 1970s with

the introduction of ZSM-5 for vapor-phase alkylation of benzene with ethylene [131]. In order to maximize the production of ethylbenzene and the minimization of oligomers formation, the benzene-to-ethylene ratio is typically above 5 molar, Table 17. The vapor-phase alkylation occurs at 370–420 °C and at this temperature isomerization of ethylbenzene yields some xylenes. Any xylene produced cannot be separated from the ethylbenzene and is subsequently not converted in the ethylbenzene dehydrogenation process to make styrene. The presence of xylenes in ethylbenzene is therefore a major problem for the downstream section of a styrene plant, as recycle of xylenes with unconverted ethylbenzene has to be minimized to avoid its build up and an increase in purge streams and equipment size [132]. Since the early 1990s liquid phase zeolite-based alkylation catalysts have been introduced working at considerably lower reaction temperature (<300 °C), Table 17. Under those conditions, nearly no xylenes and oligomers are produced anymore and much less heavy byproducts are formed. Zeolites exhibiting good diffusivity of both reactants to the active site but at the same time embracing an active site vicinity that minimizes the polyalkylation are required. The Zeolites USY, Beta and MCM-22 being used commercially can operate at benzene-to-ethylene ratios significantly below 5 molar, hence reducing benzene recycle. MCM-22 produces the least amount of diethylbenzene, most probably due to the very accessible large side-pockets at the outer surface of the crystals [131, 133]. The production of high purity cumene by liquid phase alkylation of benzene with propylene has taken advantage from similar zeolitic catalysts [134–136]. Several excellent reviews have been published recently on the alkylation of aromatics [131, 137].

7 Some Emerging Applications

They are far less documented than the well-established processes described above but some have been reviewed

Table 15 Supply of various aromatics and relevant properties of the C₈ cut

Aromatic/%	Reformate	HT pygas	HT coke oven light oil + others	Equilibrium @450 °C	T _{Boil} /T _{melt} (°C/°C)
Contribution to BTX	71	23	6		
Benzene	3–10	40	65		
Toluene	13–27	20	18		
C ₈ aromatics	16–33	7	8		
Ethylbenzene	17	50	–	8.8	136.2/–94.9
<i>p</i> -Xylene	19	10		21.7	138.1/13.2
<i>m</i> -Xylene	47	25		46.9	139.1/–47.8
<i>o</i> -Xylene	17	15		22.6	144.5/–25.1
C ₉ aromatics	15–20	3	7		
Non-aromatics	25–50	30	2		

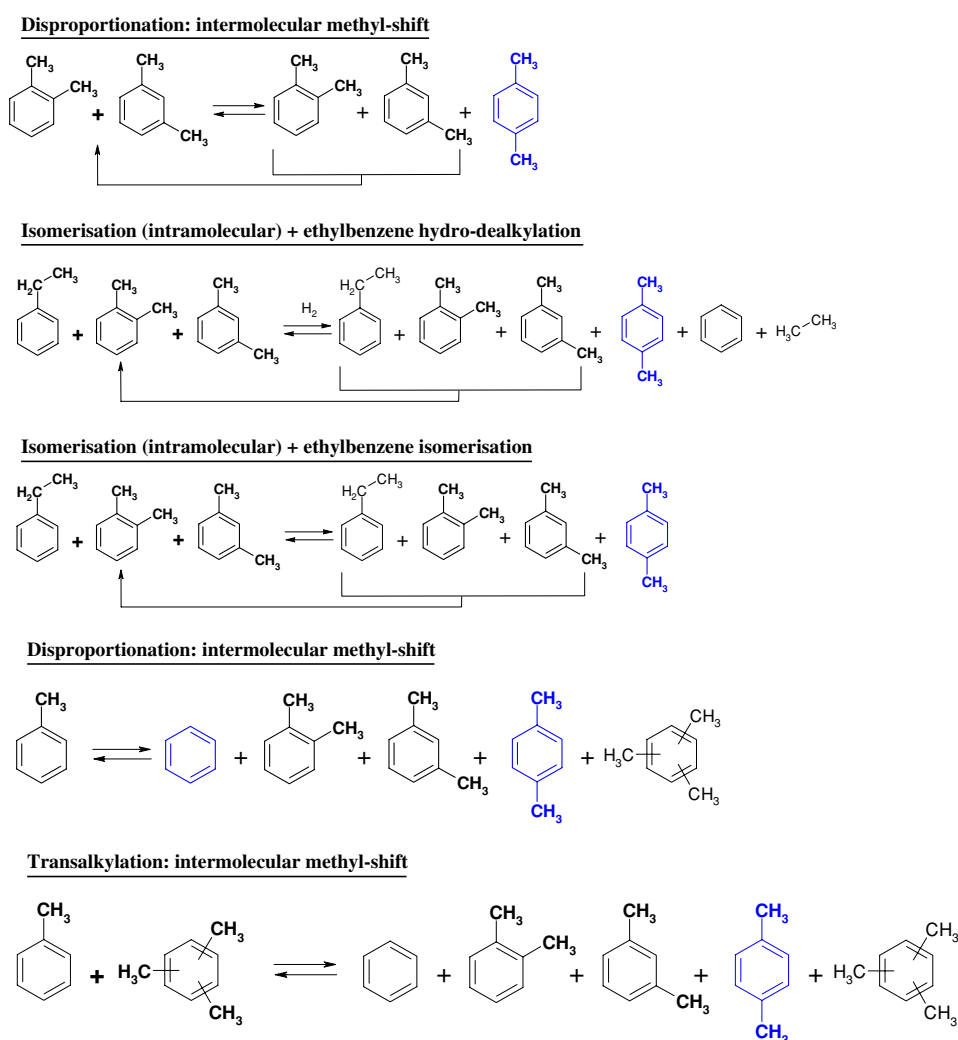
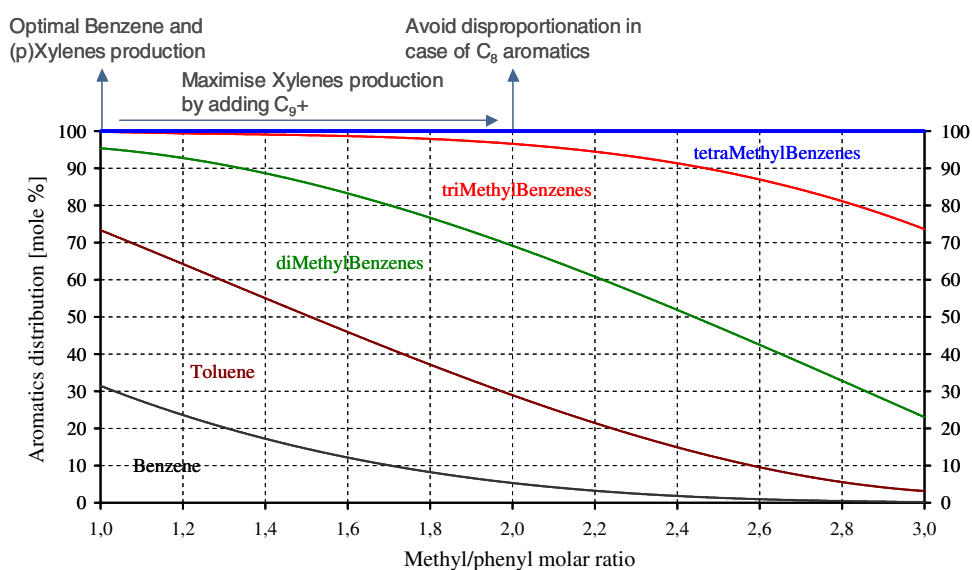
Fig. 12 Chemistry of aromatic processing**Fig. 13** Thermodynamic distribution of methyl-aromatics against methyl-to-phenyl ratio

Table 17 Overview of aromatic alkylation processes [131, 137]

	Preferred catalyst/process	Features
Ethylbenzene	ZSM-5 in gasphase >400 °C	High B/E ratio > 5 Small make of xylenes
	MCM-22/49, Beta in liquid phase	Low B/E ratio <5 Low xylene make Less oligomers
Cumene	Y in catalytic distillation	Can use diluted ethylene
	Y in catalytic distillation	Can use diluted propylene
	Mordenite (3-DMM)	Highly active → low T and hence very small amounts of n-PB
	MCM-22 Beta	
Transalkylation of multi-alkylbenzenes	Same zeolites as for liquid phase alkylation	Requires separate reactor

naphthenes over a nickel catalyst and subsequently the latter are converted by ring opening over a Pd/ZSM-5 into light paraffin's (80% yield of ethane and propane). Although, ethane is an excellent feedstock for steam cracking (~80% ultimate ethylene yield), the high hydrogen requirement for the hydro-cracking step (>10 wt% on feed basis) makes the process difficult to justify economically.

5. *Separation of C₅–C₁₁ naphtha* into normal-paraffin's and into iso-paraffin's, naphthenes and aromatics is being proposed for the optimization of feedstock for steam crackers and naphtha reformers (MaxEne[®] form UOP) [149]. Normal paraffin's are the ideal feedstock for steam crackers as they yield >20% more ethylene whereas naphthenes are the ideal feedstock for the aromatization activity in a reformer. The process is based on a simulated moving bed adsorptive separation (Sorbex[®] family of processes) using molecular sieves.
6. *Separation of water from ethanol* can now be done by means of LTA-zeolite containing membranes developed by Mitsui & Co [150, 151]. Conventionally, the last 5% of water in bio-ethanol at the azeotrope is removed by PSA (Pressure Swing Adsorption) over LTA zeolite beds. The use of a similar zeolite in a polymeric membrane, supported on ceramic tubes operating in VP (Vapor Permeation) mode, saves about 10% of the energy requirement for the production of fuel grade bio-ethanol and can even be used for more diluted ethanol streams.
7. Zeolite-based materials are now used for the *removal of olefins in aromatic streams* instead of clay materials (Olgone[®] from ExxonMobil) [152]. This removal step is based on alkylation of aromatics with the olefins present. The new zeolite-based process reduces the solid waste by more than 85% and has a higher removal efficiency. According to the patent literature,

MCM-22 is one of the most efficient zeolites for this alkylation with long-chain olefins [153].

7.2 Emerging Technologies Using New Feedstock for Existing end-Products

1. *Skeletal isomerisation of butenes and pentenes* can be performed over several 10-member zeolites, especially over ferrierite zeolite (Shell, Lyondell), but also ZSM-22 (Mobil/BP) and SAPO-11 (UOP). High selectivity for iso-butene and iso-pentene has been obtained [154, 155]. The ISOMPLUS[®] technology (ferrierite catalyst, Lyondell/CDtech) has been commercially demonstrated at the Equistar facility in Channelview on a 10000 BPD butene feed [156]. An amorphous alumina-based catalysts using continuous catalytic regeneration (ISO-5[®] technology from Axens) is being used to convert Fischer–Tropsch-derived pentenes into iso-amylene for ether production at Sasol [157] and a 2000 BPD butenes plant has been operational at Texas Petrochemicals using a Texas/Phillips technology [158]. Although, in the early nineties, it was believed that high amounts of iso-olefins would be required to respond to the rising demand for gasoline ethers, today with the MTBE-ban in the US, the need for these units does not exist anymore. Nevertheless, these developments could be used to perform the reverse isomerization (excess iso-olefins into linear olefins) to produce more feedstock for metathesis as proposed by ABB Lummus [156].
2. In the *production of 2,6-dimethylnaphthalene* (2,6-DMN, a precursor for the production of high-performance poly-ethylene-naphthenate), several acid-catalysed steps can be carried out by zeolites. In the commercially proven BP/Amoco process, a USY

- zeolite is used for the cyclization of the 5-*o*-tolyl-pentene intermediate into 2,5-dimethyltetralins, which after dehydrogenation into 2,5-dimethylnaphthalene is isomerized over a modified zeolite Beta into 2,6-dimethylnaphthalene [159]. Recently, Polimeri announced the development of a new process that produces naphthalene from low-cost cycle oils obtained during catalytic or thermal cracking [160]. It uses ZSM-12 in three separate process steps: (i) alkylation of naphthalene or methylnaphthalene with methanol using a benzenic solvent, (ii) isomerisation to maximize 2,6-DMN and (iii) a dealkylation of the remaining DMN and polymethylnaphthalenes using again a benzenic solvent.
3. *The selective cracking of C₄+ olefins* in propylene [161] is now proposed by several companies (OCP[®] from Total Petrochemicals/UOP [162], Propylur[®] from Lurgi [163], PCC[®] from ExxonMobil [164], Omega[®] from Asahi [165], Superflex[®] from KBR [166] and Sinopec [167]). These processes use modified ZSM-5 type zeolites to provide a maximum selectivity for propylene. The reaction mechanism is based on the interconversion of olefins while hydrogen-transfer and aromatization reactions are minimized as much as possible. Depending on the degree of zeolite optimization and operating conditions a wide range of olefins can be converted. In particular OCP[®], is optimized for cracking of C₄ up to C₁₀ olefins, either linear, branched or cyclic without using any diluents in the reactor [162].
 4. *The methylation of toluene to xylenes* is proposed by GTC (in alliance with Indian Petrochemicals Corp. Ltd.) [168]. GT-TolAlk[®] technology, according to patents assigned to IPCL, uses a ZSM-5 zeolite catalyst modified with gallium and selectivated by ex situ silicon impregnation [169]. GTC claims that the *p*-xylene selectivity of the GT-TolAlk[®] process is above 85 wt%. ExxonMobil and Sabic are also actively working on toluene alkylation technology. Typical process conditions are an inlet temperature of >420 °C, molar H₂/toluene ratio between 0.1 and 2, and a molar toluene-to-methanol ratio of about 4; steam is used to further increase catalyst stability. Toluene conversions are typically below 20%, with xylenes selectivity typically above 90 wt% and a *p*-xylene concentration in the xylenes stream of >85% [170].
 5. *The side-chain alkylation of toluene with methanol* to make styrene in a single step has been recently announced by Exelus. It is an alternative to the two step process, involving benzene alkylation with ethylene followed by high-temperature dehydrogenation. The new process uses a novel engineered catalyst, ExSyM[®], which consists of a proprietary zeolite with basic active sites in a highly optimized pore structure. By combining elements of reaction engineering with advanced catalytic composition, a new multifunctional catalytic system has been developed that allows significantly higher yields of styrene (>78%) at complete methanol conversion at 400 °C, WHSV of 3 h⁻¹ and atmospheric pressure [171, 172].
 6. *The conversion of methanol into light olefins* is nearing industrialization. Two families of technologies are proposed today: (i) those based on the SAPO-34 molecular sieve (UOP/Hydro [173], DCIP [174, 175], Tsinghua University [176], Sinopec [167] and Exxon-Mobil [177]) and (ii) those based on the ZSM-5 type zeolite (Lurgi [178], JGC [179] and Idemitsu [180]). SAPO-34 based processes convert methanol or dimethylether into both ethylene and propylene with a combined yield of 75–80% on carbon basis, whereas the ZSM-5 based processes produce mainly propylene and ethylene and heavy olefins as byproducts. The latter can be recycled over the same catalyst yielding more propylene, the byproducts being LPG and some gasoline. The ultimate yield of propylene is reported to be between 60 and 70% on carbon basis. The Total Petrochemicals/UOP OCP technology has been integrated with the UOP/Hydro MTO technology, which allows to crack the C₄+ olefins, produced over the SAPO-34 catalyst into additional propylene and result in >88% yield of ethylene and propylene on carbon basis [173].
 7. *Methane conversion into aromatics* is extensively studied since its first announcement in 1993 [181]. Companies like Mitsubishi [182], Mitsui [183] and ExxonMobil [184] demonstrate a high interest in this direct conversion of methane to aromatics and hydrogen. Catalysts are bifunctional, a dehydrogenation function provided by Mo or W, and an acidic function, provided by a zeolite, mostly ZSM-5. A major challenge is minimizing coke formation. Pilot test in fluidized bed reactors have been carried out in Japan [185].
 8. *Catalytic naphtha cracking* has been an elusive dream for many decades, however it has recently been revived by better knowledge of zeolite modifications [186, 187]. The main challenge is to adapt the zeolitic catalyst to obtain high selectivity for light olefins while minimizing hydrogen-transfer that would result in paraffin's and aromatics. On the other hand, as these catalytic systems are prone to coke deposition at the high reaction temperature required (600–750 °C), the catalyst need to resist to hydrothermal conditions during the regeneration step where a lot of steam is produced during combustion. It is anticipated that significantly less fuel gas (mainly methane) and highly

unsaturated gasoline will be produced over acidic zeolite catalysts, as the cracking occurs at a reaction temperature about 200 °C lower than in steam cracking. In addition, the catalyst circulation will provide a good heat balance, bringing therefore significant energy savings.

The drivers behind these applications are:

- *Technology push*: such as improvements in process efficiency (selectivity directly impacted by the zeolite catalyst)
- *Market/regulation pull*: such as regulations (on side- and by-products) and opportunities for new feedstock

8 Concluding Remarks: The Future of Zeolites in Industry and of Zeolite Research

The oil and petrochemical industries are intimately linked and face renewed challenges. These of course go well beyond the industrial use of zeolites [188, 189].

While all fossil hydrocarbons are finite resources and increasingly difficult to explore, they will however provide the vast majority of fuels and chemicals for the next decades [190]. The road towards a sustainable fossil-free future needs to be planned and managed properly in order to avoid any brutal awakening [191]. Technology will continue to contribute in two complementary ways to the overall sustainability of industry [192] by providing:

- *A license to operate*: to meet the latest specifications and regulations (health, safety, environment) on the products and processes and be a good corporate citizen
- *A license to grow*: to put new products and processes on the market that should benefit society as a whole

These two licenses are both required in order having a sustainable and profitable activity.

The petroleum industry will need to prepare the future as the production of petroleum-based fossil resources is expected to stabilize at about 95 million barrels/day, Fig. 15, before 2020 [193]. After 2020, the production of conventional petroleum is forecasted to decrease slowly and will have to be compensated by high investments in heavy oil production. Figure 16 shows the proven reserves and worldwide distribution of the three fossil resources (coal, natural gas and crude oil) [194]. It shows that the potential of natural gas and especially coal are still enormous to transform them into transportation fuels and petrochemicals. Biomass has also been reported to have a high potential, although much technological progress is needed to unlock it and to convert it using clean and efficient processes into valuable products [195]. These emerging

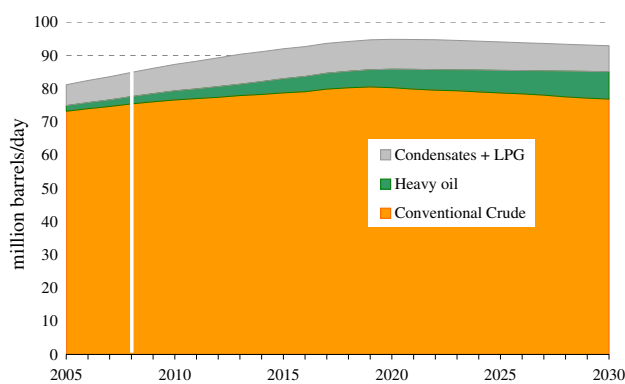


Fig. 15 Petroleum supply between 2005 and 2030, as forecasted by the Total Company as of mid 2008 [193]: 1 barrel equals 159 L or approximately 136 kg

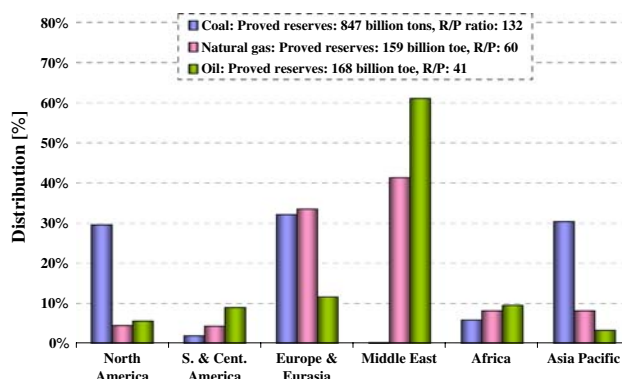


Fig. 16 Proven reserves and worldwide distribution of fossil resources: “toe” is ton oil equivalent and equals 0.805 ton natural gas and 7.33 barrels; R/P is ratio Reserves to Production; excluding Canadian oil sands that account for another 24.7 million toe [194]

feedstock present considerable challenges to the refining and petrochemical industry in order to transform them in conventional products.

Figure 17 shows a typical “van Krevelen” diagram, plotting the H/C ratio versus the O/C ratio of feedstock; Fig. 18 shows the HHV (higher heating value) versus the oxidation state of Carbon in the feedstock. They highlight that so far feedstock similar (with respect to chemical composition and energy content (HHV)) to the most desired commodity products (gasoline, diesel, polyethylene and polypropylene) have been used. They also indicate that challenging reshuffling of atoms and energy transfer will be required to transform the emerging feedstock into daily life products. So far, the known pathways are the conversion of natural gas via steam- or auto-reforming or the conversion of coal, petroleum coke and biomass via gasification into syngas. Figure 19 shows that from syngas (CO/H₂) many products can be made and that those with large scale potential are: (i) hydrocarbon-like molecules through the Fischer–Tropsch and methanol catalytic routes. It is certain that zeolites will take a prominent place in the

Fig. 17 Typical “van Krevelen” diagram of emerging feedstock and commodity products (encircled)

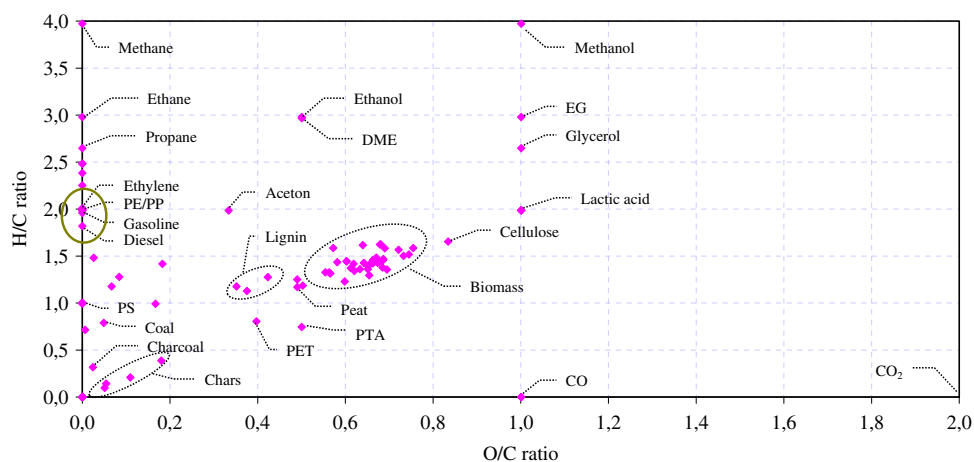


Fig. 18 Energy content against oxidation state of Carbon in emerging feedstock and commodity products (encircled): HHV is high heating value

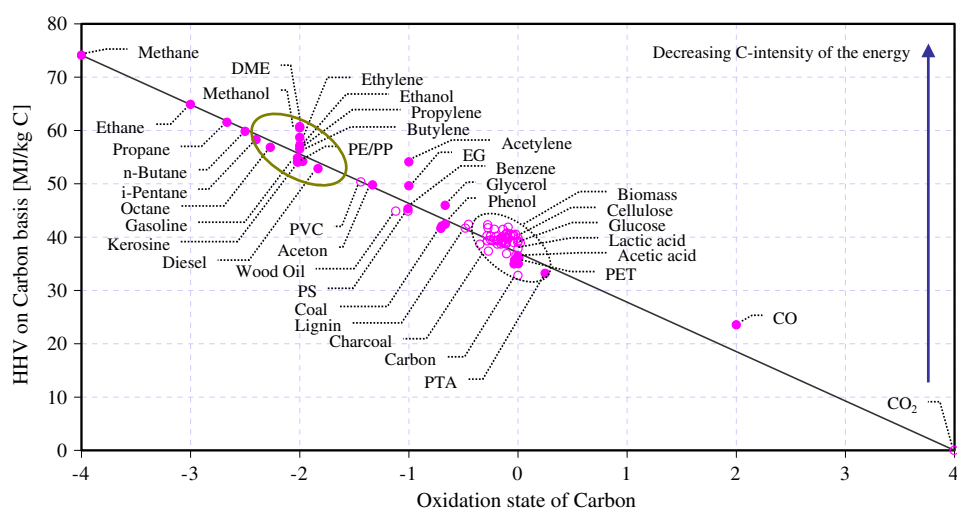
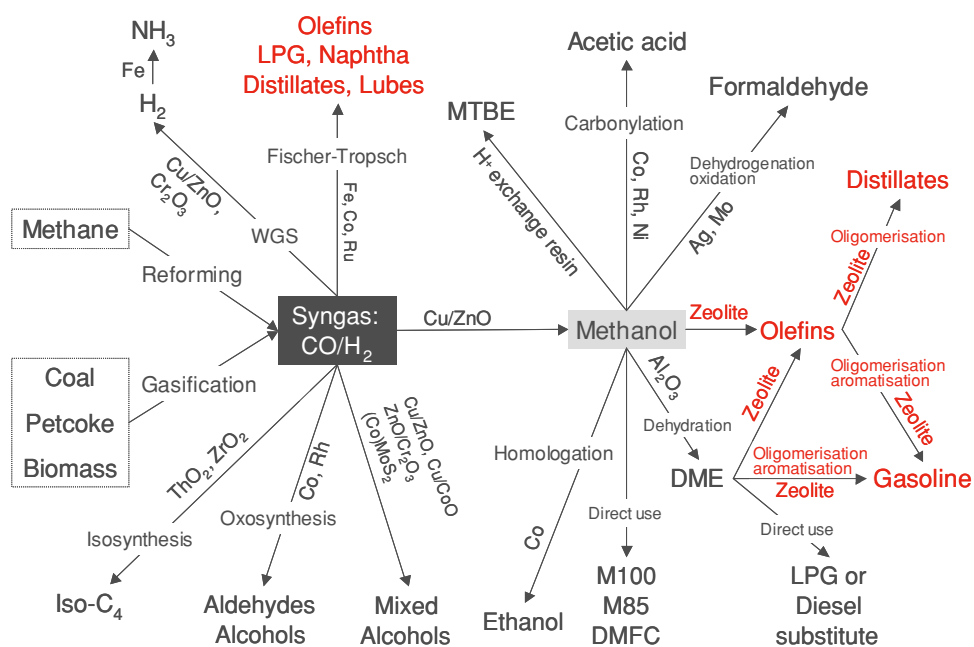


Fig. 19 Products of synthesis gas and possible chemical transformations: wording in red indicates where zeolites have high potential to contribute



development of this new syngas era that is ahead of us. The upgrading of the crude Fischer–Tropsch products will require zeolite-based catalyst to produce on-spec products. Zeolites are also the most suited catalysts for transforming methanol into olefins (cf. supra), gasoline and distillates.

Zeolites are now part of the industrial history and many examples illustrate their great contribution to oil refining and petrochemistry. They did so by providing *disruptive* (e.g. introduction of zeolites in FCC, molecular sieve adsorbents, replacement of extraction and crystallization processes, lube oil processing with shape selective catalysts...) as well as *incremental* changes (e.g. continuous improvements in FCC, HDC, better adsorbents, quality control in zeolite manufacturing, unlocking high purity aromatics from complex mixtures...). The future challenges of oil refining and petrochemicals lie mainly in:

- Energy efficiency, directly linked to CO₂ emissions
- New specifications on products, processes and overall emissions (including catalyst reclaiming)
- New fuels and lubricants to match emerging engine technologies (HCCI, CAI)
- Need to process ever challenging feedstocks from more diverse origins: gas, unconventional oils, biomass derived feedstocks, coal...
- So-called “softer” issues such as the perception of these activities, and the related ability of both the academic and industrial communities to attract the needed creative young students [189]

If one tries to translate these societal challenges in technology solutions and R&D programs, it becomes clear that zeolites will be called to contribute.

The selection of new manufacturing processes will probably have to be based on additional criteria's taking a better account of their overall footprint; in addition to the e-factor [62], energy efficiency and economic viability, intrinsic safety (choice of preventive over curative solutions) could well receive a veto power. This might for instance be the case for the olefin/paraffin alkylation refinery process [48]: it dates from over 60 years, uses potentially dangerous liquid H₂SO₄ or HF catalysts, has been optimized ever since its commercial launch and has not yet caused any major industrial accident. The barrier of entry for new [intrinsically safer] processes, based for instance on zeolites, is therefore very high. It is further increased by the yet lower performances of emerging zeolite-based technologies, given their lack of industrial experience. If a greater weight is given to the fact that introducing a zeolite-based, or any safe solid acid catalyst reduces to almost zero the probability of a major industrial accident (for instance the HF-hydrocarbons aerosol formed by leakage from a unit could be deadly over a wide area

around the refinery), opportunities will open for the emerging processes. Their performances will then benefit by climbing the commercial learning curve of any new product or process [196–198].

These formidable challenges are exciting and will need the bundling of many competences even outside of the fields of zeolite science and technology. It will be thrilling for new generations of scientists and engineers to be able to rationally design new solutions to problems such as the sustainable upgrading of biomass in environmentally benign fuels and chemicals, to reinvent processes using highly efficient catalysts and adsorbents in order to minimize energy consumption and hydrocarbon losses. It should give them the feeling they are not creating but solving problems for a better world. It will be a necessary condition to attract young students again to science and technology. It will hopefully change the perception of industrial management that R&D in general, and in particular in zeolites, is not an expense but an investment [199].

It is doubtful a single actor could master or generate all the necessary knowledge and know-how necessary; a new era of scientific and technical alliances will need to emerge. There will be a strong need for basic knowledge generation (*the role of academia*) and its application to meet new technical challenges (*the role of industry*) following mutually accepted and enforced rules (*the role of governments*). It follows that closer cooperation will have to take shape between these actors along the lines of “Open Innovation” [200] where the term Connect & Develop [201] tends to replace Research & Development. These practices are already common among innovative high-tech industries and are spreading in even more mundane applications [202]. They should be adapted to the specific cases of oil refining and petrochemicals in order to progress further and faster in the application of incremental as well as disruptive technology changes [196]. In order to be accepted, these practices will require an adequate general framework with a particular attention to intellectual property protection where every partner sees a just return on its investment.

Against that background, zeolites have a great track record and display all the required qualities to put them in an excellent position for further growth in both oil refining and petrochemistry.

Acknowledgements JPG wishes to thank the St-Nikon Foundation for its continuous support over the years in the fields of zeolite and scientific management. WV expresses his appreciation to Philippe Bodart for helping the documentation and to Total Petrochemicals for allowing the preparation of this manuscript. Finally, WV thanks Marjel, Charlotte and Marie, for patience and understanding during the preparation of this manuscript.

References

- Avidan AA (1993) *Stud Surf Sci Catal* 76:1
- Moulijn JA, Makkee M, van Diepen A (2001) Chemical process technology. John Wiley & Sons, Chichester, p 41
- Magee JS, Mitchell MM Jr (1992) Fluid catalytic cracking: science and technology. Elsevier, Amsterdam
- Guisnet M, Gilson J-P (2005) Zeolites for cleaner technologies. Imperial College Press, London
- Marcilly C (2001) *Stud Surf Sci Catal* 135:37
- Corma A, Martínez A (2005) *Stud Surf Sci Catal* 157:337
- Marcilly C (2005) Acido-basic catalysis—application to refining and petrochemistry. Technip, Paris
- Kerr GT (1966) *Inorg Chem* 5:1537
- Chen NY (2001) *Ind Eng Chem Res* 40(20):4157
- <http://www.iza-structure.org/databases>. Accessed August 2008
- Knight LM, Lewis GJ (2004) *Stud Surf Sci Catal* 154(1):171
- Lewis GJ, Miller MA, Moscoso JG, Wilson BA, Knight LM, Wilson ST (2004) *Stud Surf Sci Catal* 154(1):364
- Lewis GJ, Miller MA, WO 2005042149 (2005); Rohde LM, Lewis GJ, WO 2005113439 (2005); Jan D-Y, Johnson J, US 2006224031 (2006), assigned to UOP LLC
- Bare SR, Methanol to Olefins: development of a commercial catalytic process, presentation available on <http://w3.rz-berlin.mpg.de/%7Ejentoft/catalysis0708.html>. Accessed August 2008
- Moreau F, Moreau P, Gnep NS, Magnoux P, Lacombe S, Guisnet M (2006) Microporous Mesoporous Mater 90:327
- Corma A, Martínez-Soria V, Schnoeweld E (2000) *J Catal* 192:163
- Kuznicki SM, Bell VA, Nair S, Hillhouse HW, Jacubinas RM, Braunbarth CM, Toby BH, Tsapatsis M (2001) *Nature* 412:720
- www.moleculargate.com. Accessed August 2008
- Cherry BR, Nyman M, Alam TM, Solid J (2004) *State Chem* 177:2079
- Vartuli JC, Degnan T (2007) *Stud Surf Sci Catal* 168:837
- Schoonover MW, Cohn MJ (2000) *Top Catal* 13:367
- Karge HG, Weitkamp J (eds) (2002) Molecular sieves, science and technology, vol 3. Springer-Verlag, Berlin, Heidelberg
- de Jong KP (1998) *Cattech* 2:87
- Stiles AB, Koch TA (1995) Catalyst manufacture. CRC Press
- Pernicone N (1997) *Catal Today* 34(3–4):535
- Earl DJ, Deem MW (2006) *Ind Eng Chem Res* 45:5449
- Smit B, Maesen TLM (2008) *Nature* 451:671
- Akporiaye DE, Dahn IM, Karlsson A, Wendelbo R (1998) *Angew Chem Int Ed* 37:609
- Briker M, Vanden Bussche K, McGonegal C, Karlsson A, Akporiaye DE, Dahn IM, Plassen M (2000) *Combi* 2000, San Diego, January 2000
- Prada R (April 6, 2004) *Oil Gas J* 102(16):58 or *Appl Catal A: general* 261:247 (2004)
- The intelligence report: Business Shift in the Global Catalytic Process Industries 2005–2011 (May 2006). The Catalyst Group Resources, Inc
- World Catalysts (January 2007). The Freedonia Group, Inc
- Lacson J, Zeolites and Lauriente DH (2002, 2005), Zeolites, Chemical Economic Handbook: Marketing Research Report, SRI Consulting
- The Economics of Zeolites (2003) Roskill Information Services
- Colella C (2005) *Stud Surf Sci Catal* 157:13
- Marcilly CR (2000) *Top Catal* 13:357
- Degnan TF (2000) *Top Catal* 13:349
- Pujado PR, Rabo JA, Antos GJ, Gembicki SA (1992) *Catal Today* 13:113
- Sherman JD (1999) *Proc Nat Acad Sci USA* 96:3471
- Marcilly C (2004) In: Atwood JL, Steed JW (eds) *Encyclopedia of supermolecular chemistry*, 2nd edn. Marcel Dekker, New York, Basel, p 1599
- Kresge CT, Dhingra SS (2006) *Kirk-Othmer encyclopedia of chemical technology*, 5 edn. John Wiley & Sons, Hoboken, New Jersey, p 811
- Di Renzo F, Fajula F (2005) *Stud Surf Sci Catal* 157:1
- Barger P (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 239
- Tanabe K, Hölderich WF (1999) *Appl Catal A* 181:399
- Koottungal L, Nakamura D (2007) *Oil Gas J* October:52. www.ogjonline.com. Accessed August 2008
- Guisnet M, Gilson J-P (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 1
- Gélin P, des Courrières T (1991) *Appl Catal* 72:179
- Corma A, Grande M, Fornés V, Carlidge S, Shatlock MP (1990) *Appl Catal* 66:45
- Gélin P, Gueguen C (1988) *Appl Catal* 38:225
- Kubicek N, Vaudry F, Chiche BH, Hudec P, Di Renzo F, Schulz P, Fajula F (1998) *Appl Catal A* 175:159
- Sie ST, Krishna R (1998) *Rev Chem Eng* 14:159
- Rostrup-Nielsen JR (1997) *Catal Today* 37:225
- Méthivier A (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 209
- Jensen RH (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 75
- Wauquier J-P (1994) *Le Raffinage du Pétrole: Pétrole Brut, Produits Pétroliers, Schémas de Fabrication*. Technip, Paris, p 1
- Leprince P (1998) *Le Raffinage du Pétrole: Procédés de Transformation*. Technip, Paris
- Meyers RA (2004) *Handbook of petroleum refining processes*, 3rd edn. McGraw-Hill, New York
- Jones DSJ, Pujado PR (2006) *Handbook of petroleum processing*. Springer, Dordrecht
- de Jong KP (1996) *Catal Today* 29:171
- Sie ST (1994) *Stud Surf Sci Catal* 85:587
- Sie ST (1997) In: Ertl G, Knozinger H, Weitkamp J (eds) *Handbook of heterogeneous catalysis*. VCH, Weinheim, p 1998
- Sheldon RA (1997) *Chem Ind* 1:12
- Marin GB, Kapteijn F, van Dieën AE, Moulijn JA (2000) In: Derouane EG, Lemos F, Corma A, Ribeiro FR (eds) *Combinatorial catalysis and high throughput catalyst design and testing*. Kluwer, Dordrecht, p 239
- Schmidt F, Köhler E (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 153
- Ducourty B, Szabo G, Dath J-P, Gilson J-P, Goupil J-M, Cornet D (2004) *Appl Catal A* 269:203
- Duchet J-C, van Gestel J, Guillaume D, Monnier A, Dujardin C, Gilson J-P, Szabo G, Nascimento P (2001) *J Catal* 198:328
- Martens JA, Tielen M, Jacobs PA (1987) *Catal Today* 1(4):435
- Martens JA, Jacobs PA (1990) *Theoretical aspects of heterogeneous catalysis*. Van Nostrand, Reinhold
- Furey RL (1985) Society of automotive engineers. Technical paper series, Paper No. 852116
- Di Renzo S, Fajula F, Figueras F, Des Courrières T, US 5165906 (1992), assigned to ELF AQUITAINE
- McQueen D, Chiche B, Fajula F, Auroux A, Guimon C, Fitoussi F, Schulz P (1996) *J Catal* 161:587
- Calero S, Schenk A, Dubbeldam D, Maesen TLM, Smit B (2004) *J Catal* 228:121
- van Runstraat A, Kamp JA, Stobbelaar PJ, van Grondelle J, Krijnen S, van Santen RA (1997) *J Catal* 171:77

74. Tromp M, van Bokhoven JA, Garriga Oostenbrink MT, Bitter JH, de Jong KP, Koningsberger DC (2000) *J Catal* 190:209
75. Vu NT, van Gestel J, Gilson J-P, unpublished results
76. Enos JL (1962) *Petroleum progress and profits—a history of process innovation*. MIT Press, Cambridge
77. Freeman C, Soete L (1999) *The economics of industrial innovation*. MIT Press, Cambridge
78. Magee JS, Mitchell MM Jr (1993) *Fluid catalytic cracking: science and technology*. Elsevier, Amsterdam
79. von Ballmoos R, Harris DH, Magee JS (1997) In: Ertl G, Knozinger H, Weitkamp J (eds) *Handbook of heterogeneous catalysis*. VCH, Weinheim, p 1955
80. Habib ET, Zhao X, Yaluri G, Cheng WC, Boock LT, Gilson J-P (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 105
81. Venuto PB, Habib ET (1979) *Fluid catalytic cracking with zeolite catalysts*. Marcel Dekker, Inc., New York
82. Rase HF (2000) *Handbook of commercial catalyst: heterogeneous catalysts*. CRC Press, London
83. Roberie TG, Hildebrandt D, Creighton J, Gilson J-P (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 57
84. O'Connor P (2006) In: Lee S (ed) *Encyclopedia of chemical processing*. Taylor & Francis, New York, p 371
85. van Veen JAR (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 131
86. Maxwell IE, Minderhoud JK, Stork WHJ, van Veen JAR (1997) In: Ertl G, Knozinger H, Weitkamp J (eds) *Handbook of heterogeneous catalysis*. VCH, Weinheim, p 2017
87. Gosselink JW (1998) *Cattech* 2:127
88. Stork WHJ (1997) *Stud Surf Sci Catal* 106:41
89. Leprince P (1998) *Le Raffinage du Pétrole: Procédés de Transformation*. Technip, Paris, p 550
90. Weitkamp J, Ernst S (1990) In: Barthomeuf D, Derouane EG, Hölderich W (eds) *Guidelines for mastering the properties of molecular sieves*. Plenum Press, New York, p 343
91. Degnan TF, Kennedy CR (1993) *Chem Eng J* 39:607
92. de Jong KP (2003) *Catal Rev Sci Eng* 45:297
93. Roth WJ, Vartuli JC (2005) *Stud Surf Sci Catal* 157:91
94. Čejka J (2005) *Stud Surf Sci Catal* 157:111
95. Taylor RJ, McCormack AJ (1992) *Ind Eng Chem Res* 31:1731
96. Claude MC, Vanbutsele G, Martens JA (2001) *J Catal* 203:213
97. Ernst S, Kumar R, Neuber M, Weitkamp J (1987) *Stud Surf Sci Catal* 39:531
98. Deldari H (2005) *Appl Catal A* 293:1
99. Daage M (2005) In: Guisnet M, Gilson J-P (eds) *Zeolites for cleaner technologies*. Imperial College Press, London, p 167
100. Degnan TF (2003) *J Catal* 216:32
101. Kerby MC, Degnan TF, Marler DO, Beck JS (2005) *Catal Today* 104:55
102. Homan Free HW, Schockaert T, Sonnemans JWM (1993) *Fuel Process Technol* 35:111
103. Koskinen M, Sourander M, Nurminen M (February 2006) *Hydrocarbon Process Int Ed* 81
104. Kalnes TN, Marker T, Shonnard DR, Koers KP (2008) *Biofuels Technol* Q4:7
105. Jakkula J, Niemi V, Nikkonen J, Purola V-M, Myllyola J, Aalto P, Lehtonen J, Alopaeus V (2004) US 2004230085, assigned to FORTUM OYJ
106. Huber GW, O'Connor PI, Corma A (2007) *Appl Catal A* 329(1):120
107. Brevoord E, Janbroers S, Harte MH, Aalto P, Harlin E, Osterrom H, Mas Cabre FR (2007) WO 2007107336, assigned to ALBEMARLE NETHERLANDS BV
108. Clark RH, Wedlock DJ, Cherrillo RA (2005) *Fuel Lub* 114:1095
109. Desmarest T (2004) *Energies du Futur & environnement*, Presentation at AFTP, Paris, France, October 20–21, 2004
110. Chauvel A, Lefebvre G (1989) *Petrochemical processes 1. Syngas derivatives and major hydrocarbons*. Technip, Paris
111. Chen NY, Yan TY (1986) *Ind Eng Chem Proc Res Dev* 25(1):151
112. Miyata T, Akaishi T (Winter 1995/1996) *Hydrocarbon Technology International Quarterly* 113
113. Choi S, Oh SH, Kim YS, Seong KH, Lim BS, Lee JH (2006) *Catal Surv Asia* 10(2):110
114. Gentry J, AIChE, The 2008 Spring national meeting, petrochemicals and derivatives, paper 95E
115. Doolan P, Pujado P (September 1989) *Hydrocarbon Process Int Ed* 72
116. Mank L, Minkinen A, Shaddick R (Summer 1992) *Hydrocarbon Technology International Quarterly* 69
117. Saito S, Hirabayashi K, Shibata S, Kondo T, Adachi K, Inoue S (March 1992) NPRA annual meeting AM-92-38
118. Blom NJ, EP 0434052 (1991) assigned to TOPSOE HALDOR AS
119. Catal Rev Newslett 3:10 (1995) or O'Rear, D.J.; Scheuerman, G.L. *Zeolite Catalysis in Chevron*, Book of Abstracts, 214th ACS National Meeting; Las Vegas, NV, September 7–11, 1997 or http://www.cpchem.com/enu/press_releases_6993.asp
120. Catal Rev Newslett 6(2):7 (1993) or Solis, J. J.; Moser, M.D.; Ibanez, F.J. RZ platforming process improves profitability—first new unit at CEPESA, Algeciras, European Oil Refining Conference & Exhibition, Cascais, Portugal, June 18–20, 1997 or <http://www.uop.com/objects/RZ%20Platform.pdf>
121. Anton GJ, Aitani AM (eds) (2004) *Catalytic naphtha reforming*. Marcel Dekker, New York
122. Chemical Market Associates, Inc. (2004) *World benzene analysis*. Houston
123. Thai TC, Albright LF (2006) In: Lee S (ed) *Encyclopedia of chemical processing, thermal cracking of hydrocarbons*. Taylor & Francis, New York, p 2975
124. Méreaudeau P, Naccache C (1997) *Catal Rev* 39(1&2):5
125. Davis RJ (1994) *HCR Concise Review*. John Wiley & Sons, New York, p 41
126. Davies S (2008) *Petrochemical Industry Overview*, Chemical Economics Handbook: Marketing Research Report, SRI Consulting
127. Guisnet M, Gnep NS, Morin S (2000) *Microporous Mesoporous Mater* 35–36:47
128. Čejka J, Wichterlova B (2002) *Catal Rev* 44(3):375
129. Magne-Drisch J, Joly J-F, Merlen E, Alario F, US 6635791 (2003); Rouleau L, Lacombe S, Alario F, Merlen E, Kolenda F, Magne-Drisch J, US 6337063 (2002); Alario F, Joly J-F, Magne-Drisch J, Merlen E, Benazzi E, Lacombe S, US 6337427 (2002), assigned to INST FRANCAIS DU PETROLE Rouleau L, Lacombe S, Alario F, Merlen E, Kolenda F, Magne-Drisch J, US 6342200 (2002); Merlen E, Alario F, Martin O, Ferrer N, Lacombe S, Rouleau L, Magne-Drisch J, US 6514479 (2003); Joly J-F, Magne-Drisch J, Alario F, Merlen E, Benazzi E, Lacombe S, US 6313363 (2001); Joly J-F, Magne-Drisch J, Alario F, Merlen E, Benazzi E, Lacombe S, US 6333289 (2001), assigned to INST FRANCAIS DU PETROLE
130. Moreau P, Gnep NS, Magnoux P, Guillon E, Lacombe S, Guisnet M (2008) *Stud Surf Sci Catal* 174(2):1179
131. Degnan TF, Smith CM, Venkat CR (2001) *Appl Catal A* 221:283
132. Woodle GB (2006) In: Lee S (ed) *Encyclopedia of chemical processing, ethylbenzene*. Taylor & Francis, New York, p 929
133. Maertz B, Chen SS, Venkat CR, Mazzone DN (Autumn 1996) *Hydrocarbon Technology International Quarterly* 21

134. Guarino RF, Li CH (October 1999) *Hydrocarbon Eng* 39
135. Schmidt RJ (2006) In: Lee S (ed) *Encyclopedia of chemical processing, cumene*. Taylor & Francis, New York, p 603
136. Meima GR, Van den Aalst MJM, Samson MSU, Garces JM, Lee JG (1996) *Erdoel Erdgas Kohle* 7/8:315
137. Perego C, Ingallina P (2002) *Catal Today* 73:3
138. Degnan TF (2007) Recent progress in the development of zeolitic catalysts for the petroleum refining and petrochemical manufacturing industries. In: 15th international zeolite conference Beijing, China, August 12–17, 2007
139. Chitnis GK, Dandekar AB, Umansky BS, Brignac GB, Stokes J, Leet WA (2005) NPRA annual meeting, San Francisco, March 13–15, 2005
140. Köhler E, Schmidt F, Wernicke HJ, De Pontes M, Roberts HL (Summer 1995) *Hydrocarbon Technology International Quarterly* 37
141. Godmarks JS, Mathys GMK, Beckers HJ, Yarbrough CM, Brown SH, Lim Y-M, US 2007213575 (2007); Brown SH, Mathys GM, US 2007213576 (2007); Godmarks JS, Mathys GMK, Beckers HJ, Yarbrough CM, Brown SH, Lim Y-M, WO 2007104385 (2007), assigned to EXXONMOBIL CHEMICAL PATENTS INC
142. Knottenbelt C (2002) *Catal Today* 71:437
143. Lieber W, Wagner M (2004) *Erdoel Erdgas Kohle* 120:323
144. Hollerbach SD, Van Broekhoven EH, Nat PJ, Nousianinen H, Jakkula J (2002) ERTC 7th annual meeting, Paris, 18–20 November 2002
145. Feller A, Lercher JA (2004) *Adv Catal* 48:229
146. Mukherjee M, Dan Sunciu S (2005) *World Refining* 15(4):28
147. Petkovic LM, Ginosar DM (2004) *Appl Catal A* 275(1–2):235
148. Ringelhan C, Burgfels G, Neumayr JG, Seuffert W, Klose J, Kurth V (2004) *Catal Today* 97:277
149. Bhirud V, Foley T, Pujado P (October 9–11, 2002) *Proceedings of the DMGK-conference*, Berlin Germany, p 115
150. Morigami Y, Kondo M, Abe J, Kita H, Okamoto K (2001) *Sep Purif Technol* 25:251
151. Li Y, Zhou H, Zhu G, Liu J, Yang W (2007) *J Membr Sci* 297:10
152. Kerze AD, Sato T (March 2007) ARTC conference
153. Brown SH, Waldecher JR, Lourvanij K, WO 2007058705 (2007); Brown SH, Mohr GD, Clark MC, Lawrence S, WO 2006130248 (2006), assigned to EXXONMOBIL CHEM PATENTS INC
154. Meriaudeau P, Naccache C (1999) *Adv Catal* 44:505
155. Guisnet M, Andy P, Gnep NS, Benazzi E, Travers C (1999) *Oil Gas Sci Technol* 54(1):23
156. Weidert DJ (2000) AICHE Spring meeting, March 5–7, 2000
157. Cowley M (2006) *Energy Fuels* 20(5):1771
158. Thomas PJ, Stephen PT (1993) *Oil Gas J* 24:54
159. Lillwitz LD (2001) *Appl Catal A* 221:337
160. Girotti G (2003) ERTC petrochemicals, Paris
161. Zinger S (July to September 2005) *Petroleum Technology Quarterly* 10(4):125
162. Vermeiren W, Wei DH, James RB, Andersen JM (2003) *Hydrocarbon Eng* 8(10):79
163. Koss U (May 1999) *Hydrocarbon Eng* 66
164. Ruziska PA, Steffens TR (April 2001) AICHE Spring meeting, Houston
165. Tsunoda T, Sekiguchi M (2008) *Catal Surv Asia* 12:1
166. Tallman M, Borsos S (June 2000) EPTC, Prague
167. Teng J, Xie Z (2007) ERTC petrochemical conference, Brussels
168. Gentry JC (March 2000) CMAI world petrochemical conference
169. Das J, Halgeri AB, US 2002151758 (2002); Das J, Halgeri AB, US 2003092561 (2003), assigned to INDIAN PETROCHEMICALS CORP LTD
170. Breen JP, Burch R, Kulkarni M, McLaughlin D, Collier PJ, Golunski SE (2007) *Appl Catal A* 316:53
171. Nehlsen JP, Mukherjee M (2007) AICHE Spring meeting
172. Stephen K (19 March 2007) *Chemical & Engineering News* 46 or Mukherjee M, Nehlsen J, Dixon J, Dan Sunciu G, ERTC Petrochemicals Conference 2008, Cannes
173. Chen JQ, Bozzano A, Glover B, Fuglerud T, Kvisle S (2005) *Catal Today* 106:103
174. Liu Z (2007) CTLtec 2007—4th forum on coal conversions technologies & investments, Beijing, March 14–15, 2007
175. Highlights from DICP in *J Nat Gas Chem* (2006)15(4) [<http://www.jngc.org/download/2006-04-01Highlight.pdf>] or China Chemical Reporter (6 July 2005) 16(19):15
176. China Chemical Reporter (16 November 2007) 14 or Alperowicz N (17 November 2008) *Chemical Week* 170(35):21
177. http://www.exxonmobil.com/Corporate/Newsroom/Publications/TheLamp_3_2005/story4.asp. Accessed December 2005
178. Koempel H, Liebner W (2007) *Stud Surf Sci Catal* 167:261
179. Makoto N (2005) *J Jpn Inst Energy* 84(4):335
180. Saruwatari T, Ohue N, Wakui K, Yamakawa F, Furuswa K, Umeki T, Akiyama K, Osada K, Aoi N (2007) 4th Asian DME conference, Fukuoka, Japan, p 439
181. Wang L, Tao L, Xie M, Xu G, Huang J, Xu Y (1993) *Catal Lett* 21:35
182. *Japan Chemical Week* (6 October 2005) 46(2337):1
183. http://www.mitsuichem.com/release/2008/080814e_01.htm. Accessed August 2008
184. Iaccino LL, Stavens EL, Mohr GD, Vincent MJ, WO 2006068800 (2006); Iaccino LL, Sangar N, Stavens EL, US 2007249740 (2007), assigned to EXXONMOBIL CHEM PATENTS INC
185. Honda K, Chen X, Zhang Z-G (2008) *Appl Catal A* 351:122
186. Yoshimura Y, Kijima N, Hayakawa T, Murata K, Suzuki K, Mizukami F, Matano K, Konishi T, Oikawa T, Saito M, Shiojima T, Shiozawa K, Sawada G, Sato K, Matsuo S, Yamaoka N (2000) *Catal Surv Jpn* 4(2):157–167
187. Eng C (2007) AICHE Spring national meeting, Houston
188. Martino G, Courty P, Marcilly C (1997) In: Ertl G, Knozinger H, Weitkamp J (eds) *Handbook of heterogeneous catalysis*. VCH, Weinheim, p 1801
189. van Camp C (2005) *Catal Today* 106:15
190. Spellings J (2006) *The outlook for energy: a view to 2030*. ExxonMobil, Irving. Available at: <http://www.exxonmobil.com/energyoutlook>. Accessed December 2006
191. Lovins AB, Kyle Datta E (2005) *Winning the oil end game*. Rocky Mountain Institute, Snowmass. Available at: <http://www.oilendgame.com>. Accessed December 2005
192. van der Veer J (2002) *The successful market introduction of sustainable technology*. In: EET conference, Amsterdam, The Netherlands, March 14, 2002
193. <http://www.total.com/static/fr/medias/topic3086/sem-020608-Mosconi-vision-Total-2030.pdf>. Accessed August 2008
194. http://www.bp.com/liveassets/bp_internet/globalbp/globalbp_uk_english/reportsand_publications/statistical_energy_review_2008. Accessed August 2008
195. Junginger M, Faaij A, Rosillo-Calle F, Woods J (September to October 2006) *Renewable Energy World* 130
196. Verloop J (2004) *Insight in innovation*. Elsevier, Amsterdam
197. Christensen CM (1997) *The innovator's dilemma*. Harvard Business School Press, Cambridge
198. Foster RN (1986) *Innovation—the attacker's advantage*. MacMillan, London
199. Boer FP (2005) *Appl Catal A* 280:3
200. Chesbrough H (2003) *Open innovation: the new imperative for creating and profiting from technology*. Harvard Business School Press, Cambridge
201. Huston L, Sakkab N (2005) *Harvard Bus Rev* 84:58
202. Dearing A (2007) *Science* 315:344