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Petrochemistry and Catalysis

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Abstract

The present paper deals with the current state of affairs, as well as future directions within the field of Petrochemistry, in relation to the current state and perspectives of Catalysis – the bedrock of the greater part of Petrochemistry. We have herein outlined the socioeconomic and technological premises that underscore the development of current trends in Catalysis and Petrochemistry. The areas at the forefront of progress in the Petrochemical field have been: hydrogenation, olefin transformation, and interconversion of alchyl-aromatics. The factors underpinning current development are: materials, catalyst preparation, technology, reactions and interdisciplinary cooperation.

There is great hope for progress concerning Fischer-Tropsch processes, which will be employed in the preparation of synthesis gas obtained from the 3 major sources: natural gas (steam reformation), coal and biomass. Far from having worn out its welcome, Petrochemistry is currently undergoing a boom, in line with the demands of a growing global economy, whose existence is still heavily reliant upon the progress within this field.

Of note, one cannot envision future perspectives for Petrochemistry without considering measures of environmental protection, which have emerged as a key priority since the 1980s.

Key words: *petrochemistry, catalysis, environmental protection, technology, hydrogenation, interconversion of alkyl-aromatics, olefin transformation, Fischer-Tropsch process, biomass.*

Introduction

Petrochemistry is a field of Synthetic Organic Chemistry. Starting from a few individual hydrocarbons and petroleum fractions, one can obtain through appropiate processing extremely important products for today's civilization, notably heavy duty ones such as plastics, synthetic yarns and fibres, agricultural fertilizers, surface agents, elastomers, and solvents. Deriving from Carbochemistry – historically, the basis of Synthetic Organic Chemistry - Petrochemistry endeavours to create novel Carbon atom constructs, thereby providing some of the essential conditions for the existence of modernity itself. Petrochemistry is based mainly on the use of fossil raw materials, petroleum fractions and components, as well as natural gas which, despite having the advantage of being easy to use and process, incur the disadvantage of being exhaustible and environmentally hazardous, causing widespread pollution and being chiefly responsible for the greenhouse effect.

Our aim herein is to discuss advances in Petrochemistry, as linked to those in Catalysis.

The technical advancement during the last two decades is strictly connected with the ever growing power expenditure, which is contingent upon the exploitation of oil resources. The development of Process Manufacturing, Petrochemistry and, implicitly, Catalysis, have been influenced by a series of political and economic events, as follows:

- The 1970s Oil Crises revealed that fossil fuels are a limited resource, geographically constrained to politically and economically instable regions, the consequences of this being that:
  1. The necessity of seeking regenerable resources as an alternative to fossil fuels in regions with a high degree of power consumption (such as Europe)
  2. The gradual realization, towards the end of the 1970s, of the necessity to protect the environment from human activity-derived noxious emissions. This has had an enormous impact on fuel refinement and quality conditions: noxious flue-gas emissions from fossil fuel combustion have been reduced by two orders of magnitude since the 1970s.
- The realization, during the 1990s, of the existence of Climate Change as a consequence of the Greenhouse Effect produced by emissions of greenhouse gasses, chiefly CO_2. 21% of global CO_2 emissions originate from transportation, and 8% from the oil and gas industry. Refineries on the European continent produce an annual 100 Mt CO_2, comprising 2.9% of the annual global CO_2 production (out of a total 3.5 Gt CO_2 produced in Europe from all human activities), and 3.5% from the total annual greenhouse gas emissions in Europe of 4.1 Gt.

As concerns the European petrochemical industry, the most important characteristic is the oil refinery/petrochemistry complementarity. The main petrochemical process is steam cracking of the liquid fractions of oil, especially naphtha, yielding intermediate products demanded by the Chemical Industry: ethylene, propylene, butene, butadiene, and most importantly aromatics. Approximately 23% of propylene is currently produced in refinery installations. The recovery rate of propylene in FCC has increased from 29% during the 1980s to 80% at the present time. With regards to aromatics, petrochemistry provides 79% of benzene, 41% of toluene, but a mere 25% of xylenes, the remainder being provided by refineries. Olefine demand is steadily and consistently increasing by a rate of 2.2%/year for ethylene and 2.9% for propylene. Concerning aromatic hydrocarbons, there is also a continual increase in demands, but it is widely believed that the enormous quantity obtained after gasoline reformulation cannot be absorbed in its entirety.

Petrochemistry and Catalysis

Catalysis has incontestably, played a major role during the latter part of the 20th century. Table 1 summarizes the main historical advances in the field.

With the notable exception of steam cracking, which plays a pivotal role in Petrochemistry, the importance of strictly thermal processes has continuously decreased over the span of the last 40 years, giving way to highly performant catalytic processes /1,2/. With the possible exception of basic catalysis, which is seldom used, the petrochemical industry has made current use of all categories of catalysis, thereby benefitting from all advances made in the field of catalysis during the last five decades. Important types of catalysts, mostly heterogeneous, have been: acid, metal, oxides, sulphides, bifunctional catalysts, as well as others. One must stress the importance of employing homogenous catalysis, especially for the conversion of olefines (oligomerization, polymerization, etc.).

The development of petrochemical processes

The main petrochemical processes undergoing significant progress during recent years have been:

1. *Hydrogenation*

Extremely selective hydrogenation of different petroleum fractions metallic sulphides in the presence of sulphur compounds as impurities. The metal most commonly used as catalyst is Pd

Table 1. Development of industrial processes

Year of fabrication	Process	Catalyst	Area of industry
A. Petroleum refining			
~1860	Bach distillation	-	oil & gas
~1910	Continuous distillation	-	oil & gas
1936	Catalytic cracking and Oligomerization	$Al_2O_3 \cdot SiO_2$	oil & gas
1940	Isomerization & Hydrotreating		
1942	FCC & Alkylation	$Al_2O_3 \cdot SiO_2$, H_2SO_4	oil & gas
1950	Pt-Reforming	Pt/Al_2O_3	oil & gas
1952	HDC	$NiS \cdot MoS_2/Al_2O_3$	oil & gas
1962	zeolites in FCC	zeolites	oil & gas
1964-8	zeolites in HDC	zeolites	oil & gas
1967	RCC& Bimetallic Reforming	zeolites, $Pt+Re/Al_2O_3$	oil & gas
1974	CCR reforming	$Pt+Re/Al_2O_3$	oil & gas
1976	Catalytic dewaxing	zeolites	oil & gas
1978	Automotive converter	Three way cat.	Transport
1991	Isodewaxing	Pt/zeolites	Lubricants
2002	HDS of FCC gasoline	HDS catalysts	Environmental
2008	Deep HDS of gasoline	HDS catalyst	Environmental and gas oil
B. Petrochemistry			
1875	Sulphuric acid	Pt,V_2O_5	Chemicals
1903	oxydation of ammonia	Pt gauze	Chemicals
1913	ammonia synthesis	$Fe/Al_2O_3/K_2O$	Chemicals, Fertilizers
1923	methanol synthesis	Cu, ZnO	Chemicals
1930	Fisher-Tropsch synthesis	Fe/K/CuO/Co/supp.	Petroleum
1920-40	Hydrogenation	Ni/kiselgurh, Raney	Petrochemicals, Food
1937	Etylene oxydation	Ag/Al_2O_3	Chemicals
1936-46	Oxo Processes	Co carbonyls(homogeneous)	Chemicals
1955	Stereospecific Polymerization	$TiCl_yAl(R)_3$	Chemicals
1960	Wacker Processes	$PdCl_2$(homogeneous)	Chemicals
1963	Ammonoxydation	Bi/Phosphomolibdat	Chemicals
1964-69	Oxychlorination		
1980-95	Selective catalytic Reduction of NO	VO_x,TiO_2	Environmental control
1980-95	Gasoline from MeOH process(Mobil)	zeolit	Fuels
	Sape selective of mfc.EB Petrochemicals	new zeolites	
	Fuel ethers, MTBE,etc.	H_2SO_4, zeolites	Fuels components
	Diesel fuel from syngas	Co	Fuels

for selective hydrogenation of diolefins and alkenes from the fractions C_2-C_5 olefins and hydrogenation of alkenes from aromatic fractions without sulphur compounds. In the case of olefins hydrogenation from the aromatic fractions contaminated with sulphur compounds Ni-Mo or Ni-W type sulphides catalysts are used. Little use is made of other metals, such as: Ru is used for selective hydrogenation of benzene to cyclohexane. Adding, in the 1980ties a second metal (Ag, Au mainly) to the basic metal (Pd particularly) the catalytic performances, (selectivity mainly) increased as a result. For the total hydrogenation of the aromatics, one can use Ni for benzene hydrogenation to cyclohexane with catalyst, soluble in the homogeneous phase. Ni is substituted by Pt if feeds contain only traces of sulphur. For sulphurous feeds, the catalysts are sulphides of the mentioned metal associations.

2. *Olefins transformation*

The main use of ethane is polymerization by using ever and ever more sophisticated catalytic systems. The „Old" Ziegler-Natta catalyst is at present replaced by a metallocene type catalyst with controlled stereo selectivity. The last generation of catalysts produces new polymers grades with more and more controlled properties. The light alpha olefins produced by the oligomerization process of CPChem company (Al-alkyl catalyst),of BP company (Al catalyst), of Shell company (SHOP process with two-phase catalyst based on Ni complex) produces a large of alpha olefins, from C_4 to C_{40}. The recent IFP Alpha select process mainly produces C_4-C_8 olefins used for LLDPE (Linear Low Density Polyetylene).The tendency is to produce one product. For instance, IFP Alphabutol process (Ti based catalyst), produces high selectivity 1-butene of high puryty by ethene dimerization. It is possible now to obtain 1-hexene by ethane trimerization (Cr based Phillips – catalyst) /5/. A serie of olefin conversion processes were used to render flexible the ethane/propene ratio from of Lummus (WO_3/SiO_2), IFP (Re_2O_7/Al_2O_3 catalyst). Dimersol process (IFP homogeneous catalyst) leads to butylene dimerization to isooctane used in the synthesis of PVC type plastics/5/.

3. *Alkylaromatics interconversion*

In order to maximize p-xylene production, use was made since 1960 of xylenes izomerization on industrial scale. Significant progresses were made after 1970 by replacing amorphous acid support with much more active new several types of processes followed using these two types of zeolites. Use was made on industrial scale of some bifunctional catalysts, a noble metal associated with one of these two zeolites. Both supports isomerize the xylenes, but, while mordenite great success was achieved in selectivity to convert xylenes and ethylbenzene by using new zeolites (Table no.2) for instance that of IFP (Oparis process) /8/.

Table 2. Zeolites in the oil industry catalytic processes

Zeolite structure	Zeolites	Pore apertures (Å)	Applications
BEA	Beta	7,6x6,4	EB&cumene synthesis
FAU	Y	7,4	Cracking, hydocracking of VGO
LTL	K-L	7,1	Aromatization
MOR	Mordenite	7,0x6,5	Hydroisomerization of n-P, A8 Isomerization, trasalkylation of aromatics
MFI	ZSM-5,	5,3x5,7	FCC, dewaxing, aromatization, xylene
	Silicalite	5,1x5,5	Isomerization
AEL	SAPO-11	3,9x6,3	Isodewaxing
TON	ZSM-22	4,4x5,5	Isodewaxing
MWW	MCM-22	5,5x4	EB and cumene synthesis
FER	Ferrierite	4,2x5,4	Butene isomerization
CHA	SAPO-34	3,8x3,8	Methanol to light olefins

P-paraffins, O-olefines, N-naphtenes, A-aromatics, EB-ethylbenzene, FCC-fluid catalytic cracking

These two zeolites, mordenites and ZSM-5 are used in industrial operation such as toluene disproportionation to benzene and xylenes, trasalkylation between toluene and polymethylbenzenes C_{9+}.Great progresses were recorded by using zeolites for these processes as they promote bimolecular reactions better than any other solid. The reduced size of the ZSM-5 pores recommends it for toluene disproportionation but the selective production of p-xylene. Mordenite shows a bigger aperture of the pores and can perform to other direction of reaction, not to paraselectivity. In the benzene with ethane and propene alkylation, the zeolites used after the year 1970 knew great application due to their higher performances, compared to the old catalysts. As formal selectivity is not decisive in these two reactions, use is made of zeolites with a very different aperture: ZSM-5, MCM-22, beta and Y type are used for ethane while MCM-22, beta and Y mordenite are used for propene /9/.

The technical factors of progress

The progress recorded in the petrochemical and petroleum processing industry /10/ in the last 50ties years are mainly due to the effort done in the research work carried out by several disciplines.

1. *Materials*

A class of materials that played an important part in this development are the zeolites. The number of known structures considerably increased from 30 in 1950 to 125 in 2001. Another class of materials that played an important part in the progress of the petrochemical industry is represented by metals and particularly by the multi-metals type catalytic systems, used in numerous reaction systems, as in the case of hydrogenation/4/ (Table 3).

Table 3. Principle metals used, or of potential use, in catalysis in the refining

Catalyst	Metals	Industrial use
Monometallic	Al, Ti, Ni, Zr	Oligomerization (homogeneous catalysis)
	Cr	Selective trimerization of ethene
	Fe, Co	Fischer-Tropsch
	Ni	Oligomerization (heterogeneous), steam reforming, selective hydrogenation,
	Cu	Selective hydrogenation
	Ga, Zn	Aromatization of light alkanes
	Mo, W	Metathesis of olefins
	Ru	Selective hydrogenation, Metathesis of olefins
	Pd	Hydrocracking, Selective hydrogenation
	Ir	Hydrodecyclization
	Pt	Reforming,C_4-C_6 isomerization, isodewaxing, dehydrogenation, hydrogenation
	Re	Metathesis of olefins
Association of metals	Fe or Co with Ru	Fischer-Tropsch
	Fe or Co with Pd	Fischer-Tropsch (Pd, Pt promotor of reduction
	Mo(W) with Co(Ni)	Hydrotreatement (including hydrocracking)
	Pd with Ag or Au	Selective hydrogenation
	Pt with Ge, Sn, Re	Reforming

2. *Catalysts preparation*

The modern methods for the preparation of the industrial catalysts knew progress by ensuring the monitoring and control of the active phase status of the precursors during the unit operation provided by the manufacturing process /10/. This rigorous procedure resulted in important improvements in the last decades for apparently simply to be prepared catalysts. Furthermore, in the last two, three decades, new methods were adopted, much more sophisticated ones, and they are in a continuous development, as for instance: the implementation of new active phase

precursors, the judicious use of various interactions between the precursor and the inorganic carrier, adjustment of the gaseous atmosphere to the active phase nature during the thermal treatment.

3. *Technology*

The second half of the 20ties century brought a series of technological developments, the most sustainable ones proving to be: the fluidized bed reactors at the beginning of the `40ties, reactors with continuous catalyst regeneration applied in reforming during the 1970ties, the catalytic distilling column starting with the 1980ties for etherification and alkylation of benzene, bed reactor kettle and reactor with catalyst in suspension /3/. The last type of reactor was used in 1964 in reactions regarding benzene hydrogenation to cyclohexane and was used on large scale by the Sasol process in 1993 for Fischer-Tropsch synthesis.

4. *Reactions*

The main reactions in the petrochemical industry are known since the 1950ties and the 1960ties. Starting with the 1970ties, new reactions were discovered /8/. They include methanol conversion reaction into hydrocarbons carried out by Mobil company during the 1970ties and the aromatization reactions of light alkenes (C_3-C_4) to aromatic hydrocarbons. Some reactions whose application took place after 1970 but representing well-known reactions with long life are: isobutene etherification with methanol to MTBE (methyl-tertbutil-ether) by Snamprogetti, selective alkylation of toluene with methanol (Mobil), paraffin aromatization to C_{6+} on Pt catalyst (Elf), selective dimerization and trimerization of short-chain olefins in homogeneous phase (IFP,Phillips), methatesis (IFP, Lummus), benzene hydrogenation to cyclohexane in homogeneous phase (IFP), cyclodimerization and trimerization of butadiene to cyclooctadiene (Dow, DSM and Shell) cyclododecatriene (Shell).

5. Cooperation of various disciplines

Numerous petrochemical disciplines are the fruit of the cooperation of the specialists in chemical technology, chemical engineering and catalysis. One of the most important successes achieved by catalysis in the last 25 years is the implementation of the environment protection catalysts, purification of post-combustion gases at cars.

Knowledge Development

The recorded knowledge progresses are marked by the discovery and exploitation of numerous major concepts not sufficiently exploited for a complete understanding of catalysis claimed in the last decades can be listed /10/, as follows:

- The bifunctional catalyst concept was applied in 1849 by Weisz for RC, knowing years of numerous applications in the following years;
- The distinction done for the catalysts „sensitive to structure" and those „insensitive to structure" done by Boudart in the 1960ties;
- The concept of „Hydrogen spillover" mechanism identified in the 1960ties;
- The „strong metal-support interaction (SMSI))" was known after 1970;
- The „form selectivity" concept was identified on zeolites during the 1960ties and it was fructified in various applications after 1970;
- The reagents constraint at the level of zeolitic pores was stressed by Fraissard: this constraint in the vicinity of the walls, and later, of the active centres of these solids increases significantly the concentration of the molecules in the pores and promotes the bi-molecular reactions;
- The model of the decorated edges of the CoMoS phase (decoration achieved by Co for the MoS_2 crystal edges) was outlined by Topsoe et al at the beginning of the 1980ties by the

means of Mossbauer technique. The formulated theoretical predictions were successfully compared with the experimental results obtained.

Among the contribution of introducing new concepts in catalysis and, as a consequence, in the petrochemical industry, was the refining of catalysts preparation /10/:

- The concept of „interfacial coordination chemistry (ICC)" considers that several parts are played by the contact of a solid face and the precursor solution of the metal: solid-solvent, ionic exchange, supra-molecular ligand, reagent by thsolubilizing;
- „Organo-metallic surfaces chemistry (SOMC)" is a concept applied in the heterogeneous, homogeneous and enzymatic catalysis and to monitor the preparation of bi-metal catalysts settled on the supports.

All of these concepts shows that they include, in the preoccupations of the last decades, the wish to clarify the aspects regarding the chemical reactions, such as the mechanism and the condition of solids surface. In order to illustrate this aspect, we mention the carbon-cationic intermediates knowledge for about one century of Olah /6/ research effort, or the knowledge of the reaction mechanism implying metal catalysts and metal sulphides. The progresses recorded in studying the carbon-cationic mechanisms in the acid catalysis were made possible by applying a technique such as UV, IR, NMR and mainly ^{13}C-NMR, Raman spectroscopy, mass spectral graph, etc. A decisive part in clarifying the reaction mechanisms was played by isotopic exchange.

Present Challenges

Besides the classical preoccupations of the petrochemical industry to produce intermediates and heavy duty petrochemical products, it will answer by specific means to the present challenges, namely:

1. *Environmental protection*

With regard to the first point, without going into details, two are the directions to be followed: elimination of noxios from various environments and, second, minimizing the emissions responsible for the „green house"effect".

2. Energy conservation

The current reserves of hydrocarbons (oil and gases) deposits are estimated to be depleted between 2040-2060. Looking for new energy sources is, therefore, extremely important. At present, 90% of the energy is supplied by fossil fuels. Mention is to be made that the fossil energy resource, namely, the immense natural gas reserves captured as cristalohydrates from Gtoe, on the bottom of the Artic Ocean. Natural gas seems to be the main fossil fuel of the 21st century. Carbon deposits are estimated to be about 6 times bigger than the oil and gas deposits, being exhaustible in about two centuries. By these premises, appeal is made to a higher degree to reusable resources. The renewable resources are mainly: sun energy (the photovoltaic one, mainly), wind, hydraulic, geothermal and biomass energies. Biomass remains still insufficiently exploited. It is believed that during the 21st century the renewable resources will be fully exploited.

The present impact of the petrochemical industry over the economy

With regard to the petrochemical industry outlook, the following considerations can be done:

- The annual demand of polyolefins is high and it is believed to increase during the built next years (numerous production units are expected to be in Saudi Arabia and China) with the due increase of ethane and propene output.

- The aromatic output will exceed the demand with spreading the restrictive measures on aromatic content of the fuels for the environmental protection. In Europe, in 1998, the aromatic production was $13,5x10^6$t including 50% benzene and it grew on. The aromatic surplus due to legal restrictions for fuels will be a challenge for future processes. The aromatics can be removed by hydrogenative conversion. They can also be dehydrocyclized or used for hydrogen production by gasification.
- For pollutants removal, mention shall be made on heavy metals recycle from some used catalysts. They might be replaced by using catalysts with non-noxious elements.
- An immense future is provided for Fischer-Tropsch processes which will process the synthesis gases from the three big resources: natural gases (steam reforming), coal and biomass.
- The future fuel and one of the energy sources seems to be hydrogen as it is a clean fuel.
- Greenhouse gas pollution represents the greatest danger for the human civilization.

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Petrochimia și cataliza

Rezumat

Se discuta starea de azi si perspectivele petrochimiei, in conexiune cu starea si perspectivele catalizei, componenta care asigura functionalitatea unei mari parti din petrochimie. Sunt mentionate premizele sociale, economice si tehnologice ale liniilor de dezvoltare ale catalizei si petrochimiei actuale.Directiile principale care au inregistrat progrese in petrochimie au fost: hidrogenarea, transformarea olefinelor, interconversia alchil-aromaticelor. Factorii dezvoltarii actuale sunt: materialele, prepararea catalizatorilor, tehnologia, reactiile, cooperarea intre diferite discipline.Un viitor urias se prevede proceselor Fischer-Tropsch care vor prelucra gazele de sinteza provenite din cele 3 mari surse: gazele naturale (reformare cu abur), carbune si biomasa.Departe de a-si fi epuizat potentialul, petrochimia are in prezent o dezvoltare exploziva, pe masura dezvoltarii economice care asigura civilizatia actual.Pe langa alte ramuri care asigura dinamismul progresului economiei mondiale, petrochimia ramane una din conditiile acestui progres. Pe langa liniile de dezvoltare proprii domeniului, nu se poate gandi perspectivele petrochimiei in afara masurilor de protectie a mediului, concept ce a capatat caracter prioritar din anii `80 ai secolului trecut.