RECENT PROGRESS IN THE CATALYTIC PETROCHEMICAL PROCESSES

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CATALYSIS IS FUNDAMENTAL SCIENCE, WHICH IS DEVELOPING AT THE INTERFACE OF CHEMISTRY, PHYSICS, BIOLOGY, AND MATHEMATICS

The successes of basic research in the field of catalysis have a direct effect on solving many fundamental technological, environmental and social problems that face humanity:

1. Efficient utilisation of raw materials (oil, natural gas, etc.);
2. Development of new materials and chemicals;
3. Development of systems for environmental protection;
4. Development of new sources of energy;
5. Development of new processes and technologies.

Catalytic processes form the fundamentals of modern chemical and petrochemical industries. In developed industrial countries catalytic processes create about 20% of the GDP.

PETROLEUM OR RENEWABLE (ALGAL OIL) ?

The US 2022 advanced biofuels goal is 21 billion gallons. That's 17 percent of the petroleum that the U.S. imported in 2008 for transportation fuels. It could be obtained from algae grown on land roughly the size of South Carolina or 82931 km^2.

To produce that much algal biofuel would be needed 350 gallons of water per gallon of oil or a quarter of what the US currently uses for irrigated agriculture.

Estimated growing algae uses anywhere between 8.6 and 50.2 gallons of water per mile driven on algal biofuel.

The corn ethanol can be made with less water, but showed a larger usage range: between 0.6 and 61.9 gallons of water per mile driven.

Previously published data indicated conventional gas uses between about 0.09 and 0.3 gallons of water per mile.

REFERENCE: Mark S. Wigmosta, Andre M. Coleman, Richard J. Skaggs, Michael H. Huesemann, Leonard J. Lane. National Microalgae Biofuel Production Potential and Resource Demand. Water Resources Research. Published online April 13, 2011

BASIC FEATURES AND TENDENCIES IN CHEMICAL INDUSTRY DEVELOPMENT

1. Chemical industry is developing at a steady rate worldwide. In EU chemical industry in 2007 has 2.1% growth. Recent world crisis, however has a strong negative impact

2. The assortment of manufactured articles is constantly enlarged and renewed (now they are about 200 000). 65% of the chemical production is being transferred to other branches for secondary processing.

3. Special attention is being paid to the development of new technologies and research-consuming production at mild working conditions with a high degree of processing, low consumption of materials and high prices.

4. Under the conditions of rapidly outdated technological processes the market for selling licenses and 'know-how' becomes very important as a profitable sphere for capital investment.

5. Rapid introduction of environmentally friendly waste-free technologies

NEGATIVE FACTORS INFLUENCING THE DEVELOPMENT OF CHEMICAL INDUSTRY

1. There exists a permanent upward tendency in energy and raw materials prices, accompanied by deteriorated raw materials quality. As a result, desired products with specific properties require new complex technologies, entirely novel technological equipment, which is constantly becoming more complicated and expensive.

2. The necessity to invest considerable money in equipment and technologies for environmental protection. Nowadays the expenses for purifying facilities amount to an average of 20% of total capital invested.

3. There is a continual increase in scope and mostly in value of the research and development activities that ensure a high level and quality of new technologies, materials and information.

4. There are limitations in maximum dimensions of industrial units (reactors, columns, etc.), owing to the properties of construction materials.

OVERCOMING THE INFLUENCE OF NEGATIVE FACTORS CAN BE ACHIEVED BY:

Developing novel technologies, engineering solutions, methods and products, elaboration and innovation of new highly selective and active catalysts in industry and wide application of automation and computerization.

Availability of highly qualified scientists, engineers, industrial experts and industrial personnel.

IMPORTANCE OF THE BASIC CATALYSIS RESEARCH FOR CHEMICAL INDUSTRY

Industrial catalysis is research-intensive industry. In US it spends approximately $17.6 billion annually on research and development.

The success chemical industry in US and other developed countries is largely attributable to breakthroughs in catalysis science and technology.

IMPORTANT DIRECTIONS OF BASIC RESEARCH IN CATALYSIS

- Studies of catalytic reaction mechanisms;
- Catalytic reaction kinetics under steady and non-steady conditions;
- Physical chemistry of surfaces and solid states;
- Application of quantum chemical methods in catalytic research;
- Non-linear phenomena in catalysis
- Theory of catalyst selection and prediction of catalyst activity
- Novel catalyst supports, adsorbents;
- Development of catalysts on the basis of new materials with pre-set qualities: new micro and mesoporous materials, semiconducting materials, perovskites, layered-structure compounds, colloidal metals, amorphous metals, superconducting polymers, immobilised complexes, membranes, fibrous materials, solid superacids and bases, intercalation compounds, etc.
- Catalyst deactivation;
- Homogeneous catalysis and single site catalysis

CATALYSTS MARKET

For all types of chemical catalysts, it is estimated a total 2010 market of almost $2.7 billion, expecting to grow at annual rate of about 2.5% to more than $3 billion in 2015.

Petroleum refining catalysts is a smaller market at $1.4 billion in sales in 2010, but also are predicted to grow at about 2.5% to more than $1.6 billion in 2015.

Among the catalysts produced for the chemical and petrochemical industry, 49% are used for polymerisation, 18% oxidation processes, whereas 15, 10 and 8% go to organic synthesis, Fischer-Tropsch synthesis and hydrogenation-dehydrogenation reactions.

Growth is spurred by increasing demand for reformulated and other less-polluting gasolines, plus new regulations calling for drastic reduction in sulfur content in gasoline and diesel fuel.

Distribution of the catalyst consumption on different economic regions

	USA	European Union	Japan	World total
Oil refining	33.0	36.0	37.0	34.5
Chemical industry	37.0	18.0	19.0	31.0
Environmental protection	30.0	46.0	44.0	34.5

Structure of catalyst consumption in USA in 10^6 $ US

	1989	1994	2000
Industry general	25	75	300
Automotive industry	570	1125	1700
Chemical industry	570	685	850
Oil industry	620	735	850
USA	1785	2620	3700
World total	5100	7300	10600

Characteristics of the Industry for Catalysts Production

1. Production of catalysts has a strategic importance for the country economy.
2. Catalysts are so-called performance chemicals, which enhance the processing of other chemicals.
3. The catalyst production industry has a very complex multistep character.
4. The companies, which produce catalysts, have to support big research teams and extensive multimillion R&D programs.
5. The catalyst production is a very dynamic branch of the chemical industry.

6. In order to be able to produce various types of catalysts, the units for catalyst production should be very versatile.

7. The absolute amount of produced catalysts is not large and the catalyst production industry cannot be very profitable.

8. For selection of suitable catalysts, catalyst quality plays a decisive role, while catalyst price has only secondary importance.

9. About 30% of the newly developed catalysts and catalytic processes are not offered on the market in order to preserve the competitiveness of the owner.

10. Catalyst production industry is not an environmentally friendly industry.

11. A very high qualification of personnel is required. As mentioned above, the catalyst producing companies are located in highly developed industrial countries, since they need highly qualified staff and well-organised R&D facilities.

12. In contrast to other so-called ‘high tech’ industries, new catalyst producers are a rare phenomenon on the market, due to significant barriers. These involve a risk during introduction into practice associated with very high expenses for development, testing and production of a sample batch, probable losses in case of low quality production, conservative consumers and necessity of industrial references to catalyst quality, and a lot of expenses for R&D activities

Basic Tendencies in the Industrial Catalyst Production

Tendencies in the development of industrial catalyst production are determined by the modern state of chemical, petrochemical and oil-processing industry; it is affected by economical, technological, scientific, and other factors.

1. The endeavour of all big companies to create their own catalyst production is due to the fact that those who dominate in the production of catalysts determine the level of technical progress in industrial branches related to catalytic processes. Today there is no company that controls more than 10% of the catalyst market. The world catalyst trade is about 10 billion US dollars, which is only about 0.15% of the total volume of chemical trade.

2. Greater and greater parts of the catalysts will be produced on special orders of certain consumers. Most often consumers develop catalyst production technologies themselves.

3. The extension of produced catalyst nomenclature includes especially catalysts for new chemicals production and novel processes based on new types of raw materials.

4. In 1984, the producers offered about 700 catalysts to the oil processing industry. About 150 new catalysts were innovated in the next year, as a result of which the total number of catalysts became near 900. Among the newly introduced catalysts, there are 90 types that were designed for the process of fluid catalytic cracking. Other 111 new types of catalysts were introduced in 1986. The largest share falls again to the catalytic cracking catalysts, their number being 71. Now over 1200 types of catalysts are offered.

5. Among the catalysts produced for the chemical and petrochemical industry, 49% are used for polymerisation, 18% - oxidation processes, whereas 15, 10 and 8% go to organic synthesis, reactions involving CO and H_2 and hydrogenation-dehydrogenation reactions.

6. Expansion of assortment and volume of produced catalysts to meet the demands of environmentally protection technologies.

7. Promoting the variety of catalysts for fine chemicals synthesis.

8. Development and production of catalysts for new fields of application: catalytic combustion, gas sensors, fuel components, photocatalysis, etc.

9. Development of catalysts based on the new materials with pre-set qualities: new micro and mesoporous materials, semiconducting materials, perovskites, layered-structure compounds, colloidal metals, amorphous metals, superconducting polymers, immobilised complexes, membranes, fibrous materials, solid superacids and bases, intercalation compounds, etc.

10. The complexity of catalyst manufacture poses very tough requirements to the quality of the raw materials, technological parameter observation, and final product quality.

11. A very high qualification of personnel is required. As mentioned above, the catalyst producing companies are located in highly developed industrial countries, since they need highly qualified staff and well-organised R&D facilities.

12. In contrast to other so-called ‘high tech’ industries, new catalyst producers are a rare phenomenon on the market, due to significant barriers. These involve a risk during introduction into practice associated with very high expenses for development, testing and production of a sample batch, probable losses in case of low quality production, conservative consumers and necessity of industrial references to catalyst quality, and a lot of expenses for R&D activities.

13. All leading chemical companies, which do not produce catalysts as commercial products, have their own research programs in the field of catalysis and production of catalysts, designed for their own processes, which enable them to achieve a break-through on the market.

14. Because catalyst quality is the critical point for installations to operate, some 30% of the used catalysts are produced only to cover producers' own needs. The remaining 70% are offered on the market, half of them being customer ordered or produced in accordance with a recipe, submitted by the user. Preservation of technological secrets is the critical issue in business dealings between user and producer.

15. There are 36 catalyst-supplying companies in the USA. Eight companies from these produce catalysts for chemical and petrochemical industry and only three companies also produce catalysts for environmental protection. A similar situation exists in the European Union. The catalyst production in Japan is concentrated in the hands of some ten companies.

16. The great variety of catalysts requires a flexibility of the production facilities. It means that a whole series of catalyst articles should be produced on the same technological line. This circumstance poses very high requirements toward engineering design of technological lines, apparatus performance, and other technological equipment in the production unit.

Industrial catalysts are "performance chemicals" which should be offered on the market together with information about:

1. Reaction kinetics and kinetic model;
2. Catalytic activity and selectivity;
3. Catalyst pre-treatment regimes;
4. Catalyst deactivation kinetics;
5. Catalyst regeneration regimes;
6. Catalyst lifetime: stability, duration of operation, thermal stability;
7. Physical and mechanical properties: strength, abrasion ability, hardness, surface area;
8. Hydrodynamic characteristics of the catalyst grain and of the catalyst bed in the reactor;
9. Safety transition regimes in cases of industrial accidents;
10. Economy of the process.

Major characteristics of fine chemicals industry

- 1. Scale of production is below 5000 t/y
- 2. Expensive raw materials
- 3. Stringent product specifications
- 4. Multi-step complex technology
- 5. Big amount of by-products > 20-100 kg/kg final product
- 6. Problems of effluent disposal, safety, health hazard corrosion
- 7. Product price > US $ 50 per kg product
- 8. Users buy fine chemicals for what they are than for any function that they perform.
- 9. Major reasons for high spending are R&D of technology, raw material production, and development of process chemistry
- 10. Major sources of profit are production of advanced intermediates and bulk compound production.

Sustainable chemistry (green chemistry) characteristics

1. New products;

2. New feedstock, reagents, products;

3. New catalysts;

4. New engineering approaches and process control.

Principles to follow for sustainable (green) chemistry activity

1. Do not make waste;
2. Increase carbon efficiency of the desired product;
3. Avoid production of hazardous materials;
4. Products should preserve function at reduced toxicity;
5. Reaction products should be environmentally acceptable;
6. Avoid use of auxiliary substances or use innocuous one;
7. Energy consumption should be minimized;
8. If possible try to use renewable raw materials;
9. Avoid unnecessary modification of the process;
10. Use highly active and selective catalysts;
11. Use most advanced and fast analytical control;

GENERAL SCHEME OF PETROCHEMICAL INDUSTRY

Main source of C and H_2	Produced by	Main 1st generation	Main 2nd generation	Products families
Crude via refinery	Steam cracker	Ethylene	Vinyl chloride	Detergents
			Ethylene oxide	
		Propylene	Ethylene glycol	Pharmaceuticals
			Methylmetacrylate	Fertilizers
		Butylenes		Polymers
			Propylenoxide	
		Butadiene	Acrylonitrile	Elastomers
			Caprolactame	
		Benzene	Styrene	Fibers
			Phenol	
		Toluene	Cyclohexanone	Adhesives
			Formaldehyde	
		Xylenes	Terephtalic acid	Pigments
			Toluene diisocyanate	Paints
Natural gas	Steam reformer	Ammonia		Explosives
		Methanol		
		Hydrogen	Carbon black	

TYPICAL CATALYSTS USED IN PETROCHEMISTRY

- Supported noble metals: Pt, Pd, Rh, Ru, Re, Pt-Re;
- Supported transition metals: Ni, Co, Fe, Cu, Mo;
- Catalyst supports: γ-Al_2O_3, SiO_2, TiO_2, activated carbon, zeolites;
- Raney type metal catalyst: Ni, Cu-Ni;
- Oxide catalysts:Cr_2O_3, Fe_2O_3, Al_2O_3-Cr_2O_3, Fe_2O_3-K_2CO_3-Cr_2O_3, $Ca_3Ni(PO_4)_3$, $Bi_2O_3MoO_3$, Bi-Co-Fe-Sb-Mo-K oxide catalysts;
- Sulfides catalysts: MoS_2/Al_2O_3, WS_2/Al_2O_3, NiS/Al_2O_3, CoS/Al_2O_3;
- Micro- and mesoporous materials.

Reactors used:

Liquid phase reactions: batch reactors, stirred tank reactors, slurry reactors

Gas phase reactions: tubular reactors, multitray fixed bed reactors, moving bed reactors

MOST IMPORTANT PROCESSES IN PETROCHEMISTRY

– Selective oxidation

The total volume of produced intermediates is 215 million tons per year worth of roughly 100 billion $ US.

– Hydrogenation and dehydrogenation

These processes are used to produce about 20% of fine chemicals and pharmaceutical products.

– Organic synthesis
– Ammonia synthesis, Methanol synthesis
– Hydrogen production
– Ammoxidation, Oxychlorination
– Etherification, Esterification

PETROCHEMICAL INDUSTRY– GENERAL REMARKS

1. The yields of useful products of many current commercial processes like propylene oxide, formaldehyde, and 1,4-butanediol are low.

2. In some cases the selectivity towards the main product is low and significant amounts of co-products are produced (e.g., acetone is produced in phenol production from cumene, and t-butanol is produced in propylene oxide production from propylene and isobutane).

3. The economics of the production of many products like acrolein, acrylic acid, methanol, acetic acid, phthalic anhydride, linear alcohols could be considerably improved if they could be produced from paraffins instead of olefins.

4. Many important direct catalytic processes can be introduced in the industrial practice if they required low investment and low operational costs and proceed with high yield and selectivity.

Methane activation to ethylene, methanol, or formaldehyde;
Ethane to ethylene, ethylene glycol, acetic acid, or acetaldehyde;
Propane to propylene, acrolein, acrylic acid, or 1,3-propane diol;
Butane to butene, 1,4-butane diol, or maleic anhydride;
Isobutane to methacrylic acid,
Linear long-chain alkanes to the alpha olefins or linear alcohols;
Benzene to phenol

5. Due to introduction of new technologies, including new computer developments, time-to-market for new products is reduced, production schedules and delivery time are shortened and logistics for delivery were improved. Many of these changes lead to lower production costs and improved environmental performance.

6. The chemical industry, especially the producers of high-profit fine chemicals, specialty chemicals and pharmaceuticals are facing with increasing very strong global competition.

7. As a consequence, catalytic scientists are increasingly under great pressure to accelerate the identification of new catalysts and catalyst compositions.

Major goals for improving the process of introduction of catalytic technologies in industry can be formulated as:

- Acceleration of the development new catalysts and new catalytic processes;
- Development of catalysts with selectivity approaching 100 %.

Achieving these goals will require following major tools:

- Combinatorial algorithms for high-throughput experiments;
- High-throughput synthesis of catalysts ;
- High-throughput catalyst testing;
- New fast analytical methods and instruments;
- New techniques for in-situ catalyst characterization;
- Catalyst design using both empirical and fundamental knowledge;
- Deep understanding of the reaction mechanisms.

Assessment of the applicability of the newly developed catalytic technologies should be based on several criteria:

- Technological characteristics of the new development;
- Engineering viability;
- Impact of technology advances;
- Timeliness of the impact;
- Probability of successful development;
- Cost of investment relative to the potential benefits;
- Market niche for the new products;
- Environmental impact of the technology.

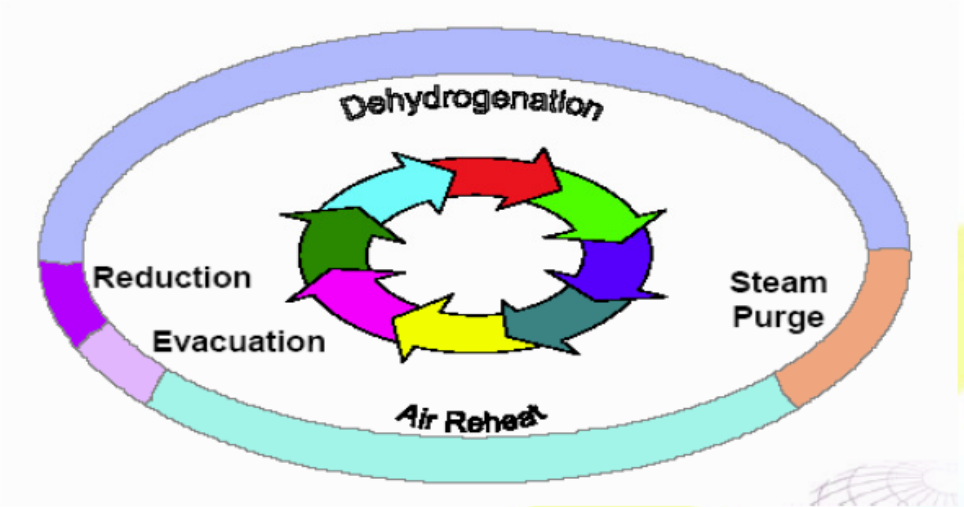
	PROPANE DEHYDROGENATION TECHNOLOGY	
	CATOFIN by LUMMUS	OLEFLEX by UOP
Reactor system	8 Horizontal fixed beds reactors in parallel	4 Vertical moving beds reactors in series
Catalyst; Catalyst life; Spent catalyst	Chromium oxide; over 3 years Spent catalysts dump-out and land filling	Pt catalysts; over 5 years Spent catalysts dump-out and Pt recovery
Catalyst regeneration; Catalyst regeneration cycle; Cycle time	In situ, Cyclic regeneration 10-20 min	Continuous catalyst regeneration 7 days
Operation conditions: temperature and pressure	600^{o}C, 0.3-1.0 bar	630-650^{o}C, 1.2-2.0 bar
Conversion Selectivity	45-50% 80-90%	35-40% 80-90%
Advantages	No separate facility for catalyst regeneration No H_2 recycle gas High conversion Lower C_3 consumption Lower catalyst cost	Safe and reliability in operation Longer catalyst life High on-stream operation
Disadvantages	Frequent changes of reactor operation conditions 12 min Use of chromium for catalyst	Complicated reactor design Separate facility for catalyst regeneration
Commercial plants	7 Plants	9 Plants

Oleflex operation cycle

1st step	Dehydrogenation
2nd step	Coke burning of the catalyst
3rd step	Pt redistribution oxidation and chlorination
4th step	Drying of catalyst
5th step	Reduction of the catalyst in moving system

III. PDH Process Technologies

CATOFIN Reactors Operation Cycle



IMPORTANT PROBLEMS IN PETROCHEMICAL CATALYSIS

Alkenes have substantial value as chemical feedstock, whereas alkanes primarily have fuel value.

The single greatest challenge in using hydrocarbon as raw material in petrochemistry is the selective, economical activation of light hydrocarbons to produce a single, more valuable product.

One of the most probable approaches is conversion of a low-energy material into a high-energy material by oxidation. For example introducing novel pathways for the selective conversion of methane/ethane to higher molecular-weight products: methane to methanol; methane to ethylene; ethane to ethylene and methane to higher molecular-weight molecules.

IMPORTANT PROBLEMS FOR CATALYSIS R&D IN PETROCHEMISTRY

Fischer-Tropsch Synthesis;
Hydrogen production;
Methanol conversion to useful chemicals;
Alkanes alkylation with carbon monoxide
Oxidative coupling of methanol to ethylene;
Direct synthesis of hydrogen peroxide;
Synthesis of amines from olefins and ammonia
Synthesis of alcohols from olefins and water;
Oxidation of benzene to phenol;
Low molecular alkene epoxidation;
Low-temperature dehydrogenation of light alkanes;
Propane oxidation to acrolein and acrylic acid;
Primary oxidation of alkanes to alcohols and diols;
Production of motor-fuel alkylate;
Technology for elimination use of cyanides, phosgene, halogens.

CONCLUSIONS

1. Industrial catalytic technologies belong to the category of the so-called ‘high tech’ industries. They are of strategic importance for any developed country.
2. It should be emphasised that without intensive research and development activities it is impossible to reach and maintain a high progress chemical industry

3. In view of the above considerations, industry should play the leading role, which is especially important. As one of the chief employers and main consumer of research products, it is expected that industry will be the main initiator that will understand and define existing and future problems and find their solution. It has to be one of the major provider of funding for R&D teams.

4. The progress of chemical industry depends on its attitude toward chemical science and interest in research work, while the good shape of science is determined by the fact how far it turns its face to the needs and prospects of developments in the industry.