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PERSPECTIVES IN CATALYSIS

THE DYNAMICS OF INNOVATIONS AND DEVELOPMENT IN CATALYST BASED TECHNOLOGIES. CATALYTIC REFORMING, CRACKING, AND AMMONIA PRODUCTION

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It is proposed that major progress in catalysis occurs in the step-wise manner. Breakthroughs which revolutionize technology occur every five to ten years. After such a breakthrough there are extended periods during which fundamental research investigating the underlying phenomena leads to better understanding and gradual improvements of the new technology. During such periods it may appear that a field or even the whole of catalytic technology is relatively mature. This is, however, a misconception because history teaches us that fields which appear mature are suddenly revitalized by a major new discovery. This is illustrated with three case histories.

For at least 50 years, between 1935 and 1985, catalysis has been one of the most important research and development areas influencing technology. Its importance has been expressed by several authors, both in terms of products produced and of monetary returns. Thus, it has been said that more than 30% of all non-agricultural products produced in the United States have seen one or more catalytic steps in the course of their production and that the world value of products from chemical catalytic technology is probably in excess of $1 trillion per year [1].

Looking at the major achievements of catalytic technology during these 50 years, it becomes apparent that there are periods of major discoveries which revolutionize industry, often an industry which was considered mature. There are also periods in which progress in technology is being made by a series of improvements in catalysts and processing. Each improvement is a relatively small step forward, but in toto they amount to large scale changes in technology. Thus, we have a somewhat step-wise progression with big steps at the time of major new discoveries and subsequent slower advances. While the breakthroughs are very frequently occurring on the basis of intuitive or empirical research, the subsequent advances in any technology are most often based on fundamental research leading to an understanding of the phenomena causing the breakthrough. This research then produces the knowledge base that permits new discoveries to occur.

Table 1 shows major catalytic innovations of a breakthrough type during the period 1936 to 1986.

Table 1 [2]
Major catalytic innovations, 1936–1986

Year of first commercialization	Event	Area of industry	Type of invention (P-new process C-novel catalyst PR-new products)
1936	Catalytic cracking	Petroleum	P
1941	Fluid-bed technology	Petroleum-petrochemicals	P+C
1942	Moving bed catalytic cracking	Petroleum	P+C
1942	Paraffin alkylation	Petroleum	P+C
1950	Catalytic naphtha reforming (Pt catalysts)	Petroleum	C
1951	Hydrocracking	Petroleum	P
1955	Ziegler–Natta polymerization	Polymers	P+C + PR
1960	Actetaldehyde from ethylene	Chemicals	C
1963	Low-pressure ammonia synthesis	Fertilizer, chemicals	P+C
1963	Ammoxidation	Chemicals	C
1964	Zeolite catalysts	Petroleum-petrochemicals	C
1964	Oxychlorination	Monomers	C
1966	Olefin disproportionation	Petrochemicals	C
1967	Bimetallic reforming catalysts	Petroleum	C
1968	Shape selective catalysis	Petroleum-petrochemicals	C + PR
1970	Low pressure methanol synthesis	Chemicals	C
1976	Emission control catalysts	Automotive	P
1978	Methanol to gasoline	Synfuels	P
1982	Crystalline alumino phosphates (Alpos)	Adsorbents	C
1984	Silica-alumino phosphates (Sapos)	Chemicals	C
1986	Boro silicates	Chemicals	C

While this list focusses on areas most familiar to the author, it indicates that on average a major discovery opening up a new field of technology seems to occur about one every three to five years. The importance of such breakthroughs is, however, often not recognized until several years after the event. In the meantime, improvements in previous discoveries' findings will continue. Major breakthroughs often have occurred and can be expected to continue to occur in fields which have been considered mature and subject only to marginal improvements.

Revolutionary inventions in catalysis fall into two categories. One is the introduction of totally new process and/or product concepts. Examples of such events are the Ziegler–Natta polymerization and the Mobil MTG process. The other category involves changes in existing technologies, particularly the introduction of novel catalysts which give greatly different product distribution and yields and which can revolutionize a "mature" industry. This paper is primarily concerned with the second category which is also easier to commercialize than the first one because it usually does not involve major engineering risks with high capital investments.

In the following, three case histories will be presented, each of which relates to discoveries in a well established area of technology, discoveries which resulted in a sudden new interest and explosive increase in number of operating units and size of production.

CATALYTIC REFORMING

In 1939 a first catalytic process for upgrading low octane number naphthas was introduced. This was the Fixed Bed Hydroforming process and the first unit went on stream in November 1940 at the Pan American Refining Company, Texas City, Texas. The commercial catalyst comprised about 9 wt% molybdenum oxide deposited on 2 to 4 mesh activated gel alumina granules [3]. Operating conditions for fixed bed hydroformers were 850 to 1000 °F, 150 to 300 psig and space velocities of about 0.5 V/V/hr. Typical units consisted of four reactors with one pair of two units in series on stream and the other pair on regeneration. Regeneration was required after every four to eight hours on stream. A heater between the two reactors compensated for the temperature drop due to the endothermic dehydrogenation reactions. Seven fixed bed hydroforming units with a total capacity of about 70,000 barrels per day were built prior and during World War II. They were primarily needed to produce toluene for TNT and high octane aviation blending components, using as feed a C_7 to C_8 boiling fraction. A fluid bed version of the hydroforming process was introduced by Standard Oil Company of Indiana. The unit was short-lived because of a major industrial accident.

After the war, no more hydroforming units were built, although most refiners had to meet the challenge of competitors on motor fuel quality and the need to produce fuels of sufficiently high octane numbers to meet the requirement of post war automobiles. In 1949 Universal Oil Products Company announced the Platforming process which was shortly followed by other processes such as Catforming, Houdriforming, TCR, Ultraforming, Power Forming, etc. All these processes used platinum on alumina catalysts with the alumina having increased acidity due to chlorination or being substituted by silica-alumina. The major advantages of these processes was that they could operate for long periods on stream without regeneration, in many cases one to two years, and, therefore, did not require alternate reactors which were on regeneration. Also, these catalysts possessed much higher hydrogenation-dehydrogenation activity than the metal oxide catalysts and consequently permitted operation at four to six times the space velocity of the earlier process. Gasoline quality as expressed in octane numbers was higher and C_{4+} gasoline yields was larger than for the fixed bed hydroforming process. This is shown for one type of naphtha in table 2.

Table 2
Catalytic reforming East Texas Virgin heavy naphtha

	Fixed bed hydroforming	Catforming
Temp., °F	930	928
Pressure, psig	200	500
LHSV, vol/vol/hr	0.5	3.0
C_{4^+} gasoline yield, vol%	85.2	93.0
Octane number, F-1 clear	91.4	94.4

Operation was at higher pressures and the active hydrogenation component kept the catalyst free from large coke deposits. The result of this invention was that over 200 reforming units were built in the United States alone and that reforming became the second or third largest refinery process.

From 1950 to 1967 many improvements were made in catalytic reforming both from a catalyst and from a processing point of view, but these were gradual improvements based on better understanding of the reactions. Only in 1967 was there another major step forward with introduction of bimetallic reforming catalysts.

This major change had been the development and introduction of catalysts containing a mixture of platinum and rhenium as hydrogenation-dehydrogenation components in combination with the halogenated alumina support. These catalysts are described in a patent issued to the Chevron Research Company and catalysts of this type were promptly produced by several catalyst manufacturers. Their great advantage was in the stability, which is illustrated in fig. 1 for

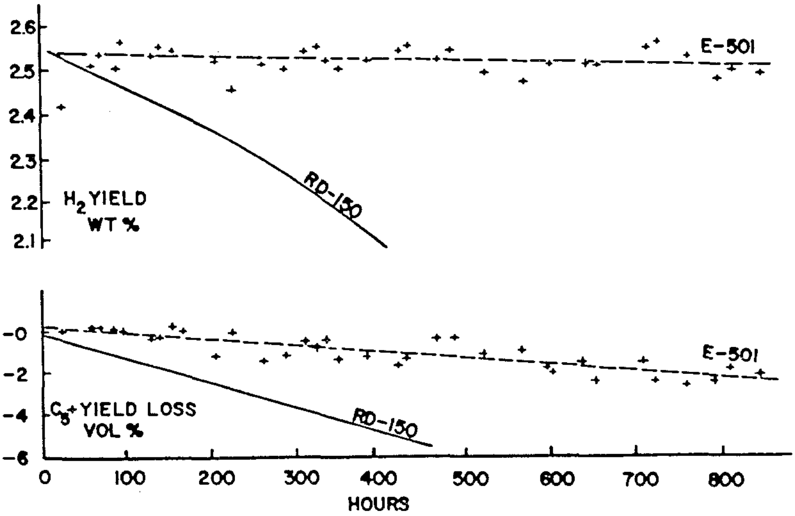

Fig. 1. Naphtha reforming at ultra-severe conditions to obtain 104F-1 octane number with Pt-alumina (RD-150) and Pt-Re-alumina (E-501) catalysts.

operations at extremely severe conditions (low pressure and high temperature) [4]. This figure shows that a conventional platinum-alumina catalyst (RD-150) deactivates relatively fast under these severe conditions while the platinum-rhenium catalyst (E-501) is stable over long periods of time.

This stability of bimetallic catalysts has permitted lowering the operating pressure without rapid loss of catalyst activity due to coking. Lower pressure resutls in greater aromatics formation and higher octane number due to thermodynamic considerations.

CATALYTIC CRACKING

The first large scale commercial catalytic cracking units were built in 1936 to 1938 and were fixed bed Houdry units. They were cyclic operation units utilizing the exothermic heat of regeneration to compensate for the endothermic cracking reaction. The catalyst, usually an acid activated clay or silica-alumina, was contained in numerous parallel tubes suspended in a molten salt heat exchanger. The great demand for high octane gasoline during the Second World War resulted in an explosive growth of catalytic cracking and in rapid engineering improvements of the original Houdry fixed bed units by installation of moving bed and fluid bed units.

In parallel with the development of new unit designs there were improvements in catalyst performance. By the mid-1950's, catalytic cracking was considered to be a "mature art." This belief was shattered when zeolite catalysts were introduced by Mobil Oil Corporation in 1964. Until then there had been a belief that crystalline materials could not make as good catalysts as amorphous substances. It was expected that they could not stand the high temperatures required in catalyst regeneration and that a broad pore size distribution was necessary to obtain the desired results. While workers at Union Carbide Corporation had pointed out in 1960 that crystalline alumino silicates could promote acid catalyzed reactions such as paraffin isomerization, Y-type zeolites became practical catalysts only after the discovery that they could be stabilized by the introduction of rare earth oxides. It rapidly became obvious that the new catalysts possessed much greater activity than the previously used amorphous silica-alumina and

Table 3 [6]
Approximate temperature for obtaining appreciable (~ 5–10%) n-hexane conversion

Catalyst	Major cations exchanged into catalyst	Temperature °C	Alpha
SiO_2-Al_2O_3 (amorphous)	–	540	1.0
Faujasite (Y-zeolite)	Ca	530	1.1
Faujasite	NH_4	350	6400.0
Faujasite	RE	< 70	> 10000

Table 4
Yields and composition of products from cracking of California Gas Oil

	Amorphous SiO_2-Al_2O_3	RE exchanged Y-zeolite	Δ increase Zeolite/ SiO_2-Al_2O_3
Conversion, vol%	36	36	0
C_5+ gasoline, vol%	22	29	7
C_4 gasoline, vol%	9	6	−3
Dry gas, wt%	5.2	3.5	−1.8
Coke, wt%	4.3	1.4	−2.9
Gasoline composition:			
% Paraffines	8.7	21.0	12.3
% Cycloparaffins	10.4	19.3	8.9
% Olefins	43.7	14.1	−29.1
% Aromatics	37.3	45.0	7.7
Octane number of gasoline, F-1	85.2	90.1	

more important that the catalysts produced less coke and much more gasoline from a gas-oil feedstock. In addition, the gasoline had a higher octane number because of the increase in aromatics content and an increase in isoparaffines with a reduction in olefins.

The zeolite catalysts were prepared by incorporating 10 to 20% of the crystalline alumino-silicate in a matrix of silica-alumina or acid activated clay. The enormous increase in catalytic activity for faujasite type cracking catalysts containing rare earth is illustrated in table 3. Full advantage of this increase in activity could not be taken because it would have required a complete redesign of units to keep them in heat balance [5].

However the increase in desirable cracked products and the composition and octane number of the gasoline as illustrated in table 4 presented a breakthrough achievement.

It meant that not only could a better product be marketed, but that the same amount of gasoline could be produced from less crude oil, thus increasing the capacity of existing catalytic cracking units and reducing the requirement for cat cracker feed. It has been estimated that in the 20 years since introduction of these new catalysts the savings in crude oil alone have amounted to more than $20 billion. The data in table 4 are for equal conversion in order to show the differences in product distribution, but in fact the higher activity of the zeolite catalyst permitted a satisfactory operation at higher conversion than previously practiced.

The success of this major discovery in cracking catalysts resulted in the rapid conversion of better than 90% of the world's catalytic cracking to the new type of catalyst. Since the general acceptance of zeolite containing catalysts for catalytic cracking, gradual changes and improvements in catalysts have been made to better comply with the demands of the changing market. However, the art of catalytic cracking has again been considered relatively mature, waiting for the next major breakthrough.

AMMONIA PRODUCTION

The catalytic synthesis of ammonia precedes the First World War with the first commercial plant being built in Germany in 1913. Even though the use of ammonia and ammonia derivatives continued to increase quite rapidly because of the demand for ammonia and urea as fertilizers, only relatively minor improvements were made in the synthesis procedure for almost 50 years. Synthesis catalysts were essentially iron oxides containing alkali promoters and alumina and calcium oxides. Nitrogen for the synthesis was obtained by air liquefaction and hydrogen primarily by steam reforming or partial oxidation of hydrocarbons. Synthesis conditions were governed by thermodynamic considerations requiring high pressure and relatively low temperature. A revolutionary breakthrough occurred about 1960. ICI in England and M.W. Kellogg Company in the United States separately developed and later joined in commercializing a process with major mechanical as well as chemical advances.

The hydrogen production by steam reforming of naphthas and gas oils could only be carried out at pressures below 100 psi. The common catalyst comprising nickel on an inert carrier did not permit operation at higher pressures because of the rapid formation of coke under these conditions. It was found that the addition of alkali to the nickel catalyst enabled one to operate at pressures as high as 600 psig. The alkali promoter catalyzed the gasification by water of any coke formed and this reaction was faster than the rate of coke deposition. The ability to produce hydrogen at pressures of approximately 500 psig made possible a major engineering improvement in the ammonia synthesis step. Whereas two or

Table 5
Ammonia plants

Year	Maximum size of single train plant tons/day
1940	100
1945	200
1950	250
1955	300
1960	350
1965	700
1968	1500
1970	2000

three compression stages had been required to carry out the synthesis at 2500 to 3000 psig with low pressure hydrogen, with hydrogen available at 500 psig only one compression stage was needed to 2500 psig. It also became possible to go from reciprocal compressors to centrifugal compressors with much greater capacity. Commercial operation was now being carried out at somewhat lower pressures than previously used namely in the order of 2000 psig even though equilibrium conditions are somewhat less favorable there than at higher pressure. However, the resulting loss in conversion was overcome by savings in operating and utility costs. Reducing pressure from 3000 to about 2000 pounds also substantially decreased reactor wall thickness and with it investment costs.

The tremendous effect of the combined chemical and engineering breakthrough which occurred about 1960 is shown in table 5.

Whereas the largest individual plant size had increased between 1940 and 1955 from 100 to 300 tons/day capacity, by 1968 plants were being built that had a capacity of 1500 tons/day and by 1975 of over 2000 tons/day in individual trains. Thus, by 1970 it was possible to build a single reactor plant producing approximately seven times as much ammonia as had been possible in 1955. The result was a very marked decrease in the cost of ammonia which in constant dollars dropped by more than one-half. This in turn spurred an enormous expansion of ammonia and with it of food production. Over 75 large scale new ammonia plants were built after 1965.

FUTURE BREAKTHROUGHS?

The three case histories presented here are typical of many other areas of catalyst based processes which were revitalized by periodic breakthroughs while they were previously considered as mature fields. While it is not possible to predict where such breakthroughs may occur in the future, one can be sure of their occurrence and relative frequency. There are many areas in which novel discoveries would be of great technological value, only a few of which are listed below.

In petroleum refining, still a major industry of vital importance heterogeneous catalysts for olefin-paraffin alkylation giving high octane isoparaffins and having no environmental or toxicological problems would catch on very fast. Already there is a trend towards the use of oxygenated hydrocarbons such as ethers or alcohols as octane enhancers in gasoline. This would be greatly accelerated by improvements in their catalytic manufacture as well as by better stabilization against peroxide formation. New uses for butane may create large markets as butane has to be removed from gasoline to comply with new volatility requirements. Synthetic fuels research has been greatly neglected in the last few years because of the low price of crude oil. A breakthrough in either direct or indirect liquefaction of coal could reverse the attitude toward synthetic fuels which will be needed at some time in the future and could be needed in the near future on the basis of strategic considerations.

The intensive work in the last few years on direct oxidation of methane is indicative of the fact that if a high yield, high selectivity process could be found to make either methanol or ethylene by direct oxidation of natural gas, such a process would have large potential.

In the chemical industry high selectivity oxidation processes are waiting to be invented for a great variety of products. The emphasis seems to be on selectivity and the discovery of selective catalysts which could be as successful as shape selective microporous crystalline catalysts such as zeolites have been in the 1960's and 1970's.

A promising field which has not yet found any major industrial application is the area of catalytic membranes. Membrane technology has come a long way permitting more and more selective separations. It is obvious that if a component of the products in a catalytic reaction can be removed continuously, it would be possible to overcome equilibrium considerations in a large variety of potential processes. Selective dehydrogenation reactions with simultaneous H_2 removal are only one example of this kind.

Asymmetric and stereospecific catalysis are still in early stages of investigation and development. Major advances in selective catalysis would be of great importance to pharmaceutical and special chemicals industries and might even impinge on biotechnology. There are indications that shape selective heterogeneous catalysts may replace homogeneous catalysts in industrial processes.

Hydrogen is in ever increasing demand and if it could be produced cheaply, could assume an enormous role as a fuel and substitute for fossil fuels at a time when the greenhouse effect may limit the amount of carbon dioxide that can be emitted into the atmosphere. Catalytic means of simple and inexpensive water dissociation are waiting to be invented.

While catalysis may periodically appear to some as a mature field, it is fully expected that it will always be in the forefront of industrial research and development and will produce many breakthroughs during the 1990's.

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