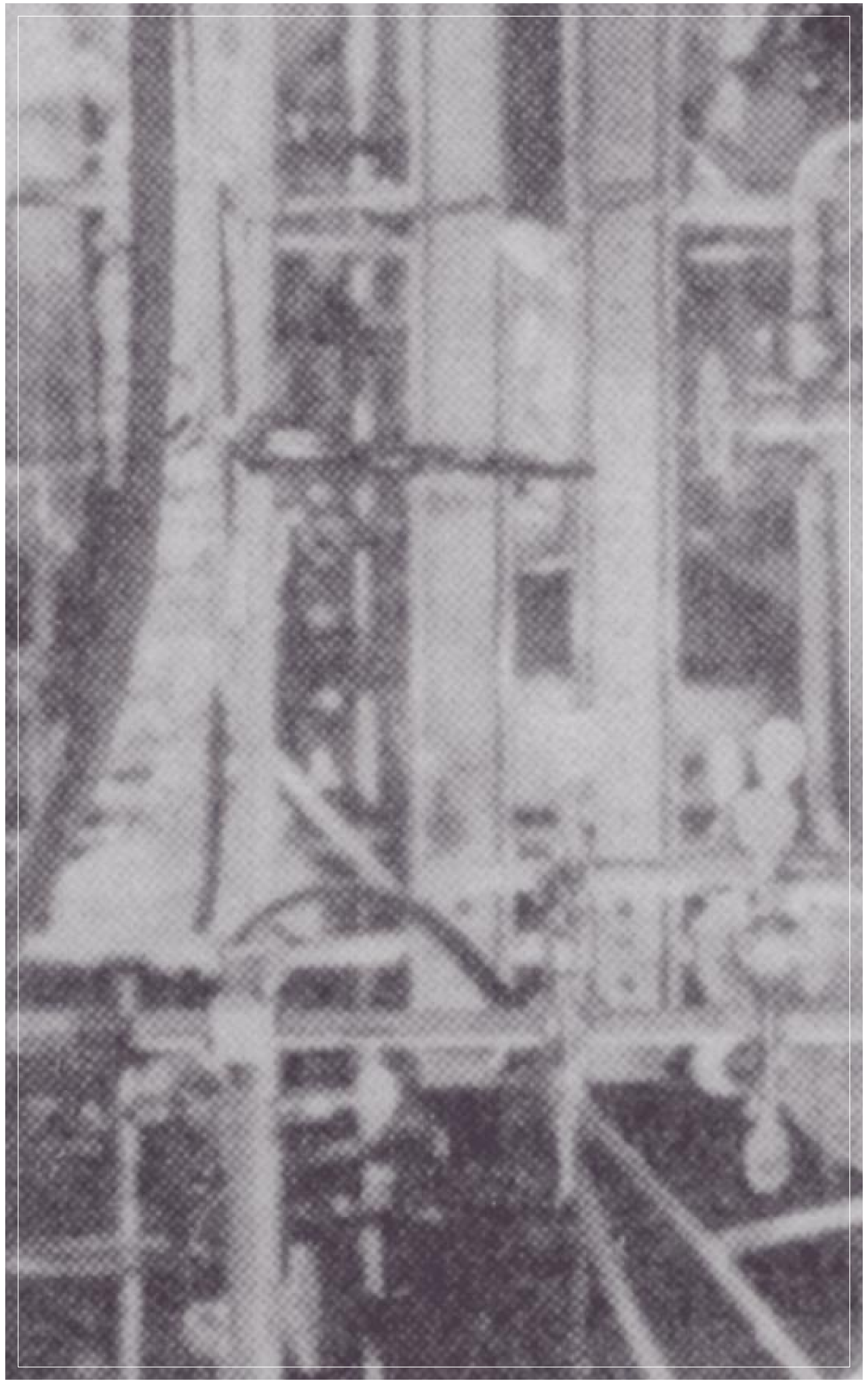


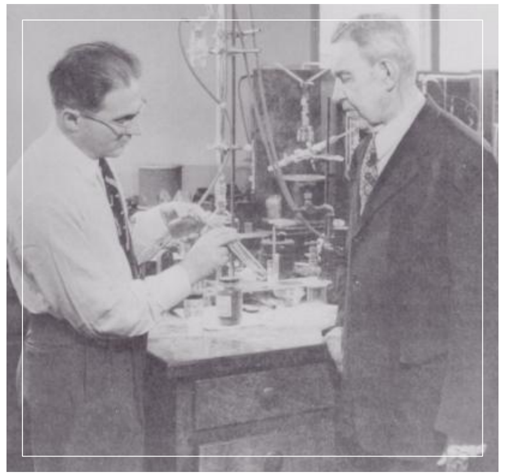
Catalysis and the oil-based industry

> **"The secret of science is to ask the right question and it is the choice of problem more than anything else that marks the man of genius in the scientific world".**
>
> C.P. Snow

One of the most important petroleum refining processes - catalytic cracking - was conceived and developed by Eugene J. Houdry in France as early as 1929 but it was after he joined Sun Oil in the USA that it was realised commercially in 1937. This was a period when industrial developments were rapid and with the discovery of rich oil-fields in Saudi Arabia in the 1940s the gradual dominance of an oil-based rather than a coal based economy was emerging. Progress was particularly rapid in the USA with contributions from Ipatieff, Pines, Plank, C.L. Thomas and Haensel. Previously coal hydrogenation had been pioneered in Germany by Franz Fischer and Hans Tropsch to give long chain hydrocarbons and by Friedrich Bergius to give liquid hydrocarbons.

The 1930's was the period when the technological applications of catalysis began to be realised. In particular the contributions of Ipatieff were immense in the area of petroleum refining and petroleum based chemicals. Prior to Ipatieff the catalysts were mainly of the Group 8 metals, but he introduced oxides such as alumina into the catalytic repertory. Ipatieff had worked in Russia between 1890 and 1929 but moved to the USA in 1930 where he shared his time between Northwestern's Chemistry Department and Universal Oil Products. He was already in his sixties but was immensely creative developing a solid phosphoric acid catalyst for polymerisation of propylene to trimers for blending with gasoline and to tetramers to be used in the manufacture of detergents. In the Second World War this catalyst was also used in the manufacture of cumene, an important component of high-grade fuel for bomber aircraft, while the discovery of alkylation and isomerization of paraffins led also to the manufacture of high octane aviation. For example n-pentane has an octane number of 62 while 2-methylbutane has a value of 90 and methyl tertiary butyl ether (MTBE) a value of 118. Also associated with this development at Universal Oil Products (UOP) was Herman Pines.

Haensel, one of Ipatieff's protégé's who had joined him from Northwestern University in 1937, was also heavily involved with catalytic reforming. He had first been concerned with demethylation and used nickel-silica-alumina catalysts for the hydrocracking of kerosenes. Then came the idea to treat a well desulphurised entire gasoline fraction over a platinum catalyst. Naphthenes were converted into aromatics, but the octane number increase was not very significant. Desulphurisation was later found to be unnecessary and alumina made from aluminium fluoride was shown to be especially good for



V.N. Ipatieff & Herman Pines

making high octane products without too serious loss of activity due to carbon formation. UOP coined the term "Platforming" which was a shortened version of 'platinum reforming' and announced it in 1949 at the Western Petroleum Refiner's Association Meeting in San Antonio. In 1950 about 2% of the U.S. gasoline pool was from catalytic reforming; by the late 1950's this had increased to 30%. The initial catalysts contained 3% platinum, and although both successful scientifically and technologically, the catalysts were expensive. Catalysts were then developed with platinum concentrations of between 0.2 and 0.7% but a major improvement took place with the development of bimetallic (Pt-Re) catalysts by Chevron.

Friedrich Bergius (Nobel prize), following the foundations laid by Bertholet, Sabatier and Ipatieff, developed the coal hydrogenation process and by 1943 Germany had 12 plants producing about 4 million tons of products per year. The catalysts were similar to those used for the oil refinery industry. It was the developments at Universal Oil Products, nearly 60 years ago and which had involved Ipatieff, Pines, Haensel and their colleagues, where high octane gasoline was produced, that was a significant factor in the performance of fighter aircraft in the Second World War.

Catalytic cracking of high-boiling petroleum fractions is probably the largest industrial catalytic process in terms of material processed and catalysed needed. As early as 1915 $AlCl_3$ had been used but it was the French chemist Eugene Houdry during the period 1924-28 that gave impetus to this area of catalysis. He developed a fixed bed process in which activated clay was the catalyst and using a series of parallel reactors operated cyclically. The fixed bed process was replaced by a moving-bed and fluidised-bed processes and the advantages of catalytic versus thermal cracking realised from the commercial value of the reaction products.

There was considerable speculation about the mechanisms, various theories were proposed and the acidic nature of the high area catalysts (SiO_2-Al_2O_3) used implicated. It was Whitmore who first suggested that the carbonium ion, now the alkyl carbenium ion mechanism, was the crucial intermediate and in due course good evidence for the strong acidity of suitably dehydrated catalysts was obtained. The use of Hammett indicators showed that silica-alumina catalysts had an acid strength greater than that of 90% sulphuric acid. The work of C.L. Thomas, at Sun Oil, was particularly noteworthy in that he provided in 1949 an explanation for their acidity based on the presence of tetravalent silicon and trivalent aluminium atoms, both tetrahedrally coordinated to oxygen atoms. To complete the structure an extra positive ion is required and by suitable methods of preparation the positive ion is a hydrogen ion. Under these conditions the catalyst is active and a correlation was shown to exist between measured acidities and catalytic activities for a range of silica-aluminas.

It is however important to recall that in 1944 Wagner, Beeck, Otvos and Stevenson reported in a series of JACS papers that when iso-butane reacted in D_2SO_4, nine H-atoms of i-C_4H_{10} were easily exchanged by D, but the tenth hydrogen - the most active one - was not. They concluded that a carbenium ion was the active species which could easily exchange its nine hydrons but a hydride transfer from another i-C_4H_{10} molecule completes the reaction chain. This concept is still relevant to mechanistic aspects of hydrocarbon reactions over solid acid catalysts used in reforming, platforming and isomerization reactions.

When in 1942 Plank, at the Mobil Research and Development Corporation's laboratories in New Jersey, was introduced to catalytic cracking the object was to improve on the silica-alumina gel catalysts. The latter was an improvement on Houdry's acid treated clay in that they were more stable, somewhat more active but there was no gain in selectivity. According to Plank 'if the gasoline yield could be increased by 1% at the expense of gas and coke it would be worth a million dollars a year to Mobil'. Rosinsky and Plank chose to study two types of materials, they were molecular sieve zeolites and silica alumina gels, but they soon concentrated on the zeolites. Weisz and Frilette at Mobil investigated commercially available NaX and CaX for the cracking of decane, both catalysts were active but exhibited different selectivities and a paper was published in 1960 in J. Phys. Chem. One of the most significant points to emerge was that the zeolites continued to function as catalysts even with coke levels present which would have resulted in the deactivation of the silica-alumina catalysts. By 1964 extensive patent rights had been acquired by Mobil for a variety of zeolites.

Fritz Haber visiting the Tamaru family. Kenzi Tamaru in the arms of his mother

In 1995 Csicery reflected on the development of shape selective catalysis, most of the catalysts were zeolitic molecular sieves and the reasons are clear: (1) they have pore-diameters with one or more discrete sizes; (2) these pore-diameters are similar to the dimensions of similar organic molecules; (3) they have exchangeable cations allowing the introduction of different cations with varying catalytic properties; (4) if these cations are exchanged to H^+ they can acquire strong oxidity. Properties (1) and (2) account for molecular sieving, properties (3) and (4) for catalytic activity.

In most technological applications of shape selective catalysts, they favour the formation of desirable isomers over less desirable ones; crack undesirable molecules to smaller fragments which can be removed; or avoid the occurrence of such undesirable reactions as coking or polymerization. The petroleum processing and chemical industries still requires improvement in shape selectivity, catalysts should be more active and more stable. New zeolite structures are being synthesised, old ones modified, heteroatoms are being substituted into existing frameworks and non-zeolitic microporous materials are being formulated. The use of optically active structure directing agents for preparing chiral molecular sieves, useful as enantioselective catalysts, is an example of future goals in zeolite chemistry.

Hydrogenation of CO to CH_4 was first observed by Sabatier while Orlov was the first to draw attention to the formation of hydrocarbons, subsequently to become known in 1925 as Fischer-Tropsch catalysis. In 1974 the oil-supply crisis stimulated interest in Fischer-

Tropsch synthesis of fuels with SASOL being particularly active in South Africa. Developments of surface sensitive spectroscopies played a vital role in establishing its mechanism carbon monoxide being shown to be dissociatively chemisorbed at iron surfaces at room temperature (Kishi and Roberts 1975). Others approached the problem differently and showed that the initiation step was not the formation of hydroxycarbene but CO dissociation (Araki and Ponec 1976; Rabo, Risch and Poutsma 1978; Petit, 1980, Biloen and Sachtler, 1979). The essential ingredients of the mechanism is:

$$CO \rightarrow C \rightarrow CHx \rightarrow CnH_{2n}$$

i.e. a step by step growth, adding CHx groups, and implying a Schulz-Flory distribution of products. An excellent review of the development of mechanistic progress in Fischer-Tropsch synthesis was given by Röper in 1983 in Catalysis in C_1 chemistry, edited by W. Keim.

The first industrial catalyst for the hydrogenation of carbon monoxide to give methanol was zinc-chromite introduced by BASF in 1923. Despite its inherent disadvantages - the use of high temperatures and high pressures - it was the major catalyst for methanol production up to the 1950's. Nevertheless there was effort being made to find alternative catalysts with the CuO/ZnO system beginning to find favour as early as 1928. The main difficulty with the CuO/ZnO catalyst was that it became easily poisoned by impurities in the synthesis gas. A break through in methanol synthesis came in the 1960s and 1970s when a low pressure process was introduced by Imperial Chemical Industries making use of a catalyst similar to that patented by Blasiak ($Cu/ZnO/Al_2O_3$) coupled with careful purification of the syn-gas. This remains the most significant catalyst for methanol production representing nearly 80% of the world supply.

During the last two decades two aspects have dominated thinking regarding the mechanism of methanol synthesis: first the crucial role of the copper surface area and second that the route to methanol is via carbon dioxide (and not CO). The evidence for this became available from isotopic labelling studies in Russia and the very detailed studies carried out at the Billingham research laboratories of Imperial Chemical Industries. The experimental observations could be rationalised through the water gas shift reaction, which explained the promoting effect of water and CO_2, coupled with the synthesis of methanol from CO_2 via the pivotal formate intermediate.

Another development was the recognition that oxygen present at the catalyst surface could act as a promoter, with Spencer recently providing a thorough analysis of the various possible ways for how chemisorbed oxygen could be involved. There has also been considerable debate concerning CO_2 adsorption on copper but what is clear is that both surface oxygen and alkali metals have an important role in that the CO_2 is adsorbed in their presence as the reactive, bent, anionic state $CO_2^{\delta-}$. It is this that is readily converted into surface formate, HCOO(a), and the following elementary steps are considered to be the most significant in methanol synthesis (Bridger and Spencer in Catalyst Handbook Ed. M. Twigg)

$$H_2 \rightarrow 2H(a)$$
$$CO + O(a) \rightarrow CO_2(a)$$
$$CO_2(a) + H(a) \rightarrow HCOO(a)$$
$$2H(a) + HCOO(a) \rightarrow CH_3O(a) + O(a)$$
$$H(a) + CH_3O(a) \rightarrow CH_3OH$$
$$H_2O \rightarrow H_2(a) + O(a)$$
$$H_2O + CO \rightarrow H_2 + CO_2$$

Although some 90% of a barrel of oil is used for fuels, i.e. energy production with the resulting products being CO_2 and H_2O, the remaining 10% is being used in various selective oxidation reactions. Based on a comparison of the weight of end products produced, Grasselli has estimated that five major reaction types account for about 90% of the top 20 organic chemicals produced in the USA by catalytic processes. These are aromatic alkylation (24%), heterogeneous oxidation (23%), dehydrogenation (15%), methanol synthesis

(16%) and homogeneous oxidation (13%). Furthermore in the area of heterogeneous oxidation there are five classes:

Allylic	oxidation of propylene to acrylonitrile
Epoxidation	oxidation of ethylene to ethylene oxide
Aromatic	oxidation of o-xylene to phlalic anhydride
Paraffinic	oxidation of n-butane to maleic anhydride
Methanol	oxidation to formaldehyde

In 1931 Lefort discovered that silver was a catalyst for the expoxidation of ethylene and is still today the main route to ethylene oxide. It was first developed by Union Carbide with a plant in 1937. A major improvement in selectivity was found in 1942 with the addition of traces of chlorides and in the 1950s a direct oxidation process was also developed by Scientific Design Co and a process using substantially pure oxygen instead of air was developed by the Shell Development Co. Most of the ethylene oxide produced is hydrolysed to ethylene glycol. Several features of this reaction are unique: first no other metal is comparable to silver in its selectivity and second the epoxydation reaction is unique to ethylene. It is now current practice to add traces of caesium to the silver and ethylene chloride to the feed in order to obtain maximum selectivity but, as usual, at the expense of activity.

Key References

[1] E.K. Rideal and H.S. Taylor, Catalysis in Theory and Practice, Macmillan & Co., (1926).

[2] Catalysis in C_1 Chemistry Ed: W. Keim, (D. Reidel Publishing Co. 1983).

[3] Principles and Practice of Heterogeneous Catalysis, J.M. Thomas and W.J. Thomas, VCH (1997).

[4] Carbon Dioxide Chemistry : Environmental Issues, Eds: J. Paul and C-M. Pradier, Royal Society of Chemistry (1994).

[5] S.M. Csiscery in 'Catalysis by microporous materials,' Eds: H.K. Beyer, H.G. Karge, I. Kiricsi and J.B. Nagy, 91, 1 (1995): Elsevier Studies in Surface Science and Catalysis.

[6] G.W. Bridger and M.S. Spencer in Catalyst Handbook, Ed: M. Twigg, Wolfe Publishing Ltd. (1989).