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C. Martin Lok's contribution to the industrial development of heterogeneous hydrogenation catalysts

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ABSTRACT

This contribution in the special issue of Catalysis Today aims to put the work of Martin Lok into historical perspective. It is shown that recent developments in industrial catalyst preparation are interwoven with the invention of fats and oils hydrogenation in the early 20th century and developments in catalyst characterization.

1. Introduction

In the spring of 2008 Dr C. Martin Lok retired after being active for about 35 years in science and technology. Most of these 35 years he has been active in heterogeneous, in particular in nickel catalysis, and during this period a total of 26 patent applications, see Table 1, that carry his name, have been filed at the European Patent Office in München, Germany. Some of these applications have resulted in the development of industrial catalysts that have been successfully applied for decades now in the food and petrochemical industry. This contribution aims to put his work into a historical perspective.

2. Heterogeneous catalysis for liquid phase reactions

In the early 1900s nickel deposited from a nickel-nitrate solution onto powdered pumice is the first mentioning of a heterogeneous catalyst that has been used in a lab experiment to prove the feasibility of liquid phase hydrogenation [1]. This first experiment, oleic acid to stearic acid hydrogenation, was carried out on the 27th of February 1901 by Wilhelm Normann (1870–1939). This scientist of only 31 years old worked in the factory Leprince & Siveke (his uncle) at Herford in Germany. He repeated these experiments using also oils, such as rapeseed oil. All these experiments clearly proved the heterogeneous nickel catalyst to be active in the liquid phase hydrogenation of organic molecules that could not be easily vapourized. It was about 7 years earlier that the two Frenchmen Paul Sabatier and Jean-Baptiste Senderens [2] had proven that vapour phase hydrogenation of small unsaturated organic molecules was possible by using reduced powdered nickel as a catalyst. It was Sabatier's belief that such a catalytic reaction was possible only in the vapour phase. Normann was the first to prove that it was also possible in the liquid phase. He obtained in 1903 a patent [3] for this invention. Normann was unable to convince his uncle Siveke to develop this invention into a commercial process, but this invention had drawn the attention of Joseph Crosfield. Their scientist Kayser visited Herford. Crosfield obtained a licence agreement with Leprince & Siveke and Normann was invited to come to Warrington to continue his experiments on a larger scale required to come to an industrial process. It implied upscaling of the hydrogenation process as well as upscaling of the catalyst manufacturing process [4].

Several years later, in 1911, Anton Jurgens purchased Ölwerke Germania at Emmerich am Rhein in Germany and he invited Normann to set up a large scale hydrogenation process and a Ni catalyst manufacturing process [4].

Anton Jurgens and Samuel van den Berg formed in 1927 the "Margarine Unie" and in 1930 together with William Heskett Lever, Unilever [5]. In 1997 Imperial Chemical Industries became the owner of the site at Emmerich and in 2002 Johnson Matthey.

Normann was also one of the first scientists who believed that it was an absolute necessity to improve the quality of this nickel catalyst continuously. He replaced the pumice by "kieselguhr". And he studied the use of a number of other metals as well [4]. At that time there were hardly any characterization techniques available. These techniques were so badly needed in order to understand the quality criteria for the production of an industrial heterogeneous catalyst.

After some time at the central Unilever Laboratory in Vlaardingen, The Netherlands, Martin was transferred to Emmerich in 1983. During his time in Emmerich, he was involved in further development and commercialisation of some of his inventions in the early 1980s. This will be discussed in the section on industrial catalyst manufacturing.

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[1] Retired.

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Table 1
Overview of European patent applications in which Cornelis Martinus Lok is the inventor or one of the inventors.

	EPO public. number	Title of patent application (filing date)
1	EP0009904	Preparation of glyceride esters (17 09 1979)
2	EP0092878	Nickel catalysts on transition alumina (21 04 1983)
3	EP0145094	Process for preparing a transition metal-silicate catalyst (12 04 1984)
4	EP0167201	Nickel/alumina/silicate catalyst, its preparation and use (19 06 1985)
5	EP0168091	Nickel/alumina catalyst, its preparation and use (19 06 1985)
6	EP0354612	Process for the preparation of nickel/alumina catalysts (28 07 1989)
7	EP0398668	Nickel/silica catalyst and the preparation and use thereof (16 05 1990)
8	EP0430543	Removal of metal soaps from hydrogenated fatty products (20 11 1990)
9	EP0496448	Preparation of hydrogenation catalysts (15 02 1992)
10	EP0660749	Nickel/silica catalyst for hydrotreating unsaturated organic compounds (09 02 1993)
11	EP0775018	Cobalt on alumina catalysts (17 07 1995)
12	EP0774451	Fatty acid isomerisation (30 10 1996)
13	EP0923525	Process for preparation of branched fatty acids (07 07 1997)
14	EP0925271	Process for the preparation of derivatives of fatty acids (07 07 1997)
15	EP1069946	Copper-containing materials (01 04 1999)
16	EP1154854	Nickel catalysts on transition alumina (11 02 2000)
17	EP1286767	Catalysts with high cobalt surface area (23 04 2001)
18	EP1733791	Preparation of a cobalt catalyst precursor (23 04 2001)
19	EP1301273	Nickel/silica hydrogenation catalysts and method of preparation (20 07 2001)
20	EP1542794	Process for preparing cobalt catalysts on titania support (25 09 2003)
21	EP1742735	Catalysts (15 04 2005)
22	EP1744829	Catalysts (15 05 2005)
23	EP1791638	High cobalt content, high cobalt surface area catalysts, preparation and use thereof (19 08 2005)
24	EP1824598	Shaped eggshell catalysts containing cobalt, use and preparation thereof (21 11 2005)

Source: http://ep.espacenet.com.
Other named inventors are: Christopher J. Adams; Sharon Bale; Stephen Bailey; Hendrikus J. van den Berg; Raimond L.C. Bonné; John L. Casci; Adelheid Deryck; Jacob van Dijk; Pieter M. van Dijk; Martin J. Earle; Brigitte Feldhäuser; Keshab L. Ganguli; Gavin Gray; Jennifer T. Hamill; William R. Hodgson; Carl L. Huitson; Gordon J. Kelly; Wicher T. Koetsier; Peter Nootenboom; Johannes C. Oudejans; Heike Ritter; Glyn Roberts; Stephen D. Rogers; Kenneth R. Seddon; Jill Turner; Dirk Verzijl; John West.

3. Industrial manufacturing of heterogeneous catalysts

Unilever scientists had developed in the 1950s and 60s a strong knowledge base in fat hydrogenation catalyst preparation as well as characterization, for example by the leading experts, Coenen [6], Linsen [7], Okkerse [8] and Broekhoff [9]. In 1958, Coenen made a valuable contribution to the knowledge of the structure and texture of nickel on kieselguhr catalysts. He showed by using X-ray investigations that the catalyst consists of an irregular, porous conglomerate of flat silica platelets on which epitaxically grown and normally cubical nickel crystallites are attached. Linsen and Okkerse further studied the texture of nickel–silica catalysts. Characterization techniques were also further developed, such as nitrogen physisorption (BET) analysis by Broekhoff.

In addition, in the decades preceding Martin's active career, Unilever scientists and others had developed and patented several routes for making base metal catalysts.

For the preparation of Ni/SiO_2 or Ni/Al_2O_3 various methods are described in the literature, most of which are based on co-precipitation. Co-precipitation implies the simultaneous contacting of a mixture of sodium carbonate, a nickel salt and a waterglass (sodium silicate) solution or a sodium aluminate solution. Kruissink [10], for example, studied the properties of a Ni/Al_2O_3 catalyst that was obtained by co-precipitation. Kruissink obtained after washing, drying, calcination and reduction a Ni-on-Al_2O_3 catalyst possessing metallic nickel particles of a size larger than 5 nm.

An example of co-precipitation followed by stabilization is the patent of Helmut Klimmek and Günter Klauenberg [11]. They developed a continuous process that used two different reactors: one for coprecipitation of a nickel hydroxycarbonate and a second reactor for stabilization of the precipitate by using silica-based materials.

In addition to co-precipitation, the technique of impregnation has also been studied. In this case first the inert carrier is made and subsequently the pores are saturated with a Ni salt containing solution. It is preferred to use Ni salts that upon decomposition during calcination or reduction do not result in the deposition of unwanted molecules. The following salts have been used successfully: Ni-formate, Ni-acetate and Ni-ammonium carbonate. All these nickel salts decompose upon heating and small NiO particles remain deposited onto the inert support, which is converted into metallic nickel during reduction [12,13].

Despite all efforts in characterization and development of manufacturing processes, as Coenen concluded most of his work in 1986, "the original combination of nickel with kieselguhr is still with us, as in Normann's days" [14].

4. Overview of C. Martin Lok's patents

All in all, the person that wants to manufacture a valuable catalyst needs to find the best compromise for quite a number of process parameters in order to get the most preferred properties. In the early 1980s many pieces of a puzzle were present, as described above. According to Martin's patent list, presented in Table 1, after a brief excursion into oleochemistry (patent 1), which remained one of his favourite topics, he reverted to catalyst preparation. The final piece of the puzzle was the commercial driver of several oil crises in the 1970s. This led to an increased focus on nickel/alumina catalysts for methanation [10], to be used in the production of synthetic natural gas (SNG) from coal.

Martin's first catalyst patent (patent 2) shows the clever combination of impregnation technology and application in a range of reactions: the target SNG, but also edible oil hydrogenation. Main characteristic of this patent application were the high metal surface areas attainable by impregnation.

Also the well-known nickel/kieselguhr catalyst attracted his attention. Coenen had shown by extensive characterization [6,14] that the silica present in the guhr was restructured during coprecipitation. The interaction with nickel led to good dispersion and high surface areas. This led Martin to the work on synthetic silicas, made from "soluble" silica-precursors, such as sodium silicate (waterglass, patents 3–7). He rightly assumed the interaction with soluble silica and nickel could lead to good catalysts. This was a major development from a traditional nickel/kieselguhr catalyst.

Patent 5, inventors Keshab L. Ganguli, Peter Nootenboom and C. Martin Lok, is his first patent for a highly selective edible oil hydrogenation catalyst. The inventors recognized the need for an edible oil hydrogenation catalyst that possesses a combination of the three most important properties: high activity and selectivity, good filterability and a good mechanical strength. This combination of properties is obtained by selecting the proper narrow range of preparation conditions.

The filing date of this patent was the 19th of June 1985. Upon publication of this patent and the notice of the European Patent Office (EPO) to grant this patent three companies filed opposition against this patent. They requested the revocation of this patent on the grounds of lack of novelty, lack of inventive step and insufficiency of disclosure. One of the companies claimed that Borisova [16] describes a procedure to prepare a catalyst having a specific Ni surface area covered by the claims of EP0168091. Moreover it was explained that the term "size of the pores" does not explain whether the pore radius or the pore diameter was meant. As a result the Opposition Division revoked the patent on the ground that claim 1 did not meet the requirement of clarity of Article 84 EPC. In this decision it held that the active Ni surface area defined in claim one was already known from Borisova. It held the O_2-chemisorption method used by Borisova and described by Buyanova [17] to be a reliable method. Experimental data submitted by the Patentees did not prove that the values of the Borisova's Ni surface area were incorrect.

Unilever successes fully lodged an appeal against the decision to revoke the patent. First of all the Analytical Laboratory of the Delft University of Technology carried out experimental work to study the question whether the two chemisorption methods gave equal nickel surface areas. They came to the conclusion that by using the O_2-chemisorption the value of the specific nickel surface area is overestimated by 15%. In other words in case Borisova should have used the H_2-chemisorption method, then he should have measured a nickel surface that was 15% smaller. Unilever also explained that the wording "pore size" must be interpreted in compliance with the IUPAC [18] recommendations which were published in 1985. Moreover, it was decided to amend the first claim by including the process by which the washed precipitate should be dried. Finally the Opposition Decision communicated to the parties on the 21st of November 2002 that EP 0168091 was maintained in the amended form. All in all more then 17 years later then the initial filing date!

Martin's work was also carried out in an industrial environment. This means that very practical problems, such as the dissolution of the catalyst (nickel) by the reagent and product (fatty acid) deserved attention (patent 8).

Patent 7 is a nice example of an invention by accident and it is a beautiful illustration how inventions can be made if something in the development process goes unwillingly and unforeseenly wrong. During preparation of a nickel catalyst it was observed that the obtained product had inferior properties for edible oil hydrogenation. In order to analyze what was wrong with the catalyst Martin Lok characterized the reduced catalyst and observed a excellent nickel surface area, but a pore size distribution which was outside the acceptable range for an edible oil hydrogenation catalyst. He immediately realized that such a catalyst would be an ideal catalyst for fatty acid hydrogenation, because the smaller the pores the better the formation of unwanted Ni-soaps is suppressed. This conclusion appeared to be correct and led to the development of fatty acid catalysts [15].

In the early 1990s, once more Martin turned to chemicals and a patent on cobalt catalysts was filed. Again, high dispersion was one of the key characteristics of his invention (patent 11). In this decade, he remained actively involved in oleochemistry, leading to a range of patents in key reactions (patents 12–14). Also, the work on nickel and cobalt was completed by investigating other base metals such as copper (patents 20–24).

C. Martin Lok was a scientist that has shown to be able to design heterogeneous catalysts that fulfilled these requirements in a number of cases. His main credits can be summarized as follows:

- He was able to define parameters that could be used to control the fat and fatty acid catalyst production process, such that a constant catalyst quality can be guaranteed.
- He has identified Ni powder catalysts with new properties that have now been successfully used for many years in the industry.
- He has recognized opportunities for using existing catalyst manufacturing technology for other catalyst types that have now become valuable industrial products.

(These points are partly laid down in patents but in many cases are still part of knowhow).

It should be noted that the other named inventors in Table 1 were also of vital importance to Martin's accomplishments. The list is by no means conclusive but gives an impression of the fellow scientists, engineers, laboratory technicians and people from other disciplines that have worked with Martin over the years. Many young people have benefited from their time with Martin and are still active in the field of catalysis.

5. Conclusion

It has been clearly demonstrated in the above sections that C. Martin Lok has had a significant contribution to the development of heterogeneous Ni catalysts that can be used for liquid phase hydrogenation reactions. Several of these catalysts are now used commercially in a range of petrochemical as well as in oleochemical and edible oil hydrogenation processes. Most of these ideas were the result of hard thinking and a lot of experimental work together with using a lot of common sense and a good understanding of the process and catalyst requirements. He can look back on a fruitful career within Unilever, ICI and Johnson Matthey.

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