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Fischer–Tropsch catalysis: The basis for an emerging industry with origins in the early 20th Century

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ABSTRACT

Fischer–Tropsch catalysts, based on cobalt, are complex materials containing the catalyst support and reduction and structural promoters in addition to the cobalt metal itself. While this basic description covers both modern FT catalyst and those first commercialised, in Germany in 1930s, modern FT catalysts have vastly improved performance. While such improvements owe much to modern materials and manufacturing methods, the role of advanced characterisation techniques cannot be underestimated. Modern techniques discern details of catalyst structure that were not available during the early pioneering work, they guide current developments and offer the prospect of designing tailored catalysts.

1. The discovery period

The early 20th century was a landmark period for industrial catalysis. It was an era of great discoveries. The hydrogenation of carbon monoxide and carbon dioxide to methane over nickel catalysts was described in 1902 by Sabatier and Senderens [1] and within decades major processes, for example for the production of methanol and ammonia, were invented and commercialised. It was in this same period that the reaction of synthesis gas to produce liquid hydrocarbons was discovered. This reaction, which is now commonly described as the Fischer–Tropsch (FT) process actually dates back to 1913 when Mittasch and Schneider patented [2–5] the conversion of mixtures of carbon monoxide and hydrogen in the presence of heterogeneous metal catalysts such as, supported cobalt oxide. Using an excess of carbon monoxide they observed the formation of liquid hydrocarbons: mixtures of saturated and unsaturated species. Claim 1 of their US patent [5] reads "The process of producing compounds containing carbon and hydrogen by passing an oxide of carbon and hydrogen over a heated catalytic agent under a pressure exceeding that of 5 atmospheres". In example 1, of the same patent, while using a cobalt catalyst "...an aqueous solution of aldehydes and the like was obtained in addition to a light, oily liquid consisting chiefly of saturated and unsaturated hydrocarbons which boil up to 250 °C or even higher".

It would appear that this pioneering work was not immediately followed up because the process yielded complex mixtures rather than well-defined "single" chemicals and priority was given to commercialisation of the methanol and ammonia processes [6]. At about the same time (1913) the Kaiser Wilhelm Institute (KWI) in Műlheim, Germany, was founded to carry out research on the conversion of coal into fuels and chemicals, indeed, the Institute was commissioned to investigate new uses for coke-oven off-gases. A key realisation was that for the production of liquid transportation fuels the formation of complex mixtures of hydrocarbons was not a drawback and two scientists Franz Fischer and Hans Tropsch of the KWI continued the earlier investigations. They combined the discoveries by Mittasch and Schneider using base metal catalysts with their own findings on the transformation of formates into hydrocarbons using basic catalysts. Using base-promoted metal catalysts and a higher hydrogen/carbon monoxide ratio, a liquid fraction was produced that was termed "Synthol".

It is fascinating to read [6–9] how these scientists were able to characterise the complex product mixtures in great detail without having access to more modern separation and characterisation tools such as GLC and NMR. Individual components were separated and identified by "classical" methods: very labour-intensive procedures involving several extraction and distillation stages followed by chemical transformation and/or crystallisation steps. Characterisation of individual compounds was mostly based on melting and boiling points, chemical reactivity and chemical analysis; even the odour of the compound was used as part of the

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identification process! Techniques to characterise the catalysts themselves were almost absent and indeed catalytic materials were mostly described based on their composition and preparation methods. Still the scientists had a remarkable insight in their mode of action, the dispersion of metals and deactivation mechanisms such as poisoning, coking and sintering.

In the initial experiments Fischer and Tropsch applied high pressures and temperatures: coal-based syngas was purified from sulphur compounds and pressurised to 150 bar [6,7]. A catalyst based on potassium carbonate impregnated iron filings was used: no characterisation of the resulting material was reported. At 400–450 °C a mixture of aliphatic alcohols, aldehydes, ketones and carboxylic acids was produced and the test rig was run for weeks to produce sufficient material for characterisation. The carboxylic acids were analysed by converting the acids into silver salts, which were then fractionated by crystallisation followed by chemical analysis. Aldehydes were identified by oxidising the compounds to the corresponding acids with an ammoniacal silver solution after which the resulting carboxylic acids were converted into metal salts (as above).

To test the usefulness of the products, as transportation fuels, the oil layer was separated from the aqueous layer, de-acidified and fractionated by distillation and then subsequently road tested using a 1922 model NSU motorbike carrying two persons. The results were reported to be encouraging with the performance appearing to be similar to, or better than, a reference fuel. This, indeed, marked the beginning of an industry for the production of transportation fuels from synthesis gas.

Soon afterwards Fischer and Tropsch discovered a cobalt-based process that operated at much lower temperatures and pressures [8]. Catalysts were mixed metal oxides prepared by combining metal oxides, by mixing molten salts or by precipitation of (mixed) metals nitrates with alkali carbonates. It was during this period that most of the basic knowledge on the FT reaction was established: nickel, cobalt and iron catalysts proved to be the most effective metals for hydrogenation of carbon monoxide to hydrocarbons. Cobalt was the most active metal for higher hydrocarbons while it was confirmed that nickel favoured the formation of methane. Other discoveries followed rapidly including the addition of promoters: alkali and manganese to improve the selectivity to higher hydrocarbons and the use of copper to lower the reduction temperature of iron. Potassium proved to be a poison for cobalt catalysts. In addition, it was discovered that irreducible oxides like chromium oxide could be used as sintering inhibitors. Initially cobalt nitrate impregnated supports were used as catalysts, but soon a co-precipitated Co/ThO_2/kieselguhr catalyst was to become the standard for many years to come [9,10]. Even after commercialisation (see later) work continued with one of the many discoveries being a further FT active metal: Ru. This had many attractive features including "...long life and was easy to regenerate." It had a tendency to produce high yields of "...hard wax... which need not make the process less attractive as it could be cracked" to shorter chain species. Work was curtailed, however, due to the "scarcity" of the metal [11].

2. Commercialisation

Ruhrchemie AG acquired the exclusive patent rights to the Fischer–Tropsch process in 1934 [11–13] and only 2 years later, in 1936, the first FT plant was in operation at their site in Oberhausen, Germany. Within a short period nine plants were erected in Germany, while factories were also built in France, Japan and Manchuria, all under a Ruhrchemie licence. The production capacity at Oberhausen in 1940s was only 70,000 tpa while combined capacity of the German FT plants did not exceed 500,000 tpa [14]. All the plants operated at atmospheric or medium pressure (5–15, mostly 9–11 bar). Because of the highly exothermic nature of the Fischer–Tropsch reaction, a key issue is the removal of heat. Extensive cooling of the catalyst bed was required which led to various process designs mostly involving water cooling of multi-tube reactors. The atmospheric process in Oberhausen was carried out in a plant containing 52 reactors and was operated in two stages using a H_2/CO ratio of 2. The medium-pressure plant contained 72 reactors and was operated in three stages with the H_2/CO ratio increasing from 1.4 in the first step, to 1.6 in the second step to a ratio of 1.8 in the final stage. This mode of operation was claimed to limit methane formation and extend catalyst life. The medium-pressure double-tube reactor had an overall diameter of 2.7 m and contained 1984 vertical tubes of 4.5 m long and 44 mm inner diameter that contained the catalyst. In each tube there was an inner tube of 24 mm through which water coolant was circulated. In addition, the outer tubes were water-cooled.

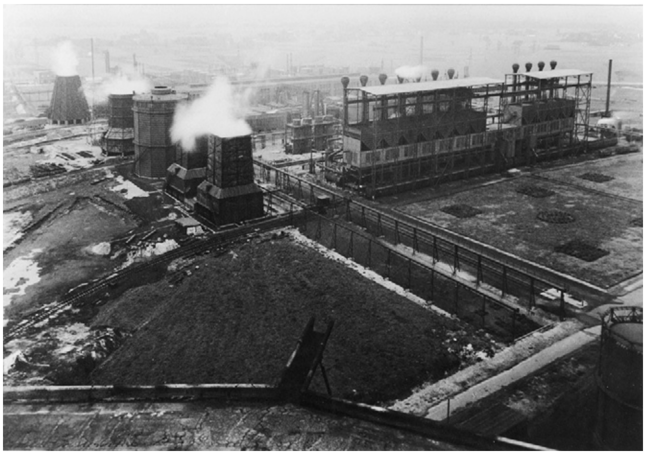

Fig. 1. Site overview Ruhrchemie FT production plant in Oberhausen, Germany, in 1930s: FT plant, cooling towers and a crane-way for catalyst filling. © OXEA Deutschland GmbH.

The plants were meant as production units mainly for chemicals rather than for fuel. Even during WWII only the "Spritfraktion", boiling less than 160 °C, and the light diesel fraction, boiling at 160–230 °C, was used as transportation fuel [14].

Figs. 1–4 provide a historic perspective of the Oberhausen facility shortly after commissioning. It is a remarkable achievement, by any standards, to have such a facility in operation within

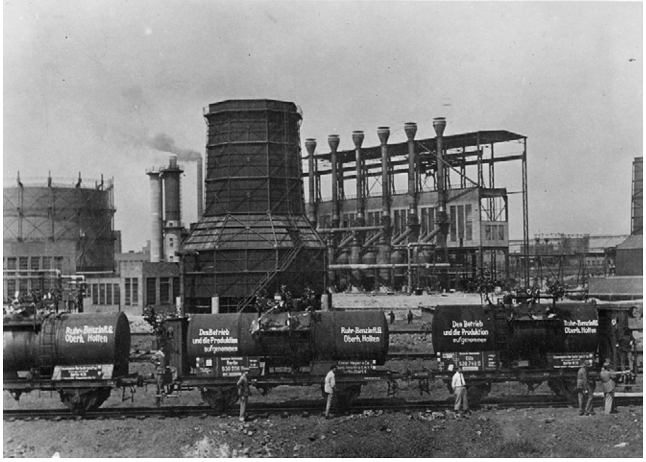

Fig. 2. FT plant and cooling tower in Oberhausen with fuel railcars in front in 1936. © OXEA Deutschland GmbH.

Fig. 3. Management of the FT plant in front of the first railcars with fuel in 1936. From left to right: Dr. Feißt, Mr. Stock, Dr. Biermann, Mr. Neveling, unknown. © OXEA Deutschland GmbH.

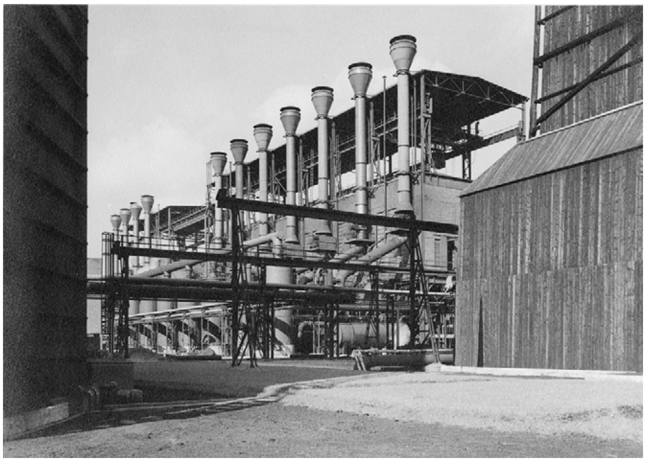

Fig. 4. Fischer–Tropsch plant in Oberhausen, 1936. © OXEA Deutschland GmbH.

12 years of the first publication from Fischer and Tropsch. Fig. 1 provides a site overview of the FT production plant in Oberhausen, Germany, in 1930s: FT plant, cooling towers and a crane-way used for catalyst transportation within the site. A 1936 view of the FT plant and cooling tower in Oberhausen with fuel railcars in front can be seen in Fig. 2. Fig. 3 was taken to commemorate the transportation, by rail, of the first commercial fuel produced at the plant in 1936 and shows some of the scientists and engineers responsible for the commissioning and operation of the Oberhausen FT plant. Fig. 4 shows the Fischer–Tropsch plant in Oberhausen, 1936 shortly before commissioning. OXEA Deutschland GmbH provided all photographs.

3. The first commercial catalyst

The FT catalyst plant in Oberhausen, now owned by Johnson Matthey, supplied a standardised cobalt catalyst to the various FT plants active during 1930s and 1940s. The initial cobalt catalyst had the following composition: Co/ThO_2/kieselguhr 100/18/100. Later, in 1938, the composition was modified and magnesium was included yielding a composition Co/ThO_2/MgO/kieselguhr 100/5/8/200 [11,13].

The choice of thoria and kieselguhr may seem strange to those currently embarking on a career in catalysis although "guhr" based carriers remain in use today. At that time kieselguhr was a standard catalyst carrier although the natural variability did provide some problems. A source material low in iron and aluminium was selected, otherwise too much methane was produced in the FT reaction. Various modifications of the kieselguhr were also carried out including acid-washing, to remove certain contaminants, and calcination (600–700 °C) to improve final product consistency. The use of thoria as a catalyst carrier, while inconsistent with modern Environment, Health and Safety standards because of its radioactivity, would have been a logical choice for a catalyst carrier: it has the highest melting point of any oxide.

The Co/ThO_2/MgO/kieselguhr 100/5/8/200 catalyst remained unchanged during WW2 and was used for both the atmospheric and the medium-pressure operations. The lifetime of the catalyst was 5–6 months for the atmospheric pressure process and 8–11 months for the medium-pressure operations [14]. The catalyst was prepared by precipitation from a solution of nitrates of cobalt, magnesium and thorium. The conditions were chosen to give the maximum "disorder" in the structure of the catalyst. The nitrate solution was added to a sodium carbonate solution at 100 °C in about 30 s thus ensuring that the super-saturation level of each metal was exceeded simultaneously: this would favour a high metal dispersion and intimate contact between the metals. Kieselguhr was added after the precipitation was complete. Other additives and promoters were identified: magnesium was thought to improve the dispersion of the cobalt and to help to reduce sintering while manganese favoured the production of high-molecular-weight hydrocarbons.

A sinter stability test was introduced and consisted of reducing the catalysts under extreme conditions i.e. at higher temperatures and for longer times than normal. Catalysts that were active after such a reduction were regarded as being resistant to sintering and hence should give a long life. Reduction took place using dry hydrogen at 360–370 °C. The degree of reduction was kept at about 60%. This reduction was considered to be the most critical step in catalyst manufacture followed closely by the need to wash the catalyst to remove sodium.

Technology was developed to transport the reduced catalysts in the pyrophoric form by rail. This was done by cooling the catalyst after reduction to room temperature under a N_2 flow, replacing the N_2 by CO_2 and transferring the contents of the reducer to a transport vessel. Ten catalyst reduction batches were required to fill this vessel [14]. Fig. 5 shows the railcar transport of reduced, pyrophoric catalyst from the catalyst plant to the FT plant. The hopper can be seen being manoeuvred onto the railcar. The purpose of this process was to facilitate a rapid start-up of the FT-reactors since the catalyst did not require any reduction or reactivation.

In an interview by British Intelligence, shortly after the WWII, Otto Roelen [11] provided additional insight into their understanding of the catalyst and the FT process after, what was, almost 10 years of successful operation. Catalyst deactivation, or "deterioration" as described by Roelen, after some months was ascribed to three potential factors and strategies were adopted to recover performance:

(i) *Pore blockage by product wax*. The catalyst was washed with solvent or treated with H_2 to restore activity.
(ii) *Poisoning by lay-down of carbon deposits or sulphur*. The catalysts were treated, at elevated temperatures, with H_2 to restore (at least partially) activity.
(iii) *Sintering*. No remedy was identified.

Interestingly, Roelen reported that there was no evidence for oxidation of the cobalt metal and he found no evidence of metal-support compound (cobalt silicate) formation.

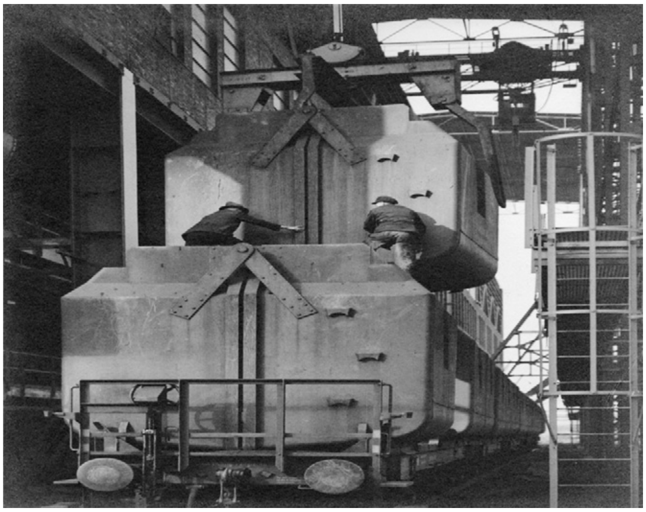

Fig. 5. Railcar transport of reduced pyrophoric catalyst from the catalyst plant to the FT plant. © OXEA Deutschland GmbH.

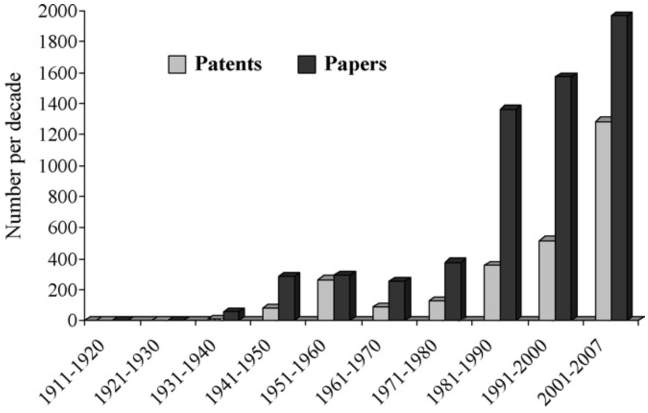

Fig. 6. Number of patents and papers published by decade.

In the same interview Roelen was asked about the relative merits of cobalt and iron-based FT catalysts. Dr Roelen stated that he believed that the choice of cobalt would be safer but thought the future lay with iron catalysts [11]. Indeed the next generation of FT plants built by Sasol in the fifties was going to be based on iron catalysts produced in the same Ruhrchemie plant in Oberhausen until the mid-1960s [12,13]. This period called the "Iron Age" by Bartholomew [15] was followed by a rediscovery of cobalt that resulted in an explosion of patents and publications. This can be seen in Fig. 6 which shows the numbers of patents and papers published by decade: Bartholemew's "rediscovery of cobalt" began in about 1980. If one takes into account the first patents by Mittasch and Schneider [2–5] and the current interest in coal-to-liquids (CTL) and biomass-to-liquids (BTL) Bartholemew's overview can be updated as provided in Fig. 6. Not all the patents disclosed cover new discoveries and indeed some can be considered as rediscoveries of what was known in the early 20th century [15].

4. Patents, assignees and mapping

Fig. 6 provides a simple, yet powerful, overview of the numbers of papers and patents published over the last 100 years that highlights the dramatic increase in publications since 1980. While this was initially "triggered" by gas-to-liquids, more recently, it has been augmented by an increasing interest in CTL and BTL. Further, more detailed, analysis of the patents published since 1980 is obviously merited and this is provided in Fig. 7. The number of patents published for each of the major assignees is shown in graphical form. Even this simple overview provides a glimpse of the differing strategies and approaches being adopted. It is easy to lose sight of the fact that Fig. 7 covers a timescale of over 25 years. Over that period only Sasol, Shell and Mossgas (now PetroSA) have operated commercial plants based on FT, yet there is considerable evidence for large and sustained R&D efforts from a number of companies: this is a formidable commitment to FT technology.

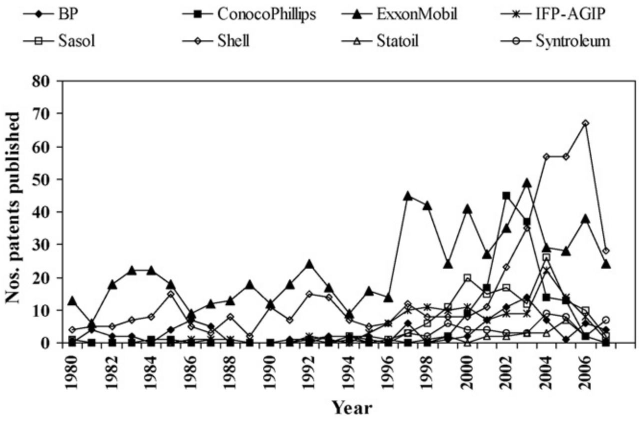

Fig. 7. Numbers of patents published, and assignee, since 1980.

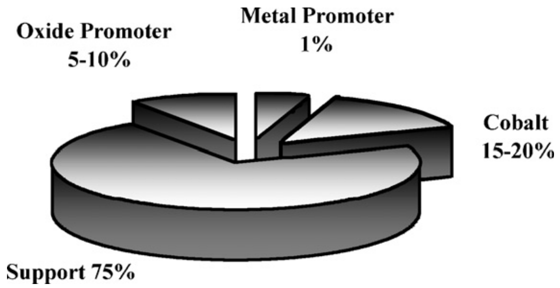

Fig. 8. Compositional overview of modern Co-based FT catalysts.

Currently, even more powerful tools exist for analysing patents. Computational methods such as Aureka's ThemeScape® software available from MicroPatent® allow contour maps to be generated based on key words or phrases in the patents. Such maps show areas of high activity and, by simple colour coding, identify the assignees interested in particular areas from the preparation of the support and catalyst to the dewaxing of product from the FT reaction.

Based on the analysis of patents modern cobalt-based FT catalysts can be described by the compositional overview given in Fig. 8. This overview is consistent with the analysis of Oukaci et al. [16]. The FT catalyst is seen to consist of a support and metal and oxide promoters. The metal promoters are usually described as "reduction promoters" with Pt, Ru, Ir and Re being those most commonly described in the patent literature. A wide range of potential oxide promoters is described. These are usually based on metals from groups IIIB, IVB, VB of the periodic table and are present to provide some structural or catalytic promotion.

5. Structure–performance relationships

Catalyst development over the years has evolved from trial and error, based almost exclusively on performance testing, to a more rational design based on quantitative-structure–performance relationships (QSPR). Central to the generation of QSPR are the vast array of modern characterisation methods. Hydrogen chemisorption became a routine technique for the measurement of cobalt surface sites and thus an indicator for FT activity; oxygen titration was used to determine the degree of reduction of cobalt to the metallic state [17].

Iglesia et al. [18] established a linear relation between cobalt dispersion and FT activity independent of the type of support for cobalt dispersions up to 10%. Selectivity could be related to the structural properties of the catalyst such as particle diameter, pore size and active site density [18]. Later de Jong and co-workers showed that for very high cobalt dispersions the activity vs. dispersion relationship is no longer linear [19].

6. Advanced characterisation techniques

Compared to the early days of Fischer and Tropsch, catalytic scientists today have access to a vast array of techniques allowing characterisation of the catalyst across the various length scales from full pellets to 0.1 nm or better. This (sub)atomic resolution allows questions to be answered about the nature and location of (metal) promoter atoms. Using EXAFS/XANES, Davis et al. [20] demonstrated direct contact of the Re promoter with the Co, while evidence for Re–Re bonds was not observed suggesting atomic dispersion of the Re. They confirmed that Re was only active above its reduction temperature indicating hydrogen spillover as a mechanism for reduction promotion. With the advent of aberration-corrected STEM (Scanning Transmission Electron Microscopy) it is now possible to form imaging probes of 0.1 nm diameter or better [21]. Using such an instrument equipped with high-angle annular dark-field (HAADF) detectors it is possible to distinguish between atoms that differ in atomic number. Bezemer et al. [22] and Morales et al. [23] have studied Mn promoted FT catalysts in such an instrument but without resolving individual atoms. Using Aberration-Corrected STEM, Shannon et al. [24] confirmed the EXAFS results of Davis et al. [20] and showed the Re, Pt and Ir promoters mainly as isolated atoms whereas Ru was present both as isolated atoms and regions of high dopant concentration within Co particles and, occasionally, as separate particles.

Fig. 9 provides an intensity profile across a Co crystallite along the {1 1 0} direction showing Re atoms in or on a Co particle [24]. Fig. 10 shows examples of Ru distribution in a Ru promoted Co-on-alumina FT catalyst determined by EELS Spectrum Imaging. The HAADF image is in the centre and the colour images above and below are colour coded as Al (from the oxide support)—red, Co—green and Ru—blue [from 24].

Li et al. recently observed that only cobalt particles containing Ru were observed to reduce to metal [25]. Therefore, for good reduction promotion a direct contact between particle and promoter and hence a good promoter distribution would seem to be essential. Scanning Tunneling Microscopy has been used to show restructuring of the Co surface after 1 h of FT reaction [26].

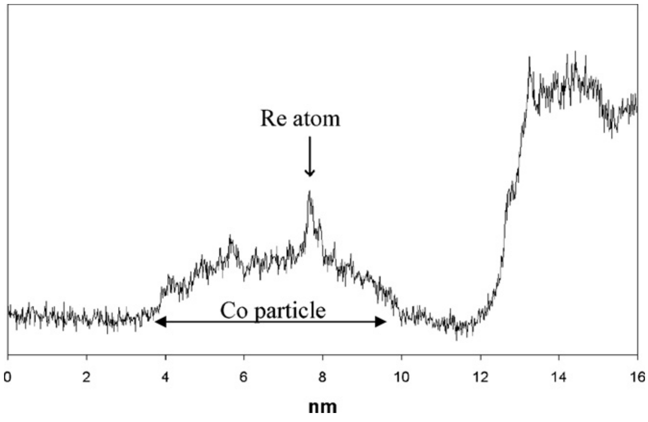

Fig. 9. Intensity profile showing Re atoms in or on Co particle along the {1 1 0} direction [24].

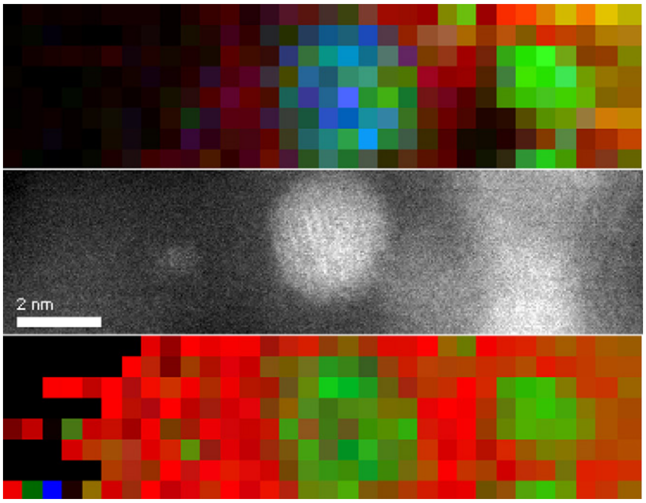

Fig. 10. Examples of Ru distribution in a Ru promoted Co-on-alumina FT catalyst determined by EELS Spectrum Imaging. The HAADF image is in the centre and the colour images above and below are colour coded as Al—red, Co—green and Ru—blue. (Al is from the oxide support). The elements are scaled to give full colour where the maximum signal from that element occurs [24].

At nm (crystallite) scale, in situ XRD is a useful technique where in a single experiment information can be obtained on changes in chemical composition, dispersion and temperature stability [27–29]. In situ XRD confirmed that the reduction of cobalt oxide occurs in discrete steps: at first a reduction of Co_3O_4 to CoO followed by the reduction of CoO to the metallic state—see Fig. 11. Upon increasing the reduction temperature it can be seen that even small 3 nm cobalt crystallites can be quite stable but gradually a bimodal distribution appears suggesting that the main mechanism of growth at higher temperatures is by crystallite coalescence rather than “Ostwald type” ripening.

Whereas a precipitated Co/ThO_2/kieselguhr catalyst was favoured in 1940s, most catalysts recently patented, are promoted cobalt catalysts made by impregnation of a preformed support like titania, silica or alumina using cobalt nitrate [16,30]. While cobalt catalysts made by deposition–precipitation from the cobalt ammine complex show a uniform distribution of small cobalt crystallites [29,31], those made by cobalt nitrate impregnation often contain clusters of cobalt crystallites of up to hundreds of nm [32]. These can be visualised by 3D TEM [33].

Other electron microscopy techniques allow the study of the passivation of cobalt catalysts. A passivated cobalt-on-alumina

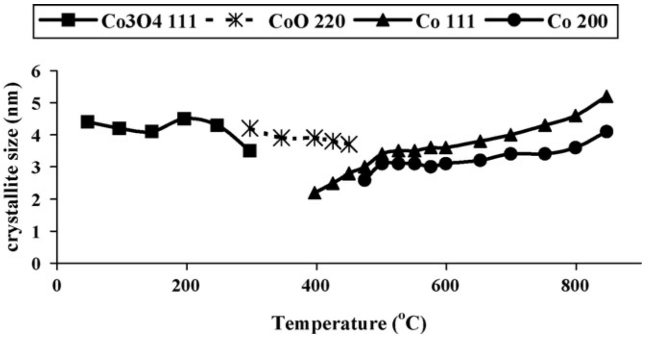

Fig. 11. Crystallite size of 22% cobalt-on-alumina catalyst during reduction [29].

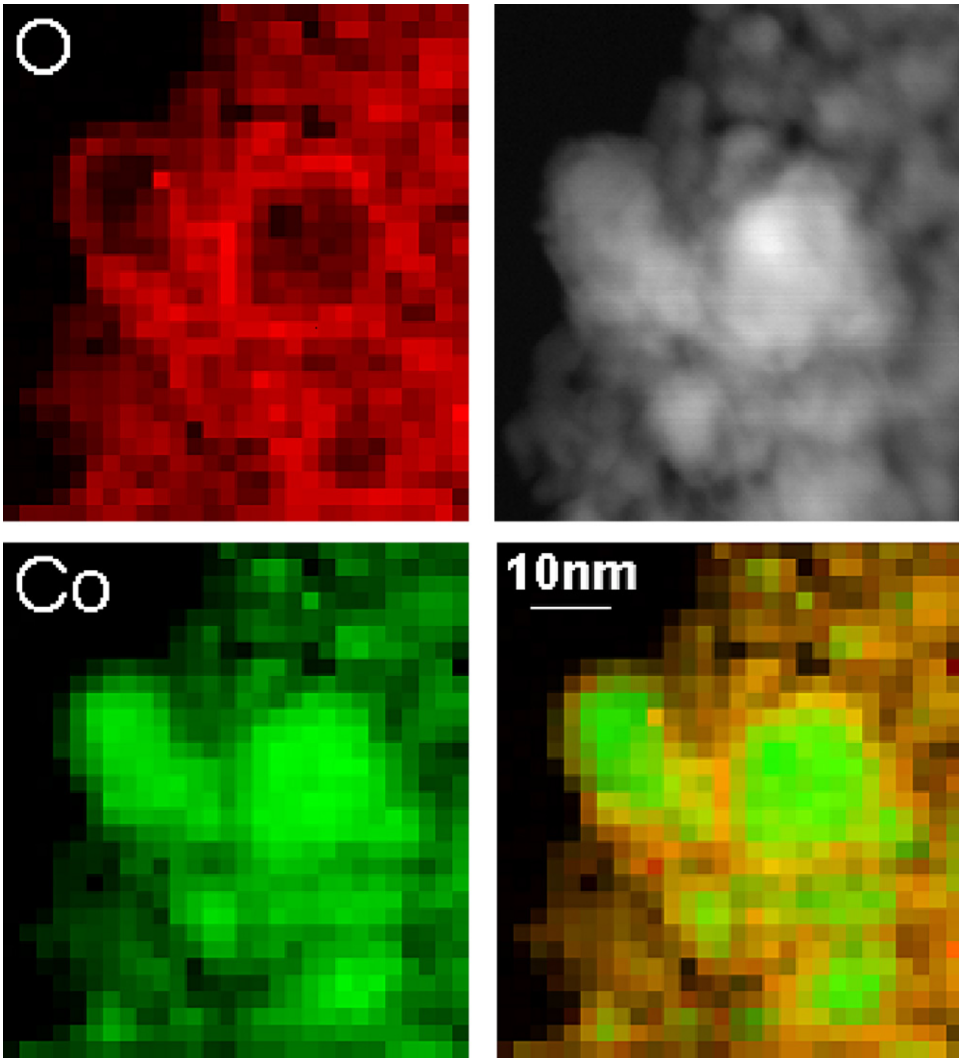

Fig. 12. SuperSTEM micrograph of reduced and passivated 20% Co-on-alumina catalyst showing a cobalt metal nucleus and a cobalt oxide skin. Elemental mapping was done using EELS. After reduction the sample was passivated using 1% O_2 in N_2 at 35 °C for 16 h. The colour images above and below are colour coded as green—Co, red—O and yellow—cobalt oxide.

catalyst was examined (after reduction the sample was passivated using 1% O_2 in N_2 at 35 °C for 16 h) and EELS spectrum imaging was employed to record a full spectrum at each pixel in a STEM image. The pixels for analysis were spaced by approximately 2 nm. Each Co particle has a metallic core and is coated by a 2–3 nm thick oxide layer containing both Co and Al (Fig. 12).

7. Conclusions

Modern Co-based FT catalysts have similarities with those developed by Fischer and Tropsch almost 80 years ago. However current catalysts have benefited from advanced manufacturing methods and characterisation techniques. Today we have the ability to probe catalyst structure with atomic-scale resolution. Using a combination of characterisation techniques, modelling and visualisation software it is now possible to assembly a “picture” of cobalt FT catalysts across four orders of magnitude of length scales.

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