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40 years in catalysis

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1. A stimulating environment

Catalysis is a fascinating field of science because it deals with change and the possibilities of influencing it.

My first encounter with catalysis was an undergraduate assignment on nickel catalysts for hydrogenation of fatty oils. The task was to find the optimum parameters for decomposition of nickel formate (Fig. 1). I studied the book of Roginskii [1] on inhomogeneous surfaces learning that there is a controlling band of active sites for each reaction step. My master thesis dealt with the kinetics of the high temperature shift catalyst under presence of high contents of sulphur [2]. The work was carried out at Haldor Topsøe. My mentor was Hans Bohlbro, who was influenced by Weller [3] and Boudart [4]. He was very careful not to draw conclusions about the mechanism from the kinetic expression. The aim was to develop rate expressions to be applied in reactor calculations. We used power law kinetics which reflected the Freundlich isotherm although the Langmuir–Hinshelwood kinetics was more suited for the computer models. In principle, the different adsorption isotherms represented different distributions of heat of adsorption, but they should rather be considered as mathematical expressions fitting the experimental rate data. The Langmuir assumptions could hardly be valid for the real inhomogeneous surfaces, but Boudart showed with the "paradox of heterogeneous catalysis [4] that the few very active sites controlling the majority of the reaction by themselves could be considered fulfilling the Langmuir conditions.

The industrial catalysis was driven by reaction engineering. Topsøe pioneered the application of computer models developed by Kjær [5] which were applied in the scale-up of the radial flow converter for the ammonia synthesis. The aim of the laboratory work was to provide accurate measurements not biased by transport phenomena. We were influenced by Satterfield and Sherwood [6] whose ideas were advocated in particular by Schoubye [7].

Catalysis was characterised by a number of theories more or less founded in experimental evidence. The trend was to explain the catalytic phenomena in terms of bulk properties of the catalysts with reference to the success of solid state physics in the field of semi-conductors. Haldor Topsøe taught us not to introduce new concepts to explain new phenomena. One should not judge a hypothesis by its effects—rather by its causes. However, it is more common to aim at an agreeable result than at a true result.

It was important parallel to the development work to carry out experiments to understand phenomena which he and Anders Nielsen had done to prove that the vanadium catalyst for sulphuric acid is a supported liquid phase catalyst [8]. The scientific approach was reflected by the thesis work of Nielsen [9], Kjær [10] and Bohlbro [2].

2. Busy times

2.1. Steam reforming

The steam reforming process was in the middle of its major industrial break-through [11] when I joined Haldor Topsøe. It was caused mainly by the use of high pressure and the extension of feedstock from natural gas to naphtha. My colleagues (Wrisberg, Houken, Gehrke, Rump, etc.) were busily engaged with the scale-up to pilot and the first industrial plants. My first tasks included work to create a better understanding of the problems. Most of the laboratory experiments were comparative studies by simulation at industrial conditions in bench-scale units. I found it a challenge to design experiments for measuring relevant parameters for the catalysts which could be used quantitatively. This included of course measurements of the intrinsic activity and for getting a better understanding of the sulphur problem to measure the sulphur uptake of the catalysts at well defined conditions in order to correlate deactivation with the amount of sulphur on the catalyst rather than in the feed. The sulphur capacity correlated with the hydrogen capacity and hence the nickel surface area as shown

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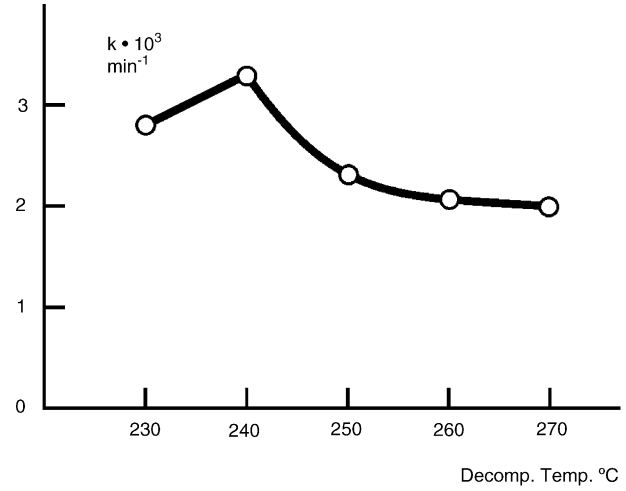

Fig. 1. Hydrogenation of peanut oil. Rate constant and decomposition temperature of Ni-formate (2.5 g Ni-catalyst, 500 g peanut oil, 180 °C, 1 bar abs) (jrn 1960).

in Fig. 2. This was published [12] almost simultaneously with results from LEED studies from the Benard group [13]. We found the same composition of the saturation layer. Sharing office with a surface phycisist, Alstrup, helped me to understand this important input from surface science to catalysis. The sulphur capacity measurements and an isotherm [14] were used for numerous studies. It allowed us to calculate the specific activity as advocated by Bond [15] or the turn-over frequency as advocated by Boudart [16] although it referred to all nickel sites on the surface. Much later the STEM studies of Besenbacher on the nickel/sulphur system [17] proved the conclusions of this early work.

The work on optimising the nickel surface area led to a new catalyst, RKN, which at the same time was alkali-free. The composition was optimised after relatively few preparations and it was operating in industry 18 months after the first laboratory tests. By using active magnesia, it was possible to eliminate the potassium promotion and the problems associated with alkali including a low specific activity [18]. The high activity and enhanced water adsorption on the magnesia support meant that the catalyst could convert heavy naphtha and even diesel if desulphurized [19]. However, the catalyst required new operating procedures and in the initial plants, there were often problems. The analysis of spent catalysts from industry (sulphur capacity, intrinsic activity, etc.) and visits to industrial reforming with problems gave me more input to the further developments than laboratory experiments.

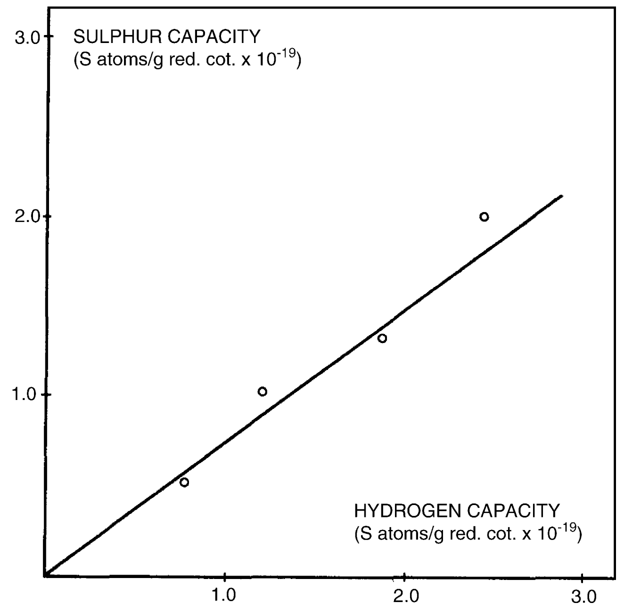

Fig. 2. Hydrogen and sulphur capacity [18].

The alkali free RKN catalyst became a strong element in the competition with ICI using an alkali-promoted catalyst. This was also reflected by a confrontation in literature [20] (Fig. 3). The work on the steam reforming reaction was carried out mainly by ICI [21] and Topsøe [18] with little input in the early 1970s from university groups [11] (Ross, Trimm, Temkin-group . . .). Dowden (ICI) [22] had ideas based on collective properties of the solids. They were strongly opposed by Sachtler [23] who argued in terms of the ‘‘individual surface atom’’—a concept which strongly influenced my own thinking. However, our own understanding of promoter effects remained vague with terms like spill-over [18].

We confirmed that the whisker carbon formed on the catalyst has a higher energy than graphite and found that the deviation depends on the nickel crystal size [24] as shown in Fig. 4. This occurred at the same time as Terry Baker’s in situ electron microscopy studies [25] leading to his temperature gradient driven mechanism. David Trimm and I agreed that it must be wrong as whisker carbon was formed by endothermic and exothermic processes as well. This resulted in joint studies [26] followed up later by his student, Bernardo [27] and his student Tavares [28]. The discussion of the mechanism for whisker growth continued with contributions by Geus [29], Alstrup [30] and others. Later, the interest in nanotubes led to repetition of much of the early studies.

Our observations were the basis for a model for kinetic carbon limits [31]. It was based on the parameters determining the induction time for growth of the carbon whisker requiring it being infinite. Froment et al. [32] developed a model based on

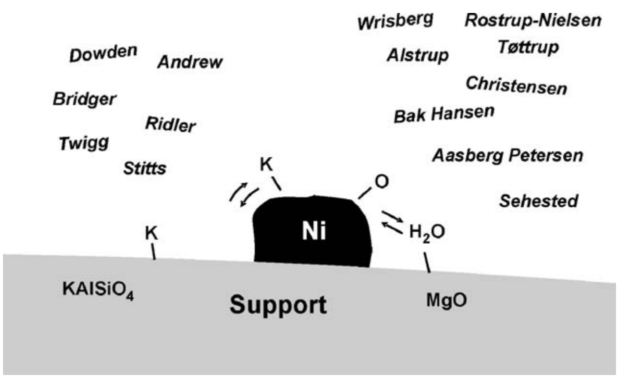

Fig. 3. Different mechanisms for steam reforming of naphtha. Both groups were right.

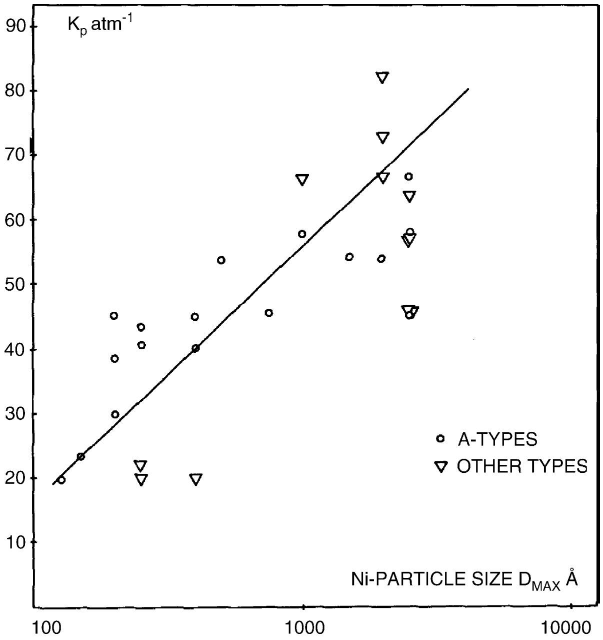

Fig. 4. CH_4 decomposition. Equilibrium constant and Ni-particle size [18].

the parameters determining the rate of whisker growth requiring it being zero.

The early work on the steam reforming catalyst formed the basis for my thesis [18].

2.2. *Towards the limits*

2.2.1. *The SPARG process*

With the improved knowledge about the reaction, it was possible to push the limits for the application of the reforming process. There was a need for a more sophisticated computer model considering the radial gradients in the reformer tube [31,33]. This was developed by Christiansen and Michelsen using the numerical method of orthogonal collocation [34]. A model is no better than the value of the constants involved. These were determined in a full size monotube pilot plant (Fig. 5) [33] and this formed the basis for exploring the limits of reaction with respect to the heat flux, carbon limits and activity.

Fig. 5. The Houston pilot plant.

One result was the SPARG process [35] breaking the thermodynamic carbon limits utilising the knowledge about the chemisorption of sulphur and the nucleation of carbon for "ensemble control". The initiative for the SPARG development did not come from surface science, but was provoked from feedback from industry. We had received a request from a Midrex reducing gas plant [36] for zinc oxide for improving the performance. The plant was operating without desulphurisation, but at conditions violating the "principle of equilibrated gas" [31]. The SPARG principle ("promotion by poisoning") is a dynamic phenomenon. The passivation of sites for nucleation of carbon means that a higher thermodynamical potential for carbon formation is required. As shown in Fig. 6, this amount to 35 kJ/mol to be compared with a few kJ/mol required for a sulphur-free catalyst [31]. The SPARG process was applied in industry to manufacture CO-rich syngas [37] and for a process for direct reduction of iron ore [38], which however was not commercialised. The SPARG process involved CO_2-reforming which was further explored with Bak Hansen [39] using noble metal catalysts to break the thermodynamic carbon limit. Results are summarized in a carbon diagram in Fig. 7 developed by Tøttrup [40].

2.2.2. *Steam cracking*

The pilot approach was also used in attempts to run the steam cracking process with naphtha as feed. The aim was to influence the thermal reactions by the presence of a catalyst. The residence time and temperature distribution expressed as the kinetic severity function is a key parameter in steam cracking and it was not possible to simulate this at laboratory scale. Hence, the need for at full-size monotube pilot.

The project was headed by Wrisberg and we collaborated with Flour Corp. My task was to optimise the catalyst. I had to conclude that the sole role of the catalyst was to change the residence time/temperature distribution in a favourable way. Alkali promotion should eliminate rapid build-up of coke. We

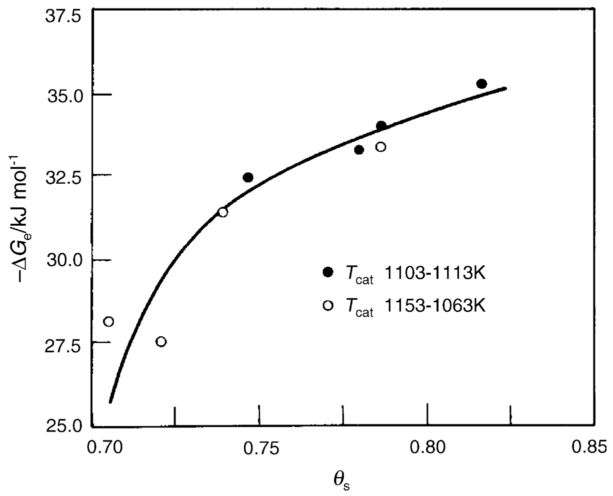

Fig. 6. SPARG principle. Carbon potential for nucleation of carbon and sulphur coverage [31].

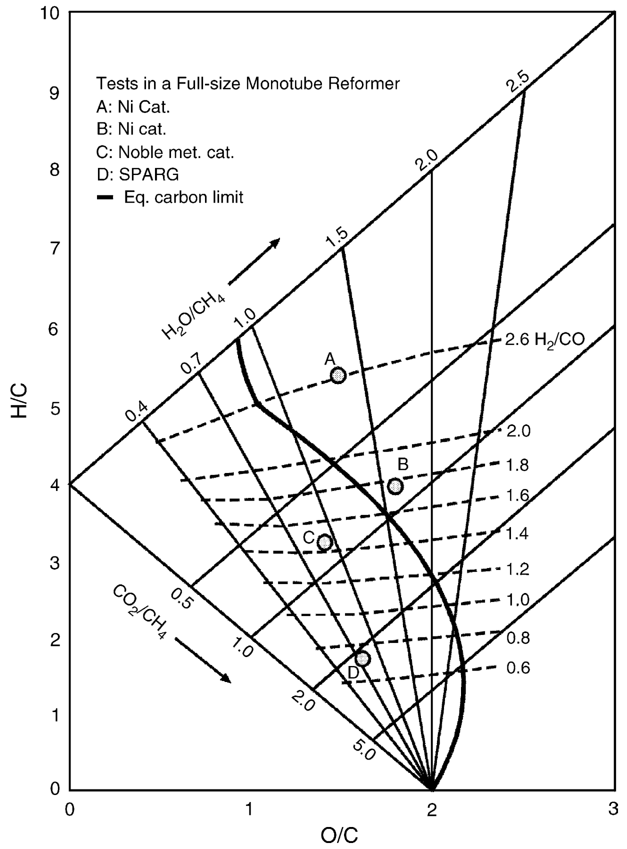

Fig. 7. Carbon limit diagram. Thermodynamic potential for carbon on the left side of the curve ($P = 25.5$ bar. Whisker carbon data ($D_{Ni} = 250$ m)) [40,41].

were able to improve ethylene yields [42] compared with the conventional process, but accompanied by a side production of syngas at the expense of high value aromatic bi-products. It was a disadvantage as the yields were evaluated in terms of gross product value per ton of ethylene. A spin-off of the work was a better understanding of carbon formation in reformers where preheaters may act as a steam cracker.

2.2.3. Autothermal reforming

The development of the autothermal reforming process (ATR) for syngas for Fischer–Tropsch synthesis was carried out primarily at pilot scale because the performance could hardly be studied in the laboratory. The process was pioneered by Primdahl [43] and optimised with Christensen [44] along with scale-up to industrial application utilizing CFD-calculations [45]. Later, this was followed by studies of catalytic partial oxidation by Basini et al. [46] on basis of the ideas of Lanny Schmidt [47].

The idea behind much of the pilot work was to identify the limits of the technology rather than demonstrating the optimum. It is easier to design for critical conditions if you know where the "cliff" is [48].

2.3. The synfuel cycle

2.3.1. Methanation

My career started with steam reforming of naphtha to syngas. During the energy crisis in the early 1970s, it was considered in the US to use low temperature steam reforming of naphtha followed by methanation to convert naphtha into substitute natural gas (SNG). At the same time, natural gas was the primary feed for tubular reforming as illustrated in the synfuel cycle in Fig. 8 [41].

The reforming steps for SNG had been pioneered by the group around Dent at British Gas [11,49], but laboratory tests showed that the RKN-catalyst could also be applied with high activity for converting heavy fuels. Very few SNG-plants were built and none with Topsøe technology which however led to the prereformer technology introduced in the 1980s [50,51].

SNG from coal was more in focus. Syngas from coal gasification was converted by methanation, the reverse reforming reaction. The high temperature methanation process (TREMP) [52] showed economic advantage because of low recycle ratio and recovery of the reaction heat at high temperature. This required that the catalyst was able to maintain low temperature activity after having been exposed to high temperatures. This was the key problem solved by the MCR catalyst which was demonstrated in relation to the ADAM/EVA scheme at Jülich involving mainly Jørn, Skov, Kiilerich Hansen and Höhlein [53].

Goodman [54] was able to correlate his measurements on well-defined nickel surfaces with our rate measurements on an industrial catalyst [55] which led him to the conclusion that methanation is a non-demanding (facile) reaction. This was in contrast to our observations on the impact of alkali on nickel indicating an even higher sensitivity than for reforming as illustrated in Table 1.

In general, the scientific literature on methanation dealt mostly with turn-over frequencies and metal support effects at low temperature of little relevance to the industrial problem. Our understanding of the sintering phenomena was, however, limited. It was not until much later by the sintering and electron microscopy studies by Sehested and Datye [56] that the phenomena could be quantified.

Again, only a few plants were built and without Topsøe technology. Another approach was sulphur resistant methanation converting the raw syngas into methane and CO_2. A special version converted the syngas into C_1–C_3 paraffins with C_2-yields above 50% thus breaking the Flory distribution [57].

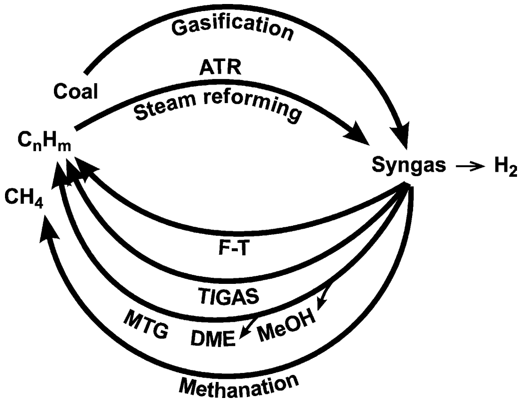

Fig. 8. The synfuel cycle [41].

Table 1
Relative specific activities at atmosphere pressure [18]

Catalyst	Alkali (wt%)	Reforming at 500 °C		Hydrogenolysis of C_2H_6 at 300 °C	Methanation of CO at 250 °C	Decomposition of NH_3 at 500 °C
		C_2H_6	CH_4			
A: Ni/MgO	0.07 Na	1.0	1.0	1.0	1.0	1.0
B: Ni/MgO		2.4	2.0	4.2	9.1	0.9
C: Ni/MgO	0.5 K	0.03	0.09	0.08	0.002	0.9
D: Ni/$MgAl_2O_4$		3.0	1.4			3.2
E: Ni/$MgAl_2O_4$	1.6 K	0.02	0.02			1.5
F: Ni/Al_2O_3		0.7			2.7	0.4
G: Ni/Al_2O_3		2.5		8.7	20.6	0.5
H: Ni/Al_2O_3		0.09			0.001	0.5
I: Ni/C		0.04	0.04	0.01	0.4	0.5

2.3.2. The TIGAS process

We developed the syngas technology for converting natural gas into synfuels, but were not involved in the Fischer–Tropsch synthesis. Topsøe came with the idea of integrating the methanol synthesis with the Mobil MTG process. The integrated synthesis loop called the TIGAS process [58] was further improved by a combined methanol/DME synthesis. The ZSM-5 zeolite was studied by Blom and Joensen with the assistance of work by Derouane [59]. With Heinemann as moderator, an agreement was made with Mobil and the process was optimised and demonstrated involving primarily Topp-Jørgensen [60].

A demonstration of TIGAS in China was given up because of lack of funding due to the Tiananmen Square incident. A spin-off was the discovery by Mikkelsen of DME as diesel fuel and the development of a DME process by Dybkjær and Bøgild Hansen [61].

Some of the synfuel processes, TREMP, TIGAS and prereforming were subject to deactivation by ‘‘gum formation’’ with a ‘‘polymer film’’ blocking the active surface. This resulted in a slow movement of temperature profiles difficult to observe if not studied at true adiabatic conditions. Frennet [62] had studied the slow transformation of adsorbed hydrocarbons and McCarty and Weiss [63] demonstrated the change of reactivity of surface carbon. We learned to characterise the phenomenon in terms of a resistance number [64].

2.3.3. Synfuels revisited

The synfuel processes have been discussed for decades with various routes in the synfuel cycle being of interest. It is only in recent years that the economy of scale, higher oil prices and concerns on flaring natural gas that synfuels have become a reality [65]. One may talk about technologies of present interest rather than new technologies as the focus in the synfuel cycle changes.

The steam cracking work taught us not to enter the fashionable field of oxidative coupling of methane. It is essential for a new catalytic process at an early stage to establish a preliminary flowsheet to identify the economic constraints and the room for improvement including the economic gain, Δp [48,65]. What does it help that the chemistry is fascinating when the process economy is poor [66].

2.4. Regulatory push

Environmental challenges represent a major room for breakthroughs in the catalytic process industry, but at the same time progress is highly determined by ‘‘regulatory push’’ [65]. There was little doubt about sulphur removal from off-gases and the WSA process developed by Schoubye [67] and scaled up in collaboration with the Danish power industry was introduced to a variety of applications. The removal of NO_x from flue gases by the SCR-reaction [68] became a question of regulations. Special design problems are associated with these ‘‘ppm reactions’’ [69] aiming at complete conversion to the ppm level. This is related to kinetics [69,70] as well as to practical problems as poor mixing and bypass [71].

Legislation is also dictating the development of refinery processes. Fuels are specified by chemical composition rather than overall empirical characteristics. Specifications for sulphur have been introduced in most parts of the world [70], whereas specifications on aromatics are not yet generally defined—although the technology is available for combined removal of both [72]. Our work on fixed bed alkylation headed by Hommeltoft [73] using triflic acid as a supported liquid phase catalyst was guided by the wish to have a more environmentally acceptable process, but regulations did not call for a shift in technology. Too often, we see legislation as arbitrary and decisions taken on a short-term basis. This means that short-termism will also influence the planning of industry which might then prefer to respond to legislation rather than to be pro-active in a long term program for more sustainable technology. This is a large challenge for the interaction between the public sector and industry.

2.5. Fuel cells and hydrogen

The steam reforming technology for hydrogen was applied to supply hydrogen for a series of prototype fuel cells from the 1970s. New compact reformers were developed in the 1980 in collaboration with EPRI. It involved new heat exchange concepts and the use of catalyzed hardware [74]. Catalyzed hardware was also involved in our efforts to develop systems for internal reforming in high temperature fuel cells in collaboration with Energy Research Corp. Bernie Baker was a pioneer in internal reforming [75]. I spent much time with him discussing the involved thermodynamics and heat balances [76]. The internal reforming system was demonstrated in a 5 kW MCFC unit with Jørn and Seier Christensen as the key persons. Later, Topsøe got involved in cell and stack development for SOFC in collaboration with Risø [77].

Fuel cells are linked to the creation of a possible hydrogen economy, although the high temperature fuel cells operate more efficiently on natural gas and other fuels.

A future ‘‘hydrogen economy’’ depends on how to solve the CO_2-problem as long as it has to be based on fossil fuels. If the CO_2-problem is disregarded, it may be more feasible to convert hydrocarbons directly in the fuel cell or to convert the fossil fuels into synfuels [65,78].

There are a number of *challenges for future* hydrogen plants [79]. The big surplus of activity in conventional reformers offers opportunities for new compact designs and the integration of the reformer with a membrane will allow full conversion at low temperature.

3. The active site

The concept of the ‘‘active site’’ has changed over the last 40 years. Although the Langmuir approach has been very efficient in establishing simplified reaction kinetics the assumptions behind it do not reflect the reality of catalysis. In general, one may question the meaning of ‘*’ in the reaction sequences [69].

In reaction kinetics, the surface inhomogenity was dealt with by the ideas of Temkin and Boudart [80]. However, the assumptions behind a simplified kinetic approach assuming a rate determining step (rds) and a most abundant reaction intermediate (mari) often break down as these concepts as well as the required ensemble may change throughout the reactor as the temperature and gas composition changes. A microkinetic analysis using stationary state assumptions as suggested by Dumesic [81] solves the rds and mari problem, but there is still a need to include the change of the active site with conversion and temperature [69].

A more detailed analysis of the ensemble was in focus in the 1960s in terms of the socalled B_5-sites introduced by van Hardeveld [82]. I tried to correlate the reforming activity with the number of B_5-sites determined by a cumbersome volumetric method for nitrogen adsorption as illustrated in Fig. 9 [18,41]. There were also some indications that the carbon formation was related to these sites, but it was not possible to come closer.

The ensemble concept was in line with the ideas of Sachtler and Ponec on ensemble control [83,84] and Boudart’s concept of demanding and facile reactions [85]. It was the idea behind the SPARG process with the carbon nucleation requiring a larger ensemble than the reforming reaction. This was supported by statistical considerations [86] meaning that even a homogeneous surface will show different concentrations of ensembles when the coverage of the dopant (sulphur) was increasing. Attempts to achieve ensemble control on Ni, Cu alloys failed [27], but was possible with Ni, Au catalysts [87].

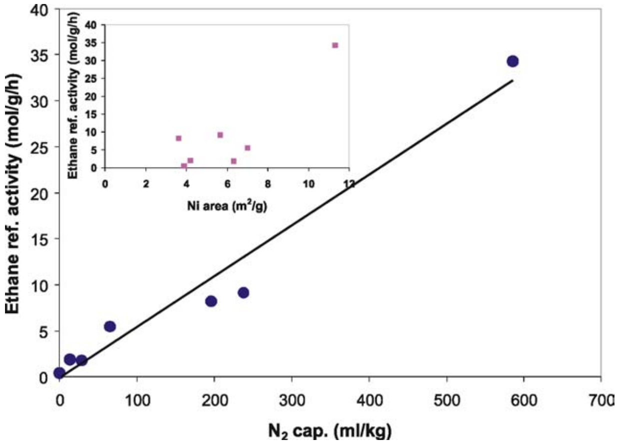

Fig. 9. Rate of steam reforming and the nitrogen adsorption capacity. $NiAl_2O_3$ ($H_2O/C_2/H_6 = 8$, $H_2O/H_2 = 10$ [41].

Surface science gave a new input to the understanding of surface heterogeneity. It was demonstrated (not the least by STM [88]) that the structures of the adsorbed layer does not reflect random adsorption.

Goodmann’s ultra-high vacuum study of methane activation on well-defined nickel surfaces [89] showed higher reactivity of open surfaces than on the dense (1 1 1) surface. Later, adsorption studies (of Chorkendorff et al. [90]) and DFT-calculations (of the Nørskov group [91]) and in situ high resolution electon microscopy (Helveg et al. [92]) showed that step sties play a key role in methane activation as well as for nucleation of carbon. This lead to a consistent description [41] of the active sites involved in the reforming reactions, thus reviving the old idea of B_5-sites.

In general, the studies have given more insight to the nature of the active site [93]. The work by Henrik Topsøe and Bjerne Clausen [94] using EXAFS and other techniques led to the understanding of the CoMoS sites for hydrotreating reactions, and in situ electron microscopy by Hansen et al. [95] demonstrated that the copper crystals in catalysts for methanol synthesis or for low temperature shift reaction changed shape (and hence exposed surfaces) reversibly with reaction conditions. The same was true for the nickel crystals during nucleation of carbon [92]. It means that the active site may adapt to the surroundings almost like enzymes or as expressed by Boudart [96]: *A catalyst is a complex and resilient self-assembly in space and time. A dead catalytic material comes to life by contact with reactants . . . a catalyst as a dead object in line with a fixed structure is a wrong model of the catalytic cycle*’’.

The success of surface science techniques almost developed into the ‘‘noble art of characterisation’’ [66] and led some to the belief that new catalysts could be developed via characterisation and by ‘‘bridging the gap’’ from measurements on well-defined systems to industrial conditions. The techniques should rather be used to formulate new experiments to enlarge our knowledge. Also, DFT-calculations may be used as a rational screening tool instead of combinatorial catalysis.

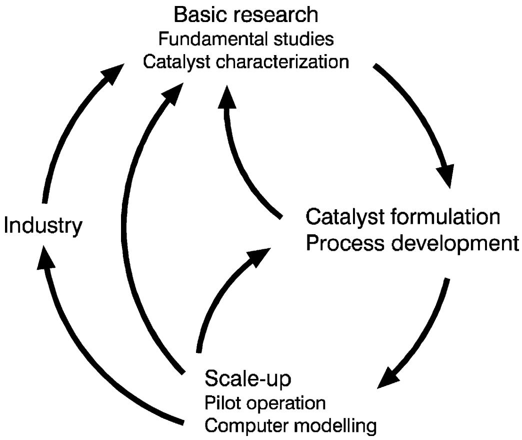

Fig. 10. The loop. Catalyst development is a learning process [96].

Most of our work dealt with catalysts and processes for commodities for which production costs are critical. This calls for process optimisation and high catalyst reliability. This is of less importance for suppliers of fine chemicals [65].

In most of the reactions, I have studied the catalytic activity was not the decisive factor, but rather secondary phenomena such as sulphur poisoning, carbon formation and sintering [97]. These phenomena are best observed in tests running close to industrial mass velocities [48]. The tools available from surface science may then be used to characterise the spent catalysts from pilot plants and industry and form the basis for design of dedicated experiments to understand and quantify the deactivation phenomenon and to give input to design of improved catalysts. In this way, catalyst development becomes a learning process [98] (Fig. 10) and the interaction between pilot work and surface studies may help in focusing fundamental studies on more relevant problems.

4. Conclusions

Catalysis is a fascinating field. It deals with processes which may provide solutions for many of the key problems we face. It provides food through the ammonia synthesis. It creates flexibility in the complex matrix of energy sources, energy carriers and conversion [64] and it contributes in minimizing pollution – but not the least it is a fascinating field of science combining several disciplines ranging from reaction engineering and kinetics to surface science – not to forget the art of manufacturing the catalyst.

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