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An industrial perspective on the impact of Haldor Topsøe on research and development in catalysis by zeolites

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ABSTRACT

The contribution of Haldor Topsøe to the advancement in zeolite science and technology is well recognized by the scientific community. He promoted the development of innovative approaches for the synthesis of zeolite-based materials, which are the basis of important research topics in which still operate numerous research groups around the world; some of the materials obtained are the basis for the development of new technologies applied also at an industrial level. In this paper, the main achievements of Haldor Topsøe in the field of science and technology of zeolites are briefly described and discussed also in view of their industrial perspectives.

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1. Introduction

The people, who had the chance to personally meet Haldor Topsøe, surely fell immediately under his spell: his curiosity and enthusiasm, the richness and the originality of his thought immediately gave the idea of an uncontainable, bursting personality. These features of his character resulted in his professional life in a real passion for the scientific research. However, this passion was not limited to the explorative studies and to new discoveries, but it was also strongly directed toward the application, the development, and the realization of the scientific topics he was studying. These principles were the basis of the creation of a large and important company such as Haldor Topsøe A/S.

One of the authors of this paper has had the privilege of meeting Dr. Topsøe and during a "Topsøe catalysis Forum" held in 2004 in the Havreholm Castle, DK Dr. Topsøe summarized him with a few handwritten lines on a sheet of paper (reported in Fig. 1) his philosophy regarding the scientific r&d: the "Triple A" approach. One "A" for "Activity," because you need to have the passion to work tirelessly to obtain relevant scientific results. The second "A" for "Ambitions" because once you have obtained some positive results you always want to find more to better understand your discoveries. The third "A" stands for "Arrogance" because if you want to improve you have to face new challenges and to take more risks in order to exploit your findings and to develop new technologies up to the industrial scale. This is in a few words the recipe to achieve both your inner and the public success.

Listening to these principles, it comes clear how Haldor Topsøe could create one of the most important companies in catalytic technologies active mainly in the fields of ammonia production, methanol and dimethylether (DME), hydrogen and syngas, SO_x and NO_x removal, sulfuric acid, refinery hydroprocessing (hydrocracking, hydrotreating, hydrodearomatization). The production of syngas and its derivatives (hydrogen, ammonia, and methanol) is probably the most important sector of activity for the company. The capacity of methanol plants is increasing to reduce investments, taking advantage of the economy of scale. The capacity of a world-scale plant has increased from 2500 MTPD a decade ago to about 5000 MTPD today. Even larger plants up to 10,000 MTPD or above are considered to further improve economics and to provide the feedstock for methanol conversion processes (e.g. the methanol-to-olefin (MTO) process). This trend has grown according to the thought of H. Topsøe who strongly supported the idea of an extensive use of methanol (and its derivative DME) as a fuel. This approach was very similar to that of George A. Olah, 1994, Nobel Prize winner, who went even further proposing an extensive use of methanol as a main energy carrier, the basis for a "methanol economy" [1].

Most of the processes developed by Topsøe are based on metal oxides catalytic systems and only a few of them involve zeolites. Nevertheless, H. Topsøe had a great interest for the zeolite science, and the works done by him and his co-workers, for example on hierarchical zeolites, are considered as a reference, as we will see in Section 3. In this paper, we will consider in a perspective view some of the relevant studies involving zeolites carried out by Topsøe.

Among the industrial processes involving zeolite catalysts, it is worthwhile citing two technologies. One is the selective catalytic

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reduction of NO_x using metal-exchanged zeolite catalysts [2], to which the Topsøe's scientists gave a significant contribution to the understanding of the NO reduction mechanism by ammonia over metal-exchanged Y zeolites [3]. The second concerns the refinery's hydrocracking process based on the use of zeolite-containing NiW catalysts [4]. In particular, the proprietary commercial catalyst, named TK-943, contains Ni and W impregnated over an extrudated mixture of a zeolite (Y or beta) and an in-house modified amorphous component. This catalyst is claimed to improve the isomerization activity and the middle distillate selectivity.

However, as anticipated above, the main industrial sector for Topsøe was that of syngas and methanol and in that field we can find a particularly relevant example of zeolite-based industrial processes: the TIGAS (Topsøe Integrated Gasoline Synthesis) process.

2. Zeolite catalysts in industrial processes: the TIGAS process

TIGAS process is designed to produce liquid fuels, mainly gasoline, starting from natural gas.

The year 1973 marked the beginning of the energy crisis that led to a strong interest in synthetic fuels, which could be obtained by feedstock different from crude oil. The methanol-to-hydrocarbons (MTH) technologies were primarily regarded as a powerful method to convert natural gas and coal into high octane gasoline. Methanol is made from synthesis gas (a mixture of carbon monoxide and hydrogen) which is formed by steam reforming of natural gas or gasification of coal. The methanol is then converted to an equilibrium mixture of methanol and DME, which can be processed catalytically to either gasoline (methanol to gasoline, (MTG)) or olefins (MTO), depending on the catalyst and the process operation conditions. In 1979, with the high demand for high-quality gasoline, the New Zealand government selected the MTG technology over the Fischer–Tropsch process for converting natural gas from their extensive Maui field to gasoline. The New Zealand plant started to produce about 600,000 ton/year gasoline from April 1986, supplying about one-third of the national gasoline demand [5]. The gasoline production section of the factory was later closed down, due to the variations occurred in gasoline market price versus the price of methanol, and only the methanol production section of the plant was kept in operation.

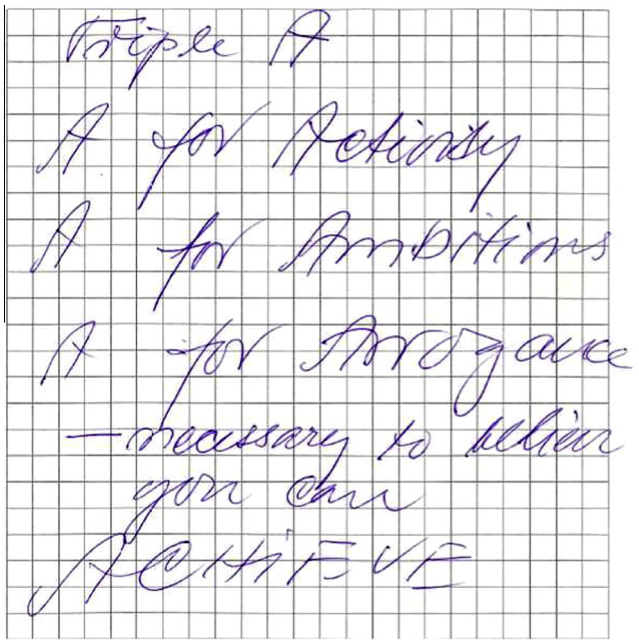

Fig. 1. The "Triple A" approach, handwritten by Mr. Haldor Topsøe: "Triple A: A for Activity, A for Ambitions, A for Arrogance, necessary to believe you can achieve."

The most likely locations for synthetic fuel plants were considered to be in remote areas, where the price of natural gas is lower. For this kind on plants, a low investment cost is a crucial factor, as the investment capital cost will represent a major part of the cost of production, due to the lower energy and feedstock price. As a consequence, several innovation efforts were dedicated to MTG process developments that could positively impact on the reduction of the investment cost. TIGAS process is a relevant example of this kind of efforts.

The basic principle in the TIGAS process is that it is designed in order to get the maximum integration between the consecutive steps [6]. The sequential steps of the MTH process are represented in Fig. 2. With the conventional MTG fixed-bed scheme, the synthesis gas has to be compressed from 15–20 to 50–100 bar before entering the methanol section; subsequently, the condensed liquid product from methanol plant is evaporated and partly dehydrated to DME before being fed to the MTG loop. In the TIGAS scheme, the steps are properly integrated in order to minimize the interconnecting unit operations.

The integration design is not trivial, mainly because the three synthesis steps should preferably be carried out at very different pressures: syngas section at 15–20 bar, methanol synthesis at 50–100 bar, MTG step at 15–25 bar. Starting from the syngas section, the synthesis gas is usually produced by steam reforming of natural gas. Maximum operating pressure is around 20 bar; higher pressures would result in an increase of the leakage of unconverted CH_4 out of the reformer. Moreover, the syngas from the steam reformer would have a composition with a surplus of hydrogen with respect to the methanol synthesis in the further step. A hydrogen purge from the loop would then be necessary. In order to increase the operating pressure of the syngas section, to reach a condition that could better match with the pressure of the second step, a two-step reforming design has been used in the TIGAS scheme. This particular feature includes a tubular steam reforming reactor combined with an auto-thermal reformer in a secondary reforming step. In the secondary reactor, the reaction is thermally self-sustained, through the combustion of part of the natural gas with oxygen. With this process configuration, the maximum operating pressure can be raised to 50 bar, approaching the oxygenates synthesis step pressure. The investment cost for the oxygen plant is more than compensated by the reduced cost of the smaller primary reactor and by the avoided cost related to the surplus hydrogen circuit.

The main feature of the TIGAS process however is the integration of the MeOH/DME synthesis and the subsequent conversion into gasoline in a single synthesis loop, without isolation of methanol as an intermediate. The MeOH synthesis normally needs pressure from 50 to 100 bar. In the conventional MTG processes, the synthesis gas is converted to methanol in a first step and methanol is stored before being converted in a second step to gasoline, after having established the MeOH–DME reaction equilibrium. In the integrated TIGAS process, there is no reason to restrict the formation of oxygenates to methanol, as the catalyst of the last step (hydrocarbon formation) can convert not only MeOH, but also a wide range of oxygenates to hydrocarbon. In the TIGAS process, MeOH can react immediately to form DME, the conversion into gasoline occurs in a single-loop process, thus eliminating the requirement for upstream methanol production and intermediate storage (see Fig. 3a and b). Without going too much in detail with the mechanism of methanol-to-hydrocarbons reaction, it can be seen from the scheme reported in Fig. 4, how the reaction path starts from MeOH and passes through a DME formation step, before the synthesis of the hydrocarbon compounds [7]. The integration in the TIGAS process is based on this sequential

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