From Science to Proven Technology
Development of new Topsoe Prereforming Catalyst AR-401

by

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Abstract
Topsøe is the leading supplier of prereforming catalyst. The RKNGR and AR-301 catalysts have both shown excellent performance in the industry and obtained large market shares. Nevertheless, Topsøe is continuously working towards developing new and improved catalysts. The recent result of Topsøe’s significant research effort is the development of a new generation of Topsøe prereforming catalyst, designated AR-401, which is now being launched.

This paper will describe the route from science to proven technology for the new Topsøe prereforming catalyst AR-401 and discuss the importance of various catalyst characteristics.

Introduction and Background

Introduction to Prereforming Technology
A prereformer is a simple adiabatic reactor operating at temperatures from 350°C to 650°C (Fig. 1). It serves as a pre-converter to a tubular or autothermal reformer converting higher hydrocarbons into methane, carbon dioxide, carbon monoxide and hydrogen using a nickel catalyst.

Fig. 1: Typical installation of a prereformer. The operating temperature range for the prereformer is from 350°C to 650°C.

The first industrial application of prereforming technology was in the old town’s gas plants based on naphtha feedstock. With the closing of the town’s gas plants, the use of prereformers almost disappeared.
Due to the rising energy prices, the technology emerged again in the early 90’s when it became interesting to design hydrogen or synthesis gas plants for lower steam to carbon ratios and use multiple feedstocks. Since then Topsøe has designed more than 60 plants based on prereforming technology.

**Benefits of Prereforming Technology**

In design of new plants the use of a prereformer introduces a number of technical and economical advantages:

In general, the downstream tubular reformer can be reduced by up to 20% in size when installed after a prereformer with reheating of the feed gas giving a direct saving in investment costs.

Due to the higher preheat temperature the reformer fuel consumption is decreased, thus resulting in savings in operation costs.

Operation with multiple feedstocks with conventional reforming catalyst installed in the tubular reformer will become feasible. The reformer sensitivity to varying steam to carbon ratios and feedstock composition is reduced, since almost all higher hydrocarbons are converted in the prereformer.

The lifetime of downstream catalysts will be extended significantly as the prereforming catalyst will absorb any traces of sulphur in the feed. With sulphur-free feed and practically all higher hydrocarbons converted, the risk of carbon formation in the tubular reformer is principally eliminated.

For existing plants, prereforming should be considered as part of a revamp when an increase in plant load or an energy consumption saving is desired.

**Future Perspectives for Prereforming Technology**

Using prereforming technology for hydrogen and synthesis gas production is now an obvious choice in most new plants; especially with the growing interest in using e.g. refinery off-gases as process feed.

Also the development of large GTL (Gas-to-Liquids) plants, where huge amounts of natural gas have to be reformed, creates a new demand for prereformers. By using a prereformer followed by an authothermal reformer, it is possible to optimise the economy balance for plants in mega-size.

**Topsøe Prereforming Catalysts**

Topsøe has been offering two different prereforming catalysts, RKNGR and AR-301, to the industry. RKNGR has a very high resistance towards carbon formation and is typically used for naphtha applications and in plants with multiple feedstocks. AR-301 is our high-activity catalyst for prereforming of natural gas and LPG.

In the development work for a new prereforming catalyst the aim has been to combine and enhance the qualities of RKNGR and AR-301; the ability to process multiple feedstocks, high activity and the ability to preserve the characteristics during a substantial lifetime. With Topsøe’s new prereforming catalyst AR-401 the expectations have been fulfilled.
Science

Catalyst Development Considerations
Developing the optimum catalyst for prereforming is to some extent a compromise between opposing factors. In this section, the following relevant prereforming catalyst characteristics are discussed:

- Content and structure of the active component
- Shape, size and surface area
- Sulphur tolerance
- Mechanical strength
- Carbon formation resistance
- Sintering characteristics

In the development of AR-401, we have combined the best characteristics from earlier generations of catalysts with the feedback we have obtained from the industry and the knowledge we have gained from our laboratory investigations. An exciting new tool is our Environmental Transmission Electron Microscope (ETEM), where atomic-scale in-situ studies of potential next generation catalysts have directed our work in the most beneficial way.

Content and Structure of the Active Component
Nickel in its reduced, i.e. metallic, form is the active component for reforming in commercial catalysts. Therefore the first consideration concerns the nickel content of the catalyst. The art of designing a prereforming catalyst is to optimise the amount of nickel in its reduced form. Nickel as NiO in the support material does not increase the catalyst activity. So simply increasing the nickel content will not necessarily improve the catalyst; actually the activity of the catalyst may even decrease at high nickel contents [1, 2], as illustrated in Fig. 2 [1].

![Activity vs Ni content](image)

**Fig. 2**: Influence of nickel content on catalyst activity. Ni/MgO catalysts. Steam reforming of C₂H₆. H₂O/C=4, p_{H₂O}/p_{H₂} = 10, 0.1 MPa, 773K [1].
It is not only the amount of nickel in the prereforming catalyst that defines the activity. Also the distribution and structure of the actual nickel crystallites are important. ETEM in-situ studies provide insight at the atomic level. It is possible to obtain information about the size, shape and detailed surface structure of the catalyst support and individual nickel crystallites. By using a combination of atomic-level observations and density functional theory (DFT) calculations, it is indicated that the surface structure of the nickel crystallite itself consists of two different types of sites – step sites and terrace sites [3], with step sites dominating the overall activity. In the photo below, a nickel crystallite with the atomic layers is depicted by ETEM.

![ETEM image of the nickel crystallite showing the atomic layers](image)

The fundamental knowledge of the reaction mechanisms on nickel crystallites has been used to design AR-401. In AR-401, the optimal nickel content has been combined with the most advantageous structure of the nickel crystallites, resulting in superior activity of the catalyst.

**Shape, Size and Surface Area**

When the right balance between nickel content and structure of the nickel crystallites has been established, easy accessibility to the active sites must be secured by optimising the surface area of the catalyst.

The reforming reaction is restricted by diffusion and consequently, the main part of the reaction takes place close to the surface. Therefore it is usually advantageous to have small catalyst tablets. The ideal catalyst tablet will have a large pore volume, large pores and a large surface area; however, this is not a simple task to achieve. A large surface area can only be obtained by small pores, which leads to higher pore restriction for the reforming reaction. Therefore, the maximum activity is achieved by optimising the pore size, pore distribution and the surface area.

The pressure drop over a catalyst bed depends strongly on the void fraction of the packed catalyst bed and decreases with increasing tablet size. The pressure drop over a prereformer catalyst bed is usually low (less than 0.3 bar) even with cylindrical tablets giving a catalyst bed with low void. However, in the large ammonia, methanol or GTL plants of today, pressure drop can be a limiting factor [4].
The shape of our prereforming catalysts has been optimised to give both high activity and low pressure drop in larger plants. The pressure drop in a prereformer reactor using Topsøe 7-hole prereforming catalyst will be one quarter of the pressure drop experienced with a standard cylindrical tablet. In Table 1, pressure drops for different tablet shapes have been compared.

<table>
<thead>
<tr>
<th>Shape</th>
<th>Nominal size</th>
<th>Relative ΔP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Topsøe 7-hole prereforming catalyst</td>
<td>11 x 6 mm with 2 mm hole size</td>
<td>1</td>
</tr>
<tr>
<td>Experimental catalyst, cylinder with convex ends</td>
<td>11 x 6 mm</td>
<td>2.5</td>
</tr>
<tr>
<td>Topsøe standard prereforming catalyst, cylinder</td>
<td>4.5 x 4.5 mm</td>
<td>4.3</td>
</tr>
<tr>
<td>Experimental catalyst, cylinder</td>
<td>3.2 x 3.2 mm</td>
<td>6.2</td>
</tr>
</tbody>
</table>

*Table 1: Comparison of relative pressure drop for different catalyst shapes.*

Exclusively looking at the pressure drop, there is no doubt that 7-hole tablets are preferable. When pressure drop is not an issue, the standard cylinder is preferable because it has a higher volumetric activity resulting in a lower catalyst volume. Thus, in order to find the optimal catalyst loading scheme for a prereformer it is important to consider the shape and size of the catalyst.

As its predecessors, AR-301 and RKNGR, the AR-401 prereforming catalyst can be supplied as small cylinder-shaped tablets and in our unique, optimised 7-hole shape characteristic for Topsøe.

**Sulphur Tolerance**

The most common poison for many catalysts, including nickel catalysts, is sulphur. Installation of an effective desulphurisation section is necessary in most plants since almost all feedstocks contain sulphur. Even with a well-functioning desulphurisation section, some sulphur may eventually reach the reforming section. Sulphur-poisoned nickel reforming catalysts have essentially no activity below 700°C [1, 5]. With a prereformer installed, the sulphur is trapped upstream the tubular reformer, thereby protecting this and other downstream catalysts from deactivation by sulphur poisoning.

The sulphur atom in hydrogen sulphide adsorbs strongly to the nickel surface:

\[
H_2S + Ni_{\text{surface}} = Ni_{\text{surface}}-S + H_2
\]

The sulphur poisons the nickel catalyst by blocking of the active sites, starting with the most active step sites, whereby fewer sites are available for the reforming reaction, resulting in a lower catalyst activity. The overall effect of sulphur poisoning is determined by the sulphur tolerance of the catalyst, i.e. the amount of active nickel sites and surface area of the catalyst [3].
During operation of a prereformer, sulphur poisoning can be detected by following the development in the temperature profiles for the reactor. Fig. 3 illustrates the changes in temperature profile, which can be seen in a natural gas based plant with severe sulphur poisoning of a prereforming catalyst.

![Temperature profile diagram](image)

**Fig. 3: Example of development in the temperature profiles for a natural gas based plant with severe sulphur poisoning of a prereforming catalyst.**

The sulphur tolerance of AR-401 has been increased considerably compared to AR-301 by ensuring a larger total number of active sites. The optimisation has been realised by modifying the catalyst recipe based on the knowledge obtained from our research in the nature of active sites.

**Mechanical Strength**

The strength of a catalyst is a critical parameter, as the catalyst both has to withstand the pressure drop across the catalyst bed and the pressure forced by the catalyst weight. The initial mechanical strength is important, but preservation of strength during operation is crucial.

A catalyst with high mechanical strength may be very compact, have a low pore volume and consequently have a low catalyst activity. Therefore, the challenge is to optimise the surface area, without sacrificing the mechanical strength.

The catalyst must be able to withstand the operating conditions to which it is exposed without any phase transformations. In addition, it is advantageous if the catalyst can tolerate condensing conditions without disintegration.

The single phased MgAl₂O₄ support of AR-401 combines mechanical strength with extended surface area. It ensures high mechanical stability of the catalyst under all kinds of operating conditions, including the ability to tolerate condensing conditions. Furthermore, AR-401 can be heated from ambient to operating temperature with process gas.
Carbon Formation Resistance
One of many parameters that need to be investigated is the resistance towards carbon formation. Steam reforming of hydrocarbons involves a risk of carbon formation, which may deposit on the catalyst and result in a deterioration of the catalyst performance. This may lead to partial or full catalyst replacement. Three types of carbon can be found in a reformer: Pyrolytic, encapsulating and whisker carbon. Below, electron microscope images of the three types are shown [3].

Electron microscope images of (A) pyrolytic carbon on MgAl₂O₄ carrier, (B) encapsulation carbon and (C) whisker carbon on Ni/MgAl₂O₄ reforming catalysts [3].

Pyrolytic carbon (A) is typically not found in prereformers due to the relatively low operating temperature.

Encapsulating carbon or gum may occur in a prereformer, when operating on heavy hydrocarbon feedstocks with a high content of aromatic components. Formation of encapsulating carbon is also linked to the temperature and steam to carbon ratio. The risk of formation of encapsulating carbon is higher at lower operating temperatures and low steam to carbon ratio. Encapsulating carbon consists of a thin hydrocarbon film or a few layers of graphite covering the nickel crystallites (B). By covering the nickel crystallites, the catalyst loses activity, i.e. deactivates. This can be observed as a change of the temperature profile in the catalyst bed, similar to the development seen in case of sulphur poisoning. Formation of encapsulating carbon does not influence the pressure drop as it is limited to the individual catalyst tablet.

Whisker carbon formation can completely destroy a nickel prereforming catalyst. Whisker carbon is filamentous carbon with a nickel crystallite at the end (C). It is formed by decomposition of methane, higher hydrocarbons or carbon monoxide:

\[
\begin{align*}
(2) \quad CH_4 & = C + 2H_2 \\
(3) \quad CxHy & = xC + \frac{1}{2}yH_2 \\
(4) \quad 2CO & = C + CO_2
\end{align*}
\]

Normally, only reactions 2 and 3 can occur at prereforming conditions.
The mechanism of whisker growths is tied to the individual nickel crystallite. In gas mixtures where the steam to higher hydrocarbons ratio is too low and the temperature above a certain limit, graphene layers grow on the nickel crystallite pushing it out. This growth continues until it bursts the catalyst tablet, which deteriorates to dust. At some point, the amount of dust formed has reached a critical level and the pressure drop across the catalyst bed starts to increase. Significant formation of carbon will result in excessive pressure drop build-up and subsequently plant outage for skimming or replacement of catalyst. Thorough research has provided Topsøe with the ability to predict the limits for whisker carbon formation, which is essential for good prereformer design.

A valuable tool for in-situ studies of whisker carbon formation is the unique Environmental Transmission Electron Microscope (ETEM) located in the Topsøe laboratories [6]. The ETEM in-situ studies allow us to follow the surface dynamic processes induced by changes in the gas composition in order to investigate the mechanisms of whisker carbon formation on an atomic level [7]. ETEM movies have been recorded to monitor the dynamics in the growth process [8]. Research based on these atomic level observations and advanced density functional theory (DFT) calculations has led to a novel understanding of the interfacial transport mechanisms involved in build up of graphene layers on the nickel atom (Fig. 4). Carbon atoms must diffuse along the nickel surface because the nickel nanoparticles remain crystalline during growth.

![Graphitic nanofiber](image)

**Fig. 4:** ETEM image of a carbon whisker and a schematic illustration of the process by which carbon whiskers are formed at the nickel crystallite during reforming [3, 7].

ETEM in-situ studies have allowed us to test the carbon limits of our nickel catalysts including AR-401, thereby enabling us to give firm recommendations for safe operation of the prereformer.

**Sintering Characteristics**

Sintering or ageing describes a process in catalysts where small crystallites grow in size. Two mechanisms have been proposed: (a) particle migration, where entire crystallites migrate over the support surface followed by coalescence, (b) Ostwald ripening (atom migration or vapour transport), where metal transport species emitted from one crystallite, migrate over the support and are captured by another crystallite [3]. The two mechanisms are illustrated in the photos overleaf.
Two series of electron microscope images of a Ni/MgAl$_2$O$_4$ reforming catalyst: Sequence (a) illustrates the particle migration and coalescence sintering mechanism. Sequence (b) illustrates the Ostwald ripening mechanism [3].

The sintering characteristics of the catalyst have a significant influence on the obtainable lifetime. The carbon limits are affected by the nickel crystallite size, the nickel surface area determines the sulphur capacity and the activity is related to nickel crystallite size [1, 5].

ETEM in-situ studies have provided fundamental knowledge of the mechanisms of sintering and this has enabled us to optimise the nickel crystallite size and distribution in AR-401 to ensure high resistance towards sintering.

**Proven Technology**

**Approval of AR-401 Prereforming Catalyst**
Prior to launching of the AR-401 prereforming catalyst, it has been extensively tested in the laboratory to ensure that it has obtained the required characteristics. Physical tests to ensure mechanical stability are performed both before and after exposure to severe conditions. The composition and structure is analysed through chemical testing. Finally, a series of operational tests with variation in operating conditions such as feedstock composition, pressure and temperature, is carried out. Initially, we test in small scale equipment and if these tests are successful; tests are carried out at industrial conditions in our prereformer pilot plant.

**Installation and Operation of AR-401**
As its predecessor AR-301, AR-401 is supplied prereduced with only a skin oxidation to assure that it is safe to handle at ambient temperature. After installation, no further reduction is required. The start-up of the prereformer with AR-401 installed follows the start-up of the fired reformer.

**Evaluation of Data Prereformer Performance**
When in operation, prereforming catalysts will deactivate over time due to ageing and a slow poisoning of the catalyst. Topsoe has implemented a simple method, denominated a $Z_{90}$ deactivation plot, to evaluate the deactivation rate [4].
Based on the measured temperature profile for the prereformer bed reported over a period of time, the $Z_{90}$ deactivation points can be calculated as described in Fig. 5. Each point is depicted in a $Z_{90}$ deactivation plot as shown in Fig. 6.

**Fig. 5:** Calculation of the $Z_{90}$ deactivation points.

**Fig. 6:** $Z_{90}$ deactivation plot for evaluation of prereformer performance.
During stable operation, the $Z_{90}$ deactivation plot will follow a straight line. The slope of this line indicates the deactivation rate. The first sign of an increase in the catalyst deactivation rate will often be seen as a changed slope in the $Z_{90}$ deactivation plot. When the $Z_{90}$ points approach the bottom of the bed, preparation for replacement of the catalyst should be made.

**Comparison with Prior Generation of Catalyst**

A preliminary comparison of the deactivation plots for AR-301 and AR-401 (Fig. 7) confirms the improved characteristics of AR-401.

![Fig. 7: Comparison of $Z_{90}$ deactivation plot for AR-301 and AR-401 at similar operating conditions.](image)

Our prereforming catalysts have operated impeccably in industrial plants for years. By launching AR-401 we have consolidated our position as suppliers of high-quality prereforming catalysts, which are second to none.

**From Science to Proven Technology**

**Industrial References for AR-401**

AR-401 has recently passed its final exam and we are proud to call it proven technology. It is currently in operation in a hydrogen, an ammonia plant and a GTL plant and it is soon to be installed in a methanol plant. Feedback from our first users indicates stable performance, high activity and low deactivation rate in accordance with our expectations.
References