The role of the methanol-synthesis catalyst
in the transition towards green methanol
Whitepaper



THE ROLE OF THE METHANOL-SYNTHESIS CATALYST

IN THE TRANSITION TOWARDS GREEN METHANOL

TOPSOE

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INTRODUCTION

The world's methanol producers are looking for ways to improve their operational economics. In order to do so, they need to maximize their methanol-loop performance, which is heavily influenced by the activity and selectivity of the chosen methanol-synthesis catalyst. Since the introduction of the first copper/zinc/alumina-based catalyst in the late 1960s, significant research has been conducted within this field with the goal of improving and optimizing catalyst performance. Such research requires fundamental insight into the catalyst function under different industrial conditions.
A plant's actual design may play a role, as it depends on the reforming section's layout; in older plants, reforming was primarily carried out in a steam methane reformer (SMR), resulting in a feed-gas supply to the methanol loop with surplus hydrogen. In recent decades, more optimized designs, based on either an SMR in combination with oxygen-enriched reforming (OSR) or a 1-step autothermal reformer (ATR), have entered commercial operation, and these plants have a more balanced H_2/CO ratio favorable for methanol synthesis. Future plants, producing green methanol or e-methanol, will be based on captured CO_2, with hydrogen being added in required quantities to balance the ratio. Typical make-up gas compositions for different plant layouts are summarized in Table 1.

TABLE 1: Typical gas compositions for different plant layouts

Front end/ feed type	UOM	One-step reforming	Two-step reforming	Coal gasification	One-step ATR (SynCOR™)	Green methanol from renewable sources (CO_2 rich)
Hydrogen	dry mol%	73.6	68.0	66.7	64.2	75
Carbon monoxide	dry mol%	15.8	22.0	28.3	28.6	-
Carbon dioxide*	dry mol%	6.8	8.0	2.8	5.3	25
Methane	dry mol%	3.7	1.5	0.2	1.5	ppm level
Other inerts	dry mol%	0.1	<1.0	2.1	0.4	ppm level

*CO_2 injection may lead to increase in CO_2 content

Alongside the varying gas compositions entering the methanol loop, reactor design influences catalyst efficiency. Earlier industrial plants were based on multi-bed quench-type reactors, or multiple adiabatic reactors with cooling in between. The introduction of more efficient boiling water-cooled (BWC) reactors in the 1980s, and the subsequent emergence of different gas-cooled reactor types, stipulated new operating-temperature regimes (ranges) that catalyst design would have to taken into account in order to accommodate increased space velocity. Table 2 provides an overview of typical operating conditions within different reactor designs.

TABLE 2: Typical space velocities for different reactor designs

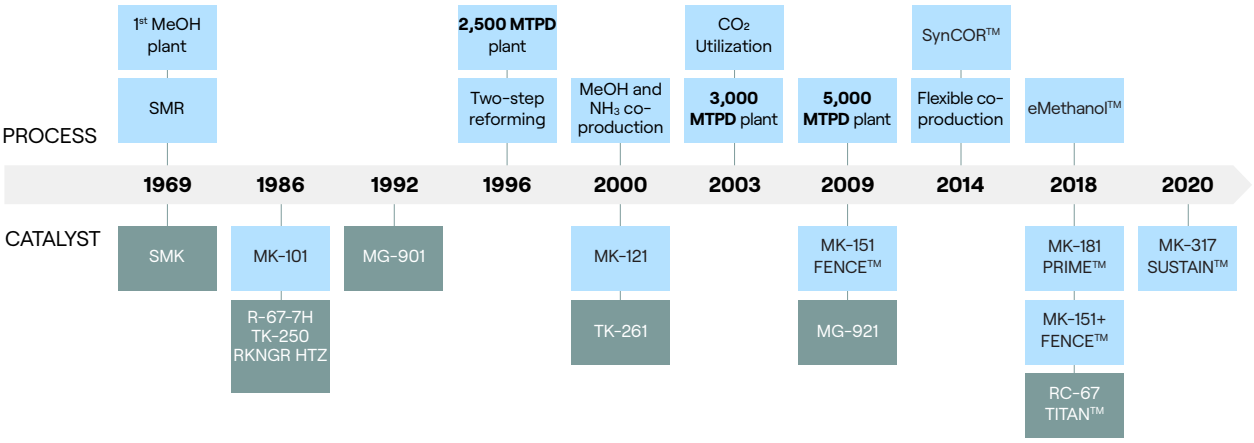
Reactor type	Typical space velocity (h-1)
Boiling-water reactor	~9000-15000
Quench reactor	~8000-9500
Gas-cooled reactor	~8000-9000

As a result, selecting the right methanol-synthesis catalyst for a specific plant is not a trivial task, and must take into account the different designs available, and the operating parameters they facilitate. Over the last few decades, Topsoe conducted a thorough investigation into the modus operandi of the methanol-synthesis catalyst, and developed an understanding of what is required in catalyst to deliver high-activity methanol-synthesis catalysts, with selectivity that can effectively accommodate different conditions and designs. That knowledge will be presented across this document, together with industrial data from select installations.

WHAT DEFINES A GOOD METHANOL-SYNTHESIS CATALYST?

In the field of methanol synthesis, Topsoe has been a significant contributor to both novel and optimal processes, as well as catalysts (Figure 1).

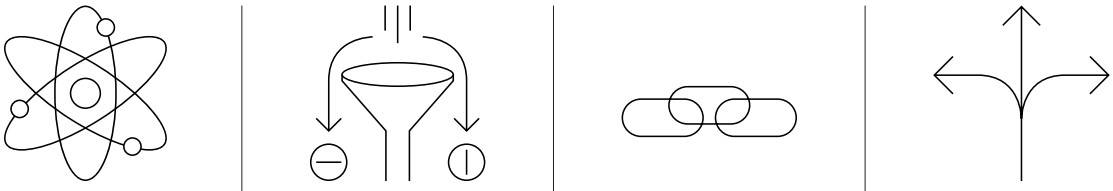
FIGURE 1: Timeline showing key Topsoe contributions to the methanol industry



Within catalyst development, our main focus has been the development of products which can function under the different operating conditions mentioned above without requiring loadings with different products.

In order to ensure effective function of a methanol-synthesis catalyst, the following objectives should be met:

FIGURE 2: Parameters that define a high-performance catalyst



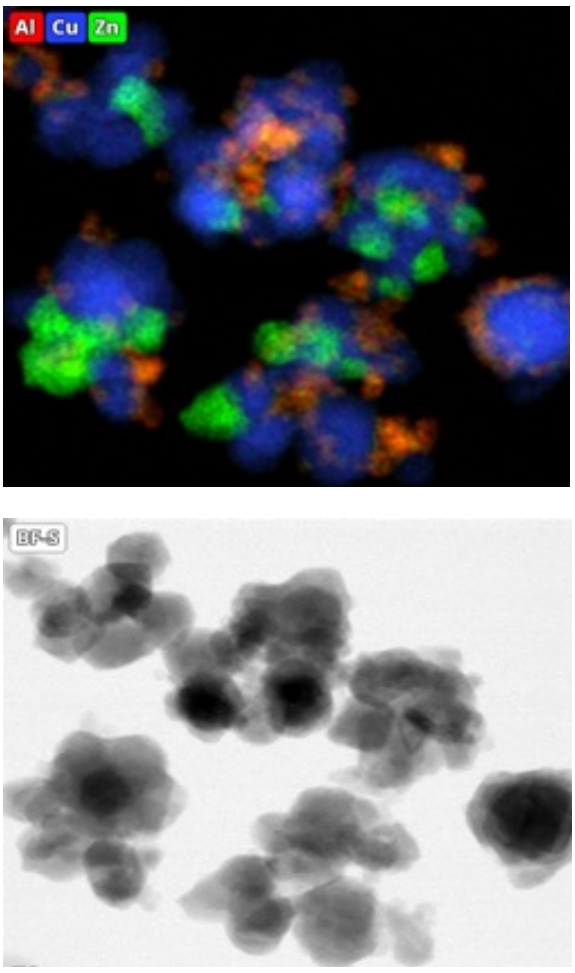
Designing a catalyst that can fulfill the four objectives displayed in Figure 2 requires a fundamental understanding of how the different components of the methanol-synthesis catalyst work under industrial conditions, especially the interaction between copper and zinc – which will be discussed in the following sections.

The Cu/ZnO/Al_2O_3 catalyst

A typical methanol-synthesis catalyst consists of copper (Cu) nanoparticles suspended in nanoparticles of ZnO and Al_2O_3, which separate the Cu particles and act as structural promotors by suppressing their growth. The intimate contact between these components is evident when imaging a spent catalyst using electron microscopy and element mapping (Figure 3).

Cu particles act as the active component in this material, while ZnO and Al_2O_3 can be regarded as structural promoters that separate the Cu particles from one another, thereby diminishing particle growth. ZnO also has the additional, even more important role of assisting Cu in producing methanol, which is explained in the following section.

FIGURE 3: Imagery of a spent methanol catalyst



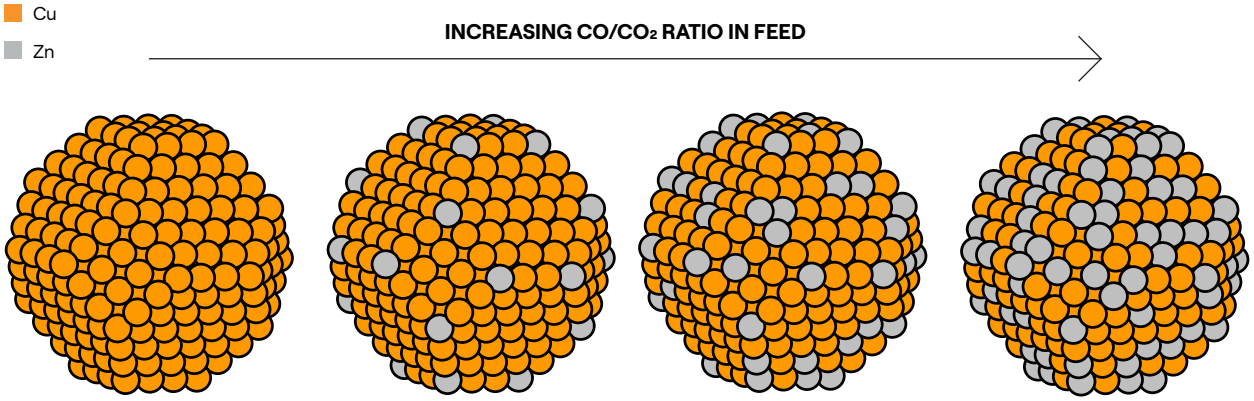
ACHIEVING HIGH ACTIVITY AND STABILITY

It is generally accepted that activity is a function of the Cu surface area, but other factors also play an important role.; While Cu can function alone as a methanol-synthesis catalyst, its activity is substantially boosted by interaction with ZnO, which demonstrates only negligible catalytic activity in low-temperature, low-pressure methanol synthesis on its own.

One of the remarkable discoveries made by Topsoe, in the last decade, involved discovering the mechanism for how zinc assists copper in producing methanol [1].

The activity boost is related to migration of Zn atoms into the surface of the Cu particles. The fraction of surface atoms in the Cu particles substituted by Zn, θ_{Zn}, is a function of the gas's reduction potential. Figure 4 illustrates the increasing fraction of Cu atoms present in the surface of active Cu particles that are substituted by zinc as a function of how reductive the gas is (represented in this case by the CO/CO_2 ratio).

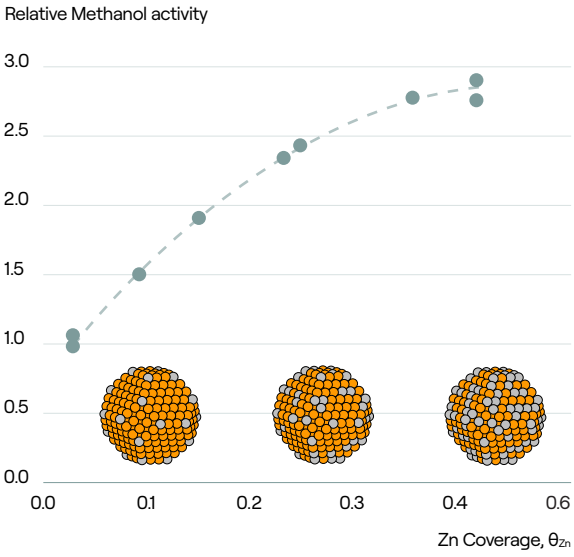
FIGURE 4: Illustration of how Cu surface atoms can be substituted by Zn atoms



The resulting fraction of Zn in the Cu surface ("Zn coverage") is between 0 and 1, and this property is critical to activity, as demonstrated by the data in Figure 5, where we see that methanol-synthesis activity is strongly enhanced by increasing the amount of Zn present in the surface of the Cu particles.

Theoretically, this activity is proportionate to the magnitude of the catalyst's free Cu surface area, which decreases as the Cu-particle size grows. Surprisingly, theory also predicts a strong dependence of the ZnO nanoparticle's size on methanol activity, as illustrated in Figure 6. The takeaway is that it is not only Cu surface area, and, therefore, Cu particle size, that determines a catalyst's performance. The synergetic interaction within the nanoparticle system implies that small ZnO particles boost the methanol activity of the $Cu/ZnO/Al_2O_3$ catalyst system to a greater extent than larger ZnO particles, due to a more efficient

FIGURE 5: Methanol synthesis activity versus the fraction of Zn in the surface of the Cu particles



promotional effect. Therefore, optimal methanol-synthesis activity requires not only small Cu particles, but also small ZnO particles.

The data in Figure 6 is built on the results of a theoretical model. As such, the expected relevance of the ZnO particle's size, in relation to methanol activity, was recently the subject of a dedicated experimental study. To further strengthen this understanding, an experiment was performed to measure activity as a function of ZnO-particle diameter, while keeping Cu surface area almost constant. It was observed that there is, indeed, a dramatic effect on methanol-catalyst activity stemming from ZnO particle size.

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These experimental observations and theoretical considerations advise that the market's most active and stable methanol catalysts are fabricated by optimized, targeted catalyst production methods that produce a catalyst microstructure which not only ensures that small Cu particles are maintained during synthesis, but also, and equally importantly, warrants stabilization of ZnO nanoparticles [2].

High-quality catalysts, where both Cu- and ZnO-particle sizes are kept small and stable during service, are more stable with respect to synthesis activity, and the deactivation rate only increases slowly with temperature. This feature is quantified in Figure 8, where the observed deactivation rates of two different catalyst formulations are plotted as a function of temperature.

Figure 8 shows that the temperature dependence of experimental deactivation rates, and, by extension, the durability and thermal stability of catalyst, are all strongly affected by the catalyst's microstructure, even though the catalyst compositions in question are similar.

FIGURE 6: Zn coverage and methanol activity versus ZnO particle size

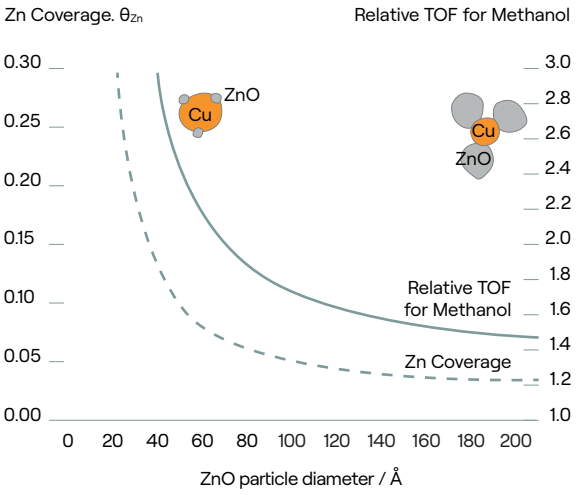


FIGURE 7: Activity divided by Cu surface area, plotted as a function of ZnO particle size

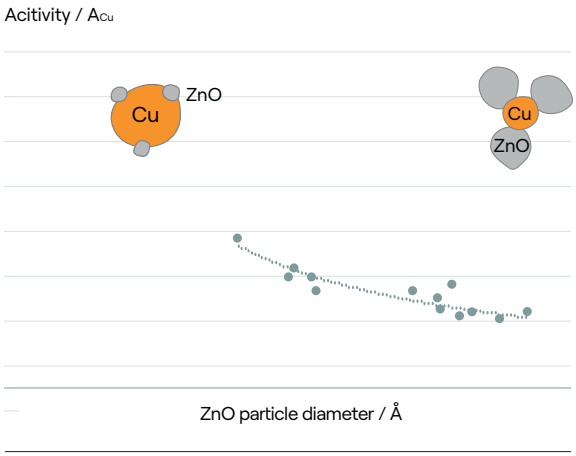
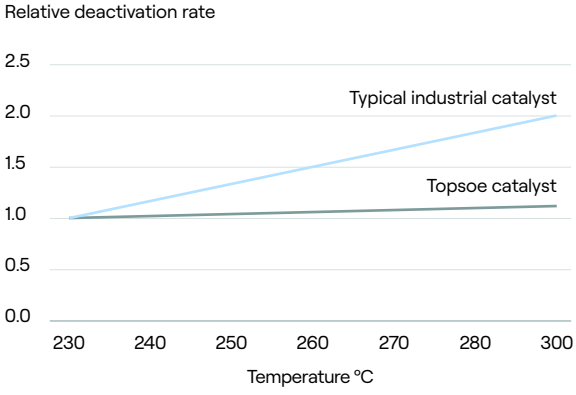


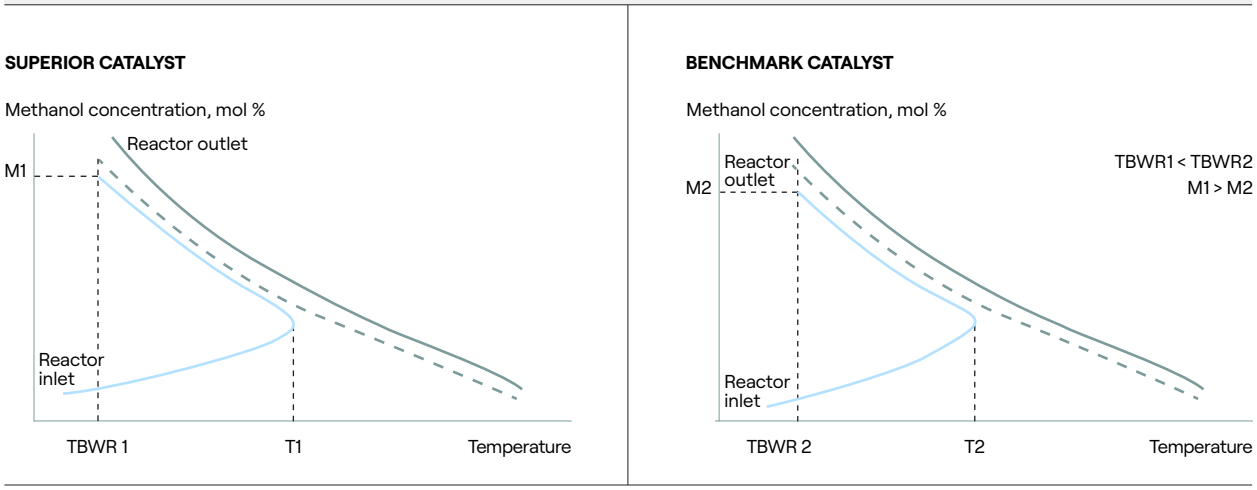
FIGURE 8: Relative deactivation rates of a typical industrial methanol catalyst and a Topsoe methanol catalyst, plotted vs. temperature



HIGH SELECTIVITY

Owing to its excellent thermostability, one type of MK catalyst can be used throughout the entire reactor without any major deactivation risk. Furthermore, its excellent low-temperature activity allows plants to operate at lower temperatures, which again allows for reduced byproduct formation and sintering effects, thereby facilitating increased catalyst lifetime. The advantage of being able to operate at low temperature is illustrated in Figure 9, and has also been noted by other authors [2].

FIGURE 9: Effect of low-temperature activity on overall performance; dotted line indicates maximum reaction-rate line



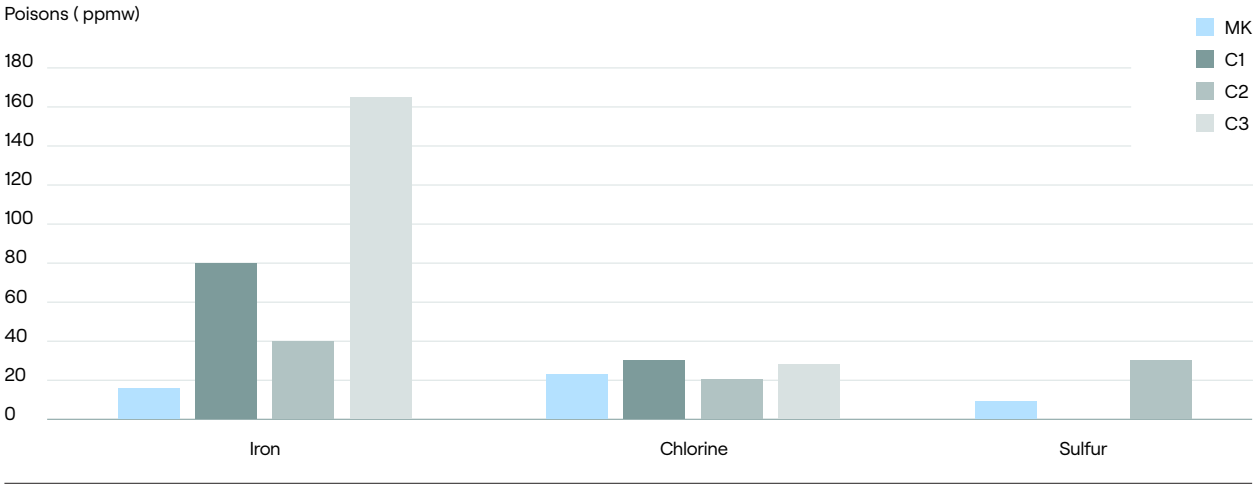
THE IMPORTANCE OF RAW-MATERIAL QUALITY IN CATALYST PERFORMANCE

It is a well-known fact that catalyst formulation is the key to optimal performance. The ingredients (i.e., the quality of raw materials) play a key role in the catalyst's success. Raw-material impurities can affect the catalyst's activity and selectivity, which negatively impacts plant performance because of a reduction in methanol output, and an increase in energy consumption along the distillation section. A particularly problematic byproduct is wax, which is formed if synthesis gas encounters iron at synthesis conditions. The iron source can either be corrosion products from upstream equipment, or the catalyst itself. This wax is deposited within the downstream coolers, leading to increased separator temperature and reduced methanol output; plants suffering from wax-formation problems are often forced to operate at reduced load to mitigate the issue.

Topsoe has developed an in-house iron carbonyl tool that can be used to identify potential iron sources and help the plant plan appropriate mitigation measures. In cases where catalyst poisons are present at the inlet of the methanol-synthesis reactor, a tailored guard solution can be installed. This is often relevant for plants where gasification generates the synthesis gas, or in plants where the use of lower-grade steel can result in corrosion products being present.

MK catalysts are produced with top-quality raw materials containing minimal impurities. This minimizes the risk associated with poor catalyst selectivity. Nevertheless, some catalysts contain significant amounts of iron, as illustrated in Figure 10, which will lead to increased wax formation.

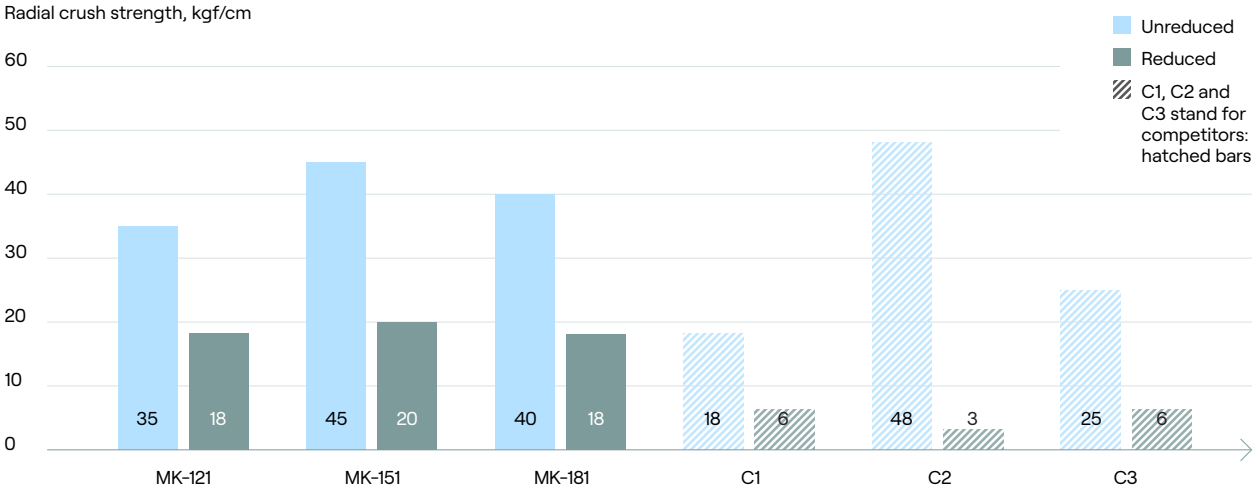
FIGURE 10: Figure 10: Impurity levels in four different catalysts



CATALYST STRENGTH

The catalyst's mechanical strength plays a pivotal role in the success of the methanol-synthesis process. It is important to note that both the unreduced and reduced strengths are important. First and foremost, the catalyst needs to have sufficient strength in its oxidized form to safeguard integrity during loading. Secondly, it is crucial that the catalyst maintain appropriate post-activation strength during service; this ensures low, uniform pressure drop across the catalyst lifetime. Our insight into the modus operandi of the methanol-synthesis catalyst, paired with our understanding of optimized manufacturing, has resulted in the availability of high-strength Topsoe methanol catalysts in both oxidized and activated states, as shown in Figure 11.

FIGURE 11: Mechanical strength of methanol catalysts in oxidized and activated states



Catalyst flexibility

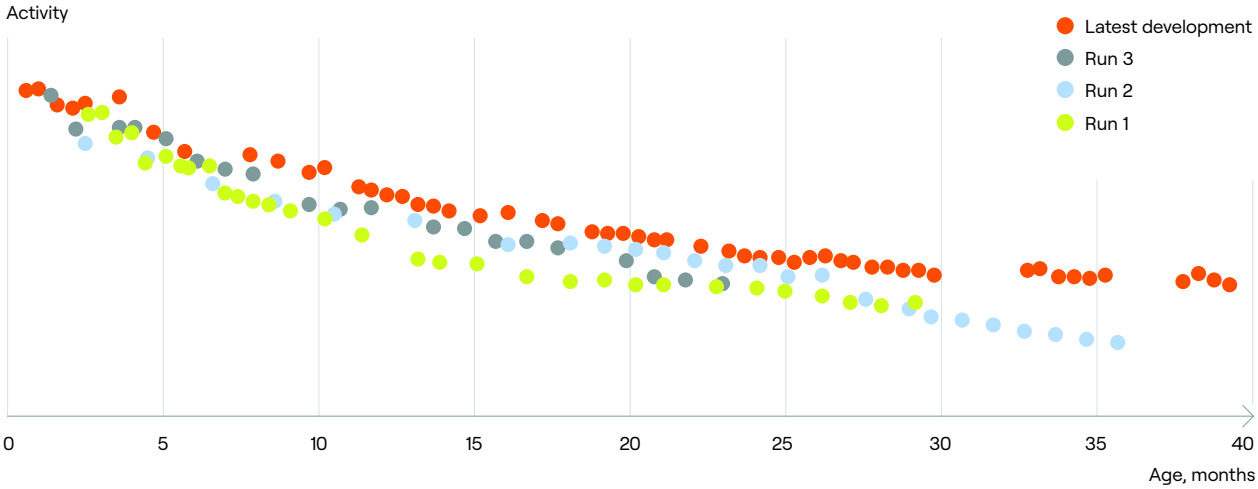
The microstructure of the Topsoe catalyst is critical to the pursuit of high activity and stability, as well as reduced shrinkage. Our proprietary cassette-loading method, developed in-house, provides for high loading density and minimal settling effects during catalyst reduction. A combination of these measures results in uniform, high-density reactor loading, allowing for operation close to the maximum reaction-rate line (shown in Figure 9) within most of the reactor, and thereby making the most efficient use of the available reactor volume. Furthermore, installation of a monolayer catalyst is fast and simple, with a low risk of mistakes, and ensures equal flow distribution within the reactor tubes.

The Topsoe MK catalyst's high operational flexibility allows for use with a wide variety of feed-gas compositions and operating conditions. This is especially relevant for operators who are able to import CO_2 from external sources for conversion to blue methanol, or for those using unconventional feedstocks.

INDUSTRIAL EXPERIENCE

The aforementioned scientific discoveries resulted in a step-change to our understanding of methanol-synthesis catalysts, which in turn led to improvement of our existing products, and the development of new ones. Our newly developed catalyst, which has been in operation at a North European methanol plant for more than three years, has demonstrated significant improvement to performance that was already excellent, as shown in Figure 12. As illustrated in the graphs, higher activity persists after three years of operation, and is remarkably stable. The operation of the latest catalyst charge, at boiling-water temperatures, demonstrates this catalyst's superior activity compared to previous charges at comparable or even lower temperatures. Furthermore, the normalized pressure drop is stable, which proves our ability to deliver another catalyst that fulfills the most important requirements for a well-functioning product capable of high activity, stability, and mechanical strength.

FIGURE 12: Comparison of activities for different charges of MK catalysts

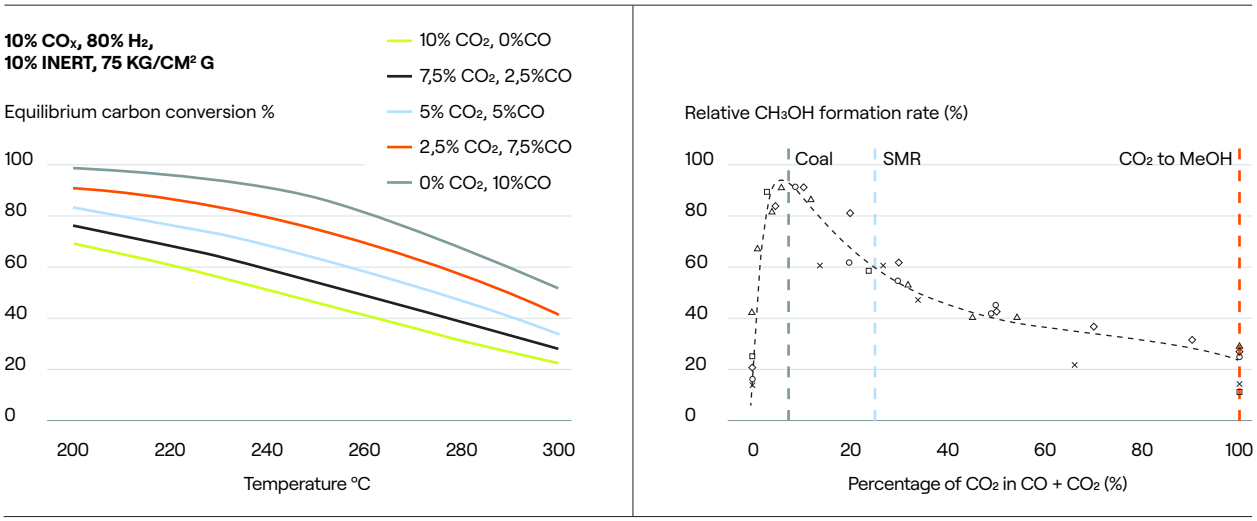


CONSIDERATIONS FOR CATALYST DESIGN WITH CO_2-RICH

Globally, greater amounts of CO_2 are being deployed in conventional methanol plants, and conversion of CO_2 using H_2 from renewable resources is also gaining ground. These developments entail significantly higher CO_2 and H_2O partial pressures along the methanol-synthesis loop. Normally, CO_2 partial pressures in conventional methanol converters range from 1.5 to 7 bar, while green methanol typically operates at CO_2 partial pressures of 5–11 bar. CO_2-rich feeds imply that methanol equilibrium is less favorable, and that traditional catalysts' activity is lower, as illustrated in Figure 13.

FIGURE 13: Fraction of carbon converted to methanol at equilibrium, depending on CO and CO_2 content (left)

Relative activities of different $Cu/ZnO/Al_2O_3$ samples adapted from [3] for different make-up gas compositions (right). "Coal", "SMR," and "CO_2 to MeOH" refer to typical make-up gases obtained by coal gasification, steam reforming of natural gas, and a CO_2 stream mixed with green hydrogen, respectively.



Fraction of carbon converted to methanol at equilibrium, depending on CO and CO_2 content (left). Relative activities of different $Cu/ZnO/Al_2O_3$ samples adapted from for different make-up gas compositions (right). "Coal", "SMR," and "CO_2 to MeOH" refer to typical make-up gases obtained by coal gasification, steam reforming of natural gas, and a CO_2 stream mixed with green hydrogen, respectively.

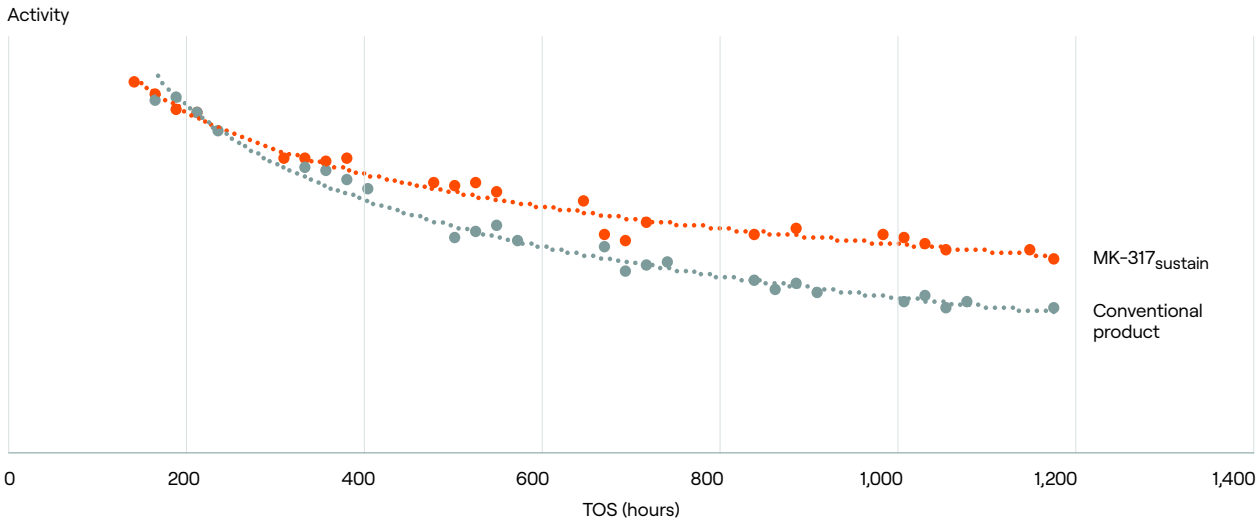
Because of Topsoe's strong commitment to assisting our customers in decarbonizing their operations, and making optimal use of their COv, we have developed a special product for high-CO_2 applications: the MK-317 SUSTAIN™, depicted in Figure 14, which can run with stable, high activity under these challenging conditions.

The exceptional stability of this product under high-CO_2 partial pressures is evident in the data provided by Figure 15, where activity is measured at a CO_2 partial pressure greater than 10 bar, and a temperature of 232°C. Even though our classical products exhibit excellent industrial performance in CO_2-rich gases, as illustrated later, Figure 15 shows that the stability of the MK-317 SUSTAIN™ is unmatched under these demanding conditions.

FIGURE 14: The MK-317 SUSTAIN™



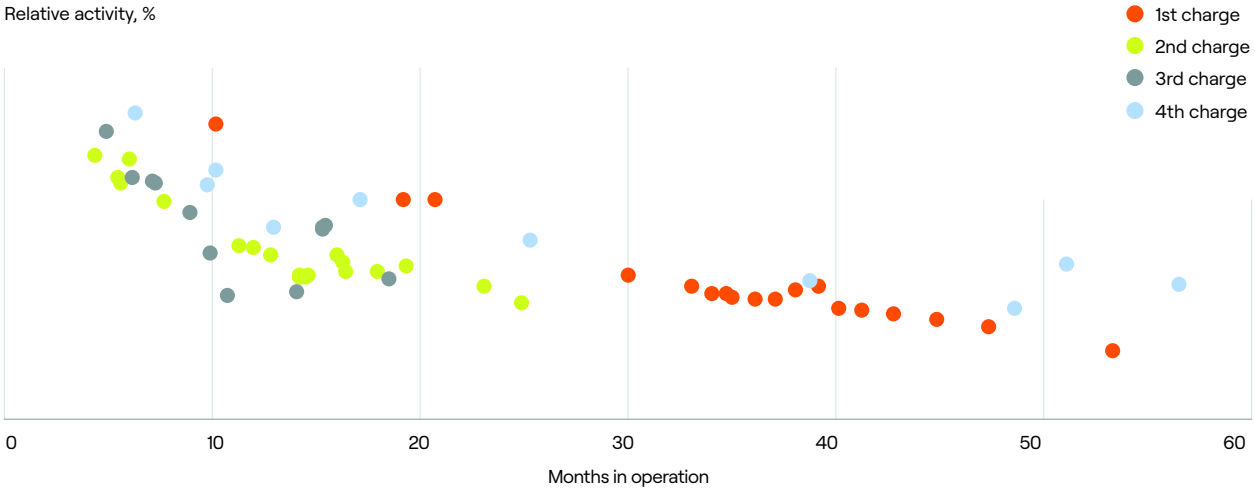
FIGURE 15: Activity levels of a classical Topsoe product and MK-317 SUSTAIN™ in a synthesis gas with a high CO_2 partial pressure (>10 bar)



Industrial performance with Topsoe catalysts in CO_2-rich feeds

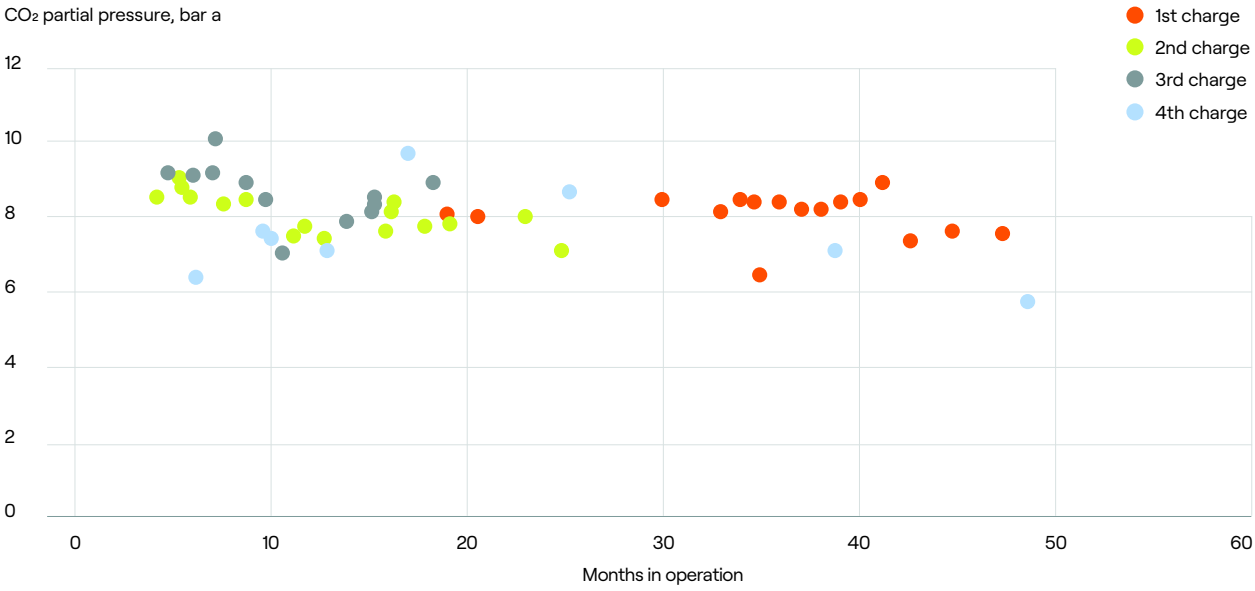
The unique formulation of Topsoe's MK catalysts allows for robust design and flexible operation, both of which contribute to superior performance in plants possessing a broad variety of feedstocks and operating conditions. One such example demonstrates the performance of previous-generation MK catalysts in a CO_2-rich feed.

FIGURE 16: Activity trends of different MK-catalyst charges in CO_2-rich gas



Figures 16 and 17 illustrate that Topsoe MK catalysts operate well and exhibit long lifetime at industrial scale when used with CO_2-rich feedstocks. Our latest development, MK-317 SUSTAIN™, is tailored for CO_2-rich feedstocks and can be expected to perform even more effectively.

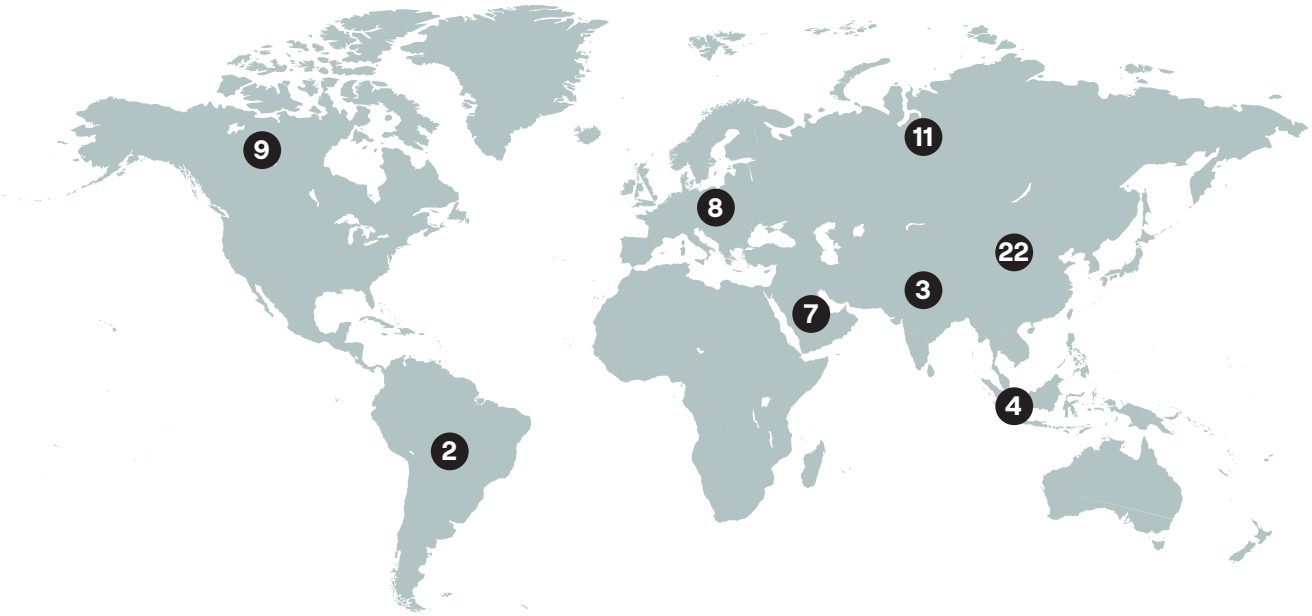
FIGURE 17: CO_2 partial pressure for different MK-catalyst charges in CO_2-rich gas



REFERENCES SITUATIONS

At present, 66 charges of Topsoe's methanol-synthesis catalysts are in operation worldwide (see Figure 18); altogether, more than 200 MK-catalyst charges have been installed in methanol plants across the globe.

FIGURE 18: MK-catalyst references



CONCLUSION

The future of methanol production will be increasingly focused on green methanol and e-methanol, and this increased focus will necessitate modifications to existing methanol-synthesis catalysts – which will, in turn, require investment in R&D that facilitates even greater understanding of how methanol-synthesis catalysts function under industrial conditions. With the recent discoveries of the copper-zinc interplay, and the knowledge of what constitutes a high-performance methanol-synthesis catalyst, Topsoe has achieved an ideal position for providing methanol catalysts that offer effective results for both fossil-, hybrid-, and renewable-based plants.

References

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Founded in 1940, Topsoe is a global leader in developing solutions for a decarbonized world, supplying technology, catalysts, and services for worldwide energy transition.

Our mission is to combat climate change by helping our partners and customers achieve their decarbonization and emission-reduction targets, including those in challenging sectors: aviation, shipping, and production of crucial raw materials.

From low-carbon or zero-carbon chemicals to renewable fuels and plastic upcycling, we are uniquely positioned to aid humanity in realizing a sustainable future.

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