

# Fertilizer Focus



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# Optimization of time-proven catalyst boosts conversion and efficiency

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The Haber-Bosch process revolutionized ammonia production by introducing promoted magnetite catalysts. Despite numerous alternatives, magnetite continues to dominate due to continuous advancements in optimizing iron crystal morphology and promoter dispersion, resulting in the most active magnetite catalyst ever developed.

Magnetite-based solutions offer exceptional longevity, with service lives so extensive that selecting a catalyst is often a once-in-a-career decision. The robustness of the catalyst is even more important when producing green ammonia as these plants will operate at fluctuating conditions depending on the electricity availability.

The catalyst chosen will significantly impact the plant's operating economics, lasting 15-20 years before replacement is needed. A poor choice can have costly consequences, however, because replacing a catalyst involves significant downtime and lost production.

## The margins matter

The Haber-Bosch process is widely regarded as one of the most transformative industrial chemistry

## Global ammonia demand is projected to rise to 470 mn t

innovations, making ammonia fertilizer readily available and fuelling dramatic increases in agricultural yields. Beyond agriculture, ammonia has become a key ingredient in pharmaceuticals, plastics, textiles, and countless other chemicals. Even minor enhancements in this mature technology can have outsized impacts, underscoring the importance of operating margins in determining both profitability and market share.

Under the Net Zero Emissions by 2050 scenario, global ammonia demand is projected to rise to 470 mn t, driven by slight increases in fertilizer use, and a 29.5% growth in industrial applications. However, the most significant demand surge will likely come from new applications, particularly ammonia's use as a marine fuel, which could account for 43% of direct ammonia use by 2050. Additionally, ammonia's role as a hydrogen carrier is set to grow due to its high energy density, ease of transport, and existing infrastructure, making it vital for the energy transition.

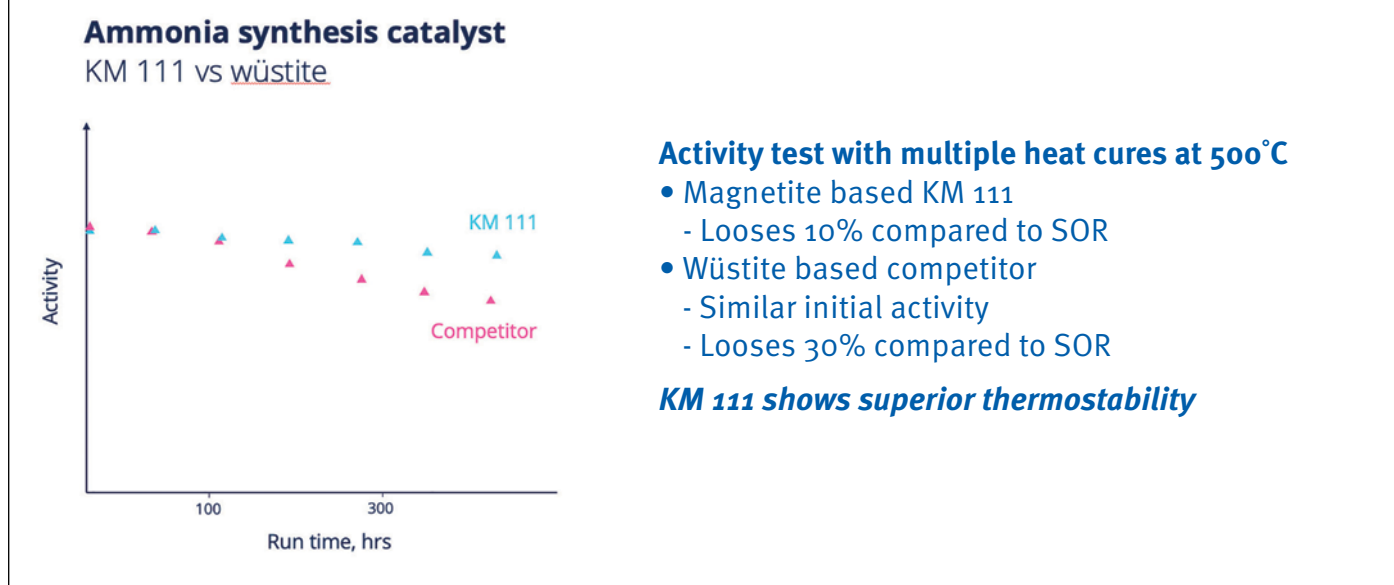
## Developments and parameters

The development of various alternative formulations and technological approaches for ammonia synthesis catalysts has been a constant over the years. About 25 years ago, a catalyst featuring ruthenium on a carbon carrier system, combined with a unique process design, generated significant buzz. However, only a few installations were ever realized due to challenges such as methanation side-reactions and the catalyst's high sensitivity to poisoning. Additionally, the scarcity of ruthenium and the complexity of the production process resulted in prohibitively high costs, rendering the process commercially unviable.

In 2005, a new iron catalyst, based on a promoted wustite phase, was introduced commercially, driven by a Chinese development initiative. This catalyst has since gained some market share in China. To evaluate the characteristics and advantages of magnetite-based versus wustite-based catalysts, it is essential to understand



**Figure 1.** Ageing experiments of commercially available magnetite and wüstite based ammonia synthesis catalysts



the key features that contribute to a long-lasting ammonia synthesis catalyst, including:

- High and stable activity
- Low deactivation rate
- Effective stabilization of pre-reduced versions

### Activity and balance

Achieving high catalyst activity requires not only the optimal amount and distribution of promoters on the iron surface but also a substantial presence of highly active Fe(111) sites. These sites, characterized by an open iron surface, allow easier access for gas reactants, thereby offering significantly higher ammonia synthesis activity compared to the more closed structures of Fe(100) and Fe(110) sites. Magnetite itself does not inherently favour any of these sites, so their formation is a factor that can be controlled and optimized during catalyst fabrication by selecting the appropriate manufacturing conditions.

While suitable promoters can partially compensate for the absence of Fe(111) sites, they can never fully achieve the same level of activity.

### The Importance of promoter distribution

The use of structural promoters such as Al, Ca, Si, and Mg is crucial in reducing the sintering of active iron sites during operation, which in turn lowers deactivation rates and maintains stable production rates in industrial units. However, to achieve optimal promotion effects, these promoters must be evenly distributed across the iron surface. On magnetite catalysts, this uniform distribution can be achieved through the appropriate techniques during catalyst fabrication.

Researchers highlight the challenges of achieving even promoter distribution on wüstite-based catalysts, which often leads to higher deactivation rates. To explore this issue further, the Topsoe Research & Development department conducted aging experiments on both magnetite and wüstite-based catalysts. The experiments, conducted at 500°C with a gas composition reflecting typical industrial conditions (a hydrogen/nitrogen ratio of 3) and at pressures of 20 MPa, revealed the impact on deactivation rates.

Accelerated aging tests reveal that magnetite-based materials lose only 10% of their activity, while wüstite-based materials experience a substantially higher loss of 30% of their Start-of-Run (SOR) activity.

### Stability of pre-reduced ammonia synthesis catalysts

In a typical ammonia synthesis reactor, the catalyst loading consists of a pre-reduced layer in the first bed and oxidic catalysts in the lower beds. The oxidic catalyst in the lower beds must be reduced in situ over several days during start-up. Some plants use pre-reduced catalyst in all beds to save start-up time and reduce the production of ammonia-containing water during catalyst reduction. This approach can save 2-3 days of reduction time, resulting in a significant increase in ammonia production.

The pre-reduced catalyst is manufactured in a separate step after the oxidic catalyst is produced. While most catalysts are pre-reduced at the same facility as the oxidic



The KM 111 catalyst

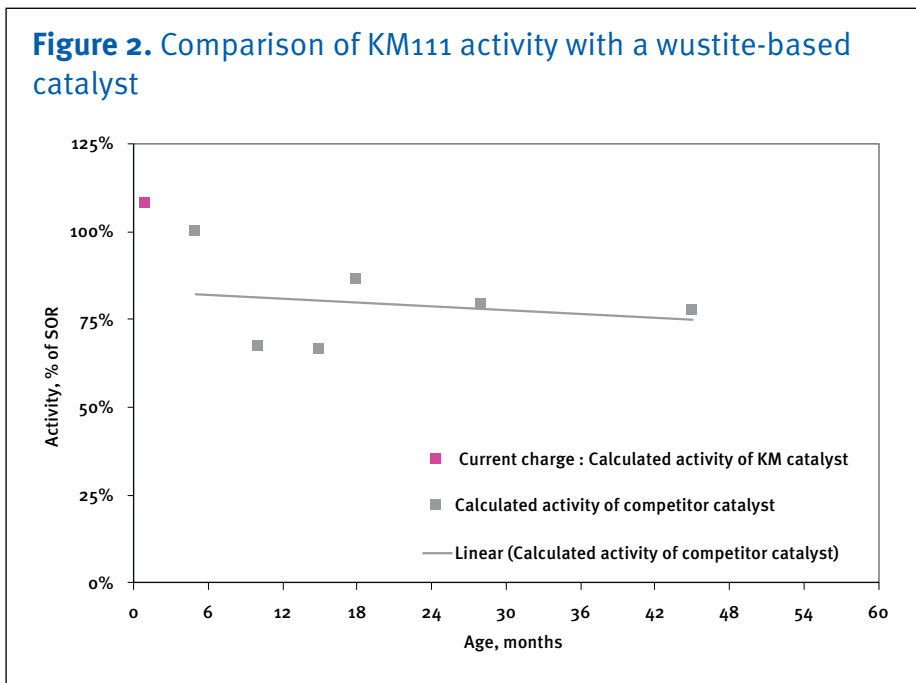
catalyst, some are handled by third parties. It is crucial that this process is carefully controlled to ensure maximum activity, as the catalyst's pore structure is formed during this reduction step. Heating rates and water content must be meticulously monitored. Researchers conducted a detailed investigation which demonstrated that fast reduction results in a narrow reaction zone progressing from the surface to the dense centre. In contrast, high H<sub>2</sub>O concentrations inhibit the reaction, leading to uneven reduction across the iron particles.

After achieving full reduction, a separate passivation step is necessary. Without proper passivation, the catalyst may begin to heat up when exposed to air, risking significant delays during loading. In most cases, this would require the reactor to be blanketed with nitrogen. If passivation is inadequate, the catalyst's activity will be lower than expected, and it should be discarded if possible.

From research investigations to market feedback

How does magnetite perform in industrial settings? After over 13 years of successful operations with the KM magnetite catalyst, one plant switched to a wustite-based catalyst.

Figure 2. Comparison of KM111 activity with a wustite-based catalyst



However, this catalyst exhibited much faster deactivation than the previous KM charge. After 10 years, the plant decided to revert to the Topsoe KM magnetite catalyst. The first 12 months of operation with the new Topsoe KM catalyst confirmed its high activity level.

Years of Topsoe's research into magnetite phases and suitable promoters, combined with industrial feedback, led to the launch of the KM 111 and pre-reduced KMR 111 catalysts in 2014. Since their introduction, these catalysts have been installed in over 70 ammonia

plants worldwide, representing 25% of the plants for which Topsoe provides catalyst solutions. A recent example is a U.S. ammonia plant that replaced a wustite catalyst with KM111 in a three-bed reactor, using pre-reduced catalyst in the first bed and KM111 in the second and third beds.

The wustite-based catalyst was replaced after four years due to mechanical issues in the ammonia converter. The plant opted for the magnetite-based KM111 due to its lower deactivation rate and higher activity, as clearly demonstrated. ■