

BASF: The right choice for nitric acid plants

BASF supplies environmental catalysts and technologies which reduce or destroy nitrous and nitric oxides emissions from nitric acid plants. Tailor-made solutions combine catalytic technology and project management services for emission reduction projects.



Technical Note



Figure 1: BASF catalysts for N_2O decomposition (left) and NO_x abatement (right)

The nitric acid (HNO_3) industry is a major source of nitrogen oxide (NO_x) emissions, including nitrous oxide (N_2O) or laughing gas. Nitrous oxide is 310 times more effective than carbon dioxide (CO_2) in trapping heat in the atmosphere. BASF offers state-of-the-art N_2O decomposition and selective catalytic reduction (SCR) De NO_x technologies (Figure 1) which reduce N_2O and nitric oxides (NO and NO_2). Both catalyst families, which were originally developed to reduce harmful impurities in nitric acid and adipic acid plants, have been

utilized for emission removal in numerous industrial applications, including off-gases from various sources. They can be used either individually or in various combinations in relevant plant configurations, as shown in Figure 2. These environmental solutions combine the strength of BASF - The Chemical Company with the expertise of its chemists and engineers for innovations that meet regulatory compliance while enhancing operations.



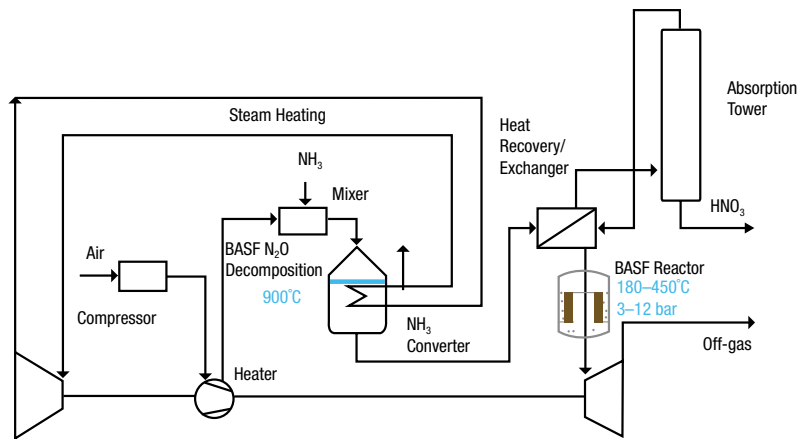


Figure 2: BASF's N₂O decomposition and DeNO_x abatement technologies in a nitric acid plant

N₂O Decomposition & Climate Gas Reduction

BASF N₂O decomposition technology supports the goals of the Kyoto Protocol including emission trading certificates. N₂O decomposition technology destroys N₂O emissions up to 100%. The decomposition of 1 ton of N₂O has the same effect as saving 310 tons of CO₂ emissions.

The catalysts are used for, but not limited to, the following worldwide industrial N₂O emission sources, such as:

- Nitric acid plants
- Adipic acid plants with referring license and design
- Caprolactam plants

Selective Catalytic NO_x Reduction (DeNO_x)

BASF offers catalysts for the selective catalytic reduction of NO_x from stationary source gases. The DeNO_x process was developed by BASF in the 60s and the V₂O₅ catalysts were developed in the 70s.

The catalysts are used for, but not limited to, the following applications:

- Nitric acid plants
- Power plants (coal, oil, gas, biomass)
- Gas turbines
- Gas and diesel engines
- Ship diesel
- Railroad engines
- Glass trough
- FCC units in refineries
- Steam crackers
- Steel mills
- Calcination plants
- Cement plants
- Waste incineration plants (municipal waste, hazardous waste, clinical waste)

BASF's Long History of Outstanding Climate Protection

With its impressive background in chemical technologies and strong desire to improve the atmosphere, BASF was designing and installing solutions for the environment before regulatory limits on harmful emissions were even established. Since the 1960s, BASF's DeNOx abatement techniques have been in place in BASF plants. This technology was expanded to third party plants worldwide in the 1970s. Starting in the 1990s, innovations for the abatement of nitrous off-gases in nitric acid and adipic acid plants have been employed.

In the 1970s, the basic configuration for the SCR process consisted of a promoted vanadium/titanium oxide catalyst that catalyzed the reaction of ammonia (NH_3) with NOx. Different operating temperatures and pressures were investigated for the initial catalyst generations. In the early 2000s, a "one size fits all" system was launched and showed outstanding properties that met the regulatory policies of global authorities. The complete single-stage system consisted of an axial radial flow (ARF) reactor, NH_3 dosing mechanism, and control and measuring unit equipment. Successful multi-stage systems have also been implemented.

A major issue requiring attention was the pressure drop over the catalyst. To analyze this, BASF initially operated their own plants with ARF reactors, taking into consideration the capital expenditures (CAPEX) and operating expenditures (OPEX) of the plants even in these early years of the SCR on a production scale level. Many niche applications of this technology followed. With continuous efforts to develop and optimize its high-performing SCR technology, BASF created a DeNOx catalyst that combines low pressure drop, high NOx conversion and selectivity, very low NH_3 slip, and close to zero ppmv generation of N_2O over the entire DeNOx system.

The N_2O decomposition catalyst followed a similar developmental process. The philosophy was to scale up the initial catalytic technologies for use in BASF plants. This was followed in the early 2000s by a transfer of this technical expertise to third party plants. BASF currently provides the highest N_2O efficiency with a possibility of greater than 90% reduction.

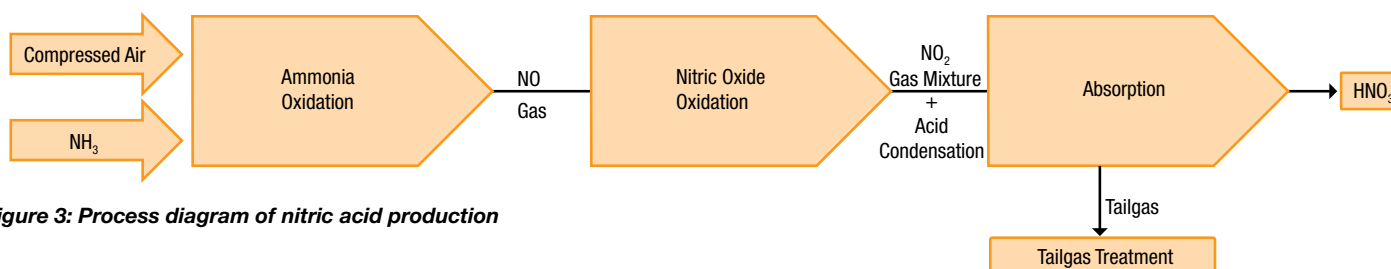


Figure 3: Process diagram of nitric acid production

Nitric Acid Production

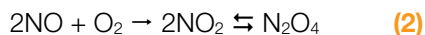
Nitric acid plants are often part of a larger production facility, such as fertilizer or explosives manufacturing. This creates significantly different operational environments. Diluted HNO₃ with a concentration range from 30–70% is produced via ammonia oxidation, nitric oxide oxidation, and absorption, as shown in Figure 3.

Ammonia Oxidation: The initial step involves oxidizing ammonia over a platinum (Pt)/rhodium (Rh) gauze catalyst to produce nitric oxide and water. This exothermic reaction uses approximately 900 kJ/mole of heat and is given by:



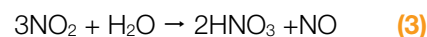
Air for this process is compressed, filtered, and preheated by a heat exchanger. The heated air is then mixed with vaporized ammonia. The ammonia-air mixture is passed to a converter where it is catalytically converted to nitric oxide and excess air. The temperature of the catalyst affects the output of the converter. Higher catalyst temperatures cause a greater selectivity towards NO production, while lower catalyst temperatures result in creation of N₂ and N₂O.

Nitric Oxide Oxidation: The NO formed during ammonia oxidation must now be oxidized. The process stream passes through a condenser and is cooled. The NO combines non-catalytically with residual oxygen to form NO₂ via the following reaction:



As seen in equation 2, the liquid dimer, nitrogen tetroxide (N₂O₄) is also generated. Low temperature and high pressure operations promote maximum NO₂ production.

Absorption: The nitric oxide mixture is pumped into an absorption tower and then absorbed into H₂O. Oxidation takes place in the free space between the trays, while absorption occurs on the sieve or bubble cap trays. The chemical reaction in the tower is:



This reaction is exothermic and continuous cooling is required within the absorber. A secondary air stream HNO₃ is pumped into the tower to re-oxidize the NO and remove NO₂ from the HNO₃. The concentration of the HNO₃ produced depends on the number of absorption stages as well as the concentration of the NO₂ entering the absorber.

Controlling Harmful Emissions the Catalytic Way

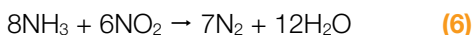
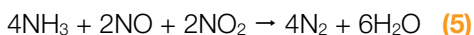
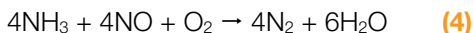
A major source of NO_x emission is the tailgas from the absorption tower. This continuous emission is heavily dependent on the process and increases can occur with:

- Insufficient air supply (Oxidation and absorption)
- Low pressure (Absorption)
- High temperature (Condensation and absorption)

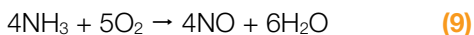
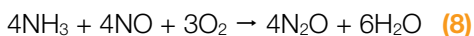
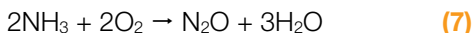
The output gases may vary within the following limits:

NO_x: 300–3,500 ppmv
N₂O: 300–3,500 ppmv
O₂: 1–4 vol %

Various control mechanisms can be implemented throughout the HNO₃ plant. While extending the absorption process can reduce tailgas NO_x emissions, catalytic reduction allows operation over a wider range of pressures. SCR utilizes a catalyst to react with the injected ammonia and chemically reduce the NO_x. Ammonia is injected before the catalyst layer at a temperature between 120°C and 450°C. This process is precisely controlled because an insufficient amount of NH₃ causes low NO_x conversion rate, while too much NH₃ results in a leakage of unconverted NH₃ from the reactor. The NH₃ is absorbed onto an active site on the catalyst where it reacts with the NO_x to produce the harmless by-products nitrogen (N₂) and water (H₂O).



However, unwanted N₂O and other emissions are also generated by the ammonia oxidation step (Equations 7–11).



The amount of N₂O formed depends on many factors, including the combustion conditions in the oxidizing unit, catalyst compositions, catalyst age, and burner design.

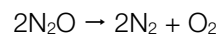
The N₂O control mechanisms are defined by their location within the production process. Primary controls are done for the oxidation process by either modifying the catalyst or optimizing the operating conditions. Secondary techniques reduce the N₂O immediately after it is formed in oxidation. The preferred location for installation is directly after the gauze in the reactor basket. Tertiary controls abate the N₂O by installing a catalytic reactor either upstream or downstream of the tailgas expander after the oxidizer. In general, the optimal location for this method is in the hottest position in the stack gas stream. Secondary and tertiary methods can achieve greater than 90% reduction. Secondary N₂O decomposition catalyst can be substituted into the oxidation stage without substantial costs through a slight increase of the Raschig Ring bed diameter and/or height in new plants or by exchange of the existing Raschig Ring bed.



Figure 4: Examples of two BASF N₂O decomposition catalysts
 a. O3-81 catalyst (top) b. O3-85 catalyst (bottom)

BASF N₂O Decomposition Technology

Decomposition technology utilizes a catalyst to initiate N₂O breakdown to N₂ and O₂, as shown below.



BASF utilizes a series of full, 100% active homogeneously extruded catalysts (Figure 4) with a very thermally stable spinell structure. A typical chemical composition is given by:

Typical Chemical Composition (wt%)	
CuO	20
ZnO	16
Al ₂ O ₃ + promoters	64

Table 1: Chemical composition of N₂O decomposition catalyst

They offer the highest temperature resistance and do not leach into the nitric acid. They are available in various geometries and sizes, including extrudates, ring tablets, and honeycombs, as shown in Table 2. An N₂O efficiency of greater than 90% is possible. The choice of shape and size depends on the plant's operating condition and the specifications that need to be met. The 3 mm catalyst offers the highest N₂O decomposition, while the 6 mm catalyst is used when a lower pressure drop is required. Various combinations that use the 3 mm, 6 mm, or both extrudates generate a higher efficiency and ensure enhanced performance for greater added-value. Honeycombs, which are tailor-made to fit the stiff catalyst bed, offer both high efficiency and low pressure drop, while maintaining a homogeneous flow. They are designed to compensate thermal reactor expansion. The gap between the honeycombs provides additional surface area for the catalytic process.

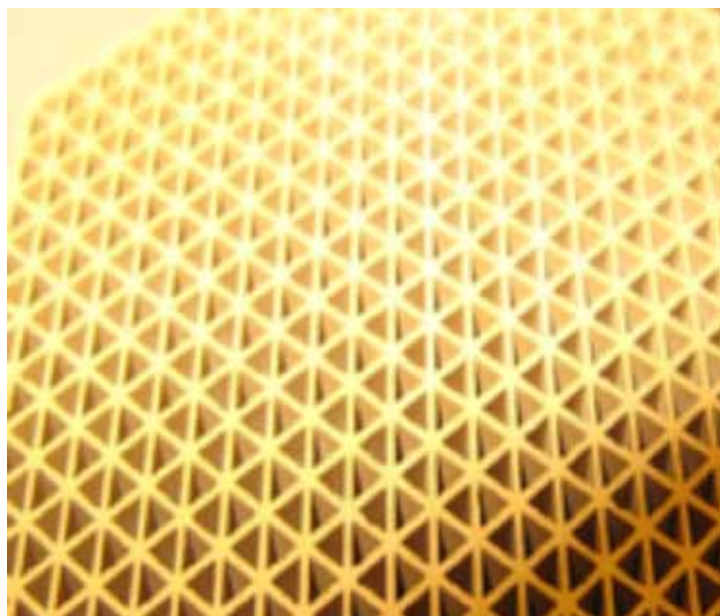
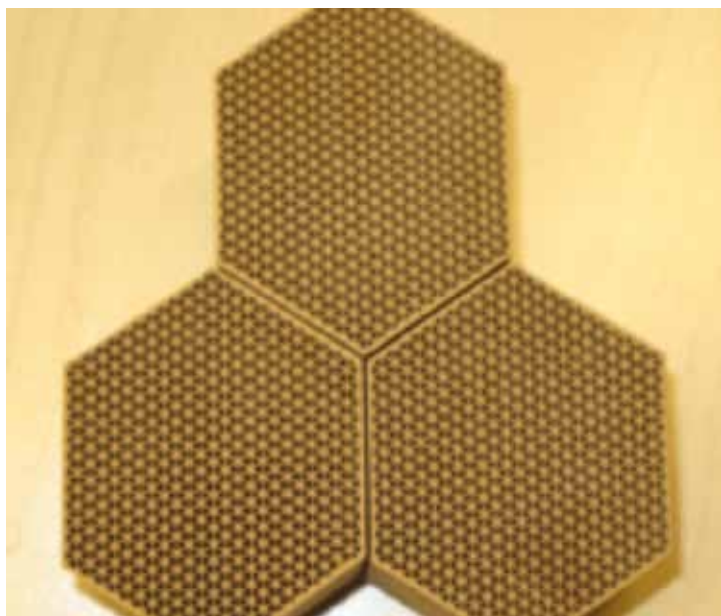


Figure 5: BASF N₂O decomposition honeycomb catalysts a. O3-88 catalyst (left) b. O3-88 catalyst: close-up (right)

Used as secondary N₂O tools, the catalysts are easy to install since they can be “dropped-in” during regular platinum (Pt) gauze exchange, as shown in Figure 6. They are poured from drums into the burner basket directly under the gauze and then leveled off by raking. Catalyst installation is not a

time-consuming process and can typically be done during a normal plant maintenance shutdown. The catalysts work with all types of Pt gauzes and can be used in low, medium, high, and dual pressure plants.

Catalyst	Shape	Size, mm	Density, kg/L	Min. Operating Temperature, °C	Max. Operating Temperature, °C
O3-81	Star Extrudates	6 (diameter)	0.9	450	>800
O3-85	Star Extrudates	3, 6 (diameter)	0.9–1.0	750	>900
O3-88	Honeycomb (Extrudates)	50–200 (length) 70 (outer diameter)	0.9	750	>900

Table 2: BASF N₂O decomposition catalysts



**Figure 6: a. Installation of a BASF N_2O decomposition catalyst (top)
b. Placing the Pt gauze over the decomposition catalyst (bottom)**

During the ammonia oxidation stage, reactions at the Pt gauze generate N_2O . With the decomposition catalyst located immediately downstream of the gauze, the N_2O is broken down into its natural components with a significant impact on the climate. In some plants, N_2O reduction of higher than 90% can be achieved.

BASF SCR DeNOx Technology

The BASF DeNOx system provided as a complete system together with our engineering partners is an “end-of-pipe” solution, which can either be installed before the expander or directly before the stack. The most advanced catalyst is O4-89 as an extrudate, but in some niche applications, especially at ambient pressure, the monolithic catalyst O4-82 can also be used. The BASF catalyst O4-89 has been successfully applied for the removal of NOx from tailgas derived from nitric acid plants, caprolactam units, gas turbines, refinery furnaces, waste incinerators, power plants, and diesel engines.

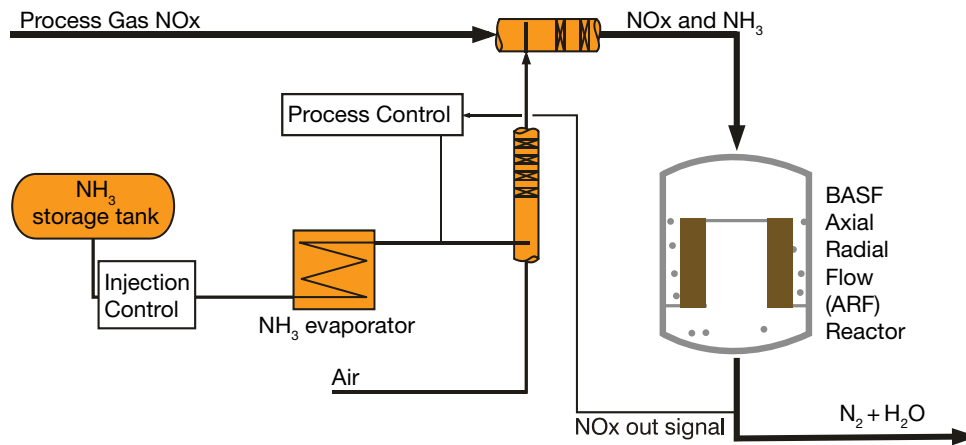


Figure 7: Block diagram of BASF SCR DeNOx technology usage in nitric acid plants for process off-gases (containing NOx)

The BASF reactor system, which consists of the ARF reactor (Figure 8), has a very low pressure drop (typically much less than 35 mbar, even with large off-gas volumes). The reactor system is CAPEX/OPEX optimized, provides excellent fluid dynamic behavior, and is easy to fill and operate. The system fits easily in the existing “plot space” and is able to fit nearly all SCR reactor locations in various chemical plants.



Figure 8: BASF state-of-the-art design ARF reactor

The BASF catalyst O4-89 (Table 3) is a very active and robust catalyst, which allows the installation within a wide temperature range. In nitric acid plants, the temperature ranges typically between 180 and 450°C and temperatures as low as 130°C can be achieved in exceptional applications. The typical operating pressure window is between 3 and 12 barg. For lower to ambient pressures, the BASF catalyst O4-82 — a monolith concept — is the preferred choice.

Physical Properties	
Color	Brown-Yellow
Geometry	Extrudate
Diameter, mm	Approx. 4.5
Active Composition	V ₂ O ₅ on metal oxide carrier
Load Density, kg/L	Approx. 1,100
Crush Strength, kg	Approx. 4

Table 3: Physical properties of BASF catalyst O4-89

The pressure drop over the catalyst system is a major issue. With the BASF system, the pressure drop can be tailored to the customers' requirements. The pressure drop with the system ranges between 35 and as low as less than 10 mbar, depending on the operating conditions. Minimal pressure drop can be obtained for both high- and low- flue gas temperatures through mechanical design of the reactor system.

The regulatory policies have increased the standards for NO_x emissions drastically, and the BASF catalyst is able to meet the aspects with emissions less than 5 ppmv. The O4-89 catalyst creates a state-of-the-art DeNO_x system with extremely low NH₃ (< 1 ppmv) slip along with a negligible N₂O formation. The cost difference for a 2000 ton/day worldscale nitric acid plant with a NO_x removal from 800 ppmv to 100 ppmv or for a NO_x removal from 800 ppmv to <30 ppmv is negligible.

BASF DeNO_x and N₂O Technologies — Moving beyond BASF Plants

Since 1997, BASF has been employing its abatement technologies on a commercial scale in plants worldwide. Starting in 1960s, new technologies have been developed, implemented, and optimized in BASF plants. Today, BASF DeNO_x and N₂O decomposition technologies are used globally in numerous nitric acid plants.

Continuous Support is the Key to Success

As part of our commitment to sustainability as well as customer satisfaction, BASF offers economic value by providing environmentally-friendly solutions and generating trust through social responsibility. This creates the flexibility needed to ensure shorter start-up times and lower overall costs. For the SCR DeNO_x system, BASF supports its customers with:

- Refills
- Revamps
- New turnkey solutions (with engineering partners)

BASF has developed a Total Service Package to meet the challenging demands of the Kyoto Protocol N₂O emissions directives. The services offered in this package support the sustainability of long-term Joint Implementation (JI)/Clean Development Mechanism (CDM) projects, from initial feasibility studies to the issuance of offset credits. The services include:

- Catalyst Engineering and Supply
 - Full catalyst design based on process simulation
 - Confidentiality license agreement
 - Supply of fresh catalyst/Disposal of spent catalyst
- Basket & Reactor Design
 - Review of existing construction
 - Two-way review of mutual experience
 - Optimization strategies for basket's engineering



The Chemical Company

- Monitoring System
 - Verification of monitoring/data processing requirements
 - Definition and recommendation of the necessary analytical instrumentation
 - Supervision of delivery, implementation, and calibration of the system
- Project Management
 - Documentation preparation
 - Verification and certification process assistance
 - Facilitation of offset credits

BASF also can provide support for voluntary emission reduction projects.

The Right Choice

BASF is the right choice for the reduction of N_2O and nitric oxides (NO and NO_2) emissions in nitric acid plants. Since 1997, BASF has been providing high N_2O reduction efficiency. BASF's flexible solutions for N_2O decomposition in nitric acid plants include easy handling capability, compatibility with any Pt gauze, and minimal impact on quality of the HNO_3 produced. The SCR DeNOx whether used alone or in conjunction with the N_2O system is an ideal solution for handling tailgas. Along with its wide range of operating window for temperatures and pressures, it achieves high NOx conversion in addition to low pressure drop and NH_3 slip. Both technologies are backed by reliable warranties and outstanding support and service that are associated with BASF - The Chemical Company. At BASF, we create chemistry for a sustainable future.

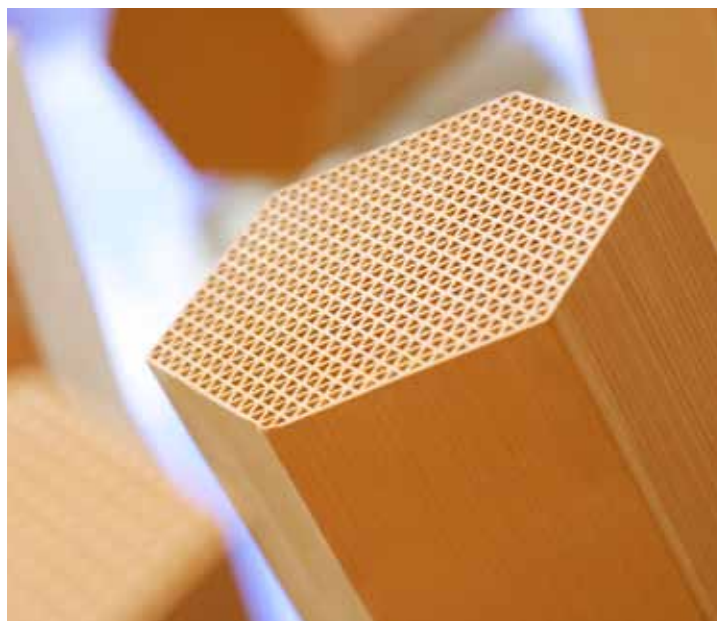


Figure 9: BASF provides technologically-advanced catalysts to meet the needs of nitric acid plants

About Us

BASF's Catalysts division is the world's leading supplier of environmental and process catalysts. The group offers exceptional expertise in the development of technologies that protect the air we breathe, produce the fuels that power our world and ensure efficient production of a wide variety of chemicals, plastics and other products, including advanced battery materials. By leveraging our industry-leading R&D platforms, passion for innovation and deep knowledge of precious and base metals, BASF's Catalysts division develops unique, proprietary solutions that drive customer success.

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