- Emissions from heavy-duty diesel vehicles contain nitrogen oxides in amounts that are damaging to human health and the environment.
- Copper-based catalysts can help mitigate these emissions but undergo reactions that cause performance degradation over time, in particular after exposure to sulphur dioxide or high temperatures.
- The CHASS project is a multi-institution project using advanced modelling and characterisation techniques to understand how catalyst degradation occurs.
- As part of its doctoral training programme, four early-stage researchers are working alongside world-leading experts to mitigate these problems.
- The final result will be an enhanced understanding of the performance of copper-based materials for the removal of nitrogen oxides.

Keeping catalysts alive with the CHASS project

While diesel cars are becoming less and less popular, heavy-duty vehicles still make extensive use of diesel engines. Diesel engines are well-suited for heavy haulage and offer excellent fuel economy, with CO_2 emission levels comparable to or less than the equivalent petrol engine.

A problem with the combustion of petrol or diesel is the production of nitrogen oxides (NOx). NOx refer to nitrogen monoxide and nitrogen dioxide, and are produced during the combustion of fuels. Nitrogen monoxide is oxidised in the atmosphere to produce more nitrogen dioxide, which is an acidic and corrosive gas responsible for photochemical smog. Nitrogen dioxide has been implicated in aggravating asthma and respiratory disorders as well as damage to vegetation and surfaces, such as furnishings and fabrics. This is why NOx emission from vehicles is strictly regulated in most places in the world via emission standards, such as the current Euro-6 emission standard in the EU.

To comply with the regulations to reduce the environmental impact of exhaust gases, all vehicles have catalysts in the exhaust system. For diesel engines, selective catalytic reduction (ammonia-SCR) is used to convert NOx into nitrogen and water via a reaction with urea, sold as diesel exhaust fluid (DEF, marketed as AdBlue® in Europe). Since the early 1990s, the implementation of SCR systems has reduced NOx emissions by as much as 95%.

While SCR technologies are very successful at removing the unwanted NOx, they also have limitations. One is that the catalysts are not very effective at low temperatures, so when an engine starts cold, the catalysts are ineffective for the conversion process. The use of copper chabazite (Cu-chabazite) catalysts minimises the cold-start problem as they are very active for SCR at 150–200 °C, and remain very efficient in the entire operating range up to 600 °C. However, like many other kinds of catalysts, Cu-chabazite catalysts suffer from degradation problems and only have a finite lifetime.

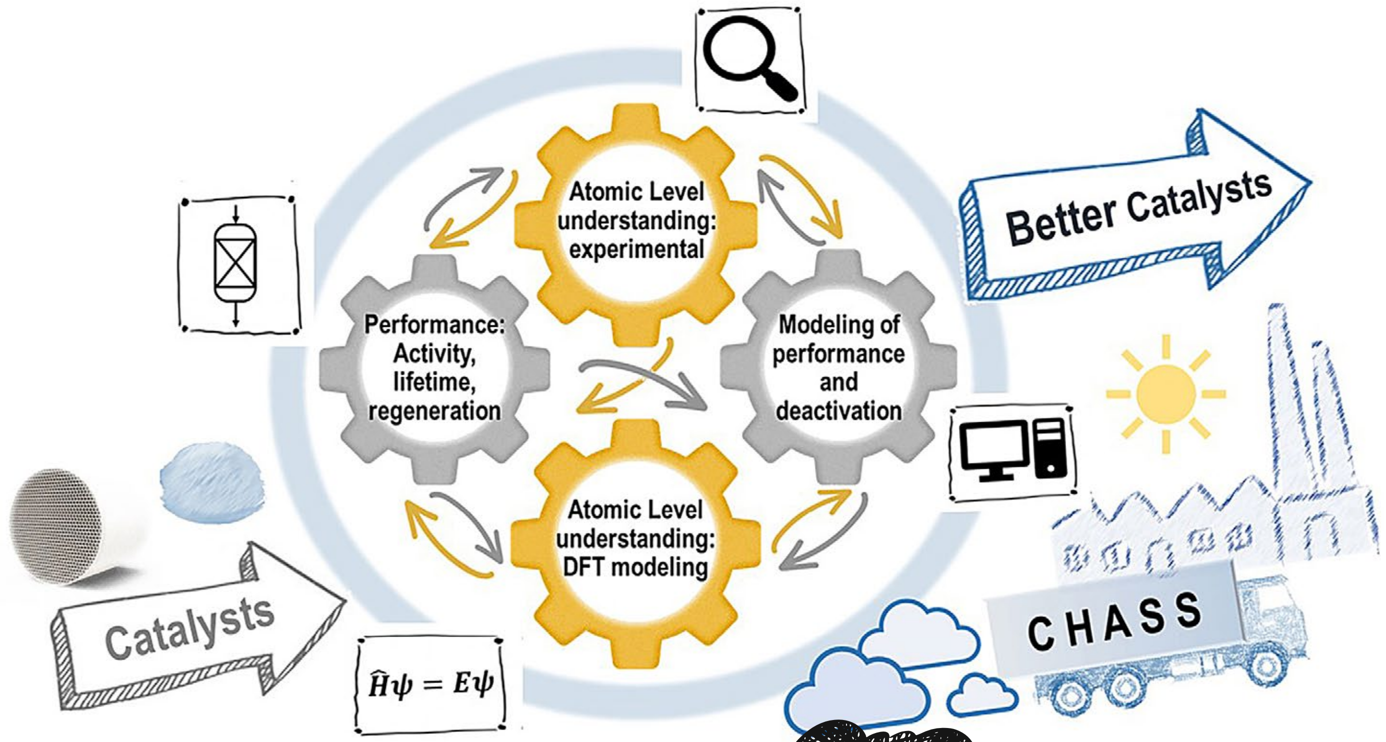
The CHASS project, an international collaboration between Umicore Denmark ApS, Umicore AG & Co. KG in Germany, the University of Turin in Italy, and Chalmers University of Technology in Gothenburg, Sweden, is tackling this problem using a 'bottom-up' approach. The PhD students, Joachim Bjerregaard, Reza Khaleghi Abasabadi, Shivangi Singh, and Vasco Correia Saltão, are working together to combine advanced computational models and characterisation methods in order to understand exactly what mechanisms lead to catalyst degradation and how the design and operation of Cu-zeolite catalysts can be improved for more effective, long-term removal of NOx from diesel exhaust gases.

Nitrogen dioxide has been implicated in aggravating asthma and respiratory disorders as well as damage to vegetation and surfaces.

Copper zeolites and catalytic cycles

Zeolites are an interesting family of crystalline aluminium-silicate materials that contain a network of small channels. The diameter of these channels is typically in the range 0.3–1.5 nanometres, allowing smaller molecules to be transported through them. This channel structure of the zeolites allows for an intimate contact with the exhaust gas, so many compounds can be bound or trapped, either for removal or to be involved in subsequent chemical reactions.

Cu-zeolites, like Cu-chabazite, are a type of zeolite with copper ions located in the channels. Copper is the active species for the SCR reaction. It has the ability to receive and donate electrons to the molecules in the exhaust gas in a continuous reaction cycle that produces nitrogen and water. A special feature of the SCR reaction in Cu-chabazite catalysts is that the active copper species is not in a fixed location in the catalyst but is continuously moving around. This mobility of the copper ions facilitates the formation of pairs of copper ions which, on one hand, is a necessary step in the SCR reaction. However, these copper pairs also react readily with sulphur dioxide, which is formed in the engine, because most fuels contain a tiny amount of sulphur compounds. This reaction with sulphur dioxide interrupts the desired reaction cycle with the NOx, damaging the activity of the catalyst.

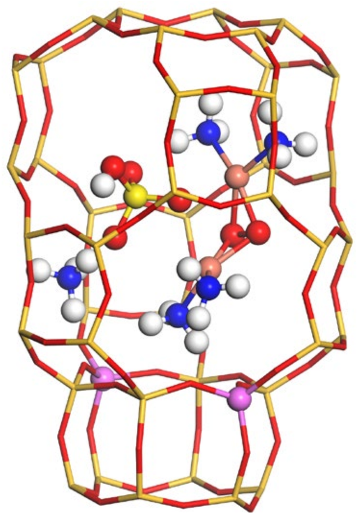


Team effort

The researchers are combining computational modelling and spectroscopic studies to look at this sulphur dioxide poisoning mechanism in detail. The computational modelling is based on Density Functional Theory (DFT), which is a quantum-mechanical modelling approach that indicates whether a given chemical structure – a spatial arrangement of atoms with particular chemical bonds – is more stable than another. With this information, it is possible to explore the relative probability of different reaction pathways that the copper might undergo and work out the most likely reaction mechanism taking place. This information could then be used to describe the deactivation process in great detail, and to modify the design of the catalysts to suppress these unwanted reactions with sulphur dioxide.

Their results will go on to influence the development of new materials or improved reaction conditions, so the SCR catalysts have a longer and more effective lifetime.

Other team members do spectroscopic measurements, which use light to monitor the reaction of sulphur dioxide with the Cu-pairs in the Cu-chabazite catalysts. As the wavelength and amount of light absorbed depends on the chemical species present, the team could identify that, when the sulphur dioxide reacts with the Cu-pairs, no further reaction of the copper by NOx and ammonia takes place. This means that the reaction with sulphur dioxide is directly responsible for the catalyst degradation.



Species formed in Cu-CHA cage by sulphur poisoning in NH_3-SCR reaction.

Apart from degradation by sulphur dioxide, high temperatures also affect the Cu-chabazite. Under such conditions, aluminium detaches from the zeolite and can react with the copper ions. Even though the copper ions hinder the detachment of the aluminium from the zeolite, it is not completely eliminated, resulting in a thermal degradation of the Cu-chabazite.

More work is needed to understand how the aluminium release affects the formation of the essential copper pairs and the reactions with sulphur dioxide. Still, the team have already taken important steps to examine how catalysts function in vehicles and some of their most crucial degradation mechanisms. Their results will go on to influence the development of new materials or improved operation conditions, so that the SCR catalysts have a longer and more effective lifetime.

Personal response

Do you have any advice for working on these kinds of interdisciplinary projects?

For a successful interdisciplinary project between academic institutes and industry, it is important that all partners recognise and respect each other's competences and interests, and know how these competences and interests support each other. The interest in industry generally is to create new business opportunities, eg via development of new technologies, while the interest of academic institutions and universities is education and the advancement of science in general. Therefore, one has to find a space where the education and scientific advancement does not collide with the commercial interests of the industrial partners. Then, all partners benefit from a collaboration. The industry gets access to the expertise and infrastructure of the academic partners, allowing them to develop the knowledge from which new commercial technologies can arise. The academic partners will develop the scientific knowledge on research questions where answers are demanded. In addition, the people that are educated in such projects will already have some experience that is relevant for industry when they finish their education.

Why do you think combining fundamental scientific studies with applications is so important?

The development of technology is always limited by our knowledge and understanding. Though often practical solutions can be found, the limitations of the applicability of a technology are not always well understood. Developing fundamental scientific knowledge strengthens the basis of our technologies, so we can make better assessments of the applicability and risks involved. At the same time, new scientific knowledge also leads us to entirely new technologies.

When do you think we will see new generations of catalysts in vehicles?

Given that we have begun to phase out fossil fuels over the coming 20 years or so, eg the ban of new fossil fuel-based vehicles in the EU from 2035 and similar arrangements in other countries, we will probably not see major changes in the catalysts that are being used in diesel vehicles, as the development of new materials typically takes 10–15 years. However, the outcome of projects like ours help to optimise exhaust systems to get the most out of the materials that we already have.

While new catalyst materials may not be on the drawing board for diesel engines, a successful introduction of hydrogen combustion engines, which have 3–4 times more water vapour in the exhaust, may ignite the development of new SCR catalyst materials. All the knowledge we develop on the current exhaust systems will then give us a strong head-start in the development of such new catalysts.

Details

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Bio

Joachim Bjerregaard is a PhD student at Chalmers University of Technology, Sweden, and research assistant at Umicore Germany.

"The possibility of working in two different scientific environments at both Chalmers University of Technology and Umicore is a unique opportunity, as it gives a broad research experience in both academic and industrial settings."

Reza Khaleghi Abasabadi is a PhD student at the University of Turin, Italy, and research assistant at Umicore DK.

"To me, CHASS is an opportunity to fight environmental pollution and provide a bluer sky to future generations."

Shivangi Singh is a PhD student at Chalmers University of Technology, Sweden, and research assistant at Umicore DK.

"I am a curious person who enjoys learning new and fascinating things. The CHASS project allows me to do applied research that works towards sustainable technologies and to apply theoretical and experimental aspects of science."

Vasco Correia Saltão is a PhD student at the University of Turin, Italy, and research assistant at Umicore Germany.

"Being part of the CHASS project means I'm able to develop my skills in both academic and industrial settings, while simultaneously contributing to a greener tomorrow, making it a very worthwhile experience."

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Collaborators

- University of Turin: Professor Gloria Berlier, Professor Elisa Borfecchia, Dr Valentina Crocellà, Professor Silvia Bordiga
- Chalmers University of Technology: Professor Henrik Grönbeck, Professor Anders Hellman, Professor Magnus Skoglundh
- Umicore DK: Ton V.W. Janssens
- Umicore Germany: Martin Votsmeier, Anke Schuler, Riccardo Bono

Further reading

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Competing interest statement

Umicore is a supplier of Cu-chabazite based catalysts for SCR to the automotive industry.