

# Car catalysator works differently than expected

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The 3-way catalysator of a car apparently works differently from the way chemists had expected. The conversion of carbon monoxide into carbon dioxide takes place not in one single step, but in at least two different steps. To date, the second reaction path was completely unknown, but it seems to work much more efficiently than the first, more familiar process. This discovery has been made by surface physicist Marcelo Ackermann from Leiden University (Netherlands). His findings call into question the chemistry of catalysators.

Because the second reaction path was not known, chemists had never properly understood what made the difference between a good and a poor performance of a catalysator. They considered the formation of a thin layer of oxide on the catalysator as detrimental to catalysis. But Ackermann has discovered how such a layer forms, and is able to demonstrate that this layer actually ensures that the catalysator works properly. Researchers can now determine precisely the atomic structure which causes a catalysator to perform more or less effectively.

Ackermann obtained his PhD at Leiden University on Tuesday 13 November. He was able to make these findings during the course of his work with a team of scientists and technical specialists who are collaborating on developing a technique which for the first time makes it possible to study catalysis at atomic level under real-life circumstances, namely at high temperature and under high gas pressure. His new method is a form of X-ray diffraction which is rendered sensitive to the structure of the surface of a crystal.

Ackermann examined the elementary steps in the catalytic oxidation of carbon monoxide (CO) on platinum and palladium. This is precisely the reaction which takes place in the familiar 3-way catalysator, which converts toxins in exhaust gases into less harmful substances. A 3-way catalysator currently consists of small particles of platinum and palladium, which catalyse the conversion of carbon monoxide (CO) into carbon dioxide (CO<sub>2</sub>) using oxygen (O<sub>2</sub>).

In chemistry, there is a tried and tested formula which describes the complete path from reactant to end product: how molecules from both reactants bind to the surface (adsorption), how they come together there and form a new reaction product, which is subsequently again released from the surface (desorption).

This formula, which has been used by chemists for more than a hundred years, gives a general description of the first known reaction path: CO and O<sub>2</sub> are adsorbed on the surface, whereby O<sub>2</sub> is split into two separate O atoms. O and CO come together on the surface, resulting in the formation of CO<sub>2</sub>.

But the process can also proceed very differently, and the formula does not describe this. The surface in this case first forms an atom-thin layer of platinum or palladium oxide. The CO molecules which come into contact with this oxide layer immediately oxidise into CO<sub>2</sub>. This process takes place only if the pressure of oxygen (O<sub>2</sub>) is relatively high in relation to the pressure of carbon monoxide (CO).

At low pressure and low temperature – conditions which are carefully created and maintained within advanced laboratory environments – this second process is never observed. There is no possibility for the oxide layer to form under such conditions. Chemists, including Gerhard Ertl, this years winner of the Nobel Prize for Chemistry, have therefore always assumed that the formation of an oxide layer must be

disadvantageous for the catalytic reaction, and have systematically wrongly interpreted results in which platinum and palladium oxides have been observed.

By measuring the structure of the oxide layer during the catalytic oxidation of CO, the researchers have also for the first time examined the effect of the reaction on the oxide layer. They saw that this thin and shiny oxide layer coarsens as a result of the reaction. This confirms the scenario that CO actually takes the oxygen for the oxidation to CO<sub>2</sub> from the layer of platinum or palladium.

The empty space which the removed oxygen atom has left behind in the oxide layer is then replenished by fresh oxygen molecules from the gas phase, which maintains the oxide layer. Under specific conditions, the surface, by coarsening, will spontaneously switch backwards and forwards between an oxidised and non-oxidised state. Consequently, the reaction rate will increase and slow down.

The research into chemical processes on fixed surfaces is currently the focus of considerable attention. The Nobel Prize for Chemistry this year was awarded to Gerhard Ertl for his surface work. The interest from the industry sector in Ackermann's research was recently emphasized with the launch of the public-private research programme NIMIC, a partnership between the TU Delft, Leiden University, and a number of different industries and research institutes aimed at revealing at atomic scale key processes which are important for industry and medicine.

Source: Leiden University

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