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# tce

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## troubled waters

how to measure, contain and clear up a deep-sea oil leak

REACTOR TECHNOLOGY | CATALYSIS | CONSULTANTS & CONTRACTORS FILE INSIDE

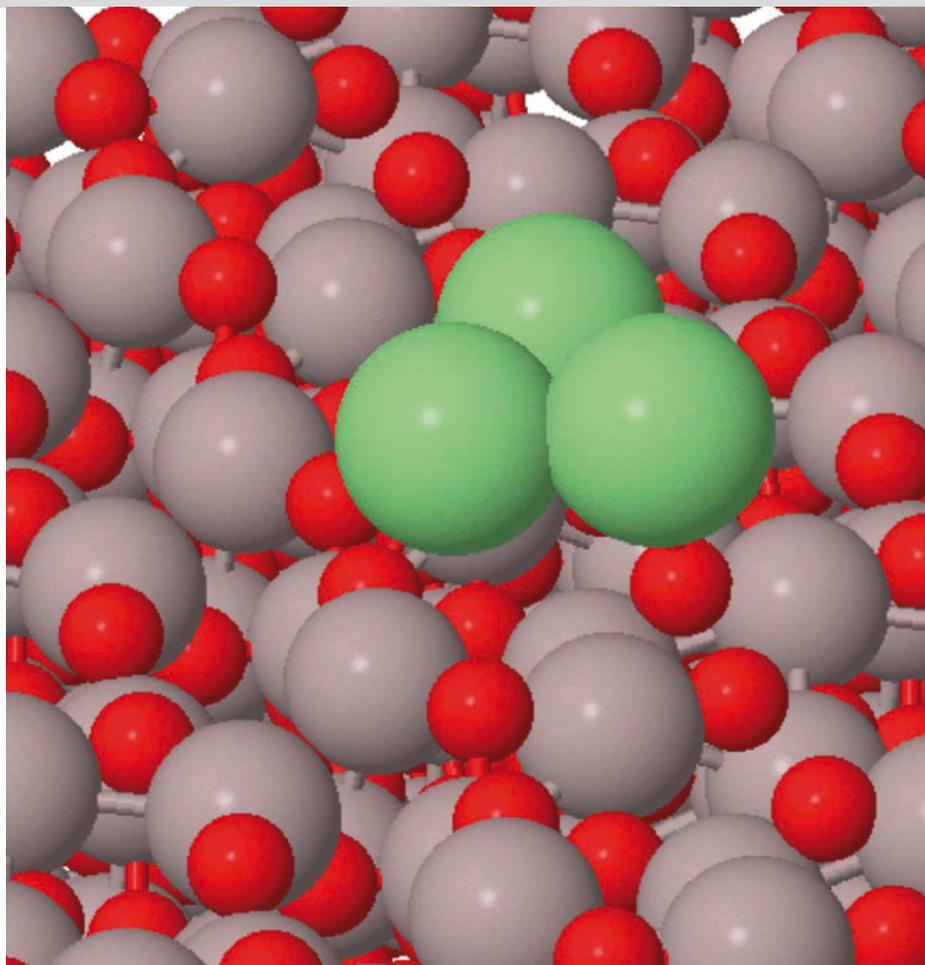
**FINDING a direct oxidation method for propylene epoxidation, the production of propylene oxide from propylene, is considered the 'holy grail' of propylene oxide catalysis.** Fundamental research led by scientists at Argonne National Laboratory has shown that nanostructured silver catalysts may provide a route to such a direct oxidation process that is more environmentally friendly than currently used catalytic chemistries.

### current status

Propylene oxide (PO) is one of the most important commodity materials produced by the chemical industry. Over 5.8m t was produced in 1999, and this rate is increasing by about 4%/y. Virtually all of the propylene oxide produced is used to make other chemical derivatives. About 65% is used in the production of polyether polyols, which are, in turn, mainly used in making polyurethanes. Propylene oxide is also used to produce propylene glycol, polypropylene glycol, propylene glycols ethers and propylene carbonate. Current commercial technologies for producing propylene oxide either use chlorine to promote the oxidation of propylene or involve oxidation of other compounds. These technologies are less efficient than direct oxidation of propylene because they generally generate significant amounts of other products, some of which are environmentally unfriendly.

The chlorohydrin process involves the use of chlorine for epoxidation of propylene. This was the original process used for PO production and is similar to the methods used for ethylene oxide production before discovery of an efficient direct oxidation method based on silver catalysis. The first step in the chlorohydrin process is the synthesis of propylene chlorohydrin from propylene and chlorine. The second step is the dehydrochlorination of propylene chlorohydrin to form PO. The process is then completed by purification of the crude propylene oxide to eliminate byproducts

“ **nanostructured silver catalysts may provide a route to such a direct oxidation process that is more environmentally friendly than currently used catalytic chemistries** ”



# Tiny trimer, big result

**Larry Curtiss** and colleagues describe a new silver nanocatalyst for greener propylene oxide

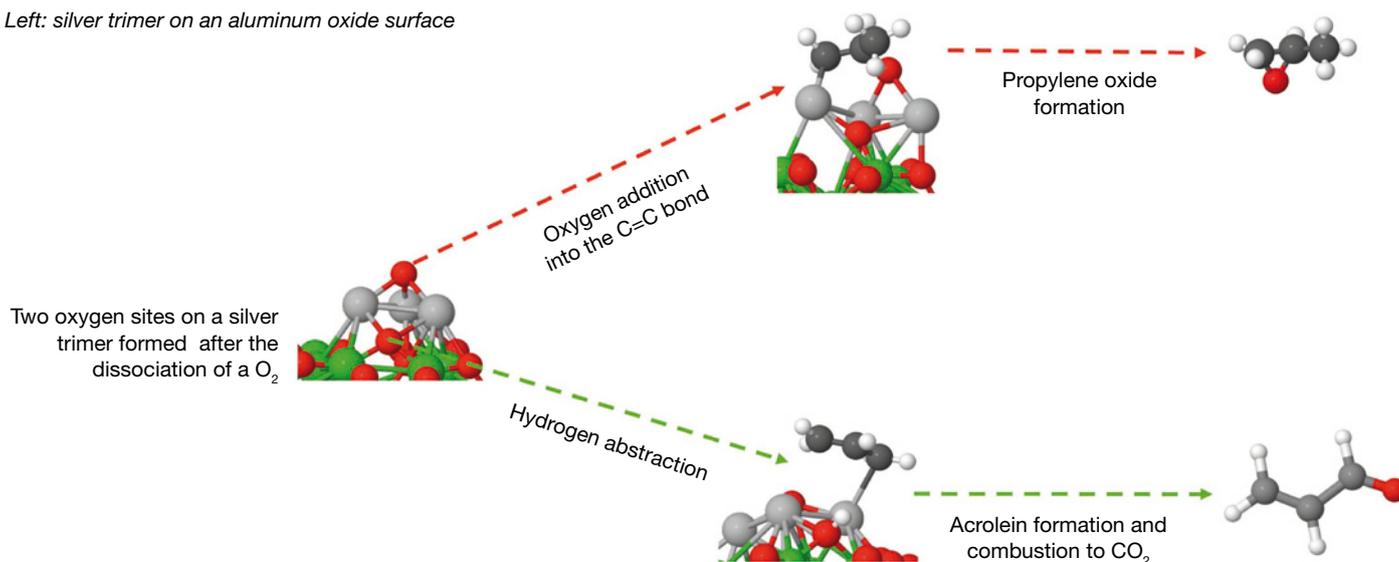
and by treatment of associated brine waste. The chlorohydrin process has several drawbacks, including the production of the wastes mentioned above and the use of significant quantities of chlorine. New plants that employ this method are no longer being constructed.

### improved processes

Several improved processes for PO production are based on indirect oxidation and are being deployed in newer plants. One such approach (the Halcon process) is based on oxidation of propylene with organic hydroperoxides. The organic

hydroperoxides are formed from oxidation of organics such as ethylbenzene and isobutene in the presence of catalysts, which results in co-products that often must be co-marketed with PO. Sumitomo Chemical, however, has developed a promising new hydroperoxide process based on cumene without significant production of co-products by recycling them back to cumene. Another indirect oxidation method is based on the use of hydrogen peroxide for epoxidation in the presence of a catalyst. This process, while efficient, suffers from the high cost of hydrogen peroxide. On-site production of hydrogen peroxide, as recently pioneered in the hydrogen peroxide

Left: silver trimer on an aluminum oxide surface



to propylene oxide (HPPO) route developed collaboratively by Dow and BASF, has some potential to alleviate this drawback. Other companies have been also working on using the hydroperoxide process for propylene-oxide production.

Due to the inherent problems in the processes described above, there has been a major effort to find direct oxidation methods for the production of propylene oxide from propylene. If an active and selective catalyst for direct oxidation could be developed, the potential economic and environmental impact would be considerable. Silver has been used as a successful catalyst in the epoxidation of ethylene with high selectivity in both the lab and on the industrial scale. By analogy, using silver for the epoxidation of propylene to propylene oxide might seem a promising approach, but this strategy has been studied for decades with little success. One of the main problems is selectivity, as the combustion of propylene is favoured over propylene oxide formation under direct oxidation conditions.

### new catalysts from nanoscience

Design of materials at the nanoscale provides an opportunity for the development of novel catalysts. Small metal clusters and nanoparticles often possess unique catalytic properties and thus have the potential to circumvent limitations of conventional catalysts. In the case of propylene epoxidation, such catalysts, based on silver, might solve some of the problems mentioned above by being active for addition of oxygen to the C=C double bond in propylene while, at the same time, having low activity for byproducts such as  $CO_2$ .

In work recently reported in *Science*, two

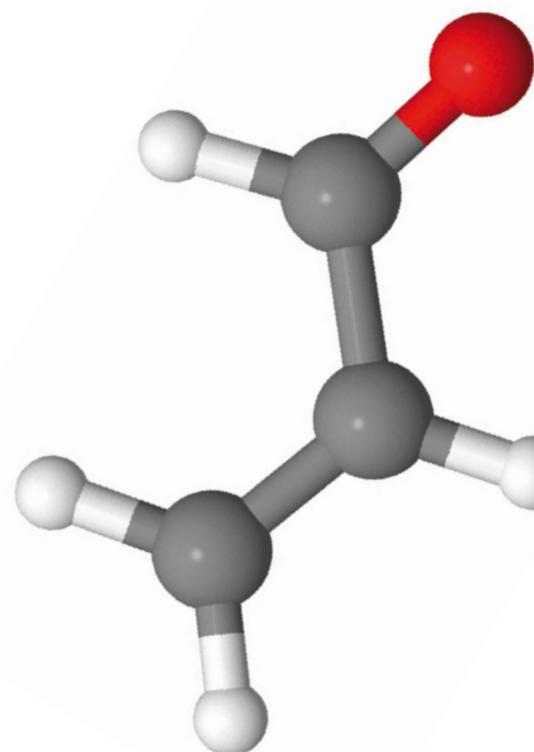
new silver nanoarchitectures have been found to exhibit unprecedented catalytic activity and selectivity for propylene epoxidation. The silver nanoarchitectures were synthesised by depositing mass-selected clusters from a molecular beam on an ultrathin amorphous alumina film produced by atomic layer deposition. The nanoarchitectures included size-selected silver trimers ( $Ag_3$ ) supported on alumina and ultra-small nanoparticles, just 2 nm tall and 4 nm in diameter, that result from aggregation of the silver trimers at temperatures of around 110°C.

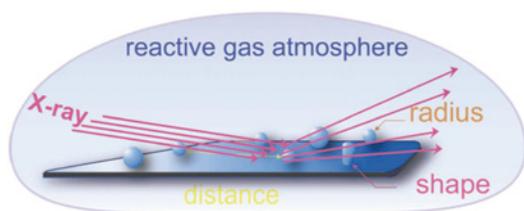
Catalytic tests on the silver trimers revealed that propylene oxide, acrolein, and carbon dioxide are the dominant reaction products. The rate of both propylene oxide and acrolein formation increases sharply with temperature, starting at room temperature, while the onset of combustion is observed at 60 °C. The catalytic performance of the silver aggregates is even better than that of the silver trimers. Overall, the rate of propylene oxide formed per surface silver atom on both catalysts is much higher than that reported for any previous silver catalyst, and the new catalysts' selectivity for propylene oxide formation over combustion at low temperatures is likewise unprecedented.

### how the new catalyst works

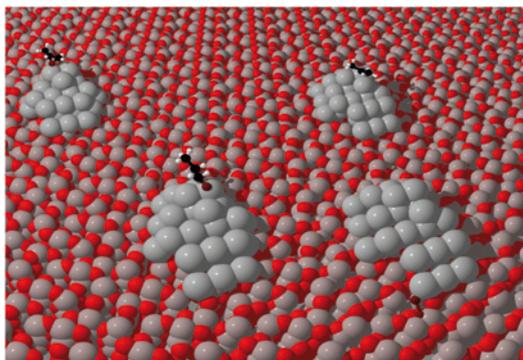
An understanding of the surprising catalytic activity and selectivity of the two new silver architectures was obtained through a combination of characterisation and density functional calculations. Characterisation of the size and shape of the supported catalyst during reaction conditions was done using *in situ* grazing incidence small

Above: Illustration of the two major reaction pathways in propylene oxidation catalysis. Small silver clusters result in the oxygen addition reaction being favourable

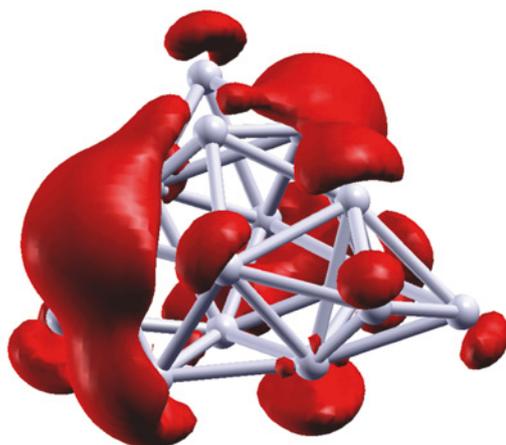




In situ x-ray characterisation



Silver aggregates on aluminium oxide surface



Spin density on clusters from modelling

Left: In situ x-ray studies have provided data on silver clusters for modelling, which has revealed that the high reactivity is due to spin density on the surfaces of the trimers and aggregates.

significant spin density, which makes it efficient for oxygen addition to a carbon-carbon double bond. In contrast, such spin density is not present on oxygen atoms adsorbed on a silver surface. This also provides an explanation for the high activity of the aggregates, which is the same per surface atom as the  $\text{Ag}_3$  clusters. The surface of the nanoparticles resulting from agglomeration of the trimers is likely to be rough, resulting in adsorbed oxygen atoms with spin density based on some density functional calculations.

### the future

The unique properties of ultra-small silver nanoparticles for propylene epoxidation are excellent examples of how new catalyst architectures, which can now be synthesised at the subnanometer and nanometer scales, provide for the control of catalytic reactions previously not possible using traditional catalytic materials. These particles, which are highly efficient catalysts for unpromoted propylene epoxidation, open a new pathway to the development of the long-sought direct oxidation method for propylene oxide production.

There are, however, many challenges to be addressed before this vision becomes a reality. Further optimisation of the catalyst may yet be possible, using, for example, further refinements to synthetic technologies or by developing silver-based nanocluster alloys. Additionally, the amount of materials that can be synthesised from the size-selected cluster deposition technique must be scaled up to permit catalytic testing on commercially-relevant quantities of materials. Although such scale up will require significant effort, recent research has hinted at promising strategies. For example, a solution phase synthesis of small metal clusters that may soon provide a viable strategy, as might the deposition of organometallic complexes containing silver atoms on oxide supports. These, or other, approaches may permit the deployment of direct propylene oxidation catalysts in commercially significant quantities, thereby permitting the realisation of the manifold environmental benefits of this novel catalytic technology. **tce**

angle x-ray scattering (GISAXS). The GISAXS measurements revealed when the sintering of  $\text{Ag}_3$  clusters begins and how it leads to the formation of silver nanostructures. The oxidation state of the catalyst was studied using x-ray photoelectron spectroscopy and revealed the silver catalysts to be metallic under propylene epoxidation. These results provided a basis for theoretical modelling to provide insight into how the new catalysts work.

Density functional calculations revealed several key features of the silver trimer that makes it a very effective catalyst for propylene epoxidation. First, it was found that dissociation of the oxygen molecule occurs at the interface of  $\text{Ag}_3$  and the alumina surface with a small reaction barrier. As a result there are two types of oxygen sites present: an oxygen at the

interface of the trimer and the alumina surface, and another oxygen at the three-fold site of the trimer. The calculations indicate that each oxygen site has unique reactivity properties for reactions involving propylene. The three-fold site is highly reactive for oxygen insertion into the carbon-carbon double bond to form an oxymetallocycle intermediate that leads to PO. In contrast, the oxygen at the interface of the silver trimer and support is found to be very active for hydrogen abstraction, which leads to combustion products,  $\text{CO}_2$  and CO.

The density functional calculations also provide an explanation for the high activity of the silver trimers for propylene epoxidation compared to a silver surface. The calculations indicate that the oxygen in the three-fold site on the trimer has

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