A New Catalyst for an Ancient Bulk Chemical

Zeolite recrystallization allows synthesis of extremely efficient gold nanoparticle catalysts. This could revive one of the oldest processes in chemical industry, namely production of acetaldehyde from ethanol. The principle may apply to a range of new catalysts.

In itself it is no great achievement to produce acetaldehyde. The annual global production of this bulk chemical with numerous applications is well above 1 million tonnes. However, research groups at DTU Chemistry and the Max-Planck-Institute für Kohlenforschung have managed to oxidize ethanol effectively and selectively into acetaldehyde by use of a novel type of zeolite catalyst with encapsulated gold nanoparticles.

"This is likely to be a favourable, green alternative to the so-called Wacker process, which dominates the world's current production of acetaldehyde. And hopefully this is just the beginning. This type of catalyst will in principle apply to a range of other reactions," says Associate Professor Søren Kegnæs, DTU Chemistry.

"On top, the materials have been well studied by advanced electron microscopy with help from DTU Cen."

Rise of the gold nano-particles

A few decades ago it came as a surprise to many, when gold nanoparticles were shown to be active and selective catalysts for several oxidation reactions with molecular oxygen despite the unreactive nature of bulk metallic gold. Since then many groups have sought to find the best practical solutions on how to make catalysts with gold nanoparticles.

The Danish-German research groups are at the leading edge of these efforts, as shown by their recent publication of an article in the journal Angewandte Chemie.

While most other attempts to encapsulate metal nanoparticles in zeolites have relied on expensive additives and complex procedures, the new approach is both simple and effective. Crystals of the zeolite silicalite-1 are modified by recrystallization, which creates intra-particle voids and mesopores. The recrystallization was performed in the presence base and a surfactant, which protects the outer surface of the crystals. Since the zeolite crystals are porous, the base will penetrate into the crystals and begin to dissolve them from within. The trick is to stop the process at the right time, when the inner voids have the optimal size. The voids will then be filled with a precursor solution containing a metal salt. In the acetaldehyde project an aqueous solution of $HAuCl_4$ was applied. Further, the material is dried and then reduced under H_2. The confined space provides ideal conditions for preparation of small and disperse gold nanoparticles inside the zeolite crystals.

In other words, the zeolite structure functions as a physical barrier which hinders the nano particles from sintering. In this way they will stay separate, leading to a large inner active catalyst surface which in turn makes the catalyst more efficient and at the same time less exposed to sintering.

A clever way to use bio-ethanol

While the researchers were certain they had created efficient catalysts, they also needed to prove it. The choice was to catalyze oxidation of ethanol into acetaldehyde. First described in 1774, acetaldehyde has numerous applications. For instance it can be processed further into acetic acid (known as vinegar in aqueous solution), and it can serve as a precursor for production of vinyl polymer. For several centuries, oxidation of ethanol was in fact the dominant route, but since the beginning of 1960'ies, with the invention of the Wacker process, which oxidates ethylene using a homogeneous palladium/copper system, ethylene has been the primary feedstock.

"We chose the ethanol process, because bio-ethanol receives large attention these years, since it is a renewable resource," Søren Kegnæs explains.

Most interest targets the use of bio-ethanol as a fuel or fuel component, but this has a drawback, since the direct synthesis of ethanol from biomass normally yields ethanol with a 90 % water content.

"If you want to use ethanol as fuel you need to get rid of the water content, which will cost you a rather high amount of energy. It would thus be interesting to find an alternative use of the bio-ethanol in which a high content of water is not a problem. This is the case for the production of acetaldehyde," notes Søren Kegnæs.

"Also, this revival of ethanol as source for production of acetaldehyde has some benefits in comparison with the use of ethylene, since ethylene is produced from crude oil which is a non-renewable resource."

Strong Danish-German cooperation

DTU has patented the new type of catalysts.

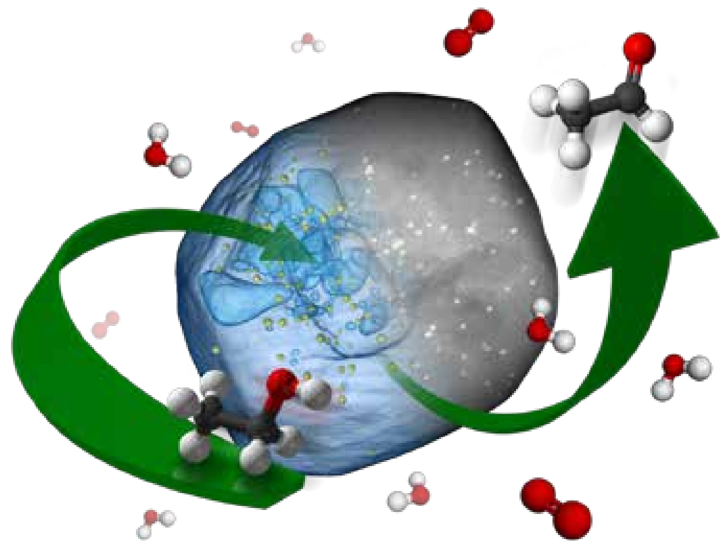
"We hope that industry will be interested in cooperation on this," says Søren Kegnæs.

At the time of this interview the article on the novel zeolite catalyst has just been published in Angewandte Chemie. It is thus too early to evaluate the impact.

"My feeling is that this very article will not in itself be enough to have industry call us and inquire about cooperation. But recently we have had another article on design and synthesis of advanced nanoparticle catalysts accepted by Angewandte Chemie, so we are getting closer," Søren Kegnæs remarks.

He further emphasizes the cooperation with the Max-Planck-Institute initiated in early 2013. The cooperation was made possible by a grant from the Danish Council for Independent Research (FTP).

"The cooperation takes place in a very open atmosphere, with a high degree of sharing ideas and having students visit for shorter or longer periods of time."



An artistic representation of the catalyst based on results from STEM microscopy. The figure also shows how bioethanol diffuse into the porous zeolite and gets converted into acetaldehyde on the encapsulated gold nanoparticles.

Published article

The text is based on the scientific article published in *Angewandte Chemie.*

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Next step ...

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CONTACT

Associate Professor
Søren Kegnæs
Inorganic Chemistry, CSC
skk@kemi.dtu.dk