

## **On the sintering of silver catalysts for ethylene oxidation.**

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Selective oxidation of ethylene to ethylene-oxide is an important process for the base chemicals industry. Ethylene-oxide and its derivative mono-ethylene glycol form the building blocks of many chemical products. Catalysts for this process are unswervingly based on Ag dispersed over an  $\alpha$ -alumina carrier.

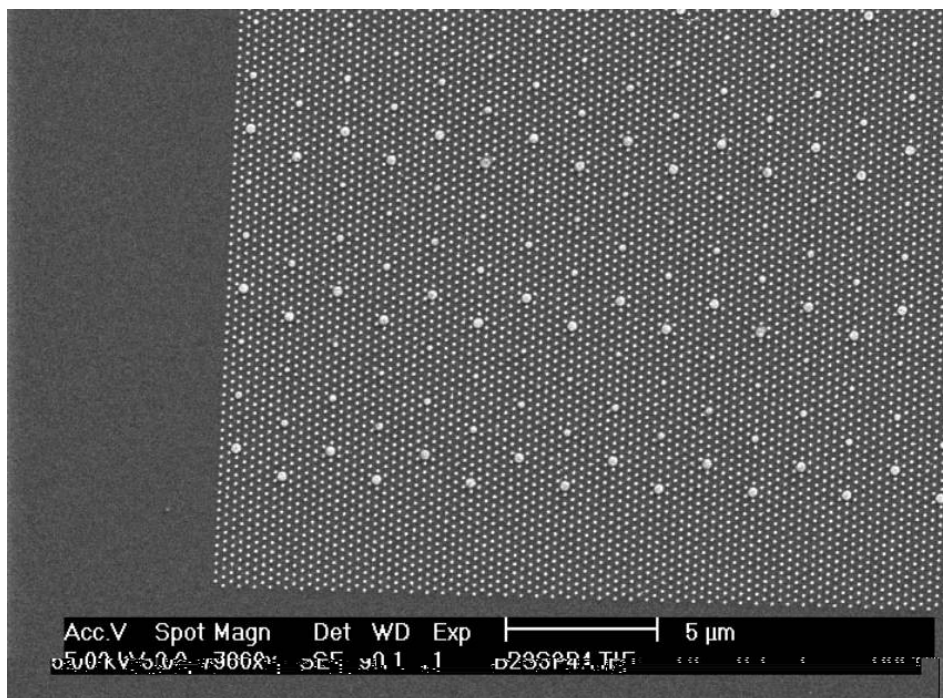
Virtually all catalysts deactivate, some slowly, some quickly but inevitably performance deteriorates over time. Ethylene oxidation catalysts are no exception to this rule. After prolonged use the catalysts become deactivated, probably due, at least in part, to sintering of the metal particles. In fresh catalysts silver is present (in catalytic terms) as relatively coarse particles. Yet this is still a thermodynamically unstable state and the system will strive to reduce its free surface energy by increasing the particle size and consequently reducing the number of particles. However the particles do not grow boundlessly and in practice an upper particle size limit is generally observed. The resulting loss of surface area leads to a reduction of the catalyst activity. To compensate for this loss in industrial practice the temperature is generally raised sufficiently so that conversion remains constant. Such an increase in temperature is usually accompanied by a loss of selectivity. When practical and/or economical limitations are reached catalyst change-out is required.

As the commercial catalysts described above are complex in nature, it was decided to study simplified systems to learn more about the principles of the processes taking place during deactivation. Spincoating and electron beam lithographic (EBL) techniques were used to prepare model catalysts. The advantages of EBL include control of silver particle size/shape, mutual arrangement and interparticle distances. In that regard this methodology<sup>1</sup> is unique for catalytic applications. In the Figure a typical sample is shown. In collaboration with the Delft Institute of Microelectronics and Submicron Technology (DIMES) in The Netherlands several series of samples were designed, prepared and tested under various industrially relevant reaction conditions. Changes in particle size distribution were monitored over time by scanning electron microscopy. Also the movement and growth of individual particles was monitored over prolonged periods of time.

The catalytic properties of some model catalysts were analysed using conventional microflow equipment. Chemical composition and surface areas were obtained using x-ray photoelectron spectroscopy.

These model experiments demonstrated that metal surface areas or particle size distributions do not provide sufficient information to explain the mechanism of

activity loss. Sintering is a local phenomenon where some particles on the surface grow at the expense of the smaller ones in their direct environment while other parts can remain unchanged for prolonged periods of time.



SEM picture of a model catalyst made by electron beam lithography; 3 different sizes (120, 180 and 270 nm) are embedded in a hexagonal matrix of 90 nm particles

To design effective commercial catalysts it is common practice to add various performance promoters. Their presence complicates the study of catalyst deactivation as they may influence the rate of sintering and their relative concentration with respect to surface silver atoms is consequently time dependent.

Some selected results will be presented to illustrate our observations and discussed in the light of the prevalent sintering mechanisms: classic Ostwald ripening, dynamic and static coalescence, sometimes referred to as Smoluchowski<sup>2</sup> ripening.

#### References

1. A. Avoyan et al, Topics in Catalysis, 10 (2000) 107
2. M. von Smoluchowski, Physik. Zeitschr. XVII, (1916) 557