Dynamics of silver particles during ethylene epoxidation

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Dynamics of silver particles during ethylene epoxidation


Abstract

Structural changes in α-Al₂O₃ supported silver particles during ethylene oxidation under industrially relevant conditions (20 bar and 225 °C, with and without chlorine) were investigated by quantitative TEM. Identical locations of two powder samples with average silver particle sizes of 41 nm and 127 nm were investigated in the fresh state and after 60 h of ethylene oxidation with and without chlorine. Without chlorine, silver particles were only slightly affected with a tendency for smaller (<30 nm) particles to shrink. These silver particles even rapidly disappeared in the presence of chlorine. Particles larger than 100 nm tended to break up into smaller ones, indicative of a chlorine-induced re-dispersion process. These results confirm the dynamic nature of silver particles during the EO reaction and emphasize the role of chlorine on the observed substantial morphological changes of the active silver phase.

1. Introduction

Ethylene epoxidation to ethylene oxide (EO) is a major chemical process with a global annual production of approximately 35 million tons [1]. Silver is the only catalyst sufficiently active and selective for commercial EO production [2]. Industrially, EO selectivity close to 90% is achieved by adding small amounts of promoters such as Cs, Re and Mo to α-alumina-supported silver catalysts. Gaseous organochlorine compounds (e.g., vinyl chloride, VC) are co-fed in trace amounts with the reaction mixture to improve the EO selectivity further [3,4]. VC is combusted in situ, leading to chlorine deposition on the catalyst. Chlorine affects the silver epoxidation catalyst in various ways. It poisons unselective vacancies, thereby reducing the direct combustion of ethylene to carbon dioxide [3]. Chlorine is also thought to increase the amount of “electrophilic oxygen” species, which are involved in the oxidation of ethylene to EO [4]. Furthermore, the presence of chlorine can significantly alter the structure of silver particles as recently shown by our group [5]. Pore formation and redispersion of large silver particles into smaller ones during the ongoing EO reaction were affected by use of a chlorine promoter. The mechanism of the chlorine-induced redispersion of silver is not understood yet and, therefore, the main topic of the present contribution.

Active phase dispersion is a key aspect with respect to activity, selectivity and stability of heterogeneous metal catalysts. A main cause of catalyst deactivation is a loss of metal dispersion and, therefore, of active sites [6]. Sintering proceeds mainly via Ostwald ripening, involving the growth of larger nanoparticles at the expense of smaller ones due to transport of small mobile, possibly atomic species over the support surface. Another sintering mechanism, called Smoluchowski ripening, involves mobile nanoparticles on the support surface and their coalescence into larger ones. A change in particle size during reaction can also lead to a change in the active sites catalytic surface. This structure sensitivity involving amongst others different activity of terrace, steps, kinks and other specific topologies is well understood for metal nanoparticles [7]. Substantial changes in the active site distribution at metal nanoparticle surfaces are typically observed for sizes smaller than 10 nm. Although surfaces are usually assumed to be static, there is increasing evidence that the surface of metal nanoparticles can also change due to strongly adsorbed reaction intermediates [8–11]. Moreover, in some cases metal nanoparticles can even display liquid-like behavior during the ongoing reaction [12].

For ethylene epoxidation, non-classical structure sensitivity is typically observed in the sense that profound changes in reaction rate occur in the range of 10–200 nm [13–18]. In a recent work, we emphasized the dynamic nature of silver particles during the EO reaction [5]. The sintering of silver particles observed in ethylene/oxygen mixtures could be partially reversed by addition of chlorine to the same feed. These findings were based on comparing averaged values of the
2.2. Catalyst deposition on Si3N4 TEM grids

The obtained powders were characterized with XRD and scanning TEM on the same locations as during the first analysis. Then, the same sample was added on top in order to break surface tension and distribute the liquid over the entire grid surface. Afterwards, the wafer was left to dry in air. Following this procedure, a thin layer of catalyst could be reproducibly deposited on the silicon nitride TEM grids. Silicon nitride is considered as a stable and inert material under the employed reaction conditions and is thus not expected to influence the restructuring of the silver particles. The Si3N4 TEM grids were analyzed with TEM.

2.3. Catalyst characterization

The powder catalysts were characterized by XRD and scanning TEM (STEM). For STEM we employed High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) on the TU/e CryoTitan (FEI, now Thermo Fischer Scientific) at room temperature. STEM images were acquired using a probe convergence angle of 10 mrad, a dwell time of 2 μs and a camera length of 89 mm in combination with a Fischione HAADF STEM detector. Dry STEM sample preparation involved sonication of the samples in pure ethanol (Biosolve, Extra dry, 99.9%) and applying a few droplets of the suspension to a 200 mesh Cu TEM grid with a holey carbon support film. Prior to imaging, the supported samples were left in an oven at 40 °C overnight to remove residual ethanol. XRD patterns were recorded with a Bruker D8 Endevor powder diffraction system using Cu Kα radiation. The scanning speed was 6.0° min⁻¹ in the range of 5–90°. Crystallite sizes were determined using the Scherrer equation on the Ag(220) diffraction peak located at 2θ = 64.7°.

The Si3N4-TEM wafers were imaged with TEM. TEM micrographs were acquired on a FEI Tecnai 20 transmission electron microscope type Sphera (FEI, now Thermo Fischer Scientific), equipped with a LaB₆ filament and operated at an acceleration voltage of 200 kV. TEM images were recorded on a CETA II 4k x 4k CMOS camera. For analysis of the TEM images an in-house written Matlab script was used to measure the size of the individual particles and to label them for later re-analysis. In case of identical particle imaging, the size was determined by manually selecting two points at opposing edges of the nanoparticles, choosing typically the shortest and longest axes.

After TEM analysis of the freshly prepared TEM grids, the wafers were used as catalysts in the epoxidation of ethylene. The TEM samples were placed in a specially designed high-pressure reactor with space for 6 TEM grids (Appendix S1). For pre-treatment a gas mixture containing 10 vol% oxygen balanced with helium was fed in the reactor at a total flow of 20 mL/min at 20 bar pressure. The reaction gas mixture contained 10 vol% O₂ and 5 vol% ethylene, which was balanced with helium at a total flow rate of 20 mL/min. Before reaction, the pre-treatment gas was stabilized at a pressure of 20 bar for 2 hours, followed by temperature-programmed heating to 225 °C (ramp rate 20 °C/min) and dwelling for 3 hours. The reaction was started by replacing the pretreatment gas with the reaction gas. After 60 hours the reaction was terminated by replacing the reaction gas by helium and cooling the reactor to room temperature. The TEM grids were then analyzed by TEM on the same locations as during the first analysis. Then, the same reaction procedure was repeated, using a reaction gas mixture that contained 1 ppm vinyl chloride (VC) for 60 h. After terminating the reaction by replacing the reaction gas by helium and cooling the reactor to room temperature, the TEM wafers were analyzed again.
3. Results and Discussion

We investigated in detail the morphological changes of differently sized silver particles on α-Al₂O₃ prepared according to a procedure relevant to industrial practice [21]. By adjusting the silver loading to either 5 wt% or 10 wt% and varying the pre-treatment gas environment, the obtained average particle sizes were 41 ± 16 nm and 127 ± 47 nm, respectively. These catalysts are denoted as Ag(41) and Ag(127). The most important physio-chemical properties of these catalysts are listed in Table 1. By XRD analysis, it was determined that Ag(41) and Ag(127) have crystallite sizes of 20 nm and 27 nm, respectively. This means that an average silver particle in Ag(127) consists of ~100 primary silver crystallites, while a typical silver particle in Ag(41) contains only ~8 crystallites. Thus, larger particles contain significantly more grain boundaries than smaller particles, which we demonstrated before to substantially affect the EO reaction [17].

We first present catalytic performance data of Ag(41) and Ag(127) to understand how the EO reaction with and without VC affected the size and size distribution of the silver particles in silver catalysts. The catalysts were tested in a feed of 5 vol% ethylene and 10 vol% oxygen balanced by helium at a temperature of 225 °C and a total pressure of 20 bar for 60 h. In another experiment, they were tested in the same way followed by exposure to the same feed containing 1 ppm VC for 60 h. Then, a final TEM analysis was carried out.

A typical example of the resulting TEM images is given in Fig. 3. Significant changes in the silver phase can be observed following the exposure to different reactive gas atmospheres. To facilitate viewing, a few characteristic events are marked in Fig. 3, which emphasize that the silver particles undergo restructuring during the EO reaction. Before we discuss the results from IAA and IPA, we will first discuss the various events that we noted in our image analysis and will classify them. A full overview of the observed events is given in Appendix S2.

By analyzing the changes in detail, we observe both growth of silver particles (SI Figure S2) and shrinkage of silver particles, the latter to the extent that some particles even disappear from the field of view (green

Table 1
Parameters used to control particle size for Ag/α-Al₂O₃ catalysts.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>He / O₂ (%)</th>
<th>T (°C)</th>
<th>Ag content (wt%)</th>
<th>d (nm) ¹</th>
<th>n (%) ²</th>
<th>XRD (nm) ³</th>
<th>d (nm) 60 h ⁴</th>
<th>d (nm) 60 h VC ⁵</th>
<th>d (nm) 60 h + 60 h VC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(41)</td>
<td>100 / 0</td>
<td>275</td>
<td>4.5</td>
<td>41 ± 16</td>
<td>400</td>
<td>20</td>
<td>45 ± 27</td>
<td>57 ± 19</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ag(127)</td>
<td>90 / 10</td>
<td>275</td>
<td>10.0</td>
<td>127 ± 47</td>
<td>349</td>
<td>27</td>
<td>191 ± 81</td>
<td>129 ± 65</td>
<td>113 ± 52</td>
</tr>
</tbody>
</table>

¹ Determined by ICP-OES, ² Determined by HAADF-STEM, ³ Determined by Scherrer equation applied to the Ag(220) reflection, ⁴,⁵ vol% ethylene, 10 vol% oxygen, 20 bar, 225 °C.

Fig. 1. Reactivity data for Ag(41) and Ag(127) (a) Ethylene conversion rate at 20 bar and 20 bar + VC (b) EO selectivity at 20 bar and 20 bar + VC.
circle Fig. 3 and SI, Figure S3). From inspection of multiple images, we infer that especially smaller particles disappear from the images, indicating an Ostwald ripening mechanism. The disappearance of silver particles may also mean that the particles shrank to a size below the detection limit in our bright-field TEM imaging. The blue circle in Fig. 3 displays an example of particle coalescence, where two particles are so close to each other that they merge into one particle, which points to some mobility of the silver particles [23]. Although in Fig. 3 (blue circle) such a coalescence event is clearly observed, it also stands out that the shapes of the initial particles remain preserved. In general, we did not observe extensive migration of silver particles over the support surface, so particle coalescence is likely limited to proximate particles (SI, Figure S4). An example of the earlier reported pore formation for the present catalysts is shown in Figure S5 [5]. Such pore formation is most likely induced by oxygen diffusion along the grain boundaries. Together with pore formation, re-dispersion of silver particles was also suggested based on average particle sizes determined by TEM. Fig. 3 presents a case of such re-dispersion observed for a single particle (red circle). The image suggests that a large silver particle breaks up during the reaction in several roughly equally sized particles. Another example is provided in SI Figure S6. Accordingly, we conclude that processes that cause the particles to slowly shrink such as etching cannot explain the observed re-dispersion. Further analysis of such break-up events will be discussed below.

3.1. Identical Area Analysis (IAA)

To obtain a more detailed insight into the individual particle size evolution, IAA was applied. Fig. 4 displays the same imaged areas of Ag (41) for the three investigated stages including the particle size histograms derived thereof. The corresponding numerical data are listed in Table 2. Additional images are provided in the Supporting Information S7. After 60 h EO reaction, the average silver particle size increased slightly from 38 nm for the fresh sample to 40 nm for the used sample. These sizes are nearly similar to the average size of 41 nm obtained after calcination by analyzing a larger number of particles (n = 400). After repeating the EO reaction in the presence of VC for 60 h, a slight increase of the average particle size to 47 nm was observed. The
amount of silver particles in the imaged area decreased from \(n = 53\) for the fresh samples to \(n = 24\) after 60 h EO reaction. When the reaction was continued in the presence of VC for 60 h, the number of particles decreased to \(n = 24\). Thus, the ongoing EO reaction leads to the disappearance of particles and this change is more pronounced in the presence of VC. A more detailed inspection of the particle size distribution shows that the fresh sample contains 13 particles smaller than 30 nm. Whereas this was virtually unchanged after 60 h EO reaction (14 particles), there were only 2 particles smaller than 30 nm after the reaction with VC. For comparison, the fresh sample contained 40 particles larger than 30 nm (but smaller than 100 nm), 28 of such particles after 60 h EO reaction and 22 after the EO reaction in presence of chlorine.

A similar set of measurements was carried out for the Ag(127) sample and the corresponding data are given in Table 2 (additional images in Appendix S8). Similar to Ag(41), the changes in the average particle size were minor after 60 h EO reaction without VC. In the fresh sample, the average particle size was 119 nm (\(n = 117\)), while it was 124 nm (\(n = 89\)) after the EO reaction. In stark contrast with Ag(41), carrying out the EO reaction with VC led to a significant increase of the number of visible silver particles (\(n = 165\)), a decrease of the average particle size to 94 nm and an increase of the fraction of particles smaller than 100 nm from 47% to 70%. These changes are highlighted in Fig. 5 as events in which silver particles break up into smaller ones.

From these ILI experiments, we infer that the most significant changes occur when VC is introduced. The presence of VC in the EO reaction feed leads to a significantly lower amount of particles smaller than 30 nm, yet otherwise only leads to a small increase of the average particle size of the Ag(41) catalyst. The influence of chlorine on larger particles predominant in Ag(127) is very different. Strikingly, particles larger than 100 nm can break up into smaller ones. In Fig. 5c, a thin (low contrast) layer is deposited on the support material between the particles that broke up. This suggests that increased wetting plays a role in this re-dispersion process.

### 3.2. Identical Particle Analysis (IPA)

A more detailed analysis of changes in the morphology at the single particle level is possible by IPA. For Ag(41), a number of particles from Fig. 4 were selected for an analysis of their size following the different reactions. Fig. 6 shows the size of individually tracked particles after the EO reaction without and with chlorine as a function of the original size of the silver particle. Data points above the diagonal represent particles that have grown larger than the original size, particles below the diagonal implies a decrease of the particle size. After 60 h EO reaction without VC, a minor decrease in size of small particles can be

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**Fig. 4.** TEM images of Ag(41) deposited on the Si$_3$N$_4$ wafer for (a) fresh, (b) spent 60 h (c) spent 60 h + 60 h VC and corresponding histograms (d), (e) and (f).

**Table 2**

| Sample                  | \(d\) (nm) | \(\sigma\) (nm) | \(n\) (\() | \(n_{d < 30}\) (\() | \(f_{d < 30}\) (%) | \(n_{d < 100}\) (\() | \(f_{d < 100}\) (%) |
|-------------------------|------------|----------------|------------|----------------|----------------|----------------|----------------|---|
| Ag(41)-fresh            | 38         | 12             | 53         | 13             | 25             | 0              | 0              |---|
| Ag(41)-60 h             | 40         | 16             | 42         | 14             | 33             | 0              | 0              |---|
| Ag(41)-60 h + 60 h VC   | 47         | 18             | 24         | 2              | 8              | 0              | 0              |---|
| Ag(127)-fresh           | 119        | 56             | 117        | 0              | 0              | 52             | 44             |---|
| Ag(127)-60 h            | 124        | 66             | 89         | 0              | 0              | 42             | 47             |---|
| Ag(127)-60 h + 60 h VC  | 94         | 50             | 165        | 2              | 1              | 115            | 70             |---|
noted, while some large particles grow in size. The changes after 60 h further EO reaction with VC are more pronounced in the sense that a large fraction of particles were not visible anymore. We can distinguish from the data that silver particles that disappeared had an average size of 34 nm and the ones that remained of 57 nm. Based on the limited particle mobility from our image analysis, the loss of silver dispersion is most likely due to Ostwald ripening. In this case, we speculate that mobile silver chloride species with a much lower Tamman temperature (228 °C) than silver (481 °C) play a role in the more pronounced sintering in the presence of chlorine. Earlier studies have demonstrated that the exposure of silver particles to organochloride promoter can lead to the formation of silver chloride [24,25].

Following a similar approach for Ag(127), a subset of the particle size evolution data is shown in Fig. 7. The particle size does not change substantially during the EO reaction without chlorine. The imaged area does not contain silver particles smaller than 30 nm. During the reaction with chlorine, the changes are however much more pronounced. A significant fraction of the silver particles larger than 100 nm break up into smaller ones. We can also observe that the few observed silver particles with an initial size smaller than 100 nm are much less affected by the EO reaction with chlorine.

Re-dispersion of nanoparticles of platinum, gold, and silver by organo-halide compounds such as 1,2-dichloropropane has been observed before [26–28]. In these cases, the metallic nanoparticles were completely dispersed into very fine clusters, presumable via metal-halide intermediate species involving an etching process. Based on the ILI results, the re-dispersion of silver particles into smaller ones does not involve etching or similar processes, which would have caused the particles to gradually shrink. Instead, the presence of chlorine causes a significant change of the shape of the silver particles, leading to the formation of multiple particles and, finally, disintegration of the original silver particle into smaller ones. Earlier, we established that the decreasing average size of relatively large silver particles during the ongoing EO reaction in the presence of chlorine requires the presence of all three gas-phase compounds ethylene, oxygen and VC [5]. From this, we conclude that a simple model in which the surface wobserved here. Our earlier data show that the primary crystallite size of the silver particles is hardly affected by these treatments. Together with the much lower tendency of smaller particles to break up, we infer that the grain boundaries between crystallites are involved in the break-up of the
silver particles. The mechanism for these profound morphological changes remains unknown, but it resembles the break up of supported metal particles observed during oxidation-reduction cycles [26, 29]. Fig. 8 highlights the complexity of the break-up process by showing that, between the smaller particles being formed from a larger one, there is a thin layer visible, which may hint at increased wetting of the support surface. This layer may be made up from silver chloride [24, 25], resulting in a different interaction between the silver particle and the support. Further detailed analysis is required to understand the mechanistic origins of these changes in particle size and shape. For instance, EDX analysis might help to resolve the presence of chlorine, although the preservation of the reactive state is likely not ideal from the chemical point of view.

Summarizing, Ostwald ripening appears to be relevant in the particle size growth of relatively small silver particles during the ongoing EO reaction and that ripening is accelerated by the presence of chlorine. Presumably, this is due to the formation of mobile silver-chloride species based on Taman temperature considerations. A catalyst containing on average particles of 100 nm responds differently to the EO reaction. The particles either remain the same or increases in size during the EO reaction without chlorine. In the presence of chlorine, however, particles larger than 100 nm break up in smaller ones, leading to a higher silver dispersion.

Finally, we briefly discuss the influence of these morphological changes on the reaction rates. Without chlorine, the reaction rates are higher for the smaller particles in line with a higher dispersion. After a short activation time, the small-particle catalyst shows a slowly decreasing reaction rate, which might be attributed to slow Ostwald ripening. The activation period for the large-particle catalyst is much longer, which we observed earlier and attributed to a slower build-up of oxygen at the more numerous grain boundaries in comparison with the small-particle catalyst. Notably, after the activation period the reaction rate does not change much, which is in line with the nearly constant particle size during the EO reaction without chlorine. It is difficult to make firm statements about the relation between size changes in the presence of chlorine, because chlorine strongly suppresses the reaction rate.

4. Conclusions

We employed quantitative TEM imaging of identical locations of α-Al2O3 supported silver particles under industrially relevant conditions (20 bar and 225 °C) in order to explore the influence of the ongoing EO reaction without and with chlorine on the size of individual silver particles. We compare two catalysts with average silver particles of ∼41 nm and ∼127 nm. The evolution of the silver particles depended on the size and the presence of chlorine. Without chlorine, silver particles were only slightly affected with a tendency for smaller particles to slightly shrink. When chlorine was present during the EO reaction, the changes were very pronounced and depended on the particle size. Silver particles smaller than ∼30 nm disappeared from the areas imaged, pointing to Ostwald ripening as a primary sintering mechanism in which we suspect the formation of mobile silver-chloride species to be involved. Larger particles sized below 100 nm were not affected substantially by the EO reaction with chlorine. However, particles larger than 100 nm broke up into smaller particles in the presence of chlorine, resulting in a re-dispersion of the silver active phase during the ongoing EO reaction. Although the underlying mechanism of this break up of silver particles is unclear, these findings confirm the dynamic nature of the silver phase during the EO reaction and emphasize the role of chlorine in Ostwald ripening of small particles and re-dispersion of larger particles into smaller ones. The use of a thin silicon nitride windows in a TEM grid placed in a catalytic reactor in combination with identical location imaging has several advantages over current in situ TEM holders: (i) industrial relevant pressures can be used to study the evolution of the EO catalyst, (ii) much longer reaction times can be applied, not limited by available microscopy time, and (iii) much larger areas can be imaged, allowing the acquisition of statistically more relevant data at a particular stage of the reaction. The presented approach can be applied to a wide range of chemical reactions and reaction conditions.

CRediT authorship contribution statement

A.J.F. van Hoof: Methodology, Investigation, Data curation, Formal analysis, Validation, Writing - original draft, Visualization.
R.C.J. van der Poll: Investigation, Formal analysis, Validation. H. Friedrich: Conceptualization, Methodology, Software, Supervision. E.J.M. Hensen: Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

We declare that the submitted work has not been published previously, that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

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