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Influence of Ag particle size and Ag : Al_2O_3 surface ratio in catalysts for the chloride-promoted ethylene epoxidation

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ABSTRACT

Ethylene epoxidation is catalyzed by α-alumina supported silver catalysts. The influence of silver particle size has been a topic of debate, and was typically investigated without the industrially essential chloride promoter. We studied the catalyst behavior in the presence of chloride. Transient behavior was observed in the first tens of hours on stream, not as a result of particle growth, but due to the gradual change in the nature of the active silver site in the presence of chloride. Different strategies were used to tune the particle size: either varying the silver loading or varying the decomposition atmosphere. Increasing the particle size from 13 to 50 nm by changing the Ag loading from 2 to 15 wt% increased the selectivity from 35 to 80%. However, increasing the 15 wt% Ag particle size from 48 to 184 nm by varying the heat treatment led to a decrease in selectivity from 80 to 50%. Changing the Ag particle size with both strategies also changes the Ag : Al_2O_3 surface ratio. The ethylene oxide selectivity is actually correlated to the Ag : Al_2O_3 surface ratio, rather than to the particle size in this size range. This can be explained by its influence on the probability of a formed ethylene oxide molecule to subsequently further react over support surface groups.

1. Introduction

Ethylene oxide is produced by selectively oxidizing ethylene. It is mainly used for the synthesis of ethylene glycol, which serves as anti-freezing agent and as a building block for the production of polymers, e.g. polyurethanes (PU) for insulating materials [1]. With an estimated annual production of 32–35 Mt [1–3], the production of ethylene oxide is one of the largest petrochemical conversions worldwide. Typically, ethylene epoxidation catalysts consist of silver particles deposited on an inert support material [4,5]. Silver is the only metal that can selectively oxidize ethylene to ethylene oxide due to its mild oxidizing behavior [6]. Ethylene can either be partially oxidized to ethylene oxide, or be fully oxidized to CO_2 and water on the silver surface [6,7]. During reaction conditions, the silver surface is partially oxidized [8,9], and the nature of the adsorbed and subsurface oxygen is believed to play an important role in the fate of an ethylene molecule. Strongly bound (nucleophilic) oxygen is thought to be the result of reconstruction of the silver surface upon adsorption [10,11]. Weakly bound oxygen coexists on the silver without reconstruction of the silver surface and has an electrophilic nature [7,10]. Several studies have suggested that ethylene oxide formation is induced by electrophilic oxygen species while total combustion is promoted by nucleophilic oxygen species [7,11–13]. Once ethylene oxide is formed, it can isomerize to acetaldehyde, which is subsequently oxidized to CO_2 and water. The isomerization reaction is facilitated by support surface (hydroxyl) groups [14], and the subsequent combustion takes place on the silver surface. The ratio between the different reaction rates and concentrations of active sites to catalyze the reactions influence the total selectivity towards ethylene oxide [15,16].

With an estimated CO_2 emission of 0.3 Mt per produced Mt ethylene oxide [1], a high selectivity towards ethylene oxide (EO) instead of CO_2 is critical. In industry, several approaches are applied to increase EO selectivity. An inert support material, α-alumina, is used as support for the silver particles. α-Alumina typically has a low specific surface area (ca. 1 m^2 g^{-1}) and a low density of support hydroxyl groups (1–6 OH nm^{-2}) [15]. These properties combined are beneficial for the ethylene oxide selectivity, as the undesired isomerization reaction of ethylene oxide to acetaldehyde is reduced. Another strategy to increase EO selectivity is operating at low conversions. The EO selectivity decreases with increasing conversion [13] due to subsequent reactions of EO [17].

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A third strategy to increase the EO selectivity is by co-feeding a gaseous organochloride (e.g. ethyl chloride) [18–20]. An *in situ* study found that upon decomposition of the organochloride on the silver surface, chloride species block oxygen vacant sites on the silver, causing a loss in activity [21–23]. Meanwhile, chloride species are thought to increase the concentration of electrophilic oxygen and decrease the concentration of nucleophilic oxygen, leading to a higher EO selectivity [21].

The effect of particle size on ethylene oxide selectivity has been a topic of debate for several decades [2,24–28]. In these studies, silver catalysts with a broad range of silver particle sizes (13–656 nm) have been investigated, and particle sizes were typically varied by changing the silver weight loading of the catalyst (0.1–56 wt% Ag). The consensus in these studies is that ethylene oxide selectivity increases with increasing silver particle size, due to structure effects [24,25]. In a recent study in our group, a synthesis method was developed to vary silver particle sizes at constant silver loadings (15 wt%) by using different decomposition atmospheres [29]. Heating the silver precursor in a reducing atmosphere resulted in small particles (20 nm), whereas an oxidizing atmosphere led to larger particles (200 nm). This study was conducted without a chloride promoter, and found that EO selectivity was independent of silver particle size, as opposed to other studies. Typically, selectivity trends are correlated to particle sizes determined before catalysis [2,24,26,27,29]. However, these and other studies state that silver particles restructure and/or grow during the reaction [30,31]. Hence, it is important to correlate observed behavior to the real particle sizes during catalysis.

Industrially, a chloride promoter is always added to the feed, which greatly influences activity and selectivity [32]. This inspired us to study the changes taking place in the catalysts during the first tens of hours on stream, and to revisit the silver particle size effect in ethylene epoxidation. We synthesized silver catalysts with varying silver particle sizes (13–95 nm), by either changing the silver loading (2–15 wt%) or by changing the decomposition atmosphere at constant silver loadings. Using H_2 titration as a characterization technique, we show that after the first tens of hours on stream, the ratio between active silver and alumina surface areas is the most important factor influencing ethylene oxide selectivity, also in the presence of chloride, rather than for instance silver particle size of as-prepared catalysts before testing.

2. Materials and methods

2.1. Catalyst preparation

Silver nanoparticles were deposited onto an α-alumina carrier through incipient wetness impregnation, based on a procedure described elsewhere [29,33]. 8 m^2 g^{-1} α-alumina extrudates (Al-4196, BASF) were sieved to a fraction below 212 μm. This support has a high α-alumina phase purity (100% of the alumina is in the α-phase and it does not contain significant amounts of any other inorganic phases) and is hence suitable as support for ethylene epoxidation catalysts. Silver oxalate was used as silver precursor, which was synthesized prior to the impregnation. Typically, an aqueous solution of silver nitrate (≥ 99.0%, Sigma-Aldrich) was added to an aqueous solution of oxalic acid (≥ 99.0%, Sigma-Aldrich) (2:1 mol ratio). The white silver oxalate precipitate was centrifuged and washed three times in MilliQ water and once in ethanol, after which it was left to dry overnight in air at room temperature. Please note that great care should be taken when handling silver oxalate species, as they are shock sensitive.

Prior to the incipient wetness impregnation, the alumina powder was dried in vacuum for 2 h at 200 °C. Silver oxalate was dissolved in a mixture of MilliQ water/ethylenediamine (99%, Sigma-Aldrich) (4:1 mol ratio), forming a silver ethylenediamine oxalate complex which is known to lead to uniformly spaced and adherent silver particles compared to other silver precursors [33,34]. The dried powder was impregnated with this solution up to 90% of its pore volume, aiming for a silver loading of 2, 8 or 15 wt%. The impregnated materials were dried for ca. 20 h, in their respective flask, at 60 °C in stagnant air and were carefully mixed after 10, 30 and 45 min of drying. A heat treatment of 2 h at 215 °C with a heating ramp of 5 °C min^{-1} was performed to decompose the silver precursor, except for one catalyst which was heated for 12 h at 350 °C with a heating ramp of 2 °C min^{-1} to obtain a different particle size. All heat treatments were performed in a U-shaped flow-reactor (internal diameter of 1.8 cm) with ca. 2 g of material, subjecting the powders to a top-to-bottom gas flow through the bed. An overview of the catalysts with corresponding decomposition conditions is shown in Table 1.

2.2. Characterization

Scanning electron microscopy (SEM) was used to analyze the silver catalysts particle size, using a FEI Helios G3 UC microscope at 5–10 kV in immersion mode. Two-sided carbon tape was used to attach the sample powder to the sample holder. The sample was sputter coated with a 7.5 nm PdPt layer to create a conductive layer over the sample. For every catalyst, over 200 silver particles were measured using ImageJ software. From these measurements, the surface-averaged particle size ($d_{p,s}$) and standard deviations ($\sigma_{p,s}$) were calculated (Eq. 1).

$$d_{p,s} \pm \sigma_{p,s} = \frac{\sum_{i=1}^{n} d_i^3}{\sum_{i=1}^{n} d_i^2} \pm \sqrt{\frac{1}{n} \times \sum_{i=1}^{n} (d_{p,s} - d_i)^2} \tag{1}$$

The accessible (active) silver surface area was characterized with H_2-titration measurements using a Micromeritics ASAP 2020 instrument, based on a method developed by Vannice et al. [27,35]. Typically, 200 mg of fresh catalyst was tested and 50–100 mg of used catalyst. Samples were loaded in a U-shaped quartz reactor between two layers of quartz wool and were evacuated at 100 °C for 30 min, with a heating ramp of 10 °C min^{-1}. Thereafter, the samples were heated to 170 °C with a heating ramp of 10 °C min^{-1} and flushed with O_2 for 30 min, which was followed by an evacuation of 30 min and a treatment with H_2 for 125 min in order to clean the Ag surface. After an additional evacuation step of 60 min, the samples were treated with O_2 for 60 min to oxidize the Ag surface to form Ag-O species. Physisorbed O_2 was removed with an evacuation step of 30 min, prior to the final H_2-titration measurement. The specific silver surface area (A_{Ag}) was calculated using Eq. 2.

$$A_{Ag} = N_A \times V_{ads} \times SF \times A_{atom} \tag{2}$$

N_A is Avogadro's number ($6.023 \cdot 10^{23}$ mol^{-1}), V_{ads} is the adsorbed H_2 volume determined from the Y-intercept from the isotherm (mol g^{-1}), SF is the stoichiometry factor of 1 (1 H_2 molecule reacts with 1 Ag-O species to form H_2O), and A_{atom} is the atomic cross section of a silver atom (0.0869 nm^2). Assuming spherical particles (6 V/A), the silver particle diameter can be calculated from the silver surface area and volume of silver in the sample.

Domain sizes of the alumina supported silver particles were determined with X-ray diffraction (XRD). A Bruker D2 Phaser with a Co K_α source ($\lambda = 0.1789$ nm) was operated at 30 kV and 10 mA.

Table 1
Overview of prepared materials labelled as [*wt%*]Ag_[*gas atmosphere during heat treatment*]. All catalysts were heated for 2 h at 215 °C with a heating ramp of 5 °C min^{-1}, except for 15Ag_25%O_2 which was calcined at 350 °C for 12 h with a heating ramp of 2 °C min^{-1}.

Catalyst	Ag weight loading (%)	Decomposition atmosphere	GHSV (h^{-1})
2Ag_25%O_2	2	25% O_2 in N_2	7 000
8Ag_25%O_2	8	25% O_2 in N_2	7 000
15Ag_50%H_2	15	50% H_2 in N_2	5 200
15Ag_100% N_2	15	100% N_2	3 500
15Ag_100% O_2	15	100% O_2	2 400
15Ag_25%O_2	15	25% O_2 in N_2	7 000

Diffractograms were measured in the range of 20–80° 2θ, with a step size of 0.030° with 1 s step^{-1}. The measured diffractograms were compared with Ag and α-alumina crystal structures from the PDF-4+ 2016 database (04–004–2852 for α-alumina and 00–004–0783 for Ag) and analyzed with Bruker TOPAS software to calculate the Ag crystallite sizes.

2.3. Catalytic measurements

The silver catalysts were tested in the epoxidation of ethylene. Catalysts (90–150 µm sieve fraction) were diluted with SiC (212–425 µm) with a 1 : 5 mass ratio. The SiC had been washed in nitric acid (HNO_3, 65%, AnalaR Normapur®, 10 mL g_{SiC}^{-1}) and calcined at 800 °C to remove impurities. Initial experiments were performed with 100 mg of catalyst to keep the amount of Ag per experiment constant (15 mg). In subsequent measurements the Ag surface area was kept constant, based on H_2 titration measurements, meaning that the catalyst loading was varied accordingly. The diluted catalysts were loaded in a quartz reactor (4 mm internal diameter) between two layers of quartz wool. The catalysts were tested at 215 °C in a flow of 7.5 vol% ethylene, 2.1 or 7.5 vol % oxygen and 1.8 ppm ethyl chloride in helium. Reaction products were analyzed with an online Interscience Compact GC supplied with two separate channels (Porabond Q column and Molsieve 5Å column). Ethylene conversion, ethylene oxide selectivity and carbon mass balance were calculated using Eqs. 3–5. Calculations on mass transfer limitations can be found in the Supplementary Information (Section C) and indicate that no mass transfer limitations are expected in our systems.

$$Conversion_{Ethylene} = \frac{p_{Ethylene_0} - p_{Ethylene_{out}}}{p_{Ethylene_0}} \times 100\% \quad (3)$$

$$Selectivity_{Ethylene\ oxide} = \frac{p_{Ethylene\ oxide}}{p_{Ethylene\ oxide} + 0.5 \times p_{CO_2} + p_{Acetaldehyde}} \times 100\% \quad (4)$$

$$Carbon\ mass\ balance = \frac{p_{Ethylene_{out}} + p_{Ethylene\ oxide} + 0.5 \times p_{CO_2} + p_{Acetaldehyde}}{p_{Ethylene_0}} \times 100\% \quad (5)$$

p_x is the partial pressure of molecule x (in Pa). The carbon mass balance is 100 ± 3% for all used datapoints.

3. Results and discussion

3.1. Catalyst structure

Catalysts were synthesized with silver weight loadings of 2, 8 and 15 wt% on an 8 m^2 g^{-1} α-alumina support. Silver particle sizes were varied by either changing the silver weight loading or by subjecting the impregnated material with 15 wt% silver to different decomposition atmospheres. Fig. 1 shows SEM images of a series of catalysts, with 2 wt % Ag (Frame A), 8 wt% Ag (Frame B), and 15 wt% Ag prepared with different decomposition atmospheres (Frames C-F). The silver particles are visible as light grey spheres on the darker grey α-alumina support. The 15 wt% Ag catalysts prepared in reducing, inert, or oxidizing atmosphere show different Ag particle sizes. A reducing atmosphere resulted in small particles (Frame C), inert atmosphere led to slightly larger particles (Frame D), and oxidizing atmoshere resulted in the largest silver particle sizes (Frames E and F), which is in line with literature [29]. A higher calcination temperature and longer calcination time for 15Ag_25%O_2 resulted in larger particles compared to 15Ag_100%O_2.

Silver particle sizes are often determined with scanning or transmission electron microscopy [2,15,30,36]. However, electron microscopy techniques only offer analysis of a very small amount of sample, which encouraged us to explore bulk techniques to gain insights that are more statistically relevant. UV/Vis is used as supported silver nanoparticles display surface plasmon resonance, where peak position and intensity can be used to calculate the particle size [31,37]. However, this calculation is based on several assumptions, e.g. particle shape, support environment, and oxidation state. As O_2 chemisorption is rather insensitive in case of silver, a specific chemisorption technique has been developed in which pre-adsorbed oxygen is titrated with hydrogen, offering an enhanced sensitivity [27,35,38]. The volume of adsorbed hydrogen is used to calculate the silver particle size. XRD is a bulk technique that can be used to determine the crystallite size. Table 2 shows an overview of the Ag particle sizes, specific Ag surface areas, and crystallite sizes. When increasing the Ag loading from 2 to 8 wt%, the surface averaged Ag particle size ($d_{p,s}$) determined with SEM shows an increase from 41 to 58 nm. When varying the decomposition

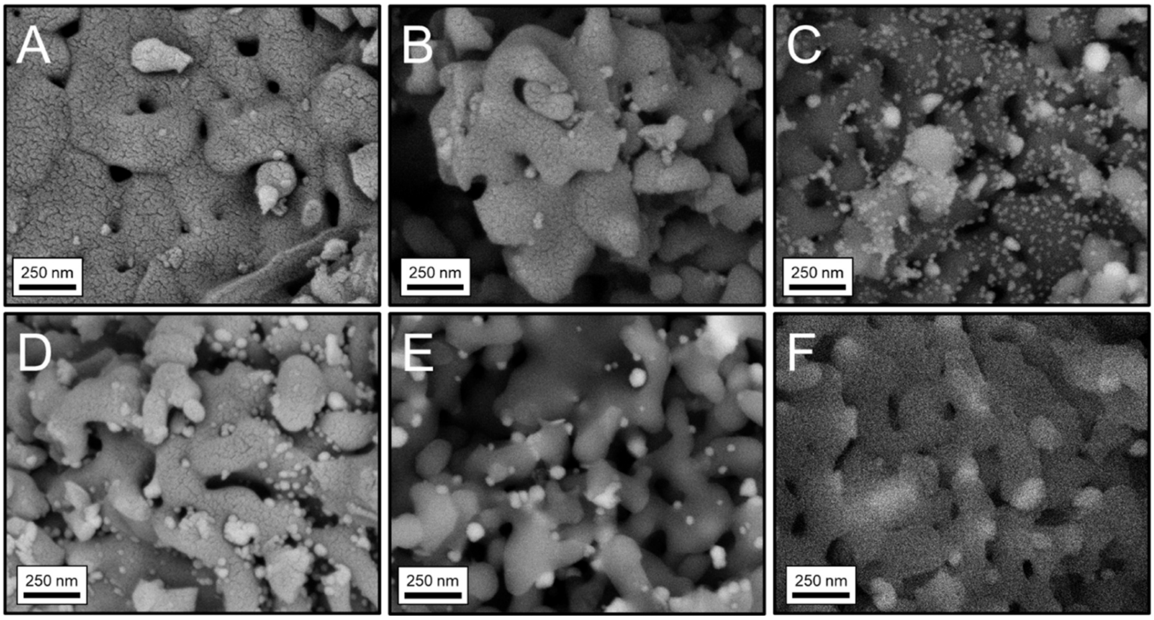

Fig. 1. SEM images of silver catalysts with different silver weight loadings on 8 m^2 g^{-1} α-alumina: : 2Ag_25%O_2 (A), 8Ag_25%O_2 (B), and 15 wt% silver catalysts (C-F) prepared with different decomposition atmospheres: 15Ag_50%H_2 (C), 15Ag_100%N_2 (D), 15Ag_100%O_2 (E), and 15Ag_25%O_2 (F).

Table 2
Ag particle sizes determined with SEM and H_2 titration measurements, together with calculated Ag crystallite diameters from XRD data. Catalysts are labelled as [*wt%*]Ag_(*particle size from H_2 titration*).

Catalyst	Decomposition atmosphere	SEM	H_2 titration		XRD
		Ag particle diameter $d_{p,s}$ (nm)	Ag surface area (m^2 $g_{catalyst}^{-1}$)	Ag particle diameter (nm)	Ag crystallite diameter (nm)
2Ag (13)	25% O_2 in N_2	41 ± 14	0.96	13	9.4 ± 0.5
8Ag (31)	25% O_2 in N_2	58 ± 20	1.40	31	15.9 ± 0.6
15Ag (36)	50% H_2 in N_2	42 ± 19	2.29	36	12.8 ± 0.2
15Ag (47)	100% N_2	52 ± 26	1.81	47	15.5 ± 0.4
15Ag (50)	100% O_2	102 ± 50	1.65	50	16.3 ± 0.4
15Ag (95)	25% O_2 in N_2	167 ± 65	0.85	95	28.0 ± 0.7

atmosphere from reducing to oxidizing at a constant Ag loading of 15 wt % the surface averaged particle sizes increase from 42 nm to 167 nm. Histograms of the measured silver particle sizes are shown in Fig. S1. The trends in specific Ag area and corresponding particle size derived from H_2 titration (Fig. S2) are in line with the SEM data. The fact that surface-area derived particle sizes are generally smaller than those derived from SEM, can be explained by the resolution of the SEM instrument, as particles smaller than 15 nm are difficult to detect. Another explanation could be that when converting the Ag surface area to particle diameter, the particles are assumed to be spherical whereas the sample could also contain more hemispherical particles. Crystallite sizes determined with XRD (Fig. S3) follow the trend of SEM and H_2 titration and are in the range of 9–28 nm, implying that the Ag particles are polycrystalline and hence consist of multiple crystalline domains, which is in line with literature [2]. As H_2 titration is a direct measurement of the active silver surface area, particle size information in the following sections will be based on this technique.

3.2. *Equilibration of the catalysts during ethylene epoxidation*

Catalysts with 15 wt% silver and with different particle sizes were tested in the ethylene epoxidation reaction, at 1 bar pressure. The concentrations of both ethylene and oxygen were 7.5% and the ethyl chloride concentration was 1.8 ppm in the feed throughout the tests. Please note that great care should be taken when handling with ethylene and oxygen, as this 1 : 1 ratio is within the flammable range. This ethyl chloride level is within the industrially used range [32]. Catalysts with only silver are relatively insensitive to the ethyl chloride concentration with respect to selectivity. The gas flow was varied during the tests to obtain different ethylene conversions at the same temperature. As an example, Fig. 2 A gives the ethylene conversion as a function of time for 15Ag(36) and 15Ag(95). An overview of the ethylene conversion (and ethylene oxide selectivity) as a function of time for catalysts with 36, 47, 50 and 95 nm particle sizes is shown in Fig. S4, with equal amounts of Ag in the reactor.

During the first 15–20 h of the experiments, the catalysts went through an equilibration period in which the conversion reached a maximum of 15–45% prior to decreasing to ca. 2%. Generally, the larger the Ag particles, the shorter the equilibration period when testing a similar amount of silver in the reactor. The equilibration times of all Ag catalysts were determined by fitting the derivatives of the conversion curves (Fig. S5), where the equilibration time was defined as 10% of the derivative minimum (Table S1). Catalysts with 47 and 50 nm Ag particles have equilibration times of 8–10 h and the catalyst with 36 nm particles equilibrated after 20 h. However, with the Ag particle size, the available specific silver surface also changes (Table 2). Fig. 2B shows the equilibration times as a function of the available silver surface area in the reactor. This suggests that the equilibration time correlates with the available Ag surface area in the reactor. The equilibration time as a function of particle size with the same amount of Ag in the reactor is shown in Fig. S6. To have a similar Ag surface area as 100 mg 15Ag(36), 270 mg of 15Ag(95) was tested (Fig. 2A), resulting indeed in almost equal equilibration times. After the calibration period all conversions are similar for the different catalysts, indicating that the active Ag surface area is the same.

One possible explanation of the transient conversion behavior in the first tens of hours could be a structural reorganization of silver particles in the presence of ethyl chloride, as the presence of mobile AgCl species may induce restructuring [30]. To our knowledge, the equilibration period of a (chloride-promoted) Ag/Al_2O_3 catalyst has not been studied before, as high temperature pre-treatments are usually applied in oxidative environment [2,30,39,40]. A combination of oxidative atmosphere and high temperature has been found to increase Ag particle sizes [31], therefore it is difficult to distinguish whether particle growth occurs during the conditioning treatment or during the catalytic test. It is hence worth determining potential particle growth during the equilibration period. To investigate this, 15Ag(36) was tested for 6, 10, 20 and 35 h as catalyst for ethylene epoxidation. Fig. 3A shows the ethylene conversion of tests of 6, 10, and 20 h, illustrating that the experiments were reproducible. After each test, the catalysts were characterized with SEM and H_2 titration: particle size distributions determined with SEM

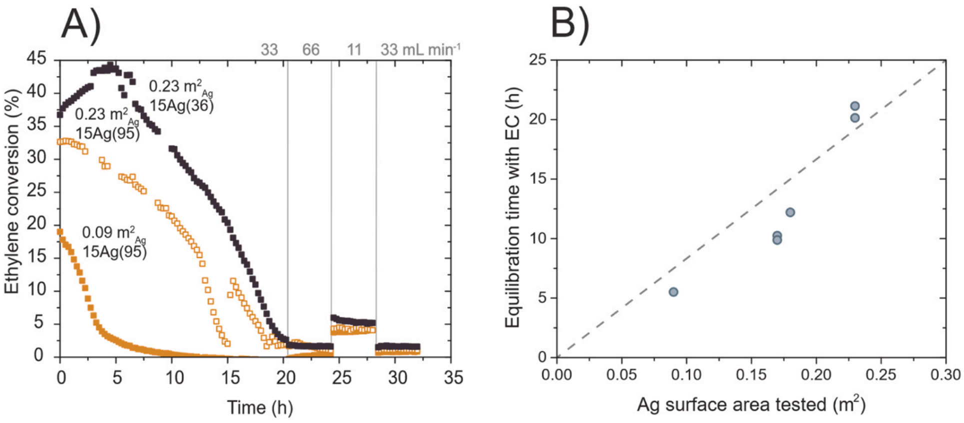

Fig. 2. (A) Ethylene conversions of 15 wt% Ag catalysts with different particle sizes. In (A) the catalyst loading of 15Ag(95) was increased from 100 mg (■) to 270 mg (□) to match the silver surface area of 15Ag(36) (■). Total gas flows are denoted above the graph in grey. (B) Equilibration times as a function of loaded Ag surface area in the reactor tested with ethyl chloride. The dotted line is added to guide the eye.

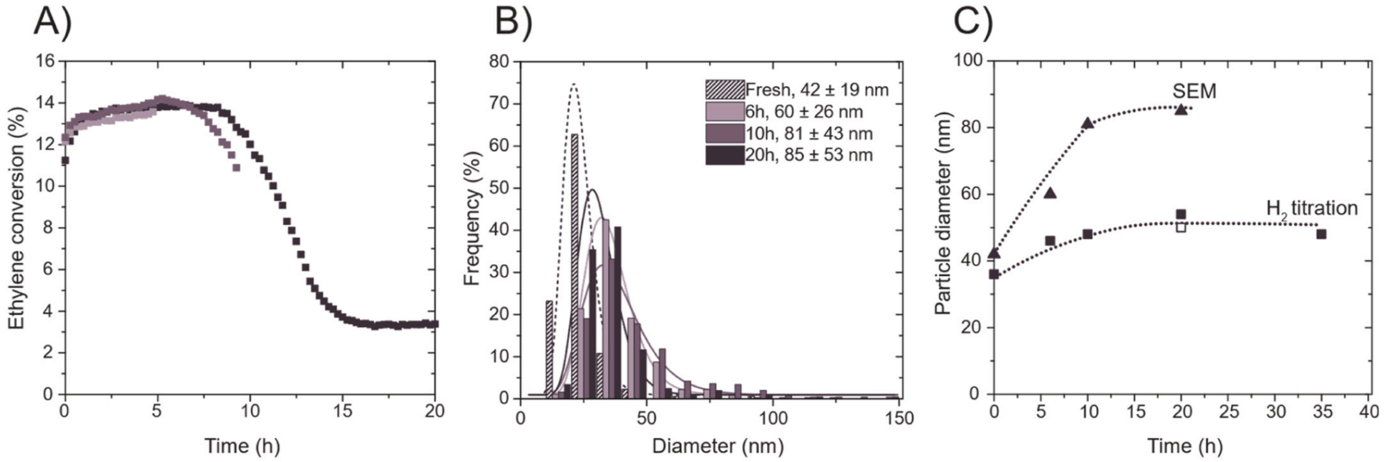

Fig. 3. Ethylene conversion of 15Ag(36) (A), with corresponding particle size distributions from SEM (B), and Ag particle sizes as a function of reaction time determined with SEM and H_2 titration (C) during the three different experiments of 6, 10 and 20 h at 215 °C with 2.1% O_2, 7.5% C_2H_4 and 1.8 ppm ethyl chloride. 2.1% O_2 was used instead of 7.5% to also study the effect of varying O_2 concentrations on the equilibration period and particle size. The open symbol in Frame C is a test of 20 h without ethyl chloride. Lines are added to guide the eye.

are shown in Fig. 3B and the particle size evolution over time is depicted in Fig. 3C. For the H_2 titration measurements the apparent particle size is derived from the experimentally measured active surface area, assuming spherical Ag particles with a fully accessible and active surface.

The SEM particle size distributions shown in Fig. 3B show a modest growth of the particle diameter upon catalysis. After 6 h the particle size had increased from 42 to 60 nm, and it stabilized after 10 h to a surface averaged particle size of ca. 80–85 nm. The H_2 titration data show a similar trend; a modest decrease of active silver surface area upon catalysis, which results in a slightly increasing equivalent Ag particle diameter (assuming spherical particles with a fully accessible and active surface area) as shown in Fig. 3C. After 6 h the equivalent silver particle size increased from 36 to 46 nm, and it stabilized at a value of ca. 50 nm. Hence the large decrease from a maximum conversion in the first tens of hours cannot be explained by a growth in Ag particle size as measured by H_2 titration.

The same catalyst was also tested for 35 h with an increased oxygen concentration (7.5% instead of 2.1%). With more oxygen in the reactant feed, the equilibration period was longer (15 h vs 20 h) (Fig. S4). Oxygen and chlorine are known to competitively adsorb on Ag surface sites [41], hence more oxygen would make it more difficult for chloride to interact with the surface, and leads to an elongated equilibration period. This further points to the fact that the equilibration period might be related to the interaction between chloride and the Ag surface. Even though in literature a more oxidative atmosphere at temperatures above 200 °C, albeit in the absence of chloride, induced Ag particle growth due to mobile Ag-O_x species [31], under our conditions the longer reaction time and higher oxygen concentration did not increase the silver particle size.

In literature, it is stated that chloride leads to restructuring of Ag nanoparticles [30]. Hence as a reference, a catalytic test was conducted without ethyl chloride in the gas feed. The conversion and selectivity data of this test can be found in the Fig. S7, while its particle size determined with H_2 titration is indicated as an open symbol in Fig. 3C. Particle size distributions measured with SEM are shown in Fig. S8. Interestingly, after this test the silver particle size is very similar to the test with ethyl chloride. The mild particle growth and severe loss in activity in the presence of ethyl chloride occur in the same timeframe. However, testing without ethyl chloride led to a similar Ag particle size while the ethylene conversion remained stable at 13% and did not decrease over time (Fig. S7). Please note that it has been industrially observed that bare Ag catalysts are too active to control, and chloride is essential to moderate the activity [32]. This confirms that the explanation for this remarkable equilibration period is a gradual change in the nature of the active site at the silver surface, induced by interaction with the chloride promoter.

The active surface areas of catalysts with 2, 8 and 15 wt% Ag were also characterized with H_2 titration and SEM after 20–30 h on stream (Table 3), i.e. after the equilibration period (which is sometimes also referred to as "break-in" or "settling" period). Histograms of the measured silver particle sizes are shown in Fig. S9. All catalysts had undergone particle growth and more or less doubled in size, also those with lower silver weight loadings (2Ag(13) and 8Ag(31)). In literature on particle size effects, conclusions are often drawn from fresh particle sizes [2,25,29], but it is clear that this is not representative for the longer term particle size, hence we will use the particle sizes after 20–30 h on stream to gain insights into activity and selectivity trends.

3.3. Influence of Ag particle size on activity and selectivity

Catalyst activity can be presented in different ways: the silver time yield indicates the ethylene conversion normalized to silver weight, which is important from an industrial point of view, while the turnover frequency gives the activity per active surface atom, which is of fundamental interest. The Ag particle size effect has been investigated without ethyl chloride in the stream [29]. Ag particles in the range of 50–70 nm showed the highest weight-normalized activity (using fresh particle sizes) which is in line with literature [24,25]. Here, we report on the silver particle size effect, using equilibrated silver particle sizes and

Table 3
Silver particle sizes after 20–30 h of h hcatalysis at 215 °C with 7.5 vol% oxygen and ethylene and 1.8 ppm ethyl chloride in the gas feed, determined from H_2 titration. Catalysts are labelled as *[wt%]Ag_(fresh particle diameter from H_2 titration)*. For comparison surface averaged particle diameters ($d_{p,s}$) measured with SEM are shown.

Catalyst	H_2 titration		SEM
	Fresh Ag particle diameter (nm)	Equilibrated Ag particle diameter (nm)	Equilibrated Ag particle diameter $d_{p,s}$ (nm)
2Ag(13)	13	35	58 ± 26
8Ag(31)	31	74	71 ± 29
15Ag (36)	36	48	53 ± 24
15Ag (47)	47	76	87 ± 35
15Ag (95)	95	184	141 ± 59

in a chloride-containing feed. Silver time yields (STY) and apparent turnover frequencies (TOFs) as a function of particle size are shown in Fig. 4. The STY decreases with increasing particle size, with the highest activity for 35 nm silver particles, the smallest measured in our series (Frame A). The TOF does not show a clear particle size independence (Frame B) in the experimental particle size range. Compared to literature [2,29], the addition of ethyl chloride seems to have shifted the optimum size to smaller particles.

The selectivity to ethylene oxide (EO) is an important performance indicator of silver catalysts, with CO_2 being the undesired side product of this reaction. The selectivity strongly decreases with increasing conversion, which is why it is important to compare catalyst selectivity at similar conversions or as a function of conversion [13]. Fig. 5 shows the selectivities to EO as a function of ethylene conversion for the series of 15 wt% silver catalysts. At conversions of 1.5%, catalysts 15Ag(36), 15Ag(47) and 15Ag(50) show EO selectivities of 75–80%, with the selectivity somewhat decreasing with larger particle size. The catalyst with the largest particles, 15Ag(95), only has a selectivity of ca. 50%. This is unexpected, as in literature larger particles are reported to be more selective to ethylene oxide [2,25]. However, in those studies particle size was not the only factor that was varied: large particles were obtained by increasing the silver weight loading (and not by using different decomposition atmospheres as in our study) which meant that simultaneously the silver loading and interparticle distance were varied [2,24,25,27].

To unravel whether the difference with literature is related to the influence of silver weight loading, we also prepared catalysts with different particle sizes by varying the silver weight loadings. Catalysts with 2 and 8 wt%, containing particles of 13 and 31 nm, respectively, were compared to a 15 wt% Ag catalyst (Table 2), with catalyst loading adjusted to test similar silver surface areas. For 0.17 m^2_{Ag} per experiment, 100 mg of 15Ag(50) was compared to 120 mg of 8Ag(31) and 170 mg of 2Ag(13) (Fig. 6). After 10–12 h, all catalysts showed a stable conversion of approximately 2% (Frame A). Ethylene oxide selectivities are shown in Frame B, with 2Ag(13) having a selectivity of 35%, 8Ag (31) of 50% and 15Ag(50) of 80%. From this dataset it seems that larger particles lead to a higher selectivity, as was also concluded in literature [2,27]. However, in these experiments it is not only the silver particle size that is varied, but also the silver weight loading and hence also other factors such as interparticle distance and the ratio between Ag and Al_2O_3 surface have changed.

The ethylene oxide selectivity is plotted in Fig. 7 as a function of the Ag : Al_2O_3 surface ratio. To make a direct comparison between the different catalysts, selectivity datapoints are shown at similar conversions (1.1–1.3% and 1.6–1.9% conversion). Table S2 summarizes the surface ratios and selectivity datapoints. A clear trend of selectivity versus Ag : Al_2O_3 surface ratio is found, despite the wide variation in particle size (35–184 nm) and silver weight loading (2–15 wt%). This strongly suggests that other effects identified are indirect, and the metal: support surface area ratio is the predominant factor determining the selectivity for chloride-promoted Ag catalysts in ethylene epoxidation. This can be rationalized by the increased probability per ethylene oxide molecule to isomerize on support surface groups (being reported in literature as the primary cause for isomerization [14,15]) when the metal : support ratio is lower, leading to isomerization of ethylene oxide to acetaldehyde, which subsequently combusts to CO_2 and water.

Less catalyst is required when using smaller silver particles, simply because the specific silver surface area is higher. Interestingly, larger particles do not always give higher ethylene oxide selectivities, as well distributed small silver particles can outperform the large particles if they have a higher Ag : Al_2O_3 surface ratio and smaller interparticle distance, limiting the undesired side-reaction on the support. Also in the presence of chloride, which decreases the activity and increases the selectivity of Ag catalysts in the epoxidation of ethylene, a decisive factor influencing selectivity remains limiting the likelihood of an ethylene oxide molecule to subsequently isomerize on the support surface, and hence the ratio between Ag and Al_2O_3 active surface. Varying the silver particle size by either changing the silver weight loading or the decomposition atmosphere changes the Ag : Al_2O_3 ratio significantly.

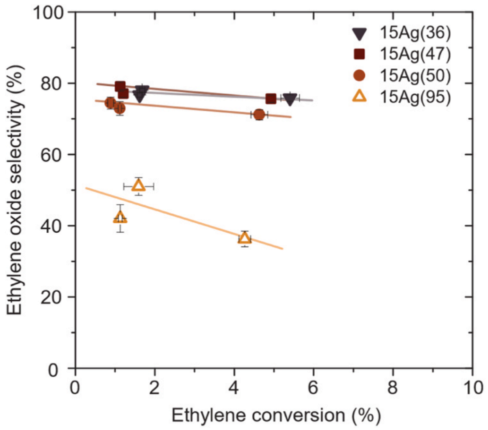

Fig. 5. Ethylene oxide selectivity versus ethylene conversion of the 15 wt% Ag catalysts with different Ag particle sizes after 30 h on stream. Lines are added to guide the eye.

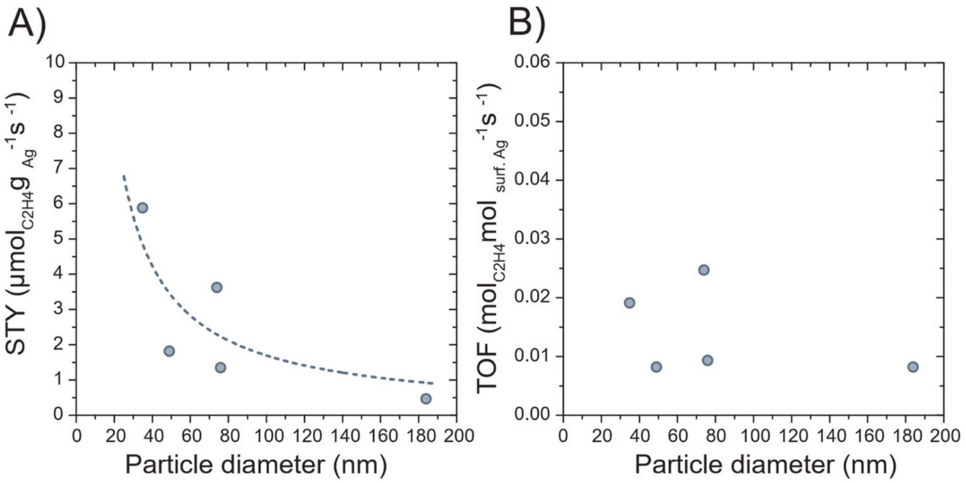

Fig. 4. Silver time yield (STY) (A) and apparent turnover frequency (TOF) (B) as a function of silver particle size after 20–30 h on stream. For these calculations, equilibrated particle sizes determined with H_2 titration were used. The dotted line in (A) is a fit of 1/diameter.

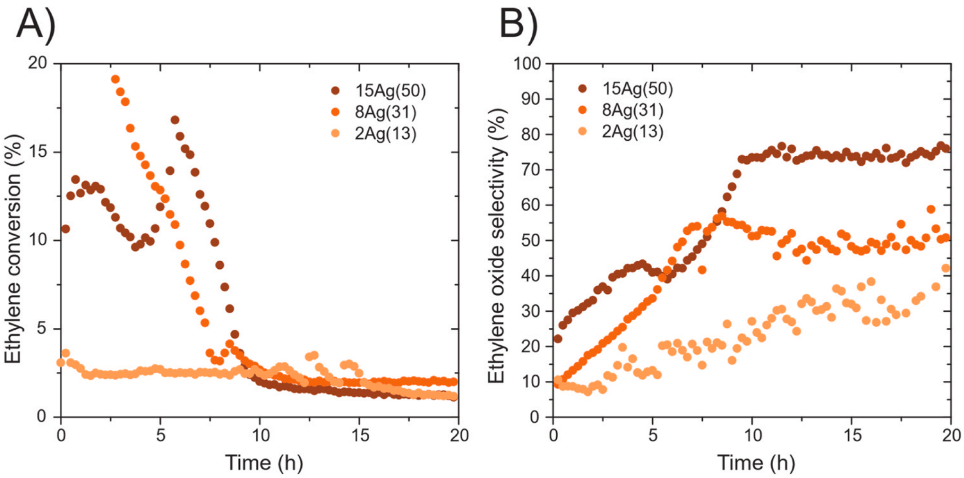

Fig. 6. Ethylene conversion (A) and ethylene oxide selectivity (B) of catalysts with 2, 8 and 15 wt% silver, 2Ag(13), 8Ag(31) and 15Ag(50), respectively. The catalyst loading was adjusted to 0.17 m^2_{Ag} to test similar Ag surface areas.

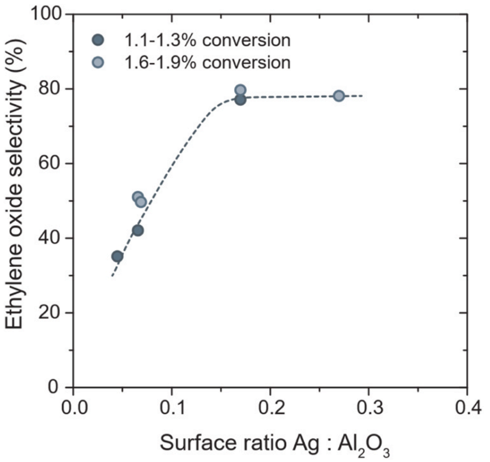

Fig. 7. Ethylene oxide selectivity as a function of the ratio between exposed silver surface and α-alumina surface areas. The dotted line is added to guide the eye.

The previously measured particle size effect [2,27] is merely a result of a change in Ag : Al_2O_3. The metal : support surface ratio is hence an important parameter to consider when comparing selectivities of different catalysts for reactions where the selectivity is determined by side reactions occurring on the support surface.

4. Conclusion

A series of supported silver catalysts with different particle sizes was synthesized by either changing the silver loading or changing the decomposition atmosphere. During the chloride-promoted ethylene epoxidation, silver particle growth occurred quickly, while the catalysts' conversions equilibrated after hours to tens of hours, depending on the specific silver surface area. Loss in activity was not explained by the mild particle growth, which also occurred for the unpromoted reaction, but by the gradual change in active Ag sites caused by interaction with the chloride. We used equilibrated particles instead of commonly used fresh particle sizes to investigate activity and selectivity trends. Catalysts with small Ag particles show a higher weight-normalized activity than large particles due to increased specific silver areas. Increasing the Ag particle size by increasing Ag loading led to an improved selectivity of 80% at ethylene conversions of 1–2%. In contrast, a decrease in selectivity was observed when increasing the Ag particle size using different decomposition atmospheres. Both routes have been used in literature, but we illustrate that both strategies introduce a bias since also the Ag : Al_2O_3 ratio is changed upon varying the silver particle size. This study shows that the probability of an ethylene oxide molecule to react with a support surface group, thus the Ag : Al_2O_3 surface ratio, is the predominant factor determining the ethylene oxide selectivity in the chloride-promoted ethylene epoxidation.

CRediT authorship contribution statement

Claudia J. Keijzer: Conceptualization, Methodology, Validation, Investigation, Writing – Original Draft, Visualization. **Luc C.J Smulders**: Methodology, Writing – Review & Editing. **Dennie Wezendonk**: Resources. **Jan Willem de Rijk**: Resources. **Petra E. de Jongh**: Conceptualization, Writing – Review & Editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2023.114447.

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