

Ethylene epoxidation over supported silver catalysts – influence of catalyst pretreatment on conversion and selectivity

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Abstract

BACKGROUND: Ethylene oxide is a key intermediate in the chemical industry. It is produced through catalytic epoxidation of ethylene. Significant economic benefits can be achieved by small improvements in catalyst activity and selectivity. The aim of this work was to study how different preparation methods and pretreatments affect the catalyst performance under industrially relevant reaction conditions. The influence of pretreatment strategy on the selectivity and reaction temperature was for the first time investigated at a constant ethylene conversion of 7%.

RESULTS: Epoxidation of ethylene to ethylene oxide was studied over a range of silver catalysts which were prepared with different thermal treatments. The influence of catalyst preparation method and catalyst pretreatment strategy on the catalytic performance was investigated. It was found that calcination resulted in lower ethylene conversion compared with pre-drying. In the latter case an induction period was observed, absent for the calcined catalyst. This induction period can be eliminated by oxidative or reductive pretreatment of the catalyst.

CONCLUSIONS: The most promising pretreatment strategy was carried out by first treating the catalyst with 1 ppm of DCE for 5 h at 230 °C followed by overnight pre-treatment in 20% ethylene at 250 °C. With this pretreatment it was possible to achieve a target ethylene conversion of 7% at 232.6 °C with a selectivity to ethylene oxide of 82.1%.

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Keywords: ethylene; ethylene oxide; silver catalyst; catalyst preparation; catalyst pretreatment

INTRODUCTION

Ethylene oxide is one of the key intermediates in the chemical industry. It is used in several important processes to obtain valuable products, such as ethylene glycol.^{1,2} Union Carbide Corporation started the first industrial process for ethylene epoxidation to ethylene oxide using direct oxidation in 1937. Since that time, the most active and selective catalyst component has been silver.¹ The desired epoxidation of ethylene to ethylene oxide is accompanied by side reactions of ethylene and ethylene oxide oxidation to carbon dioxide and water through parallel and consecutive pathways as discussed elsewhere.^{3,4}

Epoxidation of ethylene to ethylene oxide most probably occurs on an oxygen covered silver surface.^{2,5} X-ray photoelectron spectroscopy has been applied in the investigation of adsorbed oxygen species.⁶ It has been reported that an active catalyst for ethylene epoxidation has both nucleophilic ($O^{\delta-}$) and electrophilic ($O^{\delta+}$) oxygen species adsorbed on the silver particles.⁶ The nucleophilic form of oxygen is reported to be stable and acting as the adsorption site for ethylene.⁵ The nucleophilic form of oxygen, however, also takes part in the total oxidation of ethylene to carbon dioxide.⁶ Formation of the electrophilic oxygen occurs at a lower rate than formation of the nucleophilic and requires elevated oxygen pressures or reactive gas mixtures.⁷ It is believed that molecularly adsorbed oxygen reacts with the adsorbed ethylene and forms ethylene oxide.^{1,8}

Selectivity to ethylene oxide over neat silver is typically mediocre.^{9–12} It can be, however, enhanced by doping the catalysts with different promoters.¹⁰ The most commonly used promoters are cesium and rhenium.^{10,13,14} In fact, optimal promoter loadings can boost selectivity by almost 10% compared with unpromoted silver catalysts.¹⁰ It should be noted that the selectivity declines with conversion, which is typical for consecutive reactions. Ethylene oxide selectivity can also be increased by preventing total oxidation to CO_2 through co-feeding 1,2-dichloroethane (DCE).¹⁵ Addition of chlorine-containing compounds suppresses dissociative adsorption of oxygen which plays a key role in oxidation of ethylene to carbon dioxide.^{1,15–17} Optimal DCE levels for stable catalyst performance are reported to be in the range 1–2 ppm.^{18,19} It has also been reported that the selectivity can be improved by blocking sites responsible for total oxidation via addition of CO_2 to the reactor.^{20,21} The selectivity is improved

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through reactions of the dissociatively adsorbed oxygen and carbon dioxide forming carbonate species.²²

It has been reported that, during the start-up of the ethylene epoxidation in laboratory scale, a dynamic behavior of the catalyst has been observed before reaching the steady state.^{10,23} The selectivity to ethylene oxide increases with time-on-stream while the ethylene conversion goes through a maximum.^{10,24}

It has been reported that the ethylene epoxidation rate can be enhanced by illumination of the silver nanocube catalysts with visible light.¹² Christopher *et al.*¹² reported that it was possible to increase the rate four-fold with the aid of 250 mW cm⁻² of visible light. They also reported that the effect was reversible and that the ethylene epoxidation rate returned to the value without the illumination.

Besides introduction of promoters and reaction inhibitors, the selectivity to ethylene oxide can be improved by pretreating the catalyst.²⁵ Pretreatment under oxygen flow (20% in methane) at 260 °C has been reported to improve the selectivity by 2%.¹⁰ Hernández *et al.*⁴ pretreated silver-plated microreactor elements in 20% oxygen in helium at 300 °C followed by a pretreatment in 20% ethylene in helium at the same temperature. They obtained an enhancement of the initial activity and selectivity. The surface area of silver can be increased and cleaned with oxygen adsorption, outgassing, and reduction methods (OAOR).²⁶ Kestenbaum *et al.*²³ after applying OAOR for microreactor silver foils prior to ethylene epoxidation found that the treatment only slightly increased the catalytic activity, however, during the first 100 h of operation, additional active sites were formed or the activity of existing sites increased.

In the present work two different catalysts were prepared. The novelty of the work was to experimentally investigate the influence of several different catalyst pretreatment strategies on ethylene conversion and ethylene oxide selectivity under industrially relevant reaction conditions. The impact of catalyst pretreatment on the ethylene oxide selectivity and reaction temperature was evaluated at a constant ethylene conversion of 7%.

EXPERIMENTAL

Materials

Ethylene (3.5, AGA), 50 ppm 1,2-dichloroethane in helium (BOC), helium (4.6, AGA), 11.2% oxygen and 10.0% CO₂ in helium (AGA) and hydrogen (5.0, AGA) were used in the experiments. The GC calibration for ethylene oxide was made with a 3% ethylene oxide in helium gas mixture (AGA).

α -Alumina supported silver catalysts were prepared using two similar methods reported in the literature^{27–30} having different thermal treatments. The support (20 g) was vacuum-impregnated with 100 mL silver containing solution for 15 min. The silver oxalate solution was prepared according to procedures described in the patent literature^{27–30} using ethanolamine (Sigma-Aldrich) and ethylenediamine (Sigma-Aldrich) as solvents. The remaining solution was decanted and the solid material was dried at 80 °C overnight. The dried silver catalyst was exposed to a solution containing 4% cesium (CsOH, Sigma-Aldrich) and 4% rhenium (NH₄ReO₄, Sigma-Aldrich) dissolved in water by applying incipient wetness impregnation. One of the catalysts was dried overnight at 150 °C and denoted as Cat-dried, while the other one was calcined at 300 °C for 1 h and will be further referred to as Cat-calcined. During the heat treatment, the silver oxalate decomposes to metallic silver and carbon dioxide.³¹

Catalyst characterization

The catalysts were characterized by scanning electron microscopy. A Phillips XL30 FEG ESEM, with an acceleration voltage of 10 kV to acquire the backscattered electron images. Before SEM the catalysts were crushed and sieved to a fraction smaller than 180 μ m and attached to double-sided carbon tape and coated with carbon in order to prevent charging in the SEM. Approximately 100 images were taken from each sample at a horizontal full width of 6.9 μ m and 17.3 μ m. The images acquired were post-processed in ImageJ with an in-house algorithm to segment the silver particles. The areas of the silver particles were captured and converted into spherical diameter. Overlapping or merged well-defined particles were possible to separate. The non-defined particle-borders of the patchy/agglomerated particles as seen in the fresh samples are not possible to separate into individual particles. This is especially seen in the fresh Cat-dried sample of particles >250 nm.

The silver, rhenium and cesium contents of the catalysts were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Prior to analysis 0.1–0.15 g finely ground sample was extracted with 20 mL half-concentrated HNO₃ (p.a. quality) and boiled for 20 min on a heating plate. The sample solution was transferred to a 100 mL volumetric flask and filled to the mark with pure water (18.2 M Ω cm).

The contents of Ag, Re and Cs in the sample solution were quantified by an Agilent 720 ES ICP-OES instrument. Due to the low sensitivity to Cs by the ICP-OES technique, the content of Cs in the sample solution was quantified by inductively coupled plasma mass spectrometry (ICP-MS) with an Agilent 7500ce ICP-MS instrument.

Equipment

The set-up used in the experiments consisted of a 6 mm internal diameter stainless steel tube reactor heated by an electric oven. The inlet gas flows were controlled by Brooks 5850 mass flow controllers (MFC) and the pressure in the reactor was controlled by a Brooks 5866 pressure controller (PIC). The reaction temperature was monitored by a K-type thermocouple (TI) placed inside the catalyst bed. The process data (MFC, temperature and pressure) were logged by a computer during the experiments. Water was periodically released from the set-up through a valve. The temperature of the oven was measured and controlled with a Carbolite control unit.

The inlet and product gas compositions were analyzed by a GC (HP 6890) having both FI and TC detectors. The column used for separating the gases was a GS-Q. The temperature program used in the GC analysis was 40 °C isothermal for 6 min, 20 °C per min heating to 150 °C and followed by 7 min isothermal. The gas flow through the column was 12 mL min⁻¹. Temperature for FI and TC detectors was 300 °C and 210 °C, respectively. A schematic of the reactor set-up is illustrated in Fig. 1.

Catalyst pretreatment

The catalysts were pretreated in different ways prior to testing. The so-called standard (STD) pretreatment was carried out in 20% ethylene in helium overnight at 250 °C. An alternative oxidative pretreatment was performed with the oxygen gas mix (11.2% O₂ and 10.0% CO₂ in helium) overnight at 300 °C, while the reductive pretreatment was done with 40% hydrogen in helium overnight at the same temperature of 300 °C. A pretreatment in inert gas (helium) was conducted overnight at 300 °C. Finally, the standard pretreatment was modified by first exposing the catalyst to 1 ppm

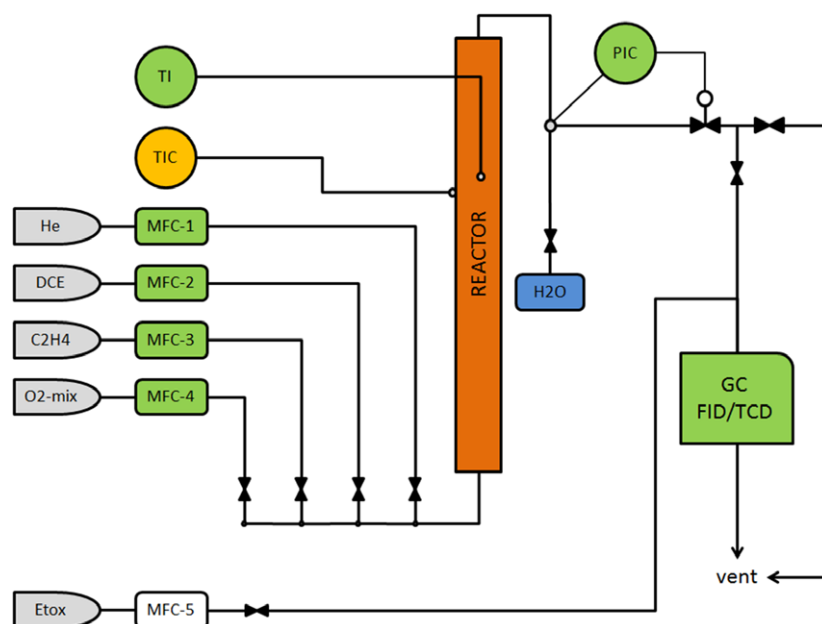


Figure 1. Reactor set-up for ethylene oxide catalysts, the symbols in green (MFCs 1–4, TI, PIC and GC) are logged to the computer.

Table 1. Silver, cesium and rhenium loadings in the applied catalysts determined by ICP-OES and ICP-MS

Catalyst	Ag (wt-%)	Cs (ppm)	Re (ppm)
Cat-dried	15.9	540	480
Cat-calcined	16.9	610	670

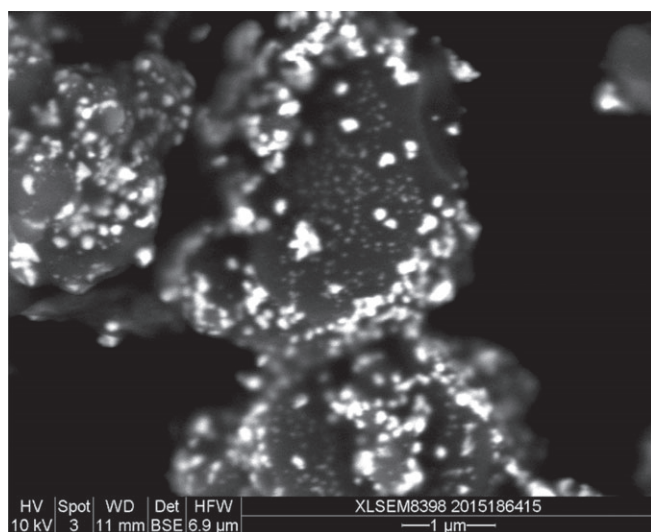


Figure 2. SEM image of the fresh Cat-dried catalyst.

of DCE for 5 h at 230 °C followed by overnight pretreatment in 20% ethylene at 250 °C (DCE + STD). The reactor was operated under atmospheric pressure during the catalyst pretreatment.

Experimental procedure

The reactor tube was filled with the catalyst (0.58 g) diluted with glass beads (2.5 g). The set-up was pressurized with helium and

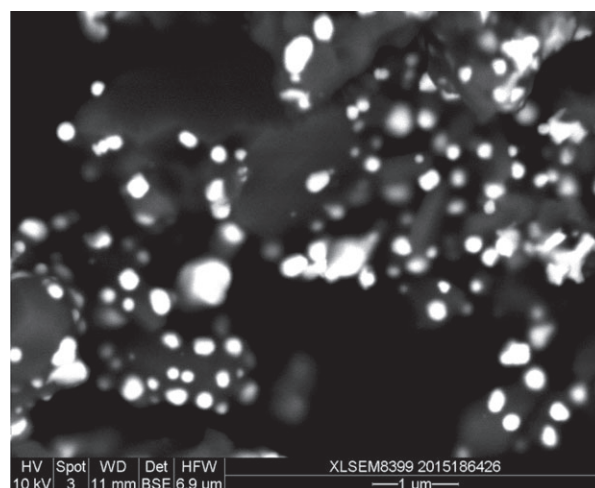


Figure 3. SEM image of the fresh Cat-calcined catalyst.

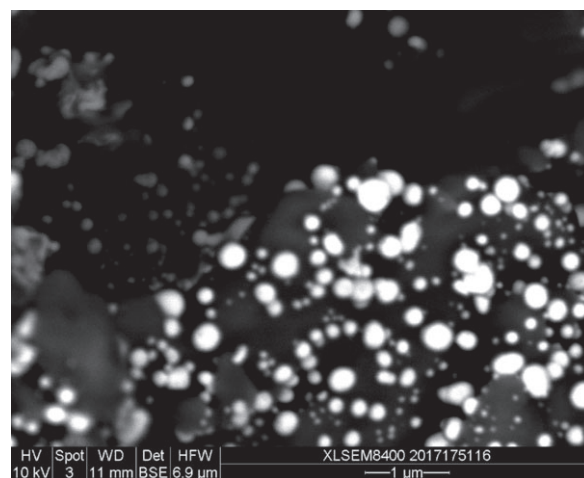


Figure 4. SEM image of Cat-dried catalyst after reaction and standard pretreatment.

Table 2. Silver particle sizes for the fresh and spent catalysts analyzed by SEM

Cat-dried	Fresh	STD	Helium	Oxidative	Reductive	DCE + STD
Mean (nm)	162	133	126	156	145	136
Standard Deviation (nm)	109	91	83	109	98	94
Number of particles	12002	10671	25944	6622	9571	16461
Cat-calcined	Fresh	STD	Helium	Oxidative	Reductive	DCE + STD
Mean (nm)	141	150	147	157	116	151
Standard Deviation (nm)	100	100	107	114	80	106
Number of particles	10787	15069	7260	7944	20762	16193

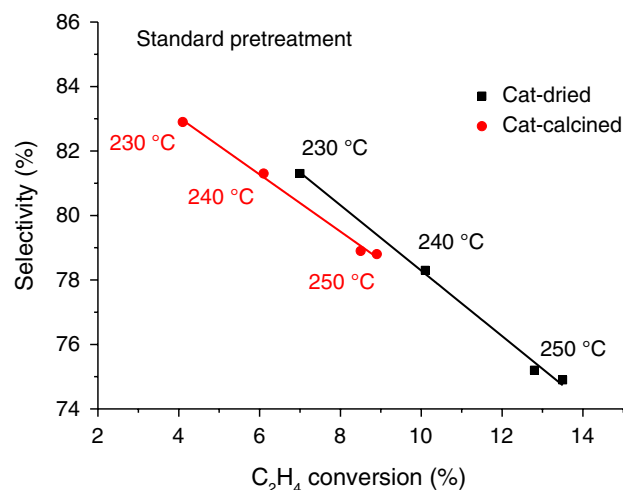
checked for leakage. The catalyst pretreatment was performed overnight with one of the above described methods. The feed gas consisted of 23% ethylene, 7.5% oxygen, 6.6% CO₂, and 1 ppm of DCE diluted in helium. The total gas flow was 100 mL min⁻¹ (STP). The temperature programming used in the catalyst testing was 20 h at 250 °C followed by isothermal holding at subsequently 240, 230 and 250 °C for 7–8 h. The overpressure was 21.6 bar. The outlet gas was continuously analyzed by GC. After the final isotherm at 250 °C, the reactor was cooled down to ambient temperature and the composition of the reactant gas mixture was analyzed by GC. The response factor for ethylene oxide was checked after every experiment with the calibration gas containing ethylene oxide. After an experiment the reactor tube was emptied from the catalyst and glass beads and cleaned with acetone and dried with compressed air before the next run.

RESULTS AND DISCUSSION

Catalyst characterization results

The metal contents in the catalysts are given in Table 1.

The metal loadings of the two catalysts were similar, however, the calcined catalyst had slightly higher concentrations of the metals. A possible reason could be that the two samples were prepared separately, i.e. two batches of alumina were impregnated with a silver solution followed with incipient wetness impregnation of the promoters. The only difference in catalyst preparation was the

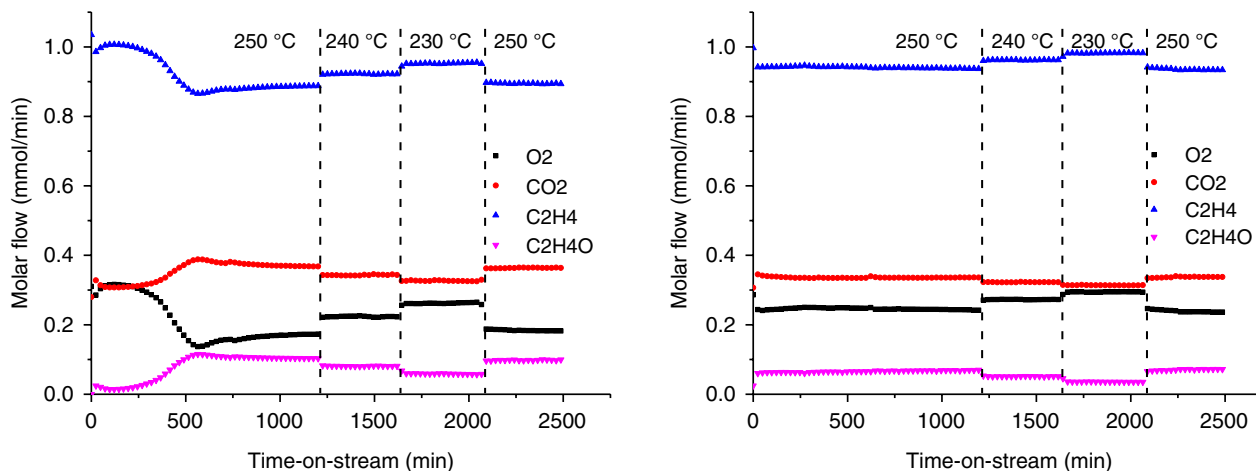
**Figure 6.** Selectivity towards ethylene oxide plotted against ethylene conversion for the dried (black squares) and calcined (red circles) catalysts.

final thermal treatment. The calcined catalyst was heat-treated at 300 °C for 1 h, while the dried catalyst was dried at 150 °C overnight.

The SEM images (Figs 2 and 3) displaying silver particles deposited on the alumina support clearly show that calcination resulted in sintering. Figure 4 shows a SEM image of the dried catalyst after reaction and standard pretreatment.

The size of the silver particles was measured with ImageJ using an in-house algorithm to segment the silver particles. The mean silver particle size, standard deviation and number of particles measured for the fresh and spent catalysts are listed in Table 2.

Contrary to the visual inspection of Figs 2 and 3, Table 2 states that the mean silver particle size for the fresh dried catalyst is slightly larger than for the fresh calcined catalyst. A possible reason for the larger particles on the dried catalyst could be agglomeration of several small particles in the post-processing of the SEM images making it difficult to separate individual particles before measuring the size.

**Figure 5.** Product gas molar flow (mmol min⁻¹) for dried (left) and calcined (right) catalysts pretreated under standard conditions, i.e. 20% ethylene at 250 °C.

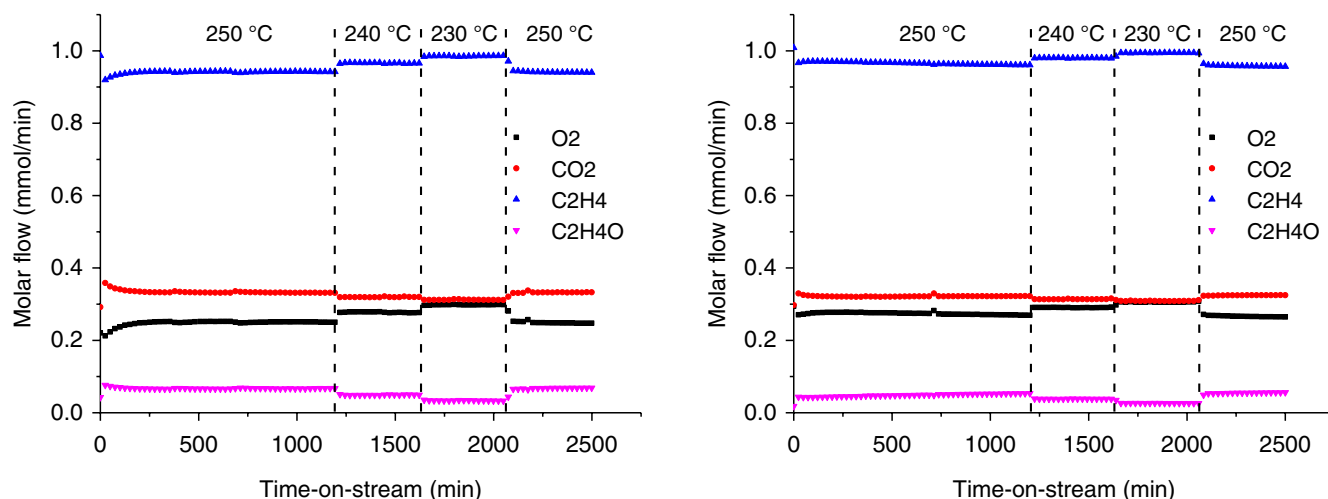


Figure 7. Product gas molar flow (mmol min^{-1}) for dried (left) and calcined (right) catalysts pretreated under oxidative conditions.

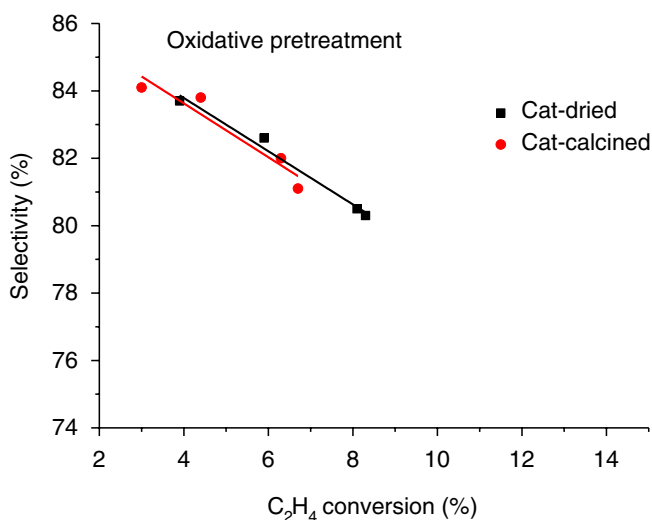


Figure 8. Selectivity–conversion plot for the dried (black squares) and calcined (red circles) catalysts pretreated under oxidative conditions.

Influence of the catalyst preparation method on conversion and selectivity

The catalysts prepared with different thermal treatments were investigated under similar reaction conditions. The molar flows of the product gases are illustrated in Fig. 5. Before the experiments the catalysts were pretreated using the standard procedure, i.e. 20% ethylene at 250 °C overnight.

From Fig. 5 it can be observed that the initial behavior of the two catalysts differs significantly. The dried catalyst has an induction period up to ca. 500 min, after which a steady state was reached. In contrast, no induction period was noticeable for the calcined catalyst. A possible reason for the difference in the initial behavior of the two catalysts could be that the organic compounds used in the catalyst preparation are removed from the catalyst surface either during calcination or during the induction period of the dried catalyst. An alternative explanation would be that silver particles sinter to larger ones, which could be more active. Recently, van den Reijen *et al.*³² reported that the turnover frequency increases until the silver particle size is larger than 70 nm and thereafter the turnover frequency is constant. The

silver time yield, defined as the moles of ethylene converted per gram of silver per s, had a maximum value over silver particles of approximately 60 nm size.³² The selectivity to ethylene oxide was reported to be independent of silver particle size. However, the selectivity at a 2.8% ethylene conversion was about 50%, which is significantly lower than the selectivity we obtained. The catalyst applied by van den Reijen *et al.* contained only silver on $\alpha\text{-Al}_2\text{O}_3$ without any promoters, this could be the reason for the lower selectivity.

The selectivity towards ethylene oxide is plotted against the ethylene conversion in Fig. 6. The selectivity and conversion are calculated as the average of the last seven data points before changing the reaction temperature. Standard deviation for the ethylene conversions are smaller than 0.09% and for the ethylene oxide selectivity the average standard deviation is 0.25% in the results presented below.

Figure 5 reveals that the dried and calcined catalysts have different activity at the same reaction temperature, with the dried one being more active. However, from Fig. 6 no major differences between the two catalysts at similar ethylene conversions can be observed. Diao *et al.*¹⁰ used a cesium and rhenium promoted silver catalyst similar to the ones applied here and reported ethylene oxide selectivity of 81.7% at 10.1% ethylene conversion.

Influence of catalyst pretreatment method

Oxidative pretreatment

The dried and calcined catalysts were pretreated with an oxidative pretreatment. The molar flows of the product gases are plotted in Fig. 7. The induction period observed with the standard pretreatment method for the dried sample was not present for the same catalyst when the oxidative pretreatment was applied. This result is in agreement with the hypothesis that the silver particles sinter during the pretreatment. The oxidative pretreatment resembles in fact calcination with the exception that the oxygen mixture contains 10% carbon dioxide and that the duration of the pretreatment is approximately 16 h, while calcination was performed in 1 h. A possible reason for the absence of the induction period is that the stabilization of silver particles occurs during the oxidative pretreatment of the dried catalyst and during calcination in the preparation of the calcined catalyst or combustion of organic residues.

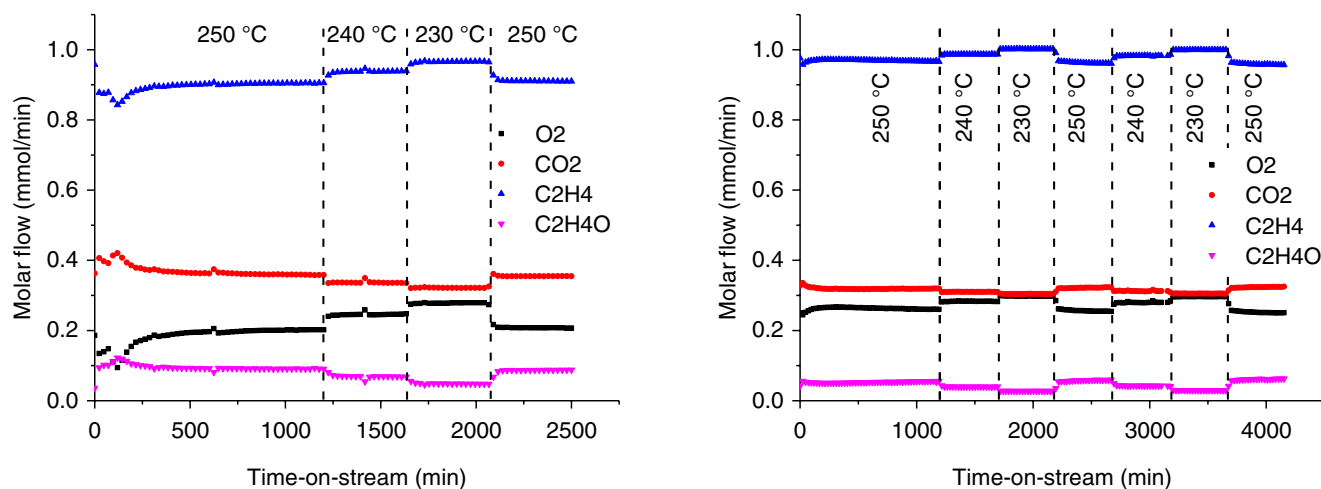


Figure 9. Product gas molar flow (mmol min^{-1}) for dried (left) and calcined (right) catalysts pretreated under reductive conditions.

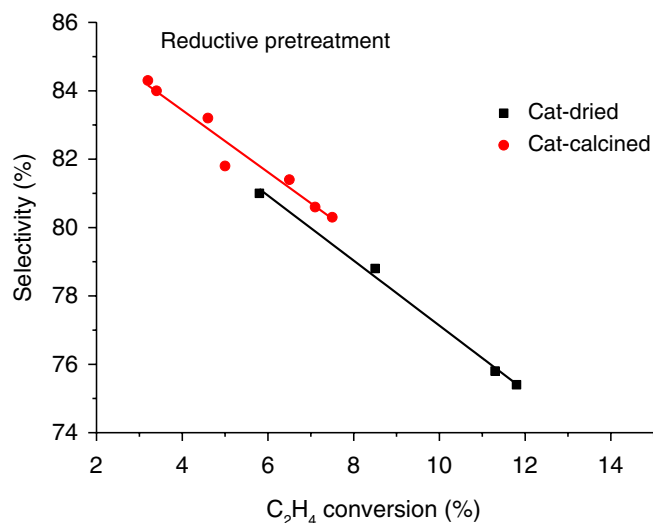


Figure 10. Selectivity–conversion plot for the dried (black squares) and calcined (red circles) catalysts pretreated under reductive conditions.

The selectivity–conversion plot displayed in Fig. 8 confirms that the selectivity at a given conversion is almost the same for both catalysts. A comparison of the results in Fig. 6 (standard pretreatment) and Fig. 8 (oxidative pretreatment) indicates that the *in situ* oxidative pretreatment of the catalysts is more beneficial than calcination as selectivity at a given conversion is slightly higher (about 1% at 8% conversion) for the catalyst pretreated under oxidative conditions. The results presented here (Figs 6 and 8) are in agreement with the results of Diao *et al.*¹⁰ who reported that *in situ* pretreatment with oxygen improves the selectivity by 1–2 percentage points compared with calcination.

Reductive pretreatment

The results from the reductive pretreatment are displayed in Figs 9 and 10.

Pretreatment in hydrogen preserved the high activity of the dried catalyst, similarly to the standard pretreatment in ethylene. The selectivity at a given conversion was comparable for the two

catalysts. A longer testing program was used for the calcined catalyst in order to investigate possible deactivation. No deactivation was observed, instead the ethylene conversion increased slightly with time.

The reductive pretreatment resembles the oxygen adsorption, outgassing, and reduction method (OAOR) for the calcined catalyst. Czanderna²⁶ reported that the silver surface area can be cleaned and stabilized with this method. It was also reported that silver starts to sinter at about 200 °C, which is in agreement with the SEM images displayed in Figs 2 and 3. Metallic silver is probably not the active phase in the epoxidation of ethylene to ethylene oxide but is quickly covered with oxygen during a change of the gas composition. Comparison between a reductive pretreatment and a standard pretreatment reveals that in order to reach a certain ethylene conversion a higher reaction temperature is needed and that selectivity to ethylene oxide is lower with the reductive pretreatment.

Helium pretreatment

The results of the helium pretreatment are illustrated in Figs 11 and 12. Although the induction period previously observed for the dried catalyst was present for the helium pretreated catalyst, the catalyst behavior was, however, different. While ethylene oxide was formed directly from the beginning of the run after ca. 4 h time-on-stream, the catalyst productivity increased and remained fairly constant until the reaction temperature was changed. The dried catalyst was more active than the calcined one. It is well known that silver oxide and oxalate decompose at around 200 °C forming metallic silver and oxygen or carbon dioxide.

The aim with the helium pretreatment was to stabilize the silver particles prior to the testing. The treatment showed no difference in the performance of the helium treated catalyst (Fig. 12) compared with the standard pretreatment with ethylene (Fig. 6) in terms of activity and selectivity.

DCE pretreatment

The DCE pretreatment results are shown in Figs 13 and 14. The induction period for the dried catalyst was almost the same for the DCE pretreatment and the standard pretreatment. The DCE pretreatment of the dried catalyst gave a slightly better selectivity compared with the calcined one.

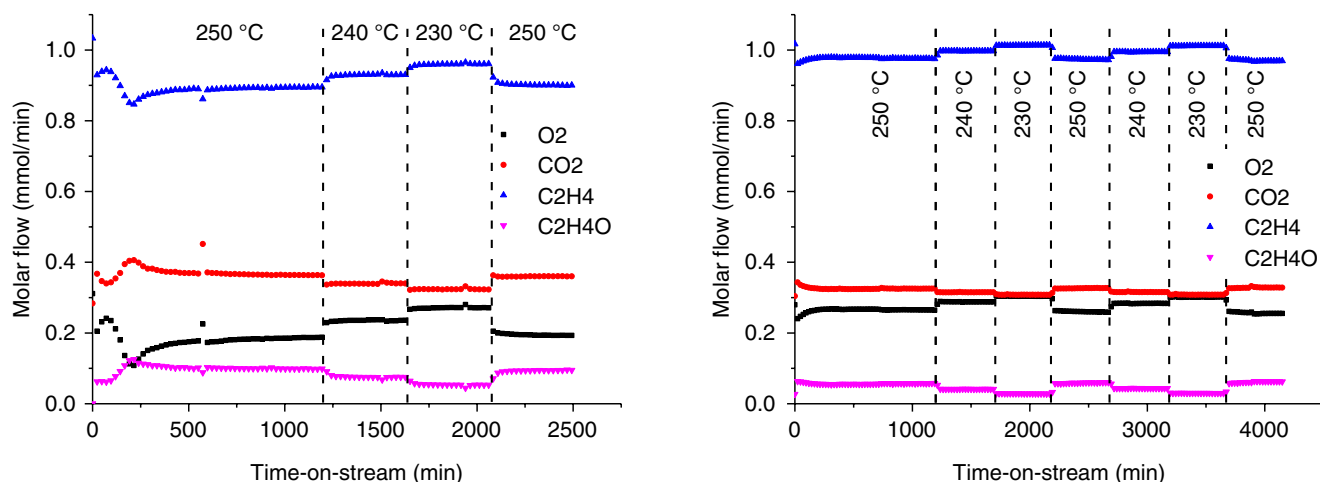


Figure 11. Product gas molar flow (mmol min^{-1}) for dried (left) and calcined (right) catalysts pretreated in helium atmosphere.

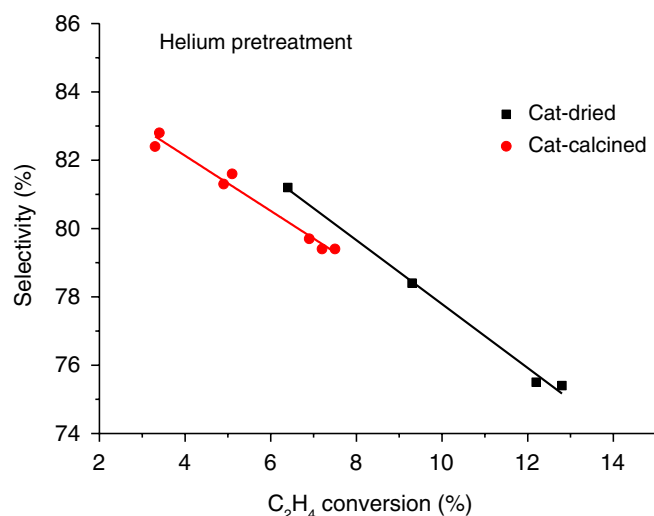


Figure 12. Selectivity–conversion plot for the dried (black squares) and calcined (red circles) catalysts pretreated under helium atmosphere.

It has been reported that silver catalysts that have been modified with the addition of DCE are more active and selective,³³ therefore the aim of DCE pretreatment was to modify the silver surface in order to achieve higher conversion and better selectivity compared with other pretreatment methods. A slightly higher ethylene oxide selectivity was achieved with the DCE pretreatment at a given ethylene conversion compared with the other pretreatment strategies.

Selectivity–conversion dependencies for all tested pretreatment strategies are displayed in Fig. 15. The conversion of ethylene is higher with the dried catalyst (circles) except for the oxidative pretreatment. The highest ethylene conversion was obtained with catalyst pretreated in 20% ethylene. Oxidative pretreatment gives slightly better selectivity to ethylene oxide at a similar conversion compared with the other pretreatment methods. The DCE pretreatment of the dried catalyst resulted in the highest selectivity at a given ethylene conversion.

Table 3 lists the reaction temperature needed to reach 7% ethylene conversion and the selectivity to ethylene oxide. The values listed are interpolated from the figures above except

the values for the Cat-calcined with the oxidative pretreatment which did not reach 7% conversion at the tested temperature interval.

Table 2 shows that the temperature needed to reach 7% ethylene conversion is less than 240 °C for the dried catalyst pretreated with different strategies except the oxidative pretreatment requiring 244.7 °C to achieve 7% conversion. The calcined catalyst is less active than the dried one and therefore the required reaction temperature is significantly higher for the calcined catalyst independent of the pretreatment method.

CONCLUSIONS

Two catalysts bearing silver supported on α -alumina were prepared with similar procedures, but different in their thermal treatments. While one catalyst was dried overnight at 150 °C, the other one was calcined at 300 °C for 1 h. The catalysts were tested under similar reaction conditions after pretreating them in 20% ethylene at 250 °C. It was found that the dried catalyst had an induction period contrary to the calcined one. A possible reason for the induction period could be removal of organic compounds used in catalyst preparation, covering the active silver particles or sintering of the silver particles into larger more active particles. The two catalysts showed similar ethylene oxide selectivities at similar steady-state ethylene conversions. Different pretreatment strategies were investigated including oxidative pretreatment with oxygen, reductive pretreatment with hydrogen, thermal treatment in inert gas (helium) and exposing the catalyst to DCE (1 ppm) before the standard pretreatment mentioned above. The oxidative and DCE pretreatment improved the performance of the dried catalyst. However, it was possible to reach 7% ethylene conversion at significantly lower temperatures with the DCE pretreatment method than with the oxidative method. The induction period became shorter with the helium pretreatment and was completely eliminated with oxidative and reductive pretreatment methods. Highest ethylene oxide selectivity (82.1%) at an industrially relevant ethylene conversion (7.0%) was reached with the dried catalyst pretreated with DCE. Furthermore, the reaction temperature required to reach 7% ethylene conversions was one of the lowest (232.6 °C) among all pretreatment strategies investigated.

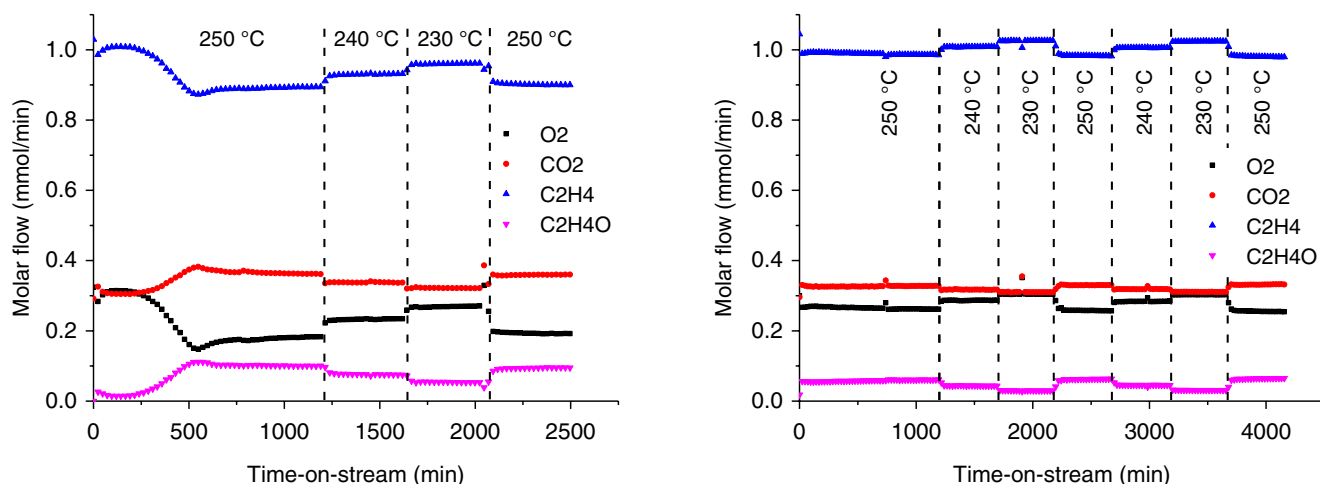


Figure 13. Product gas molar flow (mmol min^{-1}) for dried (left) and calcined (right) catalysts pretreated first in the presence of DCE (1 ppm) and then under standard conditions.

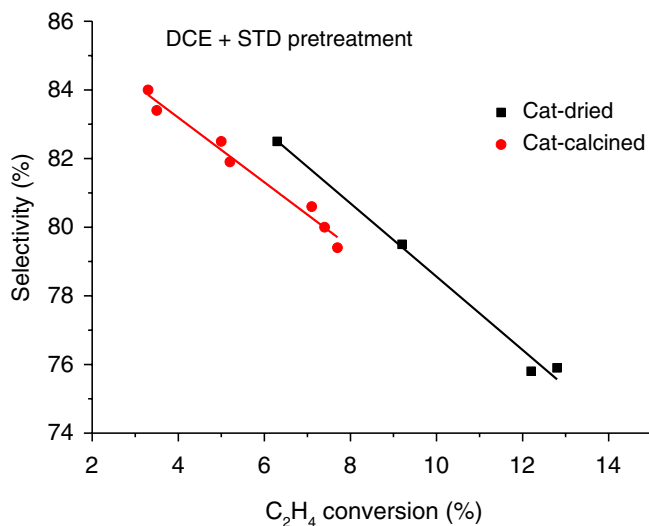


Figure 14. Selectivity–conversion plot for the dried (black squares) and calcined (red circles) catalysts pretreated first in DCE and then under standard conditions.

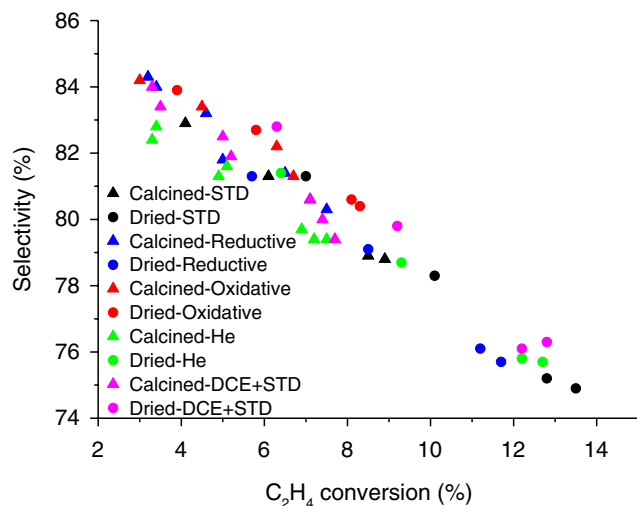


Figure 15. Selectivity–conversion plot for the dried (circle) and calcined (triangles) catalysts pretreated with different strategies.

Table 3. Temperature and selectivity at 7% ethylene conversion			
Catalyst	Pretreatment	Temperature ($^{\circ}\text{C}$)	Selectivity
Dried	STD	230.1	81.3%
Calcined	STD	242.9	80.4%
Dried	Oxidative	244.7	81.5%
Calcined	Oxidative	252.9	81.4%
Dried	Reductive	234.7	80.2%
Calcined	Reductive	249.9	80.7%
Dried	Helium	232.2	80.8%
Calcined	Helium	249.2	79.7%
Dried	DCE + STD	232.6	82.1%
Calcined	DCE + STD	248.2	80.4%

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REFERENCES

- Weissmehl K and Arpe HJ (eds), *Industrial Organic Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany (2003).
- Özbek MO and van Santen RA, The mechanism of ethylene epoxidation catalysis. *Catal Lett* **143**:131–141 (2013).
- Metcalfe PL and Harriott P, Kinetics of silver-catalyzed ethylene oxidation. *Ind Eng Chem Process DD* **11**:478–484 (1972).
- Hernández Carucci JR, Halonen V, Eränen K, Wärnå J, Ojala S, Huuhtanen M, et al., Ethylene oxide formation in a microreactor: from qualitative kinetics to detailed modeling. *Ind Eng Chem Res* **49**:10897–10907 (2010).
- Schlögl R, Heterogeneous catalysis. *Angew Chem* **54**:3465–3520 (2015).
- Demidov DV, Prosvirin IP, Sorokin AM, Rocha T, Knop-Gericke A and Bukhtiyarov VI, Preparation of Ag/HOPG model catalysts with a variable particle size and an *in situ* XPS study of their catalytic properties in ethylene oxidation. *Kinet Catal* **52**:855–861 (2011).
- Jones TE, Rocha TCR, Knop-Gericke A, Stamofl C, Schlögl R and Piccinin S, Thermodynamic and spectroscopic properties of oxygen on silver under an oxygen atmosphere. *Phys Chem Chem Phys* **17**:9288–9312 (2015).
- van Santen RA and Kuipers HPCE, The mechanism of ethylene epoxidation. *Adv Catal* **35**:265–321 (1987).

- 9 Monnier JR, *The selective epoxidation of non-allylic olefins over supported silver catalysts*, 3rd World Congress on Oxidation Catalysis, 135–149 (1997).
- 10 Diao W, DiGiulio CD, Schaal MT, Ma S and Monnier JR, An investigation of the role of Re as a promoter in Ag-Cs-Re/ α -Al₂O₃ high-selectivity, ethylene epoxidation catalysts. *J Catal* **322**:14–23 (2015).
- 11 Salmi T, Hernández Carucci J, Roche M, Eränen K, Wärnå J and Murzin D, Microreactors as tools in kinetic investigations: ethylene oxide formation on silver catalyst. *Chem Eng Sci* **87**:306–314 (2013).
- 12 Christopher P, Xin H and Linic S, Visible-light-enhanced catalytic oxidation reactions on plasmonic silver nanostructures. *Nat Chem* **3**:467–472 (2011).
- 13 Ayame A, Uchida Y, Ono H, Miyamoto M, Sato T and Hayasaka H, Epoxidation of ethylene over silver catalysts supported on α -alumina crystal carriers. *Appl Catal A Gen* **244**:59–70 (2003).
- 14 Lafarga D, Al-Juaied MA, Bondy CM and Varma A, Ethylene epoxidation on Ag-Cs/ α -Al₂O₃ catalyst: experimental results and strategy for kinetic parameter determination. *Ind Eng Chem Res* **39**:2148–2156 (2000).
- 15 Force EL and Bell AT, The effect of dichloroethane moderation on the adsorbed species present during the oxidation of ethylene over silver. *J Catal* **44**:175–182 (1976).
- 16 Voge HH and Adams CR, Catalytic oxidation of olefins. *Adv Catal* **17**:151–221 (1967).
- 17 Rocha TCR, Hävecker M, Knop-Gericke A and Schlögl R, Promoters in heterogeneous catalysis: the role of Cl on ethylene epoxidation over Ag. *J Catal* **312**:12–16 (2014).
- 18 Yeung KL, Gavrilidis A, Varma A and Bhasin MM, Effects of 1,2-dichloroethane addition on the optimal silver catalyst distribution in pellets for epoxidation of ethylene. *J Catal* **174**:1–12 (1998).
- 19 LaFarga D and Varma A, Ethylene epoxidation in a catalytic packed-bed membrane reactor: effects of reactor configuration and 1,2-dichloroethane addition. *Chem Eng Sci* **55**:749–758 (2000).
- 20 Griffe B, Blues E and Bryce-Smith D, Study of the effect of carbon dioxide on the catalytic properties of a silver catalyst in the oxidation of ethylene to ethylene oxide. *Appl Catal* **10**:303–312 (1984).
- 21 Schouten EPS, Borman PC and Westerterp KR, Influence of reaction products on the selective oxidation of ethane. *Chem Eng Process* **35**:107–120 (1996).
- 22 Tan SA, Grant RB and Lambert RM, Secondary chemistry in the selective oxidation of ethylene: effect of Cl and Cs promoters on the adsorption, isomerization, and combustion of ethylene oxide on Ag(111). *J Catal* **106**:54–64 (1987).
- 23 Kestenbaum H, Lange de Oliveira A, Schmidt W and Schüth F, Silver-catalyzed oxidation of ethylene to ethylene oxide in a microreaction system. *Ind Eng Chem Res* **41**:710–719 (2002).
- 24 Hoflund GB and Minaham DM, Study of Cs-promoted, α -alumina-supported silver, ethylene-epoxidation catalysts. II. Effects of aging. *J Catal* **162**:48–53 (1996).
- 25 Nault LG, Bolme DW and Johansson LN, Reaction rate studies of catalytic oxidation of ethane. *Ind Eng Chem Process DD* **1**:285–292 (1962).
- 26 Czanderna AW, The effect of cyclic oxygen adsorption and reduction on a silver surface. *J Phys Chem* **70**:2120–2125 (1966).
- 27 Cavitt SB, Ethylene oxide production. US Patent 4 374 260, February 15 (1983).
- 28 Iwakura T, Imamoto T and Nakashiro K, Catalyst for production of ethylene oxide. European Patent Application EP 1 529 565 A1, September 25 (1996).
- 29 Nielsen RP and La Rochelle JH, Ethylene oxide process. US Patent 4 012 425, March 15 (1977).
- 30 Lauritzen AM, Ethylene oxide catalyst and process for the catalytic production of ethylene oxide. European Patent Specification 0 266 015 B1, December 4 (1991).
- 31 Boldyrev VV, Thermal decomposition of silver oxalate. *Thermochim Acta* **388**:63–90 (2002).
- 32 van den Reijen JE, Kanungo S, Welling TAJ, Verluis-Helder M, Nijhuis TA, de Jong KP and de Jongh PE, Preparation and particle size effects of Ag/ α -Al₂O₃ catalysts for ethylene epoxidation. *J Catal* **356**:65–74 (2017).
- 33 Monnier JR, Stavinoha JL and Hartley GW, Effects of chlorine and chlorine dynamics during silver-catalyzed epoxidation of butadiene. *J Catal* **226**:321–333 (2004).