



Research article

Influence of alkali and chloride promoters on silver catalysts in ethylene epoxidation



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ABSTRACT

Commercial ethylene epoxidation catalysts consist of Ag particles supported with α -alumina and contain a mixture of promoters. High activity catalysts typically contain Cs in combination with other alkali promoters and a gaseous organochloride. We studied a series of Ag catalysts that were individually promoted with different alkali species (Li, Na, K, Rb and Cs) at equimolar loadings of 2.5 mol% ($\text{mol}_{\text{alkali}} / (\text{mol}_{\text{alkali}} + \text{mol}_{\text{Ag}})$). O₂-TPD experiments revealed that the absorption strength of oxygen onto the silver surface was influenced by the presence of the alkali species. Ethylene epoxidation experiments were performed both in the absence and presence of the industrially vital ethyl chloride promoter. Without the chloride, the alkali-promoted catalysts were less active than the silver reference catalyst and showed a decreased primary ethylene oxide (EO) selectivity. Introducing ethyl chloride to the feed increased the primary EO selectivity of all catalysts to ca. 80% without sacrificing the activity for the alkali-promoted catalysts. Systematic EO isomerization experiments revealed that the secondary reactions of EO are inhibited by alkali promoters on the silver surface rather than on the support. Larger/less electronegative alkali species such as Rb and Cs inhibited EO degradation to a greater extent than Li and Na. However, when ethyl chloride was introduced to the feed the EO conversion of all catalysts was blocked. This study hence demonstrates how the combination of chloride and alkali promoters affects the Ag sites, specifically suppressing both undesired combustion and promoting desired ethylene epoxidation when increasing the conversion.

1. Introduction

Ethylene epoxidation is one of the largest petrochemical reactions worldwide, which is catalyzed by Ag catalysts supported with α -alumina [1,2]. The desired product, ethylene oxide, is used as chemical building block for e.g. ethylene glycol, which is used for the production of polymers [3]. Silver is the only metal that is active and selective in this reaction, as it has the optimal binding strength for oxygen and is able to let ethylene oxide desorb [4]. It is believed that two types of adsorbed oxygen reside on the silver surface: weakly bound (electrophilic) and strongly bound (nucleophilic) oxygen [5,6]. The selective oxidation to ethylene oxide is thought to occur via the electrophilic oxygen, whereas full oxidation of ethylene to CO₂ and water is catalyzed via nucleophilic oxygen. A subsequent degradation reaction takes place over the support

hydroxyl groups, which is the isomerization of ethylene oxide to acetaldehyde. Acetaldehyde quickly reacts to CO₂ and water which is reported to take place on the Ag surface. To inhibit this isomerization reaction, α -alumina is used since it displays a low amount of hydroxyl groups (<1–6 nm⁻²) [7]. EO isomerization was also found to occur on the silver surface [8].

Since CO₂ is the major side product of ethylene epoxidation (0.2–0.3 Mt per Mt EO), [3] it is crucial to control the EO selectivity. In industry, several strategies are employed. One strategy is the beforementioned use of an α -alumina carrier, which limits the secondary isomerization reaction. Another approach is to run the reaction at low conversions, typically below 7–15%, as the EO selectivity inversely depends on ethylene conversion [9]. A third strategy involves the use of solid and gaseous promoters. Gaseous organochlorides (e.g. ethyl chloride) are co-

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fed with the reactants and decompose on the silver surface into chloride species, which have been reported to block oxygen vacant sites, increase the ratio of electrophilic oxygen on the silver surface and decrease the amount of nucleophilic oxygen [10]. For silver-only or alkali promoted silver catalysts, this results in an increase in selectivity, while simultaneously the total activity is decreased [9].

Besides gaseous promoters, a combination of solid promoters is used to increase the performance of silver catalysts [11]. Industrial catalysts coined as 'High Activity' typically contain alkali promoters, which from a historical perspective were discovered when sub-micrometer Ag particles had been successfully deposited using a potassium salt during their synthesis [9,12]. Despite this discovery, the most commonly studied alkali promoter for ethylene epoxidation is Cs [13–19]. The promotional effect of Cs has had multiple explanations over time. It has been reported that Cs limits the secondary reaction of EO, either by blocking α -alumina surface groups [16,20] or isomerization and combustion sites on the Ag surface [21,22]. Another study reported that Cs was bound to stepped Ag sites and blocked the adsorption of oxygen [19]. DFT studies found that alkali ions induced electric fields on a Ag(111) surface, which stabilized the transition state for EO due to its favorable dipole orientation compared to the transition state for acetaldehyde [17,23]. DFT studies including the industrially relevant chloride promoter found that CsCl_xO_y complexes coexisted on a $\text{Ag}_2\text{O}(111)$ surface, limiting the formation of oxygen vacancies [24], but to our knowledge experimental studies disentangling Cs and Cl promotional effects are limited. In addition, studies combining Re, Cs, and Cl promoters complicate the understanding of the alkali promotional mechanism even further [25–27].

In this study, we systematically investigated the individual effect of all available alkali (Li, Na, K, Rb, and Cs) on the performance of Ag catalysts in the ethylene epoxidation reaction in the absence and presence of the industrially relevant ethyl chloride. O_2 -TPD revealed that the strength of weakly and strongly adsorbed oxygen was affected by the alkali promoters with increasing electropositivity. In absence of the chloride, Rb and Cs are the least active compared to Li and Na. Intriguingly, the activity for Rb and Cs did not change in the presence of the chloride, whereas it drastically decreased for Li and Na. Furthermore, we studied the EO isomerization and combustion reaction without and with the chloride and show the remarkable interplay between the chloride and alkali promoters, which is important to consider when investigating the effect of multiple promoters.

2. Materials and methods

2.1. Synthesis of (alkali-promoted) Ag catalysts

Alkali-promoted silver catalysts supported on α -alumina were synthesized via sequential impregnation. First, silver deposition was performed following an earlier reported procedure [28], after which the alkali promoters were introduced. Prior to the first impregnation, 8 $\text{m}^2 \text{ g}^{-1}$ α -alumina extrudates (BASF, Al-4196, pore volume of 0.45 mL g^{-1}) were crushed and sieved to a fraction < 212 μm .

Silver oxalate was used as Ag precursor, which was synthesized by adding an aqueous silver nitrate ($\geq 99.0\%$, Sigma-Aldrich) solution to an aqueous solution of oxalic acid ($\geq 99.0\%$, Sigma-Aldrich) in a 2:1 mol ratio. Silver oxalate precipitated immediately and was washed three times in MilliQ® water and once in ethanol, after which it was dried in air at room temperature. Please note that silver oxalate is shock-sensitive, and should therefore be handled with great care. For the deposition of Ag, the crushed and sieved α -alumina powder was dried in vacuum at 200 °C for 2 h. Silver oxalate was dissolved in a MilliQ® water/ethylene diamine (99%, Sigma-Aldrich) solution (4:1 mol ratio). The dried α -alumina powder was impregnated up to 90% of its pore volume with the $\text{Ag}_2\text{C}_2\text{O}_4$ /MilliQ® water/ethylene diamine solution, aiming for a Ag loading of 15 wt%. The impregnated material was then dried in vacuum at room temperature for 20 h, under constant stirring to promote a homogeneous distribution. The dried samples were

transferred to a U-shaped borosilicate reactor and calcined for 2 h at 215 °C (with a 5 °C min⁻¹ ramp) in 50 vol% H₂ in N₂ (GHSV of 7000 h⁻¹).

Alkali deposition was performed with solutions of LiNO₃ (>99.99%, Sigma-Aldrich), NaNO₃ (>99%, Alfa Aesar ACS), KNO₃ ($\geq 99.0\%$, Sigma-Aldrich), RbNO₃ (99.8%, ABCR GmbH), and CsNO₃ (99.99%, Sigma-Aldrich) dissolved in MilliQ® water. The Ag/ α -Al₂O₃ catalyst was dried in vacuum for 2 h at room temperature. The impregnation was performed with 0.09 M alkali nitrate solutions, aiming for alkali loadings of 2.5 mol % compared to Ag which is below the theoretical maximum occupancy of support surface groups (Supplementary Information Section A). The impregnated catalysts were dried in vacuum for 20 h at room temperature, under constant stirring. To decompose the alkali nitrate, the samples were heated in a U-shaped borosilicate reactor for 10 min at 550 °C (with a 5 °C min⁻¹ ramp) in N₂ (GHSV of 7 000 h⁻¹). In addition to alkali-promoted Ag catalysts, crushed α -alumina powder was impregnated with 0.09 M LiNO₃ and CsNO₃ (0.45 mL $\text{g}_{\text{alumina}}^{-1}$) after which similar drying and decomposition steps were performed.

2.2. Catalyst characterization

Scanning electron microscopy (SEM) was performed to determine the average Ag particle size of the catalysts. A FEI Helios G3 UC microscope was operated at 5 kV and 0.40nA in immersion mode. Samples were attached to the SEM holder using double-sided carbon stickers (Electron Microscopy Sciences). A 7.5 nm PdPt layer was sputtered onto the powder to create a conductive layer. For each sample, at least 250 Ag particles were measured using ImageJ software. The surface averaged particle diameters ($d_{p,s}$) were calculated using Equation (1), with n the number of Ag particles and d_i the diameter of the i^{th} particle.

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

The BET surface area of pure α -alumina and of a Ag catalyst was determined with N₂-physisorption on a Micromeritics TriStar 3000 instrument, by fitting the experimental data between 0.02 and 0.25p/p₀. Prior to the measurement, the materials were dried overnight in vacuum at 200 °C. N₂-isotherms are shown in Section B of the Supplementary Information.

The strength of adsorbed oxygen was determined with temperature programmed desorption of oxygen (O₂-TPD) based on a procedure described elsewhere [29], using a Micromeritics AutoChem II instrument. For each measurement, 150 mg sample was loaded between two layers of quartz wool in a U-shaped quartz reactor. First, the sample was dried in He for 1 h at 120 °C with a heating ramp of 10 °C min⁻¹. The temperature was decreased to room temperature, after which O₂ adsorption was performed while heating the sample to 215 °C (with a heating ramp of 20 °C min⁻¹), and an equilibration time of 3 h. The temperature was decreased to 50 °C and after a stable baseline was obtained for 2 h, the O₂ desorption was monitored while heating the sample to 550 °C (with a heating ramp of 10 °C min⁻¹) in 25 mL min⁻¹ He.

Inductively coupled plasma (ICP) spectroscopy was performed at Mikrolab Kolbe (typically ca. 10 mg of sample was sent) to determine the Ag and alkali loadings within the catalysts.

2.3. Ethylene epoxidation and ethylene oxide isomerization

Prior to testing, the catalysts were sieved to a 90–150 μm sieve fraction. For each experiment, 100 mg of catalyst was diluted with 500 mg of SiC (212–425 μm), which had been washed in HNO₃ (65 %, AnalaR Normapur®, 10 mL g^{-1}) and calcined at 800 °C to remove (in) organic impurities. The SiC-diluted catalyst was loaded in a quartz reactor, with a 4 mm internal diameter, between two layers of quartz wool. The experiments were performed at 1 bar, with 7.5 vol% ethylene,

7.5 vol% oxygen, and Ethyl Chloride (EC) concentrations ranging from 0-1 ppm in balance helium, with a total gas flow of 66 mL min⁻¹. Tests without EC were performed at 215 °C for 25 h, after which the temperature was decreased to 175 °C with steps of 10 °C, and monitoring the reaction for 10 h per set temperature. Tests with 0.5 to 1 ppm EC were performed at 215 °C, allowing the catalysts to stabilize at each EC concentration for 25 h. With 1 ppm EC in the feed, the reaction temperature was varied with steps of 10 °C with 10 h per set temperature. Depending on the conversion at 215 °C the temperature was either decreased to 175 °C or increased to 255 °C to compare the catalysts at similar conversions. Reaction products were monitored with an online Interscience Compact GC, equipped with a Porabond Q column and a Molsieve 5Å column. At room temperature, the reactant concentrations in the feed were evaluated to guarantee the feed composition.

Ethylene conversion and ethylene oxide selectivity were calculated using Eqs. (2) and (3), respectively. Average conversions and selectivities were calculated after the catalysts were stabilized at each EC concentration for ca. 20 h. The carbon mass balance was calculated using Eq. (4), and was 100 ± 3% for each datapoint.

$$\text{Conversion}_{\text{ethylene}} = \frac{P_{\text{ethylene}_0} - P_{\text{ethylene}_{\text{out}}}}{P_{\text{ethylene}_0}} \times 100\% \quad (2)$$

$$\text{Selectivity}_{\text{ethylene oxide}} = \frac{P_{\text{ethylene oxide}}}{P_{\text{ethylene oxide}} + 0.5 \times P_{\text{CO}_2} + P_{\text{acetaldehyde}}} \times 100\% \quad (3)$$

$$\text{Carbon mass balance} = \frac{P_{\text{ethylene}_{\text{out}}} + P_{\text{ethylene oxide}} + 0.5 \times P_{\text{CO}_2} + P_{\text{acetaldehyde}}}{P_{\text{ethylene}_0}} \times 100\% \quad (4)$$

Ethylene oxide isomerization experiments were conducted prior to catalysis in absence of EC, and after catalysis when 1 ppm EC was co-fed. Isomerization experiments were performed at 215 °C with 0.15 vol% ethylene oxide, 0.075 vol% acetaldehyde (Linde HiQ), and 7.5 vol% oxygen in balance helium, with a total gas flow of 33 mL min⁻¹. Ethylene oxide conversion was calculated using Equation (5).

$$\text{Conversion}_{\text{ethylene oxide}} = \frac{P_{\text{ethylene oxide}_0} - P_{\text{ethylene oxide}_{\text{out}}}}{P_{\text{ethylene oxide}_0}} \times 100\% \quad (5)$$

The apparent activation energy (E_a) and pre-exponential factor (C) were calculated according to the Arrhenius equation (Eq. (6)), assuming first order kinetics, with X being either the amount of converted ethylene, formed ethylene oxide or CO₂. Arrhenius plots were based on the average of at least 5 GC datapoints at the same temperature, at temperatures ranging from 175–255 °C, including only data for which the ethylene conversion was below 25%. ln k was plotted as a function of 1000/T, and the corresponding slopes were multiplied with R (8.314 J K⁻¹ mol⁻¹) to obtain the apparent E_a . C was calculated from the intercept at 0 K.

$$\ln(k [mol_X \times g_{\text{catalyst}}^{-1} \times s^{-1}]) = -\frac{E_a}{RT} + \ln(C) \quad (6)$$

Calculations on possible heat and mass transfer limitations are shown in Section C of the [Supplementary Information](#), and it should be noted that no transfer limitations should be expected in our systems.

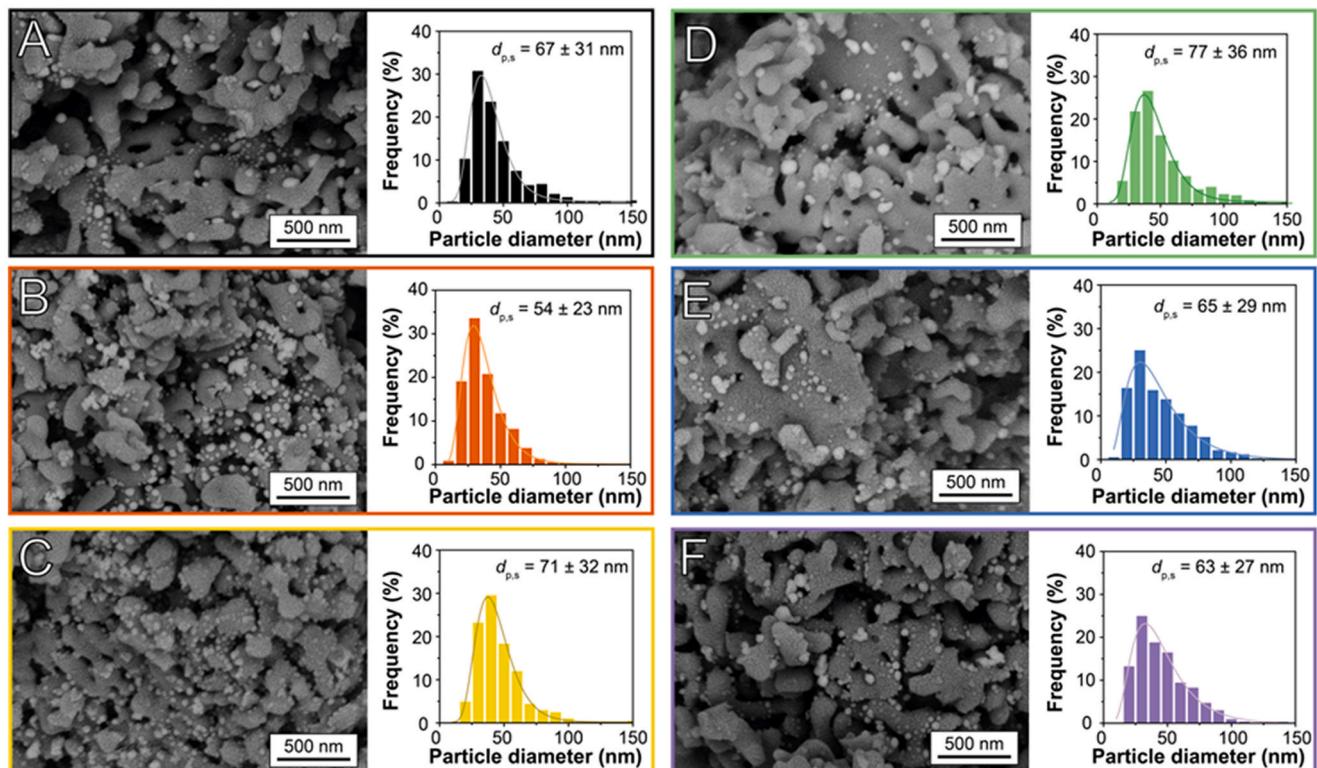


Fig. 1. SEM images of the Ag-550 catalyst (A), Li-Ag (B), Na-Ag (C), K-Ag (D), Rb-Ag (E) and Cs-Ag (F), together with corresponding histograms and the surface averaged particle diameters. For each sample more than 250 Ag particles were measured.

3. Results and discussion

3.1. Catalyst structure

The alkali promoters were introduced to a 15 wt% silver on α -alumina catalyst via sequential impregnation, which was followed by calcination at 550 °C. As a reference, a bare silver on α -alumina catalyst was also heated at 550 °C (Ag-550). Fig. 1 shows SEM images of the Ag-550 catalyst and the alkali-promoted catalysts, in which the Ag particles are visible as bright grey spheres. The corresponding particle diameter distributions illustrate that the Ag particles of all catalysts are in a similar size range (50–70 nm). Since the Ag loadings are also similar for all catalysts (Table 1), differences in catalytic activity can be ascribed to the presence of promoters and not to particle size effects or differences in Ag: Al₂O₃ surface ratios [30]. The promoter loadings determined with ICP are in line with the theoretical loading, except for the Na-Ag catalyst. One possible reason for this is the omnipresence of Na, due to the production process of alumina [31]. Trace amounts of Na and K were found in the α -alumina with ICP (0.06 and 0.05 wt%, respectively). It was assumed that the local alkali surface coverages were similar for all catalysts.

3.2. Effect of alkali species on oxygen binding strength

One of the reported effects of Cs (and alkali) promotion is that the dissociation of oxygen is facilitated [15,23]. Another study reported that Cs blocks binding sites for strongly adsorbed oxygen, which limits the full oxidation reaction [19]. In any case, the strength of the Ag-O bond plays an important role, and hence the effect of alkali promoters on the Ag-O bond strength was probed with O₂-TPD (Fig. 2). After a heat treatment at 550 °C, the reference silver catalyst (Ag-550) shows two O₂ desorption peaks at ca. 230 °C and 320 °C, which is in line with literature and can be associated with weakly and strongly adsorbed oxygen species desorbing from the silver surface, respectively [19,32]. Additional TPD profiles of Ag-215 and α -Al₂O₃ are shown in Figs. S2 and S3 shows profiles of used catalysts. When alkali promoters are present, the weakly adsorbed oxygen peaks shift to slightly lower temperatures and thus the oxygen becomes even more weakly bound. In contrast, the strongly adsorbed oxygen peaks shift to higher temperatures, as illustrated in Fig. 2B. Potentially, some errors might have been induced, for example during the sample preparation or slight differences in temperature of the pre-treatments. Nevertheless, it is clear that the adsorption strength of oxygen onto the silver surface is influenced by the presence of alkali species, with Rb and Cs showing the most pronounced effect.

3.3. Effect of alkali and chloride promoters on activity

The silver catalysts were tested in the ethylene epoxidation reaction.

Table 1

Overview of the (alkali-promoted) Ag catalysts. Ag surface averaged particle diameters ($d_{p,s}$) were determined with SEM. Ag and alkali loadings are listed. The silver on α -alumina catalysts are listed as Ag-[temperature of final heat treatment (°C)] and promoted catalysts are labelled as [alkali]-Ag.

Catalyst	Ag particle diameter $d_{p,s}$ (nm)	Ag loading ^a (wt %)	Promoter loading ^b (mol%)	
			Theoretical	ICP
Ag-215	51 ± 21	13.6	—	—
Ag-550	67 ± 31	13.5	—	—
Li-Ag	54 ± 23	12.5	2.68	2.66
Na-Ag	71 ± 32	13.4	2.44	6.84
K-Ag	77 ± 36	13.2	2.28	2.24
Rb-Ag	65 ± 29	13.6	2.44	1.73
Cs-Ag	63 ± 27	13.6	2.51	2.00

^a Of total catalyst weight.

^b Compared to the Ag loading (mol_{alkali}/(mol_{Ag} + mol_{alkali})).

In industry, a gaseous organochloride promoter is co-fed to increase the selectivity towards ethylene oxide by decreasing the fraction of nucleophilic (strongly bound) oxygen [10]. The effects of Cs and Cl have been reported to some extent in literature [14,21,26,27]. However, it is not clearly understood how the other alkali species behave in absence and presence of a chloride promoter in comparison to the commonly used Cs promoter. A recent treatise on promoted silver catalysts revealed that the optimal chloride and cesium concentrations vary depending on the promoter composition [9]. Therefore, the effect of ethyl chloride (EC) concentration on catalytic performance in the presence of different alkali promoters was investigated (Fig. 3).

Without EC the oxygen conversions vary greatly (Fig. 3A), with the Ag and Li-Ag catalyst showing the highest conversions of 95%, while Rb-Ag and Cs-Ag have a 20% conversion. Interestingly, this can be correlated to the O₂-TPD results, where the strongly adsorbed oxygen shifted to higher temperatures for Rb-Ag and Cs-Ag (Fig. 2). Having too strongly bound oxygen can result in a lower conversion, as it becomes more difficult to desorb. Increasing the EC concentration to 1 ppm drastically decreases the O₂ conversion for the Li-Ag and Ag catalysts, with almost two orders of magnitude. Catalysts promoted with heavier alkali species show a much milder response to ethyl chloride.

The trend in ethylene conversion (Fig. 3B) is similar to the oxygen conversion trend. It is fascinating that the effect of ethyl chloride on the catalyst activity is tempered by Rb and Cs, which might be an indication of the neutralization of the chloride by the alkali species. All alkali chlorides are thermodynamically stable under reaction conditions (Fig. S4). The surface averaged particle diameters after catalysis without and with EC in the feed have generally increased to 70–100 nm for all catalysts (Fig. S9), which implies that the activity differences observed were due to the presence of different promoters and not due to differences in active silver surface area. Chloride is known to competitively adsorb on sites that are active for ethylene epoxidation [33,34], which explains the decrease in the total activity upon increasing the chloride concentration.

To understand the effect of alkali promoters on the apparent activation energy, ethylene epoxidation was studied as a function of temperature in either the absence or the presence of Ethyl Chloride (EC) (Fig. S5). In absence of EC, the Rb-Ag and Cs-Ag catalysts are significantly less active than the Ag and Ag-Li catalysts over the full temperature range of 150–220 °C (Fig. S5A). The apparent activation energy (E_a) for ethylene conversion slightly decreases from 65 to 58 kJ mol⁻¹ when adding Cs to the Ag (Fig. S7, Table S6). Simultaneously, the pre-exponential factor decreases from 1.6×10^5 to 6.6×10^3 mol g_{cat}⁻¹ s⁻¹ when adding Cs (Table S6), and hence the decrease in activity could be explained by a decrease in active sites. It should be noted that the calculation of the apparent activation energies were simplified, while for example orders in oxygen have been reported to be -0.5 to 1.5 for selective oxidation and -1 to 1 for full combustion [7], and have been reported to change as a function of temperature [35].

The activity trend of the alkali-promoted catalysts with 1 ppm EC is inverted compared to the tests without EC (Fig. S5B). For an ethylene conversion of ca. 2.5%, the required reaction temperature decreased from 245 °C for Ag to 175 °C for Rb-Ag and Cs-Ag, which highlights the massive impact of EC on the activity of these promoted catalysts. As demonstrated with O₂-TPD, both strongly and weakly adsorbed oxygen species are amplified by the alkali promoters. Chloride is known to decrease or inhibit the fraction of nucleophilic (strongly bound) oxygen [10]. When ethyl chloride inhibits the more strongly bound oxygen, the effect of the more weakly bound oxygen is more pronounced. This might be the reason why the larger and less electronegative alkali species show an increased conversion.

3.4. Effect of alkali and chloride promoters on product formation

Since the Ethylene Oxide (EO) selectivity inversely depends on ethylene conversion [7], it is important to evaluate catalyst selectivity at

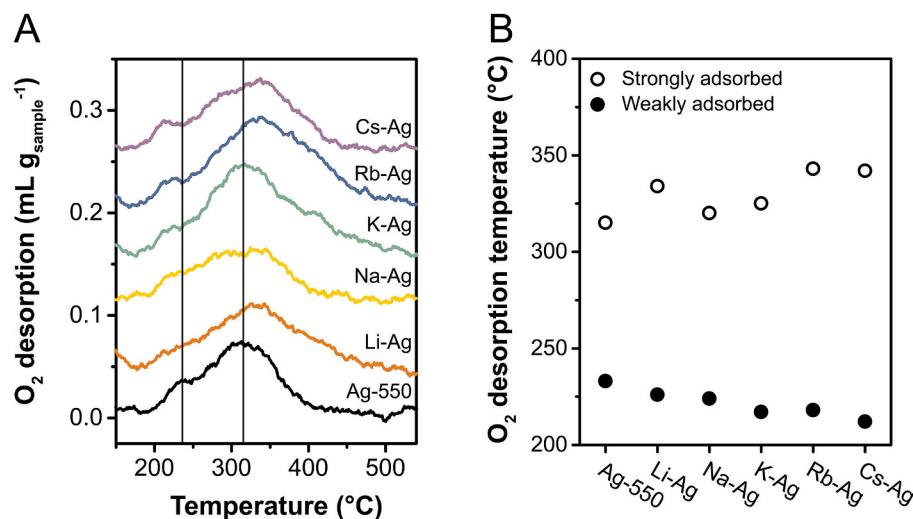


Fig. 2. O₂-TPD profiles of unpromoted and alkali-promoted Ag catalysts (A), and the desorption temperatures of the weakly and strongly adsorbed oxygen of the catalysts (B). The profiles in A have been background corrected with the signal from the α -alumina carrier.

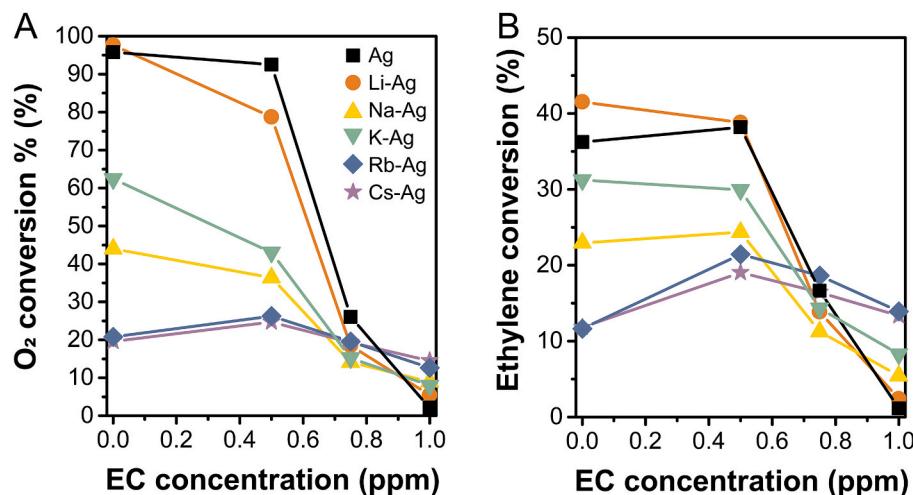


Fig. 3. Effect of Ethyl Chloride (EC) on oxygen conversion (A) and ethylene conversion (B) for the promoted and unpromoted catalysts at 215 °C in 7.5 vol% C₂H₄, 7.5 vol% O₂ and 0–1 ppm EC in He, with a total gas flow of 66 mL min⁻¹. The Ag-550 catalyst was used as Ag reference.

similar conversions or as a function of conversion, as shown in Fig. 4. It is evident that the combination of alkali and ethyl chloride promoters offers excellent selectivity enhancing effects. The (extrapolated) selectivity at 0% conversion is the primary EO selectivity on the active Ag sites. Notably, the Ag catalyst displays a similar primary selectivity both in the presence and absence of EC, highlighting that the activity-decreasing effect of the chloride causes this increase in selectivity.

In addition, the slope of the Ag catalyst is steeper than those of the alkali-promoted catalysts, which relates to the undesired isomerization and subsequent combustion of EO: a steeper slope indicates a higher degree of isomerization and subsequent combustion [7]. The corresponding values of the slopes are listed in Table S5. When adding larger/more electropositive alkali species to the silver, the slopes become less negative which suggests that there is a direct relation between the slope and the sites responsible for EO isomerization and/or (direct) combustion which are inhibited by the alkali promoters (*vide infra*). The pre-exponential factors of EO formation in absence of EC scale with both the electronegativity of the alkali species as well as the alkali cation radii (Fig. S6C–D), which makes it difficult to disentangle electronic from geometric (blocking) effects.

Without EC, the alkali promoted catalysts show a primary EO

selectivity of ca. 50%, while the Ag catalyst surpasses this. In absence of a chloride, alkali-promoted silver catalysts have been reported to be less selective than pure silver catalysts [9], which could be explained by the adsorbed oxygen becoming too nucleophilic due to the electron-donating behavior of alkali species [36]. With 1 ppm EC in the feed, the primary selectivity of all alkali-promoted catalysts increased to an astonishing 80%, which more likely seems to be caused by the chloride rather than by the alkali promoters. Interestingly, the slopes of the chloride- and alkali-promoted catalysts still show a similar trend as the experiments without chloride (Table S5). As a consequence, when Cs and Rb are added to the Ag it is possible to achieve a high selectivity (~80%) without sacrificing the conversion (~15%). The EO selectivity decreases with increasing ethylene conversion due to secondary reactions of EO [7], hence a lower slope of this dependence is favorable. The selectivity vs. conversion dependence can also be studied by varying the space velocity rather than temperature, to decouple the primary selectivity from the secondary reactions of EO [7]. Besides stabilizing the reaction intermediate, the other suggested mechanism of alkali promotion is the passivation of active support surface groups which limits the rate of EO isomerization [16,20,37] and consequently enables higher selectivities at higher conversions. However, whether alkali

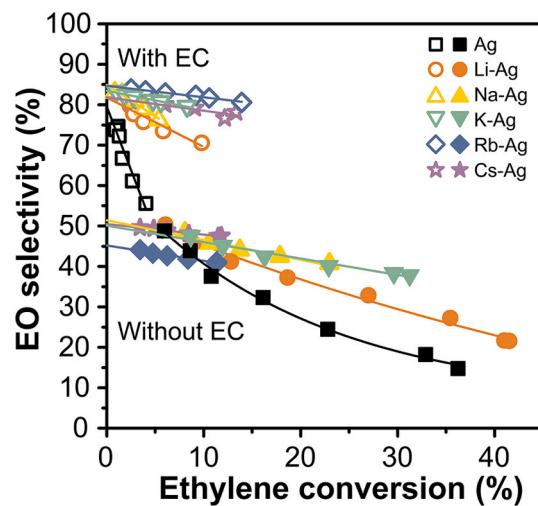


Fig. 4. EO selectivity versus ethylene conversion while varying the temperature without EC (closed symbols) and with EC (open symbols). The 15 wt% Ag on $\alpha\text{-Al}_2\text{O}_3$ (Ag-550) catalyst was used as Ag reference.

species influence the slope by passivating support surface groups or also by passivating direct combustion sites on the silver surface cannot be concluded from these ethylene epoxidation experiments only.

3.5. EO isomerization and combustion

To systematically study whether alkali promoters inhibit EO isomerization and combustion on the support surface groups or on the silver surface, dedicated EO conversion experiments were conducted with the (promoted) support and catalysts (Fig. 5). The $\alpha\text{-Al}_2\text{O}_3$ support was tested as a reference (Fig. 5A) to disentangle the promotional effect of the alkali by either blocking support surface groups, or inhibiting EO combustion on the Ag surface. The EO conversion on $\alpha\text{-Al}_2\text{O}_3$ is ca. 10% and increases to ca. 15% when oxygen is added to the feed. Adding Li or Cs to the support slightly decreases the EO conversion when oxygen is present, which is in line with previous literature [38]. It is possible that for supports containing impurities such as $\gamma\text{-Al}_2\text{O}_3$ or SiO_2 , which have a higher density of surface groups, [7] the blocking effect of alkali promoters is more pronounced compared to a pure $\alpha\text{-Al}_2\text{O}_3$ support. Nonetheless, in case of our $\alpha\text{-Al}_2\text{O}_3$ support, alkali promoters only have a limited effect of blocking the support surface groups.

To study whether the secondary reactions of EO are inhibited by alkali promoters on the silver surface rather than on the support, promoted Ag catalysts were investigated. Flowing EO resulted in a similar EO conversion as the $\alpha\text{-Al}_2\text{O}_3$ (Fig. 5B), suggesting that EO isomerization is not affected by the introduction of active silver surface. However, when oxygen is added to the gas feed there are vast differences in EO conversion. The Ag catalyst shows an EO conversion of 70%, suggesting that EO degradation is more dominant of the Ag surface than on the α -alumina support. When larger/less electronegative alkali species are present the EO conversion gradually decreases to 15%. This is interesting, since the molar ratio between Ag and the alkali is similar for all catalysts (except for Na-Ag). These EO conversions scale with both the alkali electronegativity and cation radius (Fig. S6E-F), hence it is difficult to differentiate between geometric and electronic effects. Interesting in this respect would be to study alkali and alkaline earth promoters with a similar electronegativity but with different cation radii (for instance, Ca and Li both have a Pauling electronegativity of 1.0 [39]). In earlier studies, EO degradation was reported to predominantly occur via support surface groups, and that the promoting effect of alkali species is the result of the passivation of these surface groups [16,20,37]. In contrast, we show that the alkali species strongly inhibit EO combustion on the silver surface rather than EO isomerization on the α -alumina surface groups.

After catalysis with the industrially relevant Ethyl Chloride (EC) in the feed, the EO conversion of the Ag, Li-Ag, Na-Ag and K-Ag catalysts decreased to ca. 10–20%. Considering the Ag reference catalyst, this suggests that the Ag sites responsible EO combustion are passivated by the chloride. When Li, Na, and K are present, it seems that the remaining combustion sites were passivated by the chloride. For the Rb-Ag and Cs-Ag catalysts the chloride did not further inhibit the EO isomerization behavior, but remained 15%. During ethylene epoxidation at 215 °C with EC, the EO selectivities for all catalysts are roughly similar (75–80%) despite varying ethylene conversions. It can be concluded from these experiments that both alkali and chloride promoters inhibit the secondary reaction of EO on the silver surface and do not counteract each other, in contrast to rhenium-chloride promoted silver catalysts [40].

4. Conclusions

Silver catalysts were promoted with a range of alkali species, besides the commonly studied Cs. All alkali species influenced the silver–oxygen binding strength. The catalysts were tested without and with the

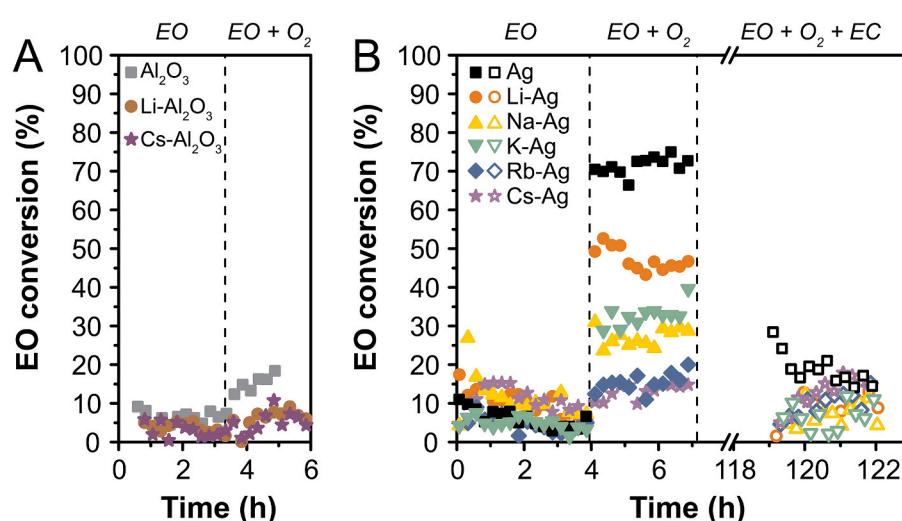


Fig. 5. EO isomerization of the bare and promoted α -alumina support (A), and of the (promoted) silver catalysts (B) at 215 °C with 0.15 vol% EO, 0.075 vol% acetaldehyde, and when indicated with 7.5 vol% O₂ and 1 ppm EC in He.

industrially relevant ethyl chloride promoter in the feed. Without the chloride, the activity and primary selectivity of alkali-promoted catalysts decreased compared to the silver reference catalyst. In contrast, chloride increased the primary selectivity of all catalysts, while the selectivity of the alkali-promoted catalysts remained higher than the reference silver catalyst at much higher activities, highlighting the impact of both promoters. We also show for the first time that both alkali and chloride species predominantly inhibit EO combustion on the silver surface rather than on the α -alumina surface groups.

CRediT authorship contribution statement

Claudia J. Keijzer: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Naud M.T. van de Ven:** Writing – review & editing, Validation, Investigation. **Remco Dalebout:** Writing – review & editing, Supervision. **Tracy L. Lohr:** Writing – review & editing, Supervision. **John R. Lockemeyer:** Supervision. **Peter van den Brink:** Supervision. **Petra E. de Jongh:** Writing – review & editing, Supervision, Resources, Project administration, 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2025.116206>.

Data availability

Data will be made available on request.

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