Promoters in heterogeneous catalysis: the role of Cl on ethylene epoxidation over Ag

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ABSTRACT: Promoters are ubiquitous in heterogeneous catalysis. The great majority of catalysts developed for commercial use are modified by promoters to enhance the yield of the desired product. Here, we report an investigation of the promotion effect using near ambient pressure X-ray photoelectron spectroscopy, whereby we directly observe a promoter modifying the active sites of a working catalyst. For a silver catalyst under ethylene epoxidation, the increase in selectivity obtained by chlorine promotion is related to modifications in the balance between electrophilic and nucleophilic oxygen species, which constitute the catalyst active sites for the selective and unselective oxidation pathways.

Introduction

Heterogeneous catalysis is an important part of the chemical technology that is responsible for the production of the materials and fuels that drive modern society. Shortly after the discovery of the first catalytic processes, it was realized that catalyst performance can be enhanced by adding very small concentrations of additional elements; known as promoters. In fact, the economic viability of most large-scale contemporary chemical processes relies on such promoters. For instance, the Fe-based catalysts used for ammonia synthesis would never be practical without the addition of potassium[1]. Empirical evidence of promotion in catalytic reactions is abundant in the literature; however, detailed mechanistic information is rarely available because of experimental limitations in determining the electronic and structural modifications that occur on the catalyst[2,3].

In the present work, we study the promotion effect of chlorine on silver catalysts in the ethylene epoxidation. This selective oxidation reaction is very attractive due to the economic importance of ethylene oxide (EO) as a versatile chemical intermediate (EO is the 14th world's most produced organic chemical). The addition of chlorinated hydrocarbons to the reaction feed is a standard industrial practice to promote the selectivity to the epoxide [4]. However, the chemical foundations of this technological procedure are still not comprehensively understood, which limits the further development of improved catalysts. To shed new light into this question, we use a state-of-the-art *in situ* surface characterization technique to correlate the modifications at the silver catalyst surface induced by chlorine promotion with the catalytic performance measured at the same time.

Materials and methods

The catalyst was a commercial Ag nanopowder with 99.5 % nominal purity, grain size < 100 nm and 5.0 m^2/g surface area (nominal values) from Sigma-Aldrich. The Ag powder was pressed as pellets consisting of 8 mm diameter, 50 mg and approximately 0.04 mm thickness that were mounted in a sapphire sample holder. *In situ* XPS characterization of the Ag catalyst under ethylene epoxidation was performed using the near ambient pressure endstation of the ISISS beamline at the synchrotron radiation facility BESSY II of the Helmholtz Zentrum Berlin. Details about the system can be found elsewhere[5]. The Ag pellet surface was positioned 1.3 mm away from the first aperture of the differentially pumped electrostatic lens stage of the spectrometer to keep a reasonable electron acceptance with a pressure drop smaller than 5 % on the catalyst surface[6]. Ethylene 3.5 and oxygen 6.0 were provided by Westfallen. 1 % Ethyl chloride diluted in helium was provided by Linde. All gases were introduced to the reaction chamber by calibrated mass flow controllers. We used an oxygen rich feed composition (C_2H_4:O_2 = 1:2) at a total flow of 4 ml/min. The reaction chamber pressure was kept constant to 0.3 mbar by regulating the outlet flow using a pressure controlling valve. The catalyst was heated from the backside by an infrared laser that was primarily absorbed by a steel plate in contact with the catalyst pellet. The sample temperature was measured by a K-type thermocouple pressed against the pellet surface and controlled by adjusting the laser power using a PID feedback loop. The feed consumption and reaction products were monitored online by a Prisma quadrupole mass spectrometer (QMS) from Balzers and a Proton Transfer Reaction MS (PTRMS) from IONICON Analytik. Quantification of product concentration and selectivity were done using a calibrated Gas Chromatograph (Varian MicroGC CP4900).

Appropriate photon energies were selected in order to measure core-level spectra for all the elements with photoelectrons with the same kinetic energy (250 eV), which provides a probing depth of 6 Å, approximated by the inelastic mean free path. The binding energy scale for all spectra was calibrated with respect to the Fermi edge. The spectra shown in the figures are intensity offset for clarity. Elemental atomic concentrations were obtained by dividing the integrated areas by the incident photon flux and the atomic photoionization cross sections calculated by Yeh and Lindau for the appropriate energies. Error bars were based on uncertainties in the areas of fitted components estimated by the integration software (CasaXPS) using a Monte Carlo algorithm. No visible effect of beam damage was present as evidenced by the comparison of spectra at different spots on the same sample.

Results and discussion

The silver powder catalyst was held at 230 °C while flowing C_2H_4 and O_2 (in a ratio of 1:2) over the catalyst surface, with the total pressure of the reaction chamber kept at 0.3 mbar, thus providing differential reaction conditions. The concentration of reactants (C_2H_4 and O_2) and products (EO and CO_2) was simultaneously measured using online mass spectrometry (MS) and gas chromatography (GC). Acetaldehyde was absent from the product stream. The initial C_2H_4 conversion was around 1 % but slowly decreased with time following the decrease of EO and CO_2 production (Fig. 1-a). The selectivity to the epoxide increase as the reaction proceed, but eventually levels off, tending to a saturation value of around 10 % (green dots in Fig. 1-a), as suggested by an extrapolation to longer TOS. See the supplementary material in appendix A for additional MS data, calibration and reproducibility tests.

Kommentar [AK1]: May be we should be more careful: "Acetaldehyde concentration in the product stream was below the detection limit of the used gas analytics".

The catalyst surface composition was monitored *in situ* during the reaction by near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). Besides silver (~ 80 %at), the main element on the catalyst surface is oxygen (12-18 %at) with minor amounts of silicon (1 %at) and sulfur (1-2 %at) impurities, within 2-3 layers . Both are typical contaminants of silver materials that are discussed in our previous work about the Ag-O system [7]. More importantly, no trace of carbon was detected on the silver catalyst surface under reaction conditions, indicating that carbon reaction intermediates are short lived in the mbar pressure range with a steady state concentration below the XPS detection limit. Considering that all oxygen ~~are~~ atoms are located at the surface, the coverage is estimated as 0.39-0.63 ML (5.4-8.6 10^{14} atom/cm^2), using the Ag(111) structure and known photoelectron inelastic mean free paths. See supplementary material appendix A for details about the coverage estimation and further discussion about contaminants. The coverage of 5.4 10^{14} atom/cm2 at the initial stages of the reaction is consistent with the Ag surface mostly covered by oxygen reconstructions. The Ag(111)-p(4x4) reconstruction has 0.375 ML giving 5.2 10^{14} atom/cm^2while the Ag(110)-c(6x2) has 0.67 ML and 5.7 10^{14} atom/cm^2. However, as the reaction proceed, the coverage increase reaching 8.6 at/cm^2. The increase in the oxygen coverage observed in situ is consistent with recent works of S. Günther et all that successfully prepared oxygen covered Ag(111) surfaces active for ethylene epoxidation at UHV conditions with 0.38 up to 0.60 ML oxygen coverage depending on the N_2O dose [8].

The identification and characterization of the surface oxygen species involved in selective oxidation reactions are highly pursued in heterogeneous catalysis, since they provide essential information for the development of kinetic models and reaction mechanisms [9–12]. In one of the proposed mechanisms for ethylene epoxidation [9,10,13], the selective and unselective reaction pathways are related to different forms of oxygen present on the catalyst surface. Oxygen atoms with higher partial charge are responsible for C-H bond cleavage – which is the first step to total oxidation – while less-charged oxygen atoms interact preferentially with ethylene's π-bond forming the epoxide ring [10,14]. These distinct oxygen species are known in the literature as strongly bound or nucleophilic oxygen (*Onucl*) and weakly bound or electrophilic oxygen (*Oelec*), respectively. Two oxygen species with distinct electronic properties have also been identified by ab initio theoretical studies [15,16] . Different forms of oxygen were also observed in alumina supported Ag catalyst by temperature programed desorption/reaction experiments [17]. Within these mechanisms, trends in selectivity are explained in terms of changes in the distribution of oxygen species on the catalyst surface. The challenging task of characterizing different oxygen species on the silver surface can be tackled by the analysis of O1s XPS spectra, since changes in the bonding characteristics of oxygen atoms result in shifts in their core-level binding energies (BE).

Figure 1-b shows representative O1s spectra measured *in situ* at different times during the epoxidation reaction. The O1s lineshape contains two main features at BE below and above 530 eV. In the beginning of the reaction, the low-BE feature is the most intense; while after 14 h the high-BE feature dominates the spectrum. The decrease of intensity for the low-BE feature and the increase of intensity for high-BE feature qualitatively follows the trend in selectivity, but proper quantification is necessary for a better assessment. The O1s quantitative analysis consisted of fitting the spectral line shapes with a set of Gaussian components, classifying the fitted components as *Onucl* or *Oelec* based on their electronic properties and reactivity [7,18], and further grouping these two classes into a single parameter as the oxygen species ratio (*Oelec/Onucl*). This procedure is discussed in more detail in the supplementary material in appendix A. The resulting oxygen species ratio *Oelec/Onucl* (Fig. 1c) and the selectivity (Fig. 1a) evolve very similarly with time, suggesting a direct correlation, in agreement with the predictions of the reaction mechanism. Consequently, the parameter *Oelec/Onucl* is henceforth regarded as a spectroscopic surface descriptor or a marker of the active sites. It is worth mentioning that the direct correlation of individual O species with the product concentration at different times is not meaningful during this dynamic period because the total catalytic surface area is not constant, as result of changes in the catalyst's particle size (see supplementary Fig A2).

The dynamics of a non-promoted catalyst under reaction conditions enabled us to establish a spectroscopic descriptor that captures trends in selectivity. This descriptor can be used to assess the promotion effect. After 14 h on stream, ethyl chloride (EtCl) was added to the reactant feed in short pulses (Fig. 2a). The decomposition of EtCl on the catalyst surface led to a stepwise chlorination of the silver catalyst. The *in situ* XPS data show that the atomic concentration of chlorine on the silver surface increased immediately after each EtCl pulse, changing from 1.7 %at up to 7.9 %at (Fig. 2c and table 1), which correspond to an estimated surface coverage of 0.07 to 0.*31 ML for Ag(111) (0.9-4.3* 10^{14} atom/cm^2*)".* The promotion effect of chlorine is immediately visible in the reaction products (Fig. 2a), with CO_2 monotonically decreasing while EO slightly increases after the first EtCl pulse and then decreases after the last one[1]. As a result, the selectivity increases more than 6-fold from about 9 % to 55 % (Fig. 2a). These results agree well with detailed kinetics studies at 1 bar using chlorinated silver single crystals [19–21].

The O1s spectra measured after each chlorination step (Fig. 2b) indicate that the presence of chlorine influences the distribution of oxygen species. The most noticeable modification is the decrease of *Onucl*, but quantification revealed that *Oelec* also changed, slightly increasing after the first EtCl pulses but decreasing at the last one (Table 1). The total amount of oxygen lowered only at the last EtCl pulse. Fig. 2-d shows that the calculated *Oelec/Onucl* ratio increases almost linearly with the chlorine concentration in the surface (dots) closely following the rise in selectivity (green bars). This correlation strongly suggests that the promotion effect of chlorine is related to changes in the distribution of oxygen species on the catalyst surface.

The current knowledge about the chlorine promotion of silver catalysts is based on surface science experiments on model systems or theoretical calculations. Numerous interpretations of the

[1] Since Cl reduce the rate of both wanted and unwanted reactions, it is considered a moderator in industry.

available data have produced hypothesis and appealing ideas regarding the origin of the promotion effect, but these ideas have not yet merged into a unified mechanism. For instance, based on *ex situ* surface analysis of single crystals, Campbell and co-workers [20,21] interpreted the increase in selectivity due to chlorination as an ensemble effect, proposing that the unselective pathway is more affected because it involves more elementary steps thus requiring a larger number of active sites that are blocked by chlorine. Van Santen and Kuipers [12] proposed that chlorine decreases the total amount of adsorbed oxygen, although it increases the amount of oxygen that participates in the epoxidation by withdrawing electron density from its surroundings and consequently rendering the nearby oxygen atoms more electrophilic. A theoretical analysis based on density functional theory (DFT) suggests that subsurface chlorine promotes the epoxidation pathway by stabilizing the transition state for EO formation due to electrostatic interactions [22]. K. Waugh and co-workers[23,24] found experimental evidences that chlorine weakens the silver-oxygen bond, which is suggested to decrease the activation energy for the cyclisation of the surface intermediate relative to the unselective pathway. Based on ab initio studies, E. A. Carter and W. Goddard III proposed that chlorine and other electronegative elements promote the epoxidation pathway by blocking higher coordination sites on silver that give rise to unselective oxygen species and consequently creating more selective oxygen species at less coordinated sites[15,16]. In contrast, other DFT calculations suggest that chlorine inhibits the formation of unselective oxidation intermediates by blocking surface vacancies [25].

Our in situ XPS data reveal that chlorine directly affects the oxygen atoms in the Ag surface, but not all oxygen species are equally influenced. At lower amounts, chlorine preferentially removes *Onucl* species, while *Oelec* slightly increases (table 1). The monotonic decrease of both CO_2 and *Onucl* suggest that chlorine works as a site blocker, which promotes the selectivity by removal of nucleophilic species that are involved in the unselective oxidation pathway. At the same time, the increase of both EO and *Oelec* suggests that chlorine might also influence the selective oxidation pathway by enhancing the electrophilic oxygen species due to charge transfer, and/or rehybridization of the metal valence band orbitals. The dynamic changes in the distribution of oxygen species observed for the non-promoted catalysts might also be interpreted in the same framework of electronic modifications of surface species, but in this case, due to the incorporation of oxygen at sub-surface sites (see supplementary material), as proposed by Van Santen et al [12]. Hence, our results suggest that the overall increase in selectivity promoted by chlorine results from a combination of structural and electronic effects that act together modifying the balance of electrophilic and nucleophilic oxygen species on the silver surface, which comprise the active sites for ethylene epoxidation. At higher chlorine concentrations, the promotion effect is counter-acted by a poisoning effect, in which excess chlorine blocks oxygen chemisorption, and thereby limits the catalyst activity. We emphasize that correlating a single parameter to the catalytic performance is an over simplification that cannot capture all the nuances of a complex reaction like ethylene epoxidation. However this approach, provide valuable trends useful for catalyst optimization and testing hypothesis from reaction mechanisms

Conclusions

Our findings provide experimental evidence of an underlying surface process that explains the phenomenological correlation between chlorine promotion and selectivity based on the concept of electrophilic and nucleophilic species. In a more general sense, these results demonstrate that promoters in heterogeneous catalysis not only modify the number of active sites, but also change the chemical nature of a given site, as a result of electronic modifications induced in adjacent atoms. It remains to be shown whether practical strategies exist for further tuning of the distribution of oxygen species on silver that will produce the next generation of improved catalysts. Moreover, the approach followed in this work might benefit the study of the promotion effect in other catalytic systems, for which the common post mortem analysis using bulk techniques is not sufficient. In situ surface-sensitive spectroscopy allows not only the test of reaction models and kinetic mechanisms, but it might also unravel rational ways to effect improvements in the catalysts.

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Appendix A. Supplementay material

Supplementary data associated to this article can be found in the online version at

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Figures and tables

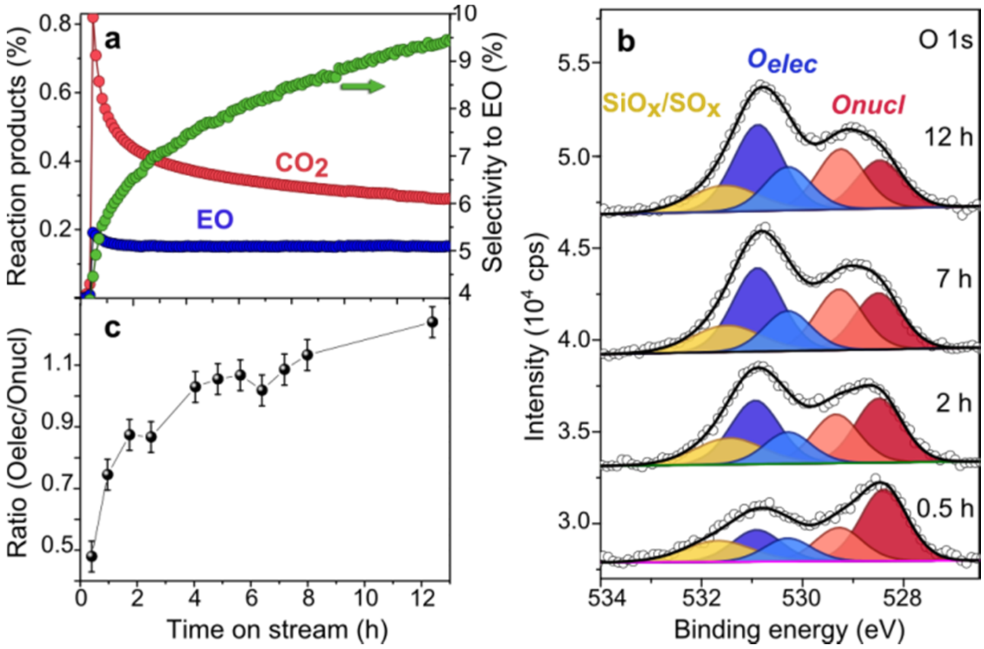

Figure 1. Dynamics of non-promoted silver catalyst under ethylene epoxidation at 0.3 mbar, 230 °C, C_2H_4:O_2 = 1:2. **(a)** Mole fraction of reaction products CO_2 (red) and EO (blue) together with selectivity to EO (green) as function of time. **(b)** Representative O1s XPS spectra measured at different times. **(c)** Ratio of electrophilic to nucleophilic oxygen species (Oelec/Onucl) as function of time.

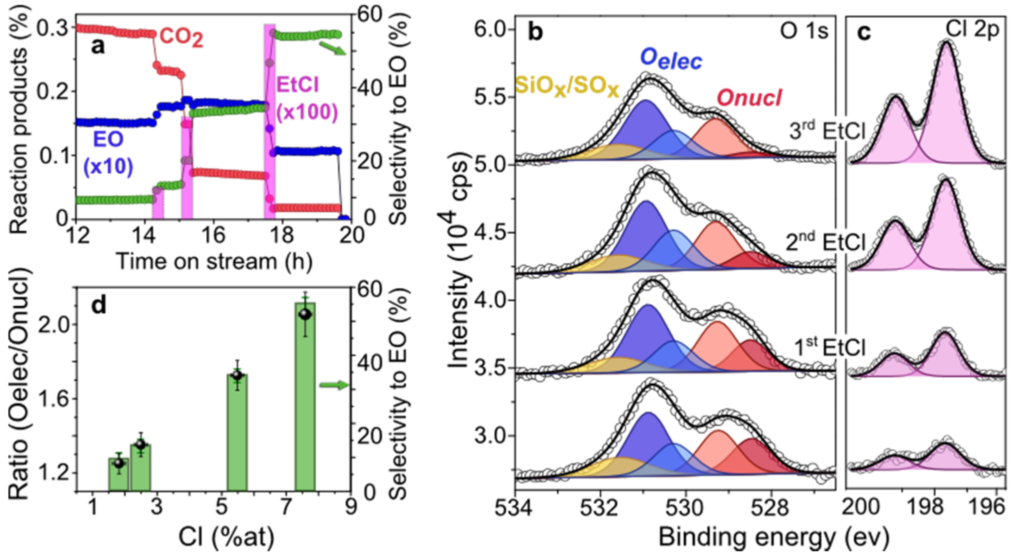

Figure 2. In situ stepwise chlorination of silver catalyst under ethylene epoxidation at 0.3 mbar, 230 °C, C_2H_4:O_2 = 1:2. **(a)** Mole fraction of reaction products CO_2 (red) and EO (blue) together with selectivity to EO (green) as function of time. EtCl pulses are represented by the purple bars. **(b)** O1s XPS spectrum before (bottom) and after each chlorination step (1^{st}, 2^{nd}, 3^{rd} EtCl pulses). **(c)** Corresponding Cl 2p spectra before and after each chlorination step. **(d)** Ratio of electrophilic to nucleophilic oxygen species *Olelec/Onucl* (black dots) and selectivity (green bars) as function of the Cl atomic concentration.

Table 1. Quantitative XPS data for silver catalysts under ethylene epoxidation during the in situ chlorination. Chlorine and oxygen species presented as atomic concentration (%at) within a probed depth of approximately 0.6 nm.

EtCl pulse	Cl (%) ±0.6[a]	*Onucl* (%) ± 0.3	*Oelec* (%) ± 0.3	Ototal (%) ± 0.3	Oratio ± 0.06
0	1.7	7.4	9.3	16.7	1.24
1st	2.6	7.0	9.5	16.5	1.36
2nd	5.6	6.0	10.6	16.6	1.77
3rd	7.9	4.9	10.0	14.9	2.07

[a] atomic concentrations. Errors propagated from the integrated area uncertainties.