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Research Note

Study of the active phase of silver catalysts for ethylene epoxidation

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Abstract

An investigation of ethylene epoxidation on α-alumina-supported silver catalysts promoted by cesium found that cesium favored the formation of strongly adsorbed electrophilic oxygen. The reactant mixture (C_2H_4 and O_2) modified the silver structure, favoring the formation of oxygen electrophilic species. In situ DRIFTS results demonstrated the formation of a thin film of silver for the cesium-promoted catalyst, decreasing the influence of the support. Similar in situ DRS profiles were observed for promoted and nonpromoted catalysts, indicating that the effect of cesium is due mainly to geometric rather than electronic effects. At iso-conversion conditions, Cs presence increased the yield toward ethylene oxide.

Keywords: Silver; Ethylene; Epoxidation

1. Introduction

In the commercial process for ethylene oxide production, a key intermediate in the chemical industry, ethylene epoxidation is performed on silver catalysts. Since the discovery of this reaction by Lefort, significant efforts have been made to improve the catalysts used in this process [1]. Applied surface science methods allowed the development of structure–activity relationships for this reaction system. The nature of surface active species and adsorbed intermediates, the effect of promoters, and the mechanism of this reactions have been intensively investigated [2–16]. There is a growing interest in analyzing these systems under reaction conditions [17], because the postreaction evacuation methodology may lead to destruction of weakly adsorbed intermediate species or changes in the surface structure. Debate continues over such matters as the mechanism of reaction and the promoter action mechanism. Considering only electronic effects, Cs should decrease the selectivity to ethylene oxide through an electronic charge donation to the atomic oxygen [8]. Actually, Grant and Lambert [9] observed that Cs addition on Ag(111) favored the CO_2 production associated with ethylene combustion but increased the selectivity to ethylene oxide formation through a second-order effect. Cs is able to neutralize acid sites on the oxide support responsible for isomerization of the epoxide to acetaldehyde, followed by combustion [18]. Campbell [10] suggested that the structure of Cs is more complex, noting the formation of CsO_3 species, which can generate some electronic or geometric effects. Serafin et al. [8] showed that Cs promotes a (1×2) reconstruction at Ag(110) and increases CO_2 release by silver in the presence of oxygen. This latter effect decreases ethylene oxide combustion, inhibiting additional CO_2 formation. It turns out that Cs acts by diminishing and stabilizing the Ag particle size, increasing the crystalline lattice defects, where the electrophilic oxygen is likely located [4,9], and decreasing nucleophilic oxygen concentration, which is responsible for the ethylene total oxidation [16]. Linic and Barteau proposed that ethylene epoxidation occurs though formation of a oxametallacycle intermediate, and that the role of Cs is to modify the electric field or dipole surface interactions, favoring the transition state that leads to ethylene oxide [19]. Similar results have been observed by microkinetic model analysis [20].

In the present work, we studied the surface properties of Cs-promoted and nonpromoted 15% Ag/α-Al_2O_3 catalysts applied in the epoxidation reaction, taking into consideration the modifications of the morphology and structure of the catalyst, as well as the influence on the reaction intermediates. We chose in situ

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characterization techniques using chemical and spectroscopic methods.

2. Experimental

Silver catalysts were prepared through impregnation of silver lactate to commercial α-alumina support (Norton, 0.5 m^2/g, 6% silica), as described by Liu and Shen [21]. A Cs-promoted sample was obtained by adding CsOH to a silver lactate solution. The sample labels and composition are described in Table 1. The samples were calcined at 350 °C for 4 h in 20% O_2/He at a total flow rate of 30 mL/min. The samples were previously submitted to a blank test by heating under He flow until 550 °C and monitored by mass spectroscopy, and no evidence of undecomposed compounds or preadsorbed oxygen was found.

Before each desorption and reaction procedure, the samples were also pretreated by heating to 350 °C in 20% O_2/He for 2 h, cooling to room temperature, and holding under a 20% O_2/He stream for 18 h. Temperature-programmed desorption (TPD) was monitored using a Balzers mass spectrometer with a QMS 200 Prisma quadrupole. For TPD of oxygen, the temperature was increased to 550 °C under an He flow of 30 mL/min. TPD of ethylene was done in a C_2H_4 flow of 30 mL/min at 0 °C for 1 h, followed by heating 550 °C as described for TPD of oxygen. In situ investigations were carried out using 20% C_2H_4 and 5% O_2 diluted in He reactant feed. Superficial reaction at programmed temperature (TPSR) was measured by heating the samples up to 800 °C under reactant flow. In situ diffuse reflectance spectroscopy UV–vis–NIR (DRS) measurements were done with a Varian-Cary 5 spectrophotometer connected to a diffuse reflectance accessory (Harrick). To separate the contribution of the support, the reflectance $r(\lambda)$ was ratioed to the reflectance of the support, and the results were calculated as function of the Shultz–Kubelka–Munk equation. DRS spectra were obtained at room temperature after the samples were exposed to a 30-mL/min reactant feed flow at 250 °C for 15 min. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed using a Thermo Nicolet Nexus 470 device with an MCT-A detector and a Spectra-Tech diffuse reflectance accessory. Interferograms were collected at 250 °C. The ethylene oxidation reaction (30 mL reactant feed) was carried out in a microreactor at atmospheric pressure under 200 mg of catalyst, with the temperature varied between 200 and 350 °C. The products were analyzed after 10 h on stream at a constant temperature reaction to ensure a stationary state [22], using a Chrompack-CP9001 TCD gas chromatograph fitted with a HAYESEP D column. The silver dispersion was calculated according to the method of Busser et al. [23], assuming a silver atomic density of 1.15×10^{-19} atoms/m^2.

Table 1
Silver content and data of silver surface coverage

Catalyst	Metal content (wt%)		Desorbed O_2 (μmol/g_{cat})	Ag dispersion (%)[a]	
	Ag	Cs		Before reaction	After reaction
15Ag	15.7	–	8.2	1.4	10.2
15AgCs	15.2	211	41.7	1.5	23.7

[a] Calculated by CO_2 chemisorption.

3. Results and discussion

Oxygen TPD results ($m/e = 32$) are presented in Fig. 1. As expected, oxygen adsorption was not observed on α-alumina, whereas silver catalysts demonstrated oxygen adsorption capacity. The addition of Cs caused a fivefold increase in the total amount of desorbed oxygen compared with the nonpromoted catalyst (Table 1). Along with an oxygen desorption peak at 430 °C, the cesium-promoted catalyst exhibited a larger peak (22.90 μmol/g_{cat}) related to more strongly adsorbed oxygen species at 500 °C. The different oxygen species on silver have been widely discussed in the literature, mainly for single crystals under low-pressure conditions [5,7–9,24,25]. These have demonstrated lower temperatures than we observed for the oxygen desorption of supported silver catalysts. Similar desorption temperatures were observed by Kim et al. [26] for supported silver catalysts. All of the studies of supported and unsupported silver attribute low-temperature desorption to molecular adsorbed oxygen and high-temperature desorption to atomic oxygen. Bukhtiyarov et al. [24] reported that Cs addition blocks the regular silver surface, which is responsible for the formation of nucleophilic oxygen; increases silver crystalline network defects, where epoxidizing oxygen species are located; and decreases the concentration of nucleophilic oxygen species, which are responsible for complete ethylene oxidation. Silver can dissociatively chemisorb molecular oxygen to form a surface silver oxide layer (Ag_2O) [3]. Silver cations (Ag^+) are needed to fix the ethylene at the catalyst surface; if these cations are located close to silver crystalline defects, where electrophilic oxygen is located, then epoxidation occurs [3].

The results of the ethylene TPD analysis are presented in Fig. 2. Ethylene desorption ($m/e = 28$) was not observed, with the appearance of only one signal referred to mass 44 (the main signal, intensity 100%), corresponding to both the par-

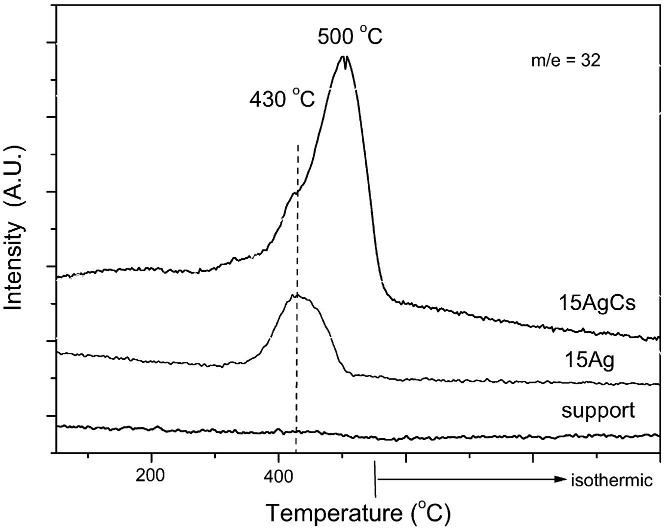


Fig. 1. O_2 TPD profiles of silver catalysts and the support ($m/e = 32$).

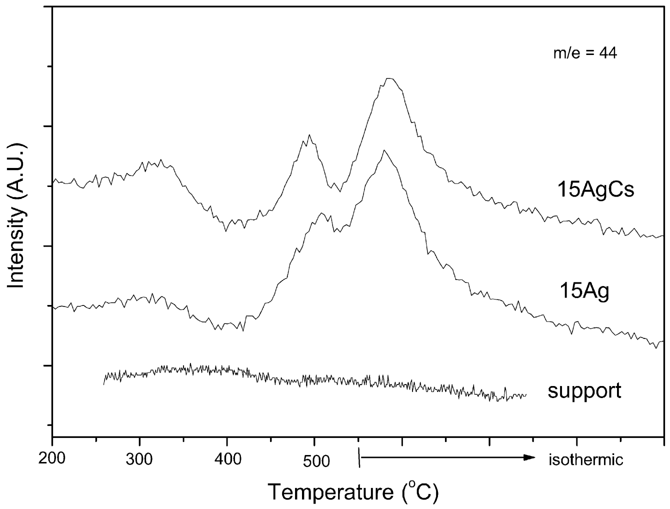


Fig. 2. Ethylene TPD profiles of silver catalysts and the support ($m/e = 44$).

tial oxidation to ethylene oxide (C_2H_4O) and total oxidation (CO_2) reaction products. Mass 29, characteristic of a secondary C_2H_4O signal [27,28], was not detected. This finding indicates preferential conversion of ethylene to CO_2. No CO_2 desorption from the support was seen, indicating that ethylene was not adsorbed on the support. The 15Ag and 15AgCs catalysts presented similar desorption profiles, indicating that the presence of Cs did not influence the total oxidation reaction. Bukhtiyarov et al. [16] reported that when Ag is exposed to the reactant feed, the surface is activated by formation of another oxygen species (O1s, 528.4 eV), increasing the ionicity of the adsorbed oxygen and favoring its participation in ethylene epoxidation. This species was identified as a subsurface oxygen species, which is dissolved into the silver matrix [7,25], and its presence is considered fundamental for epoxidation activity [6].

The silver dispersion was calculated based on CO_2 desorption for fresh samples and after reaction (TPSR), based on a 1 Ag:4 CO_2 ratio (Table 1). The fresh catalysts of 15Ag and 15AgCs presented silver dispersions of 1.4 and 1.5%, respectively, a good result compared with the reference values of 1.08% reported by Busser et al. [23]. The calculated silver surface area for fresh samples was around 1 m^2/g_{cat}, but after reaction it increased to 7.4 and 17.3 m^2/g_{cat}, corresponding to silver dispersions of 10.2% for 15Ag and 23.7% for 15AgCs. This significant improvement was probably due to the increased oxygen species diffusion in the silver matrix favored by reaction feed activation [6], which is greatly enhanced for the cesium-promoted sample due to the greater amount of silver crystalline framework defects, where these subsurface atoms are located [4,9].

Fig. 3 presents the results for the in situ DRS analyses. The 15Ag and 15AgCs catalysts show similar bands, appearing and increasing in intensity in the same wavelengths. Before the reaction, both samples had four bands: a small band at 230 nm attributed to isolated Ag^+ ion electronic transition $4d^{10} \rightarrow 4d^9\,5s^1$, a band of average intensity at 350 nm derived from clusters of oxidized silver, and a larger band at 320 nm due to the electronic transition of reduced silver species, indicating that most of the silver is deposited on alumina in the reduced form but with a significant presence of oxidized silver clusters. After reaction at 250 °C, a new shoulder appeared at 420 nm assigned to the formation of metallic silver particles [29–31]. No significant differences in silver electronic transitions during the ethylene epoxidation reaction were seen between the catalysts. This indicates that the Cs-promoting action is due mainly to geometric effects, not electronic effects. A drastic increase in silver dispersion in the presence of cesium has been observed by scanning electronic microscopy and atomic force microscopy [32].

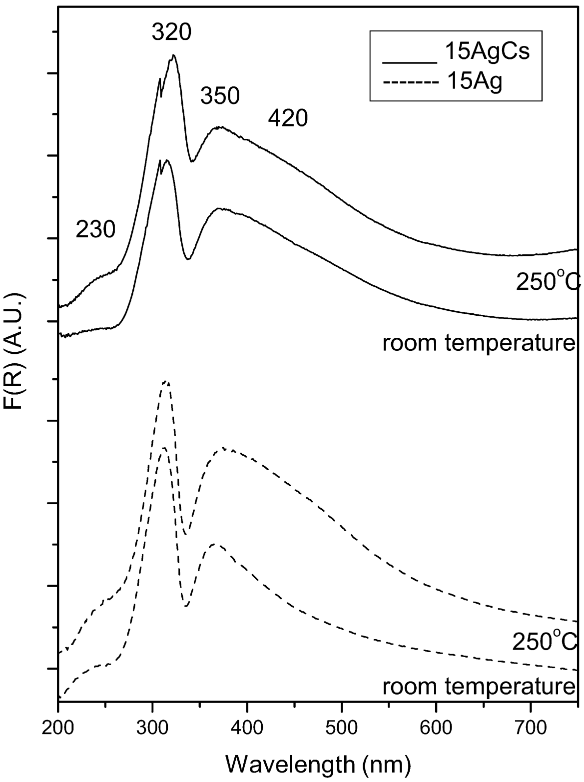
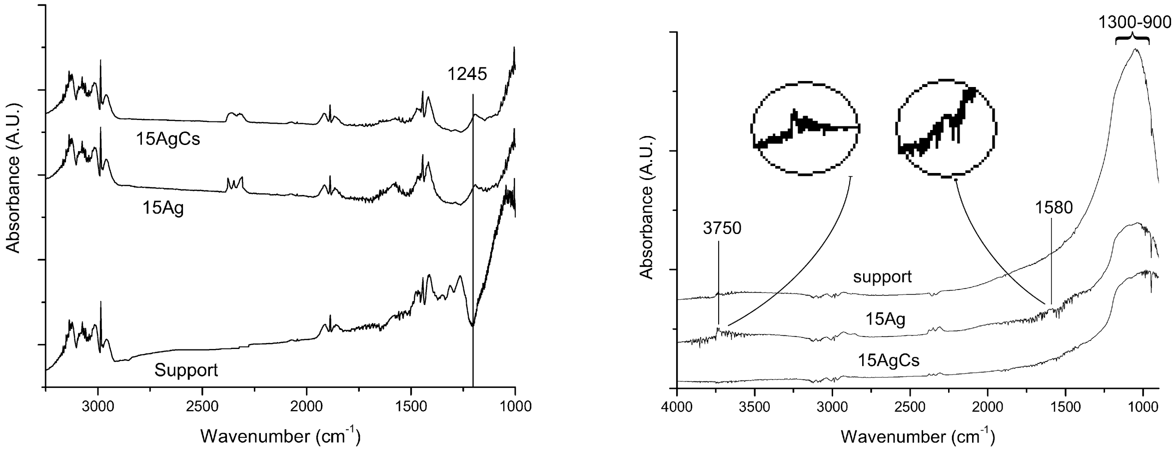


Fig. 3. In situ DRS profiles of silver catalysts.

Fig. 4 presents DRIFTS spectra under ethylene oxidation reaction conditions (250 °C, 1 atm). Two different backgrounds were used: catalyst after pretreatment with oxygen (a) and reactant mixture ($C_2H_4 + O_2$) (b). The adsorption bands were ascribed to different compounds according to the literature [15,22,33–35]. The spectrum for gas-phase ethylene presents bands in two regions: 3200–2900 and 1500–1400 cm^{-1}. Coadsorption of ethylene with oxygen raises another band at 1900–1800 cm^{-1}. CO_2 is present at 2370 and 2330 cm^{-1}, and C_2H_4O appears at 1245 cm^{-1}. Along with the bands characteristic of ethylene, the α-Al_2O_3 spectrum exhibits carboxylate species (1580–1260 cm^{-1}) and acetaldehyde (1043 cm^{-1}). According to some authors [6,11], C_2H_4O is formed over alumina but is immediately isomerized to acetaldehyde by Lewis Al^{3+} acid sites as surface silica hydroxyls present in commercial supports. The Ag catalysts present similar profiles with higher formation of CO_2 for 15Ag, giving rise to a band at the same region of gaseous CO_2 (2350 cm^{-1}), attributed to CO_2 adsorbed over Ag atoms. Both silver samples also show a band at



(a) (b)

Fig. 4. DRIFT spectra during ethylene oxidation reaction at 250 °C using as background: the sample (a) and reactant mixture (b).

1245 cm^{-1}, ascribed to C_2H_4O formation. The 15Ag catalyst shows a band at 1580 cm^{-1} corresponding to antisymmetrical stretching vibration of surface carboxylates, an acetate intermediate [11–13]. Thus the presence of this band for nonpromoted catalyst suggests an influence of the residual support on ethylene oxidation. These results suggest that the addition of Cs enhances the epoxidation reaction by decreasing undesirable stable compound formation. These data agree with reports that Cs favors the formation of a thin Ag film that decreases the support effect [32,37,38].

Fig. 5 presents the conversion of ethylene and the yield to ethylene oxide obtained during the catalytic runs. The 15Ag catalyst was not active at temperatures below 260 °C. When the temperature reached 280 °C, the reaction started with a gradual increase in conversion, which varied between 1 and 6%. Ethylene oxide yield increased abruptly, reaching 32%, which was the maximum yield value observed for this sample. Increasing the temperature to 300 °C increased the conversion to about 9% but decreased the yield to 24%. At 350 °C, the conversion was the same, and the yield decreased to between 7 and 4.5%. This apparent stable conversion for temperatures above 300 °C is due to a limitation of the reaction condition caused by the total consumption of the oxygen in the reactant feed, which was observed by the absence of the oxygen peak in the chromatograms. To verify deactivation, the temperature was reduced to 280 °C. The initial conversion and yield levels decreased to 5 and 16%, respectively, indicating deactivation of the 15Ag catalyst. The 15AgCs catalyst activity started at a lower reaction temperature (260 °C), but with a low conversion (1%). The ethylene oxide yield was much higher for 15AgCs than for 15Ag, reaching up to 48%. At 280 °C, the conversion did not increased significantly (2%), and the yield decreased slightly to about 45%. At 300 °C, the conversion increased gradually up to 7%, but the yield diminished to 30%. At a higher reaction temperature (350 °C), the conversion increased to 10%, but the yield decreased to 13%. After returning to 280 °C, the conversion was the twice the initial amount, but the yield diminished from 45 to 29%. In contrast to the 15Ag catalyst, the promoted catalyst exhibited increased activity with time on stream instead of deactivating. Force and Bell [33] also reported increased conversion with reaction time, reaching a maximum after 18 h. According to some authors [9,39,40], catalytic activity depends on the activation of silver surface and diffusion of oxygen species in the silver crystalline framework. The apparent lower deactivation of the 15AgCs can be explained by a better distribution of the silver particles in the silver film deposited on the support surface [32]. Table 2 gives the C_2H_4O yield at iso-conversion, showing that the presence of Cs promoted the C_2H_4O yield for all levels of iso-conversion

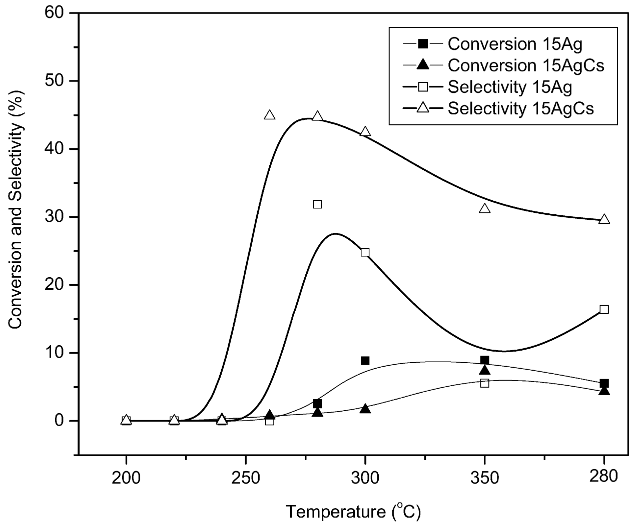


Fig. 5. Conversion and yield to C_2H_4O in ethylene epoxidation on silver catalysts.

Table 2
Yield to ethylene oxide at iso-conversion condition over silver catalysts

	Catalyst					
	15Ag			15AgCs		
Reaction temperature (°C)	280	280[a]	350	280	280[a]	350
Conversion (%)	2	5	8	2	5	8
Yield (%)	30	17	10	45	29	32

[a] After reaction at 350 °C.

tested, with an increase of up to 220% in the case of ethylene conversion of 8%. In these experiments, the maximum ethylene oxide yields were ca. 30% for 15Ag and 45% for 15AgCs.

The calculation of TOF values based on surface area of fresh 15Ag and 15AgCs catalysts were 6.02×10^{-4} mol/(s m^2) and 3.49×10^{-4} mol/(s m^2) (or 3.62×10^{20} and 2.10×10^{20} molecules/(s m^2) at iso-conversion around 2% and temperature of 280 °C, indicating that the reaction is structure-insensitive for the supported catalysts, because the factor 2 is within the criteria used for TOF. Moreover, the most important effect of Cs is stability and selectivity, as demonstrated above. The activity is directly proportional to the surface active sites, as demonstrated by the TOF value.

For comparison, Bal'zhinimaev et al. [22] found for 13.8% of Ag/α-Al_2O_3 (7 m^2/g support) a reaction rate of 4.9×10^{17} molecules/(s m^2), at around 10–15% conversion and 230 °C and a feed with excess of oxygen, which is lower than ours, because the ethylene/oxygen ratio is 4:1 in the feed. Industrially, the ethylene epoxidation reaction proceeds under pressures of 2–30 atm [41,42], with chlorine-containing hydrocarbons used as moderators. Along with Cs, the catalysts also contain Rh and Ba as catalytic promoters. Currently, working with conversion of ethylene around 8%, it is possible to reach a yield of 85% to ethylene oxide. A 60% yield to ethylene oxide for a conversion 0.58% of ethylene at atmospheric pressure and at 230 °C over 16% Ag/α-alumina catalyst has been reported [43]. At 3.4 atm with 10% Ag/α-alumina catalyst, a 79% yield at 180 °C for 1.4% conversion was obtained [36]. At 240 °C, the conversion was 10%, but the ethylene oxide yield decreased to 59%.

Our data agree with those of Bal'zhinimaev et al. [3], indicating that addition of Cs in the Ag/Al_2O_3 system results in a substantially increased ethylene oxide yield, with the activation of Ag surface by reactant feed increasing the ionicity of the adsorbed oxygen, which favors its participation in the ethylene epoxidation. Ethylene adsorption on silver occurs only after pretreatment under oxygen atmosphere and, consequently, generation of Ag^+ adsorption sites [5,16,44]. However, the presence of electrophilic oxygen species is necessary for ethylene oxide formation because it effectively epoxides the ethylene, and they are found in Ag crystalline framework defects, which are favored by the presence of Cs.

Our experimental results demonstrate that the simultaneous presence of ethylene and oxygen are necessary for activating the catalyst surface and obtaining ethylene oxide, as evidenced in the ethylene TPD experiments. According to many authors, this activation causes oxygen diffusion to inner silver layers generating the electrophilic oxygen, which is essential to the ethylene epoxidation reaction [2,6,16,45]. The surface silver state changed during reaction, with the appearance of silver reduced species indicating the Ag redox property. Moreover, the formation of acetates and aldehydes was observed when the residual influence of the support remained, decreasing ethylene oxide yield. The results, based on in situ analyses of real catalysts, confirmed observations reported for silver foil and single crystals, with participation of different oxygen species during ethylene epoxidation and are in accordance with the mechanism proposed by Bukhtiyarov et al. [16], with direct participation of nucleophilic and electrophilic oxygen species and indirect participation of subsurface oxygen. The formation of the reaction intermediate and yield toward C_2H_4O or CO_2 depend on the oxygen species that attacks the adsorbed ethylene molecule, being that the epoxidation is led by an electrophilic attack.

4. Conclusion

Cs promotional action is due mainly to geometric effects of improved silver dispersion. The increased Ag dispersion increased the amount of crystalline framework defects. The estimated dispersion of silver surface based on CO_2 desorption on fresh of 15Ag and 15AgCs catalysts and the surface sites were very similar, and when compared with the surface area of used catalysts after 90 h of reaction, increased by a factor of 5 for the unpromoted samples and a factor of 11 for the promoted samples. This significant improvement in the storage capacity of O_2 after reaction was probably due to the increased oxygen species diffusion in silver matrix during reaction.

The TOF values based on surface area of fresh 15Ag and 15AgCs catalysts at iso-conversion and constant temperature shows that the reaction is structure-insensitive for the supported catalysts. The reaction mixture was capable of modifying the silver structure, generating electrophilic oxygen. At iso-conversion conditions, the presence of Cs promoted an increase in the yield for ethylene; however, the most important effects of Cs are on stability and selectivity.

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