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Origin of enhanced ethylene oxide selectivity by Cs-promoted silver catalyst

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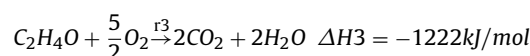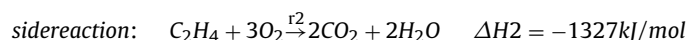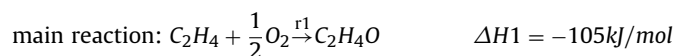
ABSTRACT

Cesium (Cs) is a key promoter to improve the selectivity of Ag catalyst for ethylene epoxidation. However, there is still no consensus in the literature about the origin of enhanced ethylene oxide (EO) electivity by Cs-promoted Ag catalysts. In this paper, the role of Cs as a promoter for ethylene epoxidation on Ag catalyst is studied by both experiments conducted under industrially relevant conditions as well as density functional theory (DFT) calculations. Ag/α-Al_2O_3 and Ag-Cs/α-Al_2O_3 catalyst are prepared by excessive impregnation and evaluated for ethylene epoxidation to determine the mechanism of selectivity enhancement for Ag catalysts that contain Cs. With the optimal loading of Cs, Ag particles of uniform size are evenly distributed on the support and EO selectivity increases from approximately 72.5%–82.0% compared with the Ag/α-Al_2O_3. O_2-TPD results indicate that Cs decreases the adsorption strength of oxygen on Ag and XPS analyses show that Cs shifts the $Ag\ 3d_{5/2}$ binding energy to facilitate the desorption of the EO precursor to form gas EO. DFT calculations demonstrate that Cs-promotor can weaken the adsorption of atomic oxygen. Electron density of atom oxygen absorbed on silver decreases with the addition of Cs on Ag(111) thereby enhancing the electrophilic attack by atomic oxygen at the electron-rich C=C bond of C_2H_4. Therefore, Cs lowers the activation energy for the formation of the oxometallacycle (OMC) and EO, while increasing the barrier for acetaldehyde (AA) formation, thereby leading to higher EO selectivity.

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1. Introduction

Ethylene oxide (EO) serves as a key chemical intermediate which is produced more than 27 Mt/y on the world-wide by the year 2017 [1] and about 70% of EO is converted to ethylene glycol (EG) by hydration. EG is one of the most important chemicals from which further products such as polyester, plastics, and engine antifreeze can be derived [2]. Direct oxidation of ethylene to EO in the presence of supported Ag catalysts has emerged as the main route for EO production since Lefort discovered the process in 1931 [3]. The competing parallel reactions are as shown below [4], where r1 represents the desired, mildly exothermic and selective pathway leading to the formation of EO. Alternatively, ethylene and/or EO can undergo combustion to CO_2 and H_2O through one or both of two highly exothermic pathways including the parallel r2 and sequen-

tial routes r3. The heat release of side reaction is 12 times more than that of main reaction. Hence, it is of great significance for industrial production to increase EO selectivity to avoid thermal runaway, cut the cost and increase profit [5].

$$\text{main reaction: } C_2H_4 + \frac{1}{2}O_2 \xrightarrow{r1} C_2H_4O \qquad \Delta H1 = -105 kJ/mol$$

$$\text{side reaction: } \quad C_2H_4 + 3O_2 \xrightarrow{r2} 2CO_2 + 2H_2O \quad \Delta H2 = -1327 kJ/mol$$

$$C_2H_4O + \frac{5}{2}O_2 \xrightarrow{r3} 2CO_2 + 2H_2O \ \ \Delta H3 = -1222 kJ/mol$$

So far, silver is the most efficient catalyst for ethylene epoxidation [6]. Numerous papers and patents have reported various of ways to increase ethylene oxide (EO) selectivity [7–11], including the usage of different silver precursors, different preparation techniques, and promoters. Among them, the use of Cs as a selectivity promoter has been discussed at length. Lambert and coworkers argued that Cs can decrease the binding strength between EO and the catalyst surface [12], thereby minimizing sequential reaction to form carbon dioxide. It has been reported that the presence of

cesium would neutralize the acid sites on support, avoiding the isomerization of EO to form acetaldehyde (AA), which finally transform to CO_2 and H_2O [13]. Cs has also been shown to favor the formation of strongly adsorbed electrophilic oxygen to form EO [14]. Moreover, it has been suggested that cesium plays a key role in binding and dispersing the silver particles on the support [15]. Linic and Barteau [16] demonstrated that a surface intermediate oxometallacycle (OMC) could be formed through the ring-closure reaction of weakly absorbed ethylene with adsorbed oxygen, and then the OMC intermediate reacted through a transition state to form EO and AA [17,18]. Though the mechanism of ethylene epoxidation changes slightly with the coverage of oxygen [19,20], the OMC is an important intermediate in the process of ethylene epoxidation. Saravanan [21] found that Cs was an electron donor for the OMC and the presence of Cs atom repelled the OMC intermediate. Linic et al. [22] suggested that Cs cations increase the selectivity by long-range electrostatic interactions that stabilize the transition state for the EO formation. Ozbek et al. [23] performed computational studies on an Ag2O(001) and found that the presence of Cs resulted in the formation of CsOx complexes and introduced the surface oxygen vacancies, which could reduce the catalyst selectivity. It is also found that Cs and Cl co-existed on the surface can result in high EO selectivity. Though many theoretical studies about the ethylene epoxidation on different silver surfaces have been developed [24,25], investigations on the reaction mechanism on Cs promoted Ag catalysts using Density functional theory (DFT) calculations are still relatively little. Furthermore, the experimental results of most literature were concluded on single crystal silver catalysts or under rigor reaction conditions inconsistent with the industrial process. Therefore, the specific role of promoter Cs in the selective oxidation of ethylene is still the subject of considerable debate.

In this work, we explored the role of Cs as a promoter for Ag catalyst through the analysis of ethylene epoxidation on unpromoted and optimal loading Cs-promoted Ag catalyst in both experiments conducted under industrially relevant conditions as well as DFT calculations. According to the previous experimental studies [26,27], addition of ppm levels of 1,2-dichloroethane (DCE) can promote catalyst selectivity, therefore, all the experiments were concluded under 0.3 ppm DCE. It was demonstrated that Cs decreased the binding energy of Ag $3d_{5/2}$, which facilitated desorption of the produced intermediate to form EO. With the combination of DFT calculations performed on pure and Cs-promoted Ag(111), we study the origin of enhanced ethylene epoxidation selectivity derived from Cs-promotor by analyzing the electronic distribution of the adsorbed oxygen and intermediate(OMC), and the activation energy along the reaction path. DFT calculations demonstrate that the presence of Cs increased the electrophilic oxygen adsorbed on Ag surface, which lowered the activation energy to form oxometallacycle (OMC) and EO, meanwhile increasing the barrier toward acetaldehyde (AA).

2. Material and methods

2.1. Catalyst preparation

The $Ag/\alpha-Al_2O_3$ and $Ag-Cs/\alpha-Al_2O_3$ catalysts in this investigation were prepared using excessive impregnation method according to the patent literature [28]. The $Ag_2C_2O_4$ was slowly dissolved into an aqueous solution containing a 3:1 M ratio of ethylene-diamine (EN) to $Ag_2C_2O_4$, and then the $Ag_2C_2O_4$-containing impregnation solution was added to the support, then the sample was heated to 300–400 °C for thermal decomposition under air atmosphere for ten minutes. The $Ag-Cs/\alpha-Al_2O_3$ catalyst was prepared using the same procedure with $Ag/\alpha-Al_2O_3$ cata-

lyst as mentioned above. Catalysts with different Cs contents were obtained by adding different amounts of CsOH solution into the $Ag_2C_2O_4$-containing impregnation solution. Ag loadings of all these catalysts maintained 15 wt%.

2.2. Catalyst evaluation

Catalysts were evaluated in a stainless steel reactor with 4 mm inner diameter. The catalysts were broken and sieved to 0.9–1.4 mm, then 1 ml sample was loaded into the reactor. Quantitative analysis of inlet and outlet gas composition was performed on an online Prima dB mass spectrum produced by Thermo Scientific. The gas was ionized by bombardment of electron current in ion source. Stand Faraday detector was used to analyze the gas concentration of 10 ppm–100%, and the concentration between 10 ppb to 10 ppm was detected by secondary electron multiplier. Gas feed composition was C_2H_4 30%, O_2 7.5%, CO_2 1.85%, ethylene dichloride (EDC) 0.1–0.5 ppm, balance N_2 at 1.7 MPa total pressure, and the gas hourly space velocity (GHSV) of 5000 h^{-1}. Temperature was recorded when EO concentration of outlet gas stream attained at 2.5 mol%. The EO selectivity was expressed as the following equation.

$$EOsel.(\%) = \frac{\Delta EO}{\Delta EO + 0.5 \times \Delta CO2} \times 100\%$$

Since ethylene oxide molecules are easily converted to carbon dioxide and water in pores with such small diameters as nanometer order, it is realized that pore diameter of carriers should be as close as possible to a desired macropore size. The surface area of $\alpha-Al_2O_3$ carrier is about 1.0 m^2/g, and the average pore diameter of $\alpha-Al_2O_3$ carrier is about 1.0 μm [29]. We approximately calculated the effect of mass transfer according to the Weisz-Prater criterion (see details in the Supporting Information). It is noted that the value of N_{w-p} is 0.0044, which is much less than 0.3. It indicates that pore diffusion can be excluded. So the value of catalyst effectiveness factor η should be approximately to be 1.0. In addition, the experimental results proved that no mass transfer effect exists for ethylene epoxidation with our evaluation conditions.

2.3. Catalyst characterization

O_2-TPD was measured using a TPDRO 1100 automated chemisorption analyzer with a Pfeiffer Vacuum Quadrupole Mass Spectrometer. 2.0 g of catalysts was exposed to 30 ml/min He for 1 h, then temperature was increased to 550 °C and kept for 1 h to remove the impurities on the sample. After the catalyst was cooled to 210 °C in He, O_2 was switched to chemisorb on catalyst for 1 h and then the sample was cooled to room temperature in He. As the baseline was stable, the catalyst was analyzed with temperature-programmed desorption from room to 550 °C.

Scanning electron microscopy (SEM) micrographs were collected using a FEI Quanta200 Scanning Electron Microscope with a tungsten electron source and three imaging modes (high vacuum, low vacuum and ESEM) to accommodate the widest range of samples for any SEM system. X-ray photoelectron spectra (XPS) was carried out with a Thermo Scientific 250 ESCALAB, the system is equipped with an X-ray source to produce Al Kα radiation for XPS measurements, and the A12p line being used with a binding energy of 74.5 eV;XRD measurement was performed using a Empyrean X-ray diffractometer operated at 40 kV and 40 mA using Cu Kα radiation, scanning range: 8–100° and Scanning rate: 0.65°/s.

2.4. DFT calculations

DFT calculations were performed using the PWSCF (Plane-Wave Self-Consistent Field) code in the Quantum ESPRESSO package. Gra-
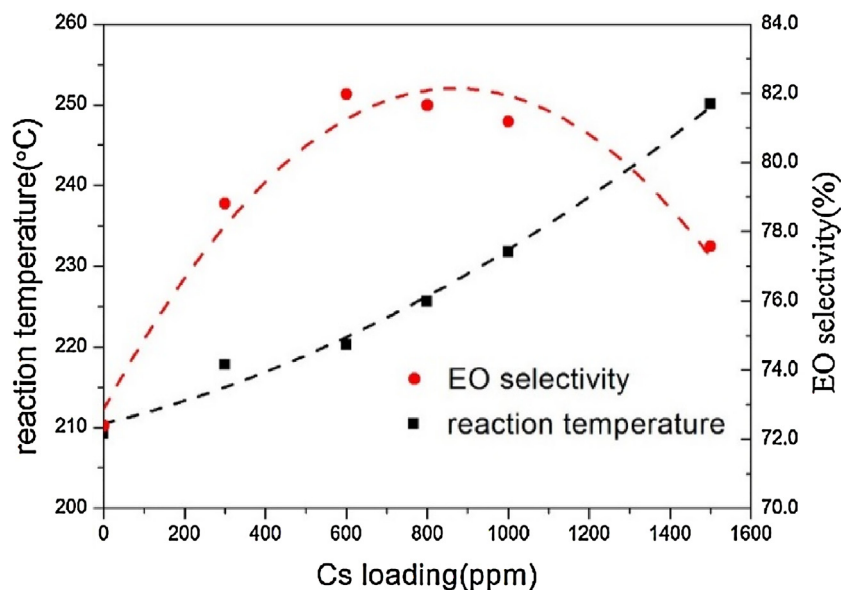
Fig. 1. The effect of promoter Cs on 15 wt% Ag/α-Al$_2$O$_3$ catalyst performance.

dient corrections are included using the Perdew-Burke-Ernzerh form of the generalized gradient approximation (GGA). The kinetic energy cutoff for the selection of the plane-wave basis set is fixed to 40 Ry. The regular Ag(111) surface was modeled with a five-layer slab, each layer contains either 9 Ag atoms (3 × 3cell), oxygen atom was absorbed on the upper Ag layer and the bottom three layers of the slab are kept fixed during structural optimizations. For calculations of the electronic properties of Ag(111) slab, Monkhorst-Pack 4 × 4 × 1 k-points with 16 k-points were used. The geometry optimizations stop when the maximum force on the atoms is less than 10^{-4} a.u. The climbing-image nudged elastic band (CI-NEB) method is used to determine the minimum-energy pathway for elementary reaction steps for ethylene epoxidation.

3. Results and discussion

3.1. Effect of promoter Cs on the performance of silver catalyst

The results of evaluation shown in Fig. 1 indicated that the reaction temperature gradually enhance as increasing of the Cs loadings, and that elevated rapidly when cesium loading was above 1000 ppm. EO selectivity increased with Cs loadings rising to 800 ppm, while higher amount of Cs resulted in the decreasing of EO selectivity, Optimum alkali promotion was achieved when a little of Cs was used, and further increasing the alkali coverage reduced catalyst activity and selectivity, which is in good agreement with the previous work [30]. The optimal Cs loadings ranged from approximately 600–800 ppm, on which EO selectivity was about 82.0% and reaction temperature was approximately 220 °C. Reaction temperature on catalyst without Cs was 209 °C, and EO selectivity was 72.5%, enhancing approximately 10% because of the addition of proper amount of Cs.

The addition of Cs has a negative influence on the activity of silver catalyst, which is in good agreement with the study reported by Barteau [31] who demonstronted that the catalyst activity is sensitive to alkali metal loading, and it suppress all activity by adding larger amounts of alkalis. However, the optimal Cs loading was different from the result reported by Diao et al. [4], who suggested that the best quantity of Cs is 300–450 ppm. The optimal loading of promoter Cs is influenced by varied α-Al$_2$O$_3$ carriers used in the catatlyst and the silver concent loaded on them.

3.2. Effect of Cs on size and distribution of silver particles

Fig. 2 presents the SEM micrographs of 15%Ag/α-Al$_2$O$_3$ catalyst and 15%Ag-600ppmCs/α-Al$_2$O$_3$ catalyst. The massive and flat regions depicts the crystal plates of α-Al$_2$O$_3$ carrier, and the smaller white particles are the supported Ag particles. It can be seen from picture (a) that the size of Ag particles in 15%Ag/α-Al$_2$O$_3$ catalyst are not uniform. The diameter of the large grains are more than 100 nm while the small ones are less than 50 nm. Large particles are mainly distributed on the margin of the carrier, while smaller particles are distributed on the surface of the carrier. Crystal plates are partially exposed, which would result in the decrease of EO selectivity because the weak acidity of α-Al$_2$O$_3$ led to complete oxidation of ethylene [32]. However, in the presence of Cs, Ag appears to wet the α-Al$_2$O$_3$ surface and Ag particles are evenly in size and distribute uniformly on the crystal plate of the support [15,33], which benefits the catalytic performance of silver catalyst [34].

3.3. O$_2$-TPD characterization

The oxygen species held on a 15%Ag/α-Al$_2$O$_3$ and 15%Ag-600ppmCs/α-Al$_2$O$_3$ catalysts were studied by temperature programmed desorption (O$_2$-TPD), without considering of oxygen adsorbed on the α-Al$_2$O$_3$ support [14], as presented in Fig. 3. There are two peaks for desorbed oxygen in both catalysts, corresponding to the Ag-O bonds of different bond strengths [35]. The temperatures for different oxygen species desorption are 275 °C and 320 °C in Ag/α-Al$_2$O$_3$, respectively. In contrast, the temperatures are 270 °C and 305 °C in Ag-Cs/α-Al$_2$O$_3$, respectively. The results are consistent with the previous work by Couves [36]. Our results show that oxygen desorbs from the silver catalysts in two states with different desorption temperatures, corresponding to oxygen desorbing from Ag(111) and from a highly stepped or defected Ag surfaces, respectively, in which EO and CO$_2$ produced coincidently.

From Fig. 3, we can also conclude that the maximum desorption temperature declines in different degree by the addition of Cs. The desorption temperature of strong Ag-O bond decreases about 15 °C while that of weak Ag-O bond reduces about 5 °C. The concentration of strongly adsorbed oxygen decreases and that of weakly adsorbed oxygen has no obvious change, resulting in the decreasing of total amounts of adsorbed oxygen. Addition of Cs decreases the intensity
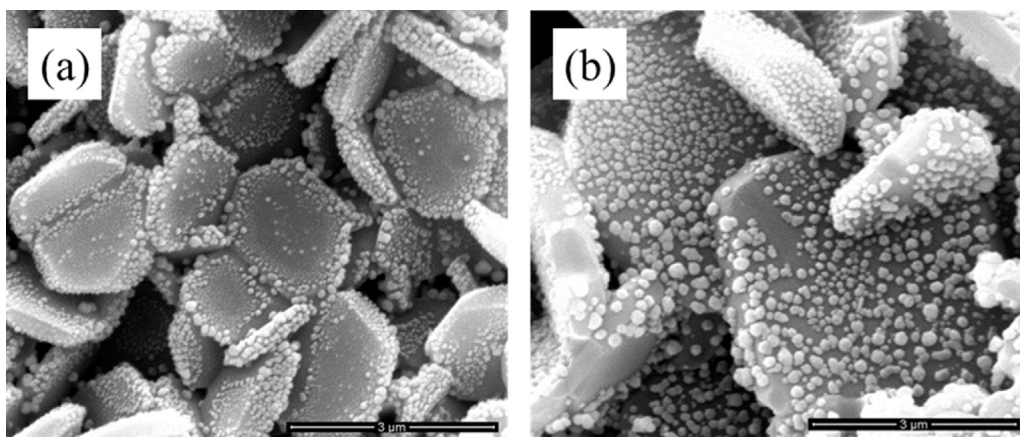
Fig. 2. SEM micrographs demonstrating the size and distribution of Ag on α-Al$_2$O$_3$ carrier: (a) 15%Ag/α-Al$_2$O$_3$, (b) 15%Ag-600ppmCs/α-Al$_2$O$_3$.
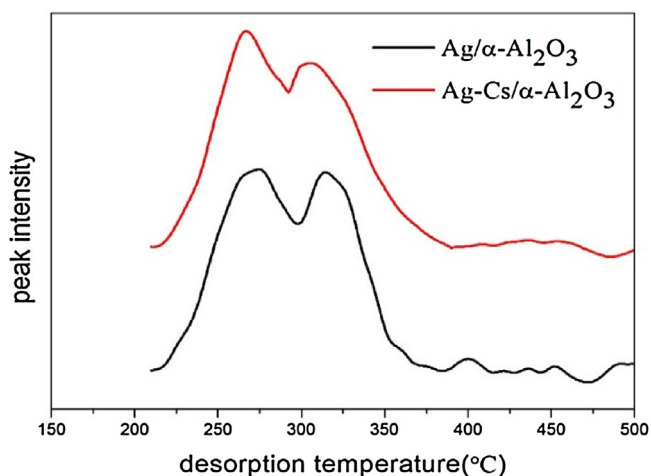
Fig. 3. Effect of Cs on the desorption of oxygen from silver catalyst.

Fig. 4. Ag 3d$_{5/2}$ XPS spectra recorded on Ag/α-Al$_2$O$_3$ and Ag-Cs/α-Al$_2$O$_3$ catalysts.

of Ag-O bond and the concentration of strongly adsorbed oxygen, which resulted in the increase of reaction temperature and higher selectivity for ethylene epoxidation reaction.

3.4. XPS characterization

In order to better explore possible electronic interactions between Ag and Cs, XPS studies were conducted on 15%Ag/α-Al$_2$O$_3$ and 15%Ag–600 ppm Cs/α-Al$_2$O$_3$ catalysts. The XPS results in Fig. 4 show us the Ag 3d$_{5/2}$ binding energies of silver catalysts. The binding energy (BE) of Ag 3d$_{5/2}$ is 367.7 eV for Ag/α-Al$_2$O$_3$, while it is 367.6 eV for Ag-Cs/α-Al$_2$O$_3$ catalyst. The addition of Cs lowers the BE value by 0.1 eV suggesting the transfer of e$^-$ from the highly polarizable Cs$^+$ to metallic Ag, which is consistent with earlier result from Monnier et al. [37]. Higher charge and lower binding energy of Ag would result in desorption of the EO precursor to form gas EO. The result is in good agreement with the view from Diao et al. [4], who suggested that promoter Cs reduced the binding energy of Ag and the activation energy from EO precursor to gas EO, avoding further oxidation to form CO$_2$, enhancing the selectivity of EO.

3.5. XRD characterization for silver catalyst

Fig. 5 shows the XRD results of α-Al$_2$O$_3$ carrier and supported silver catalysts with different composition. The peaks assigned to Ag(111), Ag(100) and Ag (110) are in 38.1°, 44.4° and 64.8° of 2θ angel, respectively, and the other peaks are attributed to the α-
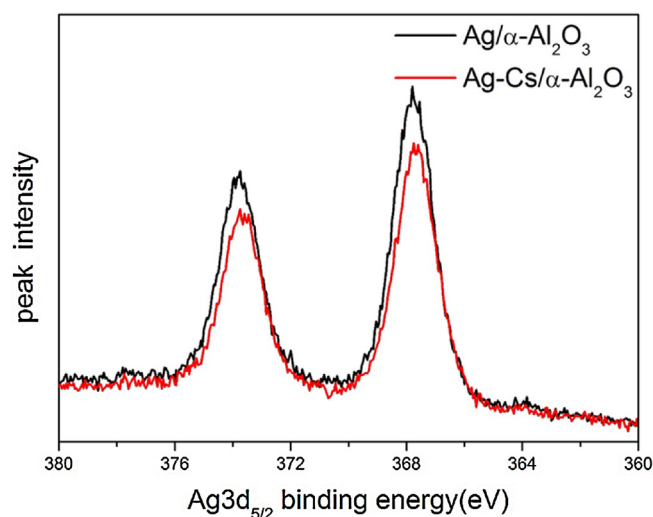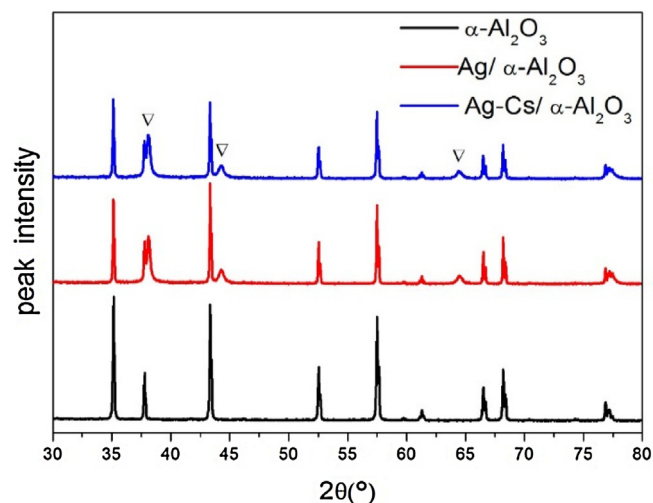

Fig. 5. XRD characterization of α-Al$_2$O$_3$ carrier and supported Ag catalyst.

Al$_2$O$_3$. The strength of the peak assigned to Ag(111) is maximum, the sequent is Ag(100) and the Ag(110) surface is minimum, as literature has reported that major metallic Ag exists stably in the form of Ag(111) in silver catalysts [38]. Therefore, ethylene epoxidation was mainly calculated on the surface of Ag(111) in next section.
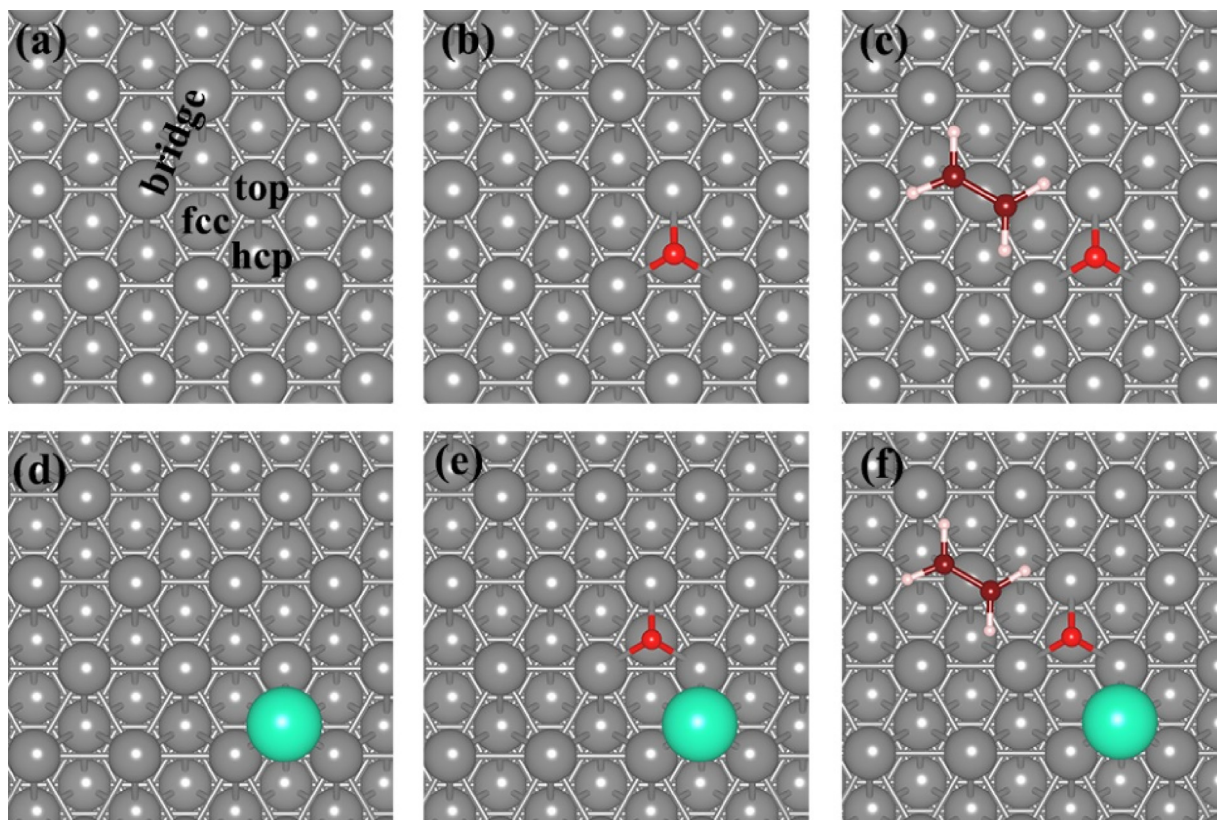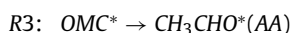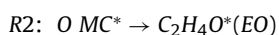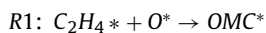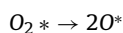
Fig. 6. Platform of optimized structure of (a) Ag(111), (b) optimal site of binding. oxygen on Ag(111), (c) absorbed molecular ethylene and atomic oxygen on Ag(111), (d) Cs-Ag(111), (e) optimal site of binding oxygen on Cs-Ag(111), (f) absorbed molecule ethylene and atomic oxygen on Cs-Ag(111). (Ag: gray, O: red, C_2H_4: dark red, H: light pink, Cs: green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.6. DFT calculations

In order to unveil the origin of Cs enhanced catalytic selectivity of silver catalyst for ethylene epoxidation, we employed density functional theory (DFT) calculations to investigate the differences of oxygen adsorption and the activation barrier for ethylene oxide formation between pure Ag(111) and Cs-promoted Ag(111) surface. According to the proposed mechanism, oxometallacycle (OMC) intermediate is formed through the reaction of weakly absorbed ethylene reacts with adsorbed oxygen and then it is converted into EO and AA through ethylene epoxidation and complete combustion, respectively, and the elementary reactions are shown below:

$O_2* \rightarrow 2O^*$

$R1: \ C_2H_4* + O^* \rightarrow OMC^*$

$R2: \ O\,MC^* \rightarrow C_2H_4O^*(EO)$

$R3: \ OMC^* \rightarrow CH_3CHO^*(AA)$

As molecular oxygen decomposed to form atomic oxygen rapidly on Ag surface [39,40], the O_2 dissociation is not considered in this paper. So the possible rate-determining steps may include weakly absorbed ethylene reacting with binding oxygen to form OMC (R1) and OMC reacting through ring closure or H-transfer to produce absorbed EO (R2) or AA (R3) [6,18,41].

To search for the minimum energy profiles (MEP) for the ethylene epoxidation, we have optimized the adsorption configuration of reactant, intermediate and product on catalysis. Top, bridge, fcc and hcp hollow sites are the four sites for oxygen adsorbed on Ag(111) [21], which are shown in Fig. 6a and the fcc has the strongest oxygen adsorption energy [38]. Suljo [22] observed that

Table 1
Adsorption energy, bond length with Ag and Loẅdin charge analysis (positive values mean electron accumulation) of atomic oxygen adsorbed on Ag(111) and Cs-Ag(111).

surface	$E_{ad}(O)$/eV	d(Ag-O)/Å	$|\Theta(O)|$/e
Ag(111)	−5.92	2.18	0.44
Cs-Ag(111)	−5.22	2.26	0.26

the positive impact of Cs on the selectivity drops off with the distance between Cs and the EO transition increasing. In general, the closer the distance of atomic Cs to oxygen adsorbed on Ag, the higher the selectivity of EO. So cationic Cs is located at the hollow site of Ag(111) and is nearby the binding atomic oxygen at fcc sites in this work. Meanwhile, the preferred ethylene adsorption position is at the top site with a hexagonal empty space around [38]. Fig. 6 shows the platform of adsorbed atomic oxygen and co-adsorbed of O and C_2H_4 on Ag(111) and Cs-Ag(111).

As shown in Table 1, the adsorption energy of oxygen is 5.92 eV on clean Ag(111), while it is 5.22 eV on Cs-Ag(111) surface. Addition of Cs reduces the adsorption energy but increases the bond length of Ag-O from 2.18 to 2.26 Å. Saravanan et al. [21] using Ag_{10} clusters model demonstrates that the binding energy of oxygen on Ag(111) is 3.21 eV, the length of Ag-O bond is 1.46 Å, and those are 2.71 eV and 3.21 Å on Cs-Ag(111) surface, respectively. Though the changes are similar in binding energy of oxygen and bond length by Cs promotion, large differences exist in calculation results by different models. Meanwhile, the reduced electron number from 0.44 to 0.26 |e| of adsorbed oxygen by the addition of Cs shows weakly adsorbed oxygen, which is benefit for the formation of the EO [16–18].
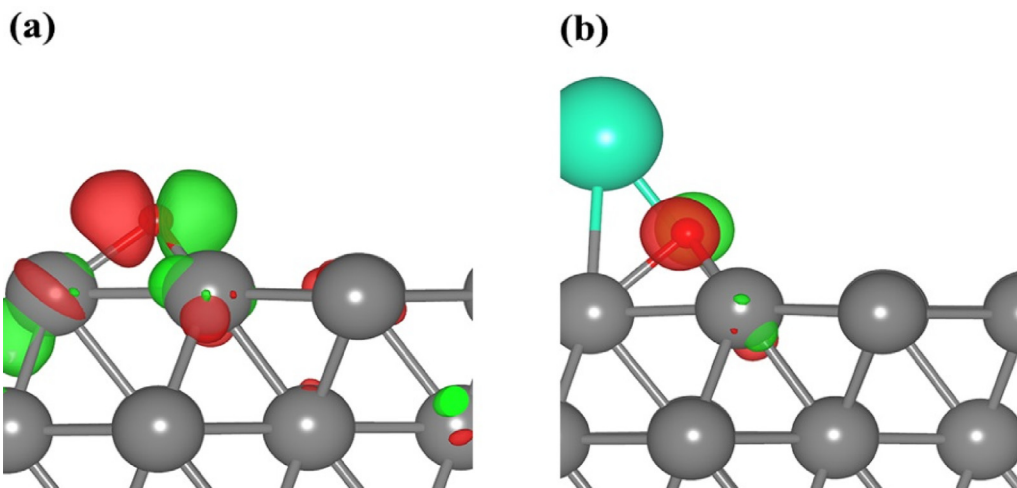
Fig. 7. Density of electron cloud in highest occupied molecular orbital (HOMO) for atomic oxygen adsorbed on (a) Ag(111) and (b) Cs-Ag(111).

Table 2
Activation energy (eV) of elementary steps R1-R3 and Adsorption energy of ethylene oxide (E_{ad}(EO), eV) on Ag(111) and Cs-Ag(111).

surface	Activation Energy (eV)			E_{ad}(EO)(eV)
	R1	R2	R3	
Ag(111)	0.47	0.72	0.73	−0.46
Cs − Ag(111)	0.39	0.57	0.78	−0.24

In order to demonstrate the role of weakly adsorbed atomic oxygen played in the enhancement of catalytic selectivity of ethylene epoxidation, a series of detailed electronic structure analysis is performed. Fig. 7 shows the highest occupied molecular orbital (HOMO) of the studied structures around the atomic oxygens absorbed on surface, indicating that atomic oxygen is the electron donation center in reaction. Comparing Fig. 7a with b, it is found that region of HOMO of atomic oxygen shrinks with the addition of Cs, mutually corroborating the decreasing excess electron number of atomic oxygen in Table 1. Strongly binding oxygen with higher electron density on Ag(111) shows nucleophilic property relative to that on Cs-Ag(111), and tends to attach the C—H bond in C_2H_4 with low electron density, facilitating the formation of AA. Oppositely, the weakly adsorbed oxygen with lower electron density on Cs-Ag(111) is regarded as electrophilic center, which prefers to react with ethylene to form EO by attacking C=C bond, because of the high electron density located in π bond of C=C bond. Fig. 8 shows the local density of state (LDOS) for C=C bond of OMC intermediate formed in the reaction between ethylene and atomic oxygen (R1) on Ag(111) and Cs-Ag(111). As known to all, the difference in the bond strength derives from the anti-bonding states, that is, the antibonding states move to lower energy level and become higher occupancy, which leads to a weaker bond, and vice versa. In the process of the OMC formation, the antibonding orbital π* in C=C bond moves below the Fermi energy furtherly on Cs-Ag(111) compared with pure Ag(111), so the stability of C=C bond is weaker on Cs-Ag(111) than that on pure Ag(111) surface, which makes atomic oxygen easily insert the C=C bond to form the target product EO on Cs-Ag(111).

Fig. 9 shows the optimized configurations along the minimum energy profiles and activation energies for all elementary steps. From Fig. 9 and Table 2, we can draw that the activation energy is 0.47 eV on Ag(111) surface while it is 0.39 eV on Cs-Ag(111) surface in the formation of the OMC intermediate. The activation energies are 0.72 and 0.73 eV from OMC to EO and AA on Ag(111) surface, respectively, and the same reactions occur on the surface of
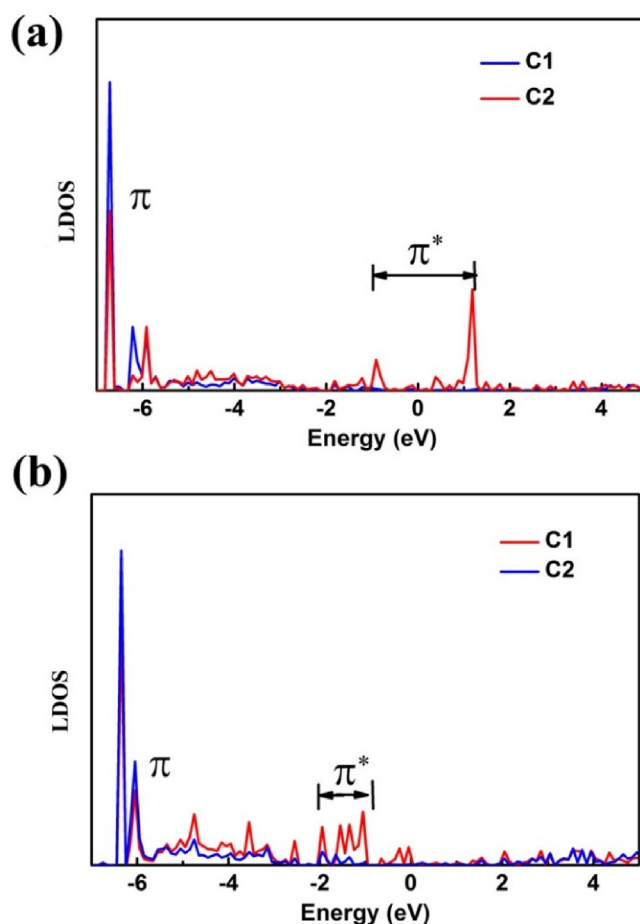

Fig. 8. LDOS for C=C bond of OMC formed on (a) pure Ag(111) and (b) Cs-Ag(111).

Cs-Ag(111), in which the activation energies are 0.57 and 0.78 eV, respectively. The difference in the activation barrier for AA and EO formation calculated on Ag(111) is 0.1 eV, while the value is 0.21 eV on Cs-promoted Ag(111). The similar activation barriers result in the lower EO selectivity [42], but the lower activation energy to produce EO and the higher barrier to form AA can enhance the selectivity from the OMC intermediate to EO. The energy difference of the activation barrier from OMC to EO and AA is much more one on
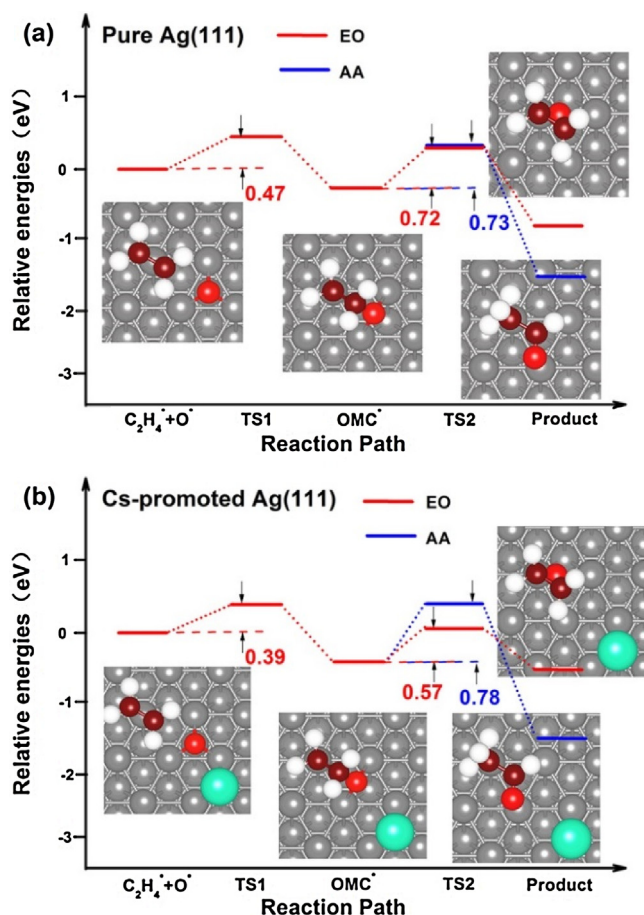
Fig. 9. Ethylene epoxidation reaction pathway and corresponding structure on (a) Ag(111) and (b) Cs-Ag(111).

influence on the activity of silver catalyst, the reaction temperature gradually enhanced as the increasing of Cs loadings. Optimal Cs loading ranged from 600 to 800 ppm in 15%Ag/α-Al$_2$O$_3$, on which EO selectivity enhanced approximately 10% to reach 82.0%. Promoter Cs maintained the proper size of Ag particles which benefited the performance of silver catalysts and made Ag particles distribute uniformly on the carrier, which improved the EO selectivity by avoiding the complete combustion of ethylene. There are two peaks of oxygen desorption for silver catalysts, and the addition of Cs decreased the intensity of Ag-O bond and the concentration of strongly adsorbed oxygen, which resulted in higher selectivity for ethylene epoxidation reaction. Binding energy of Ag $3d_{5/2}$ reduced from 367.7 to 367.6 eV when Cs promoter added to Ag/α-Al$_2$O$_3$, which facilitated desorption of the EO precursor to form gas EO, increasing the EO selectivity. Major metallic silver exists stably in the form of Ag(111) in pure and Cs-promoted silver catalysts. DFT calculations demonstrated that the addition of Cs reduced the adsorption energy of oxygen and the electron numbers around oxygen adsorbed on Ag(111) surface, but increased the length of Ag-O bond. The low electron density of adsorbed oxygen on Cs-Ag(111) easily reacted with the C=C bond in ethylene to form OMC intermediate, which means that the activation energy for OMC formation decreased on the surface of Cs-Ag(111). The activation energies for OMC transforming to EO and AA were 0.72 and 0.73 eV on Ag(111) surface, while that on Cs-Ag(111) were 0.57 and 0.78 eV, respectively. The lower activation energy to produce EO and the higher energy to form AA that resulted in the enhancing selectivity to EO.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2017.08.007.

References

[1] Ethylene Oxide (EO) (Complete Report), in, A Global Strategic Business Report Global Industry Analysts Inc., 2011, pp. 346.
[2] X. Jing, J. Huang, H. Wang, M. Du, D. Sun, Q. Li, Preparation of Ag/α-Al2O3 for ethylene epoxidation by an impregnation-bioreduction process with Cinnamomum camphora extract, Chem. Eng. J. 284 (2016) 149–157.
[3] T.E. Lefort, Process for the production of ethylene oxide, 729952, 1931.
[4] W.J. Diao, C.D. DiGiulio, M.T. Schaal, S.G. Ma, J.R. Monnier, An investigation on the role of Re as a promoter in Ag-Cs-Re/α-Al2O3 high-selectivity, ethylene epoxidation catalysts, J. Catal. 322 (2015) 14–23.
[5] H. Takada, M. Shima, Silver catalyst for production of ethylene oxide, method for production thereof, and method for production of ethylene oxide, 01669834, 2000.
[6] M.O. Ozbek, I. Onal, R.A. Van Santen, Why silver is the unique catalyst for ethylene epoxidation, J. Catal. 284 (2011) 230–235.
[7] J.C. Dellamorte, J. Lauterbach, M.A. Barteau, Effect of preparation conditions on Ag catalysts for ethylene epoxidation, Top. Catal. 53 (2010) 13–18.
[8] S. Anandhakumar, M. Sasidharan, C.W. Tsao, A.M. Raichur, Tailor-made hollow silver nanoparticle cages assembled with silver nanoparticles: an efficient catalyst for epoxidation, ACS Appl. Mat. Interfaces 6 (2014) 3275–3281.
[9] Matusz, Marek, Epoxidation catalyst, a process for preparing the catalyst, and a process for the production of an olefin oxide, US9018126, 2011.
[10] M. Rosendahl, D. Tobias, L. Torsten, K. Cornelia, W. Andreas Johanna, Process for producing a supported silver catalyst, US9, 199, 223, 2015.
[11] R. Matusz, L. Marek, Michael Alan, B. John Robert, Silver-containing catalysts, the manufacture of such silver-containing catalysts, and the use thereof, US7259129, 2004.
[12] S.A. Tan, R.B. Grant, R.M. Lambert, Secondary chemistry in the selective oxidation of ethylene effect of Cl and Cs promoters on the adsorption,

Cs-Ag(111) (0.21 eV) than that on Ag(111) surface (0.01 eV), which implies a higher selectivity to EO [6,22].

In addition, as shown in Table 2, the adsorption strength of EO on Cs-Ag(111) surface (-0.24 eV) is weaker than that on Ag(111) surface (-0.46 eV), indicating that the addition of promoter Cs promotes the desorption adsorbed EO to free EO and further increases the selectivity toward EO.

The DFT calculations demonstrate that Cs-promotor can weaken the adsorption strength of atomic oxygen, which is shown to be in good agreement with experimental observations of O$_2$-TPD. Weakly adsorbed atomic oxygen attributes to the introduction of Cs, which lowers the activation energy to form OMC and EO, meanwhile increases the barrier toward acetaldehyde (AA). Besides, XPS analyses show that Cs shifts the Ag $3d_{5/2}$ binding energy to facilitate desorption of the EO precursor to form gas EO, which is also consistent with DFT results that Cs decreases the adsorption energy of EO. Therefore, our combined experimental and computational studies uncover the origin of enhanced ethylene oxide selectivity on Cs-promoted Ag catalyst.

4. Conclusions

In this paper, the role of Cs as a promoter for ethylene epoxidation on Ag catalyst is studied by both experiments conducted under industrial conditions as well as density functional theory (DFT) calculations. Ag/α-Al$_2$O$_3$ and Ag-Cs/α-Al$_2$O$_3$ catalyst were prepared by excessive impregnation and evaluated for ethylene epoxidation to determine the mechanism of selectivity enhancement for Ag catalysts which contain Cs. The addition of Cs has a negative

isomerisation, and combustion of ethylene oxide on Ag(111), J. Catal. 106 (1987) 54–64.

[13] W.S. Epling, Gar B. Hoflund, D.M. Minahany, Study of Cs-promoted, α-alumina-supported silver, ethylene-epoxidation catalysts IV. model study, J. Catal. 171 (1997) 490–497.

[14] M.C.N. Amorim de Carvalho, F.B. Passos, M. Schmal, Study of the active phase of silver catalysts for ethylene epoxidation, J. Catal. 248 (2007) 124–129.

[15] David M. Minahan, Gar B. Hoflund, William S. Epling, D. Schoenfeld, Study of Cs-promoted, α-alumina-supported silver, ethylene epoxidation catalysts III. Characterization of Cs-Promoted and nonpromoted catalysts, J. Catal. 168 (1997) 393–399.

[16] S. Linic, M.A. Barteau, Formation of a stable surface oxametallacycle that produces ethylene oxide, J. Am. Chem. Soc. 124 (2002) 310–317.

[17] S. Linic, M.A. Barteau, Construction of a reaction coordinate and a microkinetic model for ethylene epoxidation on silver from DFT calculations and surface science experiments, J. Catal. 214 (2003) 200–212.

[18] S. Linic, M.A. Barteau, Control of ethylene epoxidation selectivity by surface oxametallacycles, J. Am. Chem. Soc. 125 (2003) 4034–4035.

[19] Vasilii I. Avdeev, G.M. Zhidomirov, Ethylene and oxygen species adsorbed on a defect oxidized surface Ag(1 1 1)- theoretical analysis by DFT method, Surf. sci. 492 (2001) 137–151.

[20] M.G. White, Heterogeneous Catalysis, Prentice Hall, New Jersey, 1990.

[21] C. Saravanan, M.R. Salazar, J.D. Kress, A. Redondo, Oxametallacycle intermediates on clean and Cs-promoted Ag(111) surfaces, J. Phys. Chem. B 104 (2000) 8685–8691.

[22] S. Linic, M.A. Barteau, On the mechanism of Cs promotion in ethylene epoxidation on Ag, J. Am. Chem. Soc. 126 (2004) 8086–8087.

[23] M.O. Ozbek, I. Onal, R.A. van Santen, Chlorine and cesium promotion of silver ethylene epoxidation catalysts, ChemCatChem 5 (2013) 443–451.

[24] N.L. Nguyen, S. Piccinin, S. De Gironcoli, Stability of intermediate states for ethylene epoxidation on Ag-Cu alloy catalyst: a first-principles investigation, J. Phys. Chem. C 115 (2011) 10073–10079.

[25] P. Christopher, S. Linic, Shape- and size-specific chemistry of Ag nanostructures in catalytic ethylene epoxidation, ChemCatChem 2 (2010) 78–83.

[26] T.C.R. Rocha, M. Hävecker, A. Knop-Gericke, R. Schlögl, Promoters in heterogeneous catalysis: the role of Cl on ethylene epoxidation over Ag, J. Catal. 312 (2014) 12–16.

[27] K.L. Yeung, A. Gavriilidis, A. Varma, M.M. Bhasiny, Effects of 1,2 dichloroethane addition on the optimal silver catalyst distribution in pellets for epoxidation of ethylene, J. Catal. 174 (1998) 1–12.

[28] Z.X. Zhang, J.Q. Jin, Z. Gao, Silver catalyst for epoxy ethane production, its preparation method and application, CN1426836A, 2003-07-02.

[29] A. Ayame, Y. Uchida, H. Ono, M. Miyamoto, T. Sato, H. Hayasaka, Epoxidation of ethylene over silver catalysts supported on α-alumina crystal carriers, Appl. Catal. A-Gen. 244 (2003) 59–70.

[30] C.T. Campbell, Cs-promoted Ag(11 1) model studies of selective ethylene oxidation catalysts, J. Phys. Chem. 89 (1985) 5189–5195.

[31] J.T. Jankowiak, M.A. Barteau, Ethylene epoxidation over silver and copper-silver bimetallic catalysts: II. Cs and Cl promotion, J. Catal. 236 (2005) 379–386.

[32] W.S. Epling, Gar B. Hoflund, D.M. Minahany, Study of Cs-promoted, α-alumina-supported silver, ethylene-epoxidation catalysts. IV model study, J. Catal. 171 (1997) 490–497.

[33] S.S. Hassani, M.R. Ghasemi, M. Rashidzadeh, Z. Sobat, Nano-sized silver crystals and their dispersion over alpha-alumina for ethylene epoxidation, Cryst. Res. Technol. 44 (2009) 948–952.

[34] S.N. Goncharova, E.A. Paukshtis, B.S. Bal'zhinimaev, Size effects in ethylene oxidation on silver catalysts. Influence of support and Cs promoter, Appl. Catal. A-Gen. 126 (1995) 67–84.

[35] V.I. Bukhtiyarov, M. Havecker, V.V. Kaichev, A. Knop-Gericke, R.W. Mayer, R. Schlogl, Atomic oxygen species on silver: photoelectron spectroscopy and x-ray absorption studies, Phys. Rev. B 67 (2003).

[36] J. Couves, M. Atkins, M. Hague, B.H. Sakakini, K.C. Waughc, The activity and selectivity of oxygen atoms adsorbed on a Ag/α-Al2O3 catalyst in ethene epoxidation, Catal. Lett. 99 (2005) 45–53.

[37] John R. Monnier, Jerome L. Stavinoha Jr., R.L. Minga, Stability and distribution of cesium in Cs-promoted silver catalysts used for butadiene epoxidation, J. Catal. 226 (2004) 401–409.

[38] M.O. Ozbek, I. Onal, R.A. Van Santen, Effect of surface and oxygen coverage on ethylene epoxidation, Top. Catal. 55 (2012) 710–717.

[39] A.I. Boronin, S.V. Koscheev, G.M. Zhidomirov, XPS and UPS study of oxygen states on silver, J. Electron. Spectrosc. Relat. Phenom. 96 (1998) 43–51.

[40] A. Ayame, S. Eimaeda, L. Feng, H. Hayasaka, Oxygen adsorption on silver catalysts during the course of partial oxidation of ethylene, Appl. Catal. A-Gen. 304 (2006) 93–108.

[41] M.L. Bocquet, D. Loffreda, Ethene epoxidation selectivity inhibited by twisted oxametallacycle: a DFT study on Ag surface-oxide, J. Am. Chem. Soc. 127 (2005) 17207–17215.

[42] P. Christopher, S. Linic, Engineering selectivity in heterogeneous catalysis: Ag nanowires as selective ethylene epoxidation catalysts, J. Am. Chem. Soc. 130 (2008) 11264–11265.