

Preparation of Ag/ α -Al₂O₃ for ethylene epoxidation by an impregnation–bioreduction process with *Cinnamomum camphora* extract

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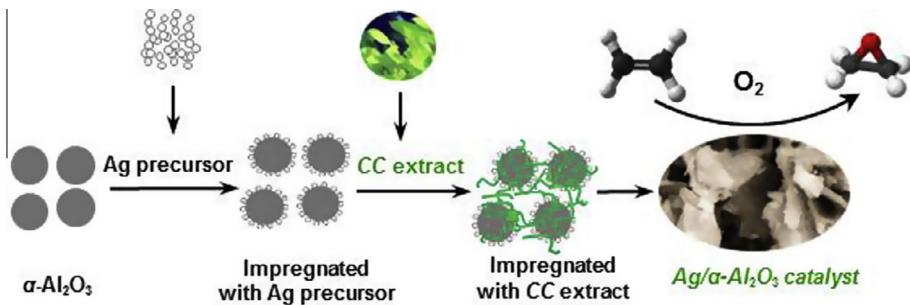
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HIGHLIGHTS

- Impregnation–bioreduction method was used to prepare the supported Ag catalyst.
- Influence of bioreduction temperature, concentration of CC extract, silver loading amount, calcination temperature and Cs addition on catalytic performance were investigated.
- The optimized catalyst 15Ag/ α -Al₂O₃-15Cs gave the EO concentrations of 1.70%, EO selectivity of 87.46% and EO STY of 223.07 g h⁻¹ L⁻¹_{cat} at 200 °C.
- The as-synthesized Ag catalyst exhibited high catalytic stability during 50 h.

GRAPHICAL ABSTRACT



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ABSTRACT

Supported Ag catalyst for ethylene epoxidation was prepared by an impregnation–bioreduction process with *Cinnamomum camphora* (CC) extract. Influence of bioreduction temperature, concentration of CC extract, silver loading amount, calcination temperature as well as Cs promoter on catalytic performance were thoroughly investigated and the catalysts were characterized. The results showed that the catalyst prepared from bioreduction process exhibited excellent performance for the ethylene epoxidation with O₂. Proper amount of Cs addition could effectively improve the catalytic performance of the catalyst. The optimal catalyst 15Ag/ α -Al₂O₃-15Cs gave the EO concentrations of 1.70%, EO selectivity of 87.46% and EO STY of 223.07 g h⁻¹ L⁻¹_{cat} at 200 °C, showing high catalytic stability with no significant decrease in the activity and the selectivity during 50 h.

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1. Introduction

As the most utilized epoxide species, ethylene oxide (EO) is an important raw material in chemical manufacturing process and accounting for approximately 40–50% of the total value of organic

chemicals [1–5]. Since the discovery of the Lefort process in 1931 [6], direct oxidation of ethylene to EO with molecular oxygen in the presence of supported Ag catalysts has emerged as the main route for EO production. To date, Ag is still the most active component for ethylene epoxidation. The increase of the EO selectivity by only 1% leads to considerable profit [7]. Hence, research and development of more efficient Ag catalyst are of great significance [8,9].

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Impregnation is the most widely used method for the preparation of supported Ag catalyst. Based on the conventional impregnation, extensive research has devoted to four main aspects: (i) Ag precursor or the impregnating solution, (ii) impregnating process, (iii) thermal treatment process of the catalyst and (iv) promoters. Silver salts include inorganic and organic salts, are used as the precursors [10–17]. Impregnating temperature, time and composition of impregnating solution would affect the activity of the catalyst. Calcination temperature and time could also influence the performance of the Ag catalyst. For example, high catalytic performance for ethylene epoxidation was achieved over the supported Ag catalyst obtained by a multi-stage calcination process with controlling atmosphere [18]. Besides, addition of promoters such as Cs, Cl, Cu, Cd, Pt, Re and other alkali metals, could further enhance the performance to some extent [12,19–22].

As a newly developed method, biosynthesis of metal nanoparticles has received increasing attention in the last decade [23,24]. Biosynthesis of metal nanoparticles by both plants and microorganisms could be used for the preparation of catalysts. In contrast with the elaborate cell cultivation, plant-mediated strategy appears to be a simple and viable method for the preparation of efficient catalyst [25–32]. For example, Ma et al. [25] prepared supported Ru catalyst with *Cacumen platycladi* (CP) extract and find the biosynthesized Ru-based catalysts showed excellent performance in hydrogenation of maleic anhydride. Ag/TiO₂ and Au/TiO₂ is prepared by using the extracts from the vascular plant *Citrus limon*, which exhibited great photo degradation effect for an organic dye [26]. Both AgAu/SiO₂–Al₂O₃ and Au/SiO₂–Al₂O₃ were obtained with *Camellia sinensis* plant extract, and the former showed better behavior for CO oxidation process, while the latter show much better performance in the CO hydrogenation process [27]. Zhan and Du et al. [28–30] prepared Au/TS-1 catalysts by using CP extract, which exhibited both good performance and stability for propylene epoxidation in vapor phase under H₂/O₂. Biosynthesized Au/TS-1 using CP extract also show excellent catalytic activity for the liquid phase epoxidation of styrene with aqueous H₂O₂ [31]. By using CP extract, bimetallic Au–Pd/TiO₂ catalysts is prepared and show excellent durability and reusability for solvent-free oxidation of benzyl alcohol to benzaldehyde with molar oxygen [32].

In our previous work, thermal decomposition with the assistance of *Cinnamomum camphora* (CC) extract was adopted to prepare active Ag/α-Al₂O₃ catalyst for ethylene epoxidation [16]. And the results show that the sintering and aggregation of Ag particles and Ag loss during the reaction were alleviated. Furthermore, comparative studies indicated that Ag catalyst prepared with silver–ethylenediamine complex performed higher catalytic activity than those with silver nitrate and silver–ammonia complex [15]. As a continuation of our previous work [15,16], a simple and convenient impregnation–bioreduction (IMP–BR) method shown in Scheme 1 is used to prepare the Ag/α-Al₂O₃ catalyst with CC

extract in this study. We concentrated on optimizing the preparation process of the Ag/α-Al₂O₃ catalysts by the IMP–BR method and developing catalytic application of the obtained catalysts for ethylene epoxidation. Influence of biomass concentration, bioreduction temperature, calcination temperature, Ag loading amount on the ethylene epoxidation was thoroughly investigated. And the addition of Cs promoter also was researched. Besides, comparative study was carried out between the optimized catalyst and industrial catalyst and the stability of the Ag/α-Al₂O₃ catalyst was tested.

2. Experimental section

2.1. Materials and chemicals

C. camphora (CC) leaves were picked up at Xiamen University. The dried CC leaves was milled to a 20-mesh powder for use. α-Al₂O₃ were purchased from Tianjin Chemical Research & Design Institute. The commercial α-Al₂O₃ was ground into a 20–40 mesh powder and calcined at 600 °C for 6 h. Other regents used in this work were bought from Aladdin Reagents (Shanghai).

2.2. Preparation of CC extract

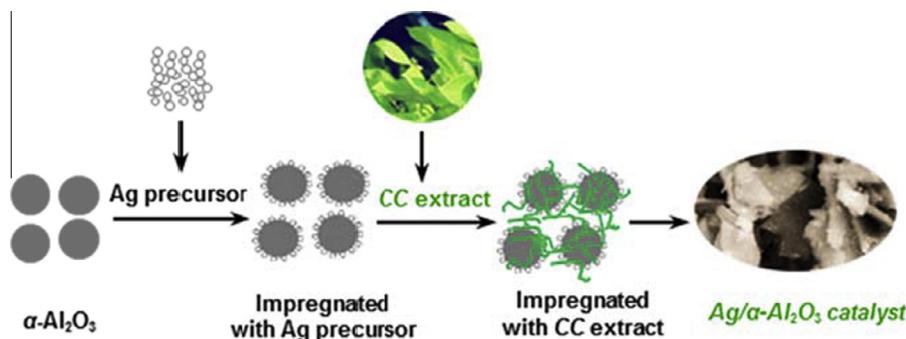
15 g CC biomass was added to 100 mL deionized water, and after 5 min boiling, the solution was filtered and transferred to a volumetric flask, diluted with deionized water to 100 mL. The concentration of this CC extract was denoted as 15 g/L, and other concentrations of CC extract were prepared as described previously by adjusting the dosage of CC biomass.

2.3. Preparation of silver–ethylenediamine complex

Silver–ethylenediamine complex was prepared from AgNO₃. First, 1.1575 g AgNO₃ was dissolved in 3.9 mL deionized water and 0.5249 g ammonium oxalate was dissolved in 7.1 mL deionized water, then mixed the above two solutions and a white precipitate was generated. The precipitate was filtered, washed and then dried under vacuum at room temperature. After that, the obtained precipitate was dissolved in 5 mL ethylenediamine–water solution (1:1, v/v) to get the silver–ethylenediamine complex solution for next use.

2.4. Preparation of Ag/Al₂O₃ catalysts

The catalyst was prepared by an impregnation–bioreduction process, as shown in Scheme 1. 1.0 g α-Al₂O₃ support was impregnated with a certain amount of silver–ethylenediamine complex solution, and dried at 50 °C for 12 h in vacuum. Then the obtained solid was dipping with CC extract in an iso-volumetric way for 24 h at indicated temperature, dried at 50 °C for 24 h in vacuum and cal-



Scheme 1. Schematic description of preparing supported Ag catalyst by an IMP–BR method with *Cinnamomum camphora* (CC) extract.

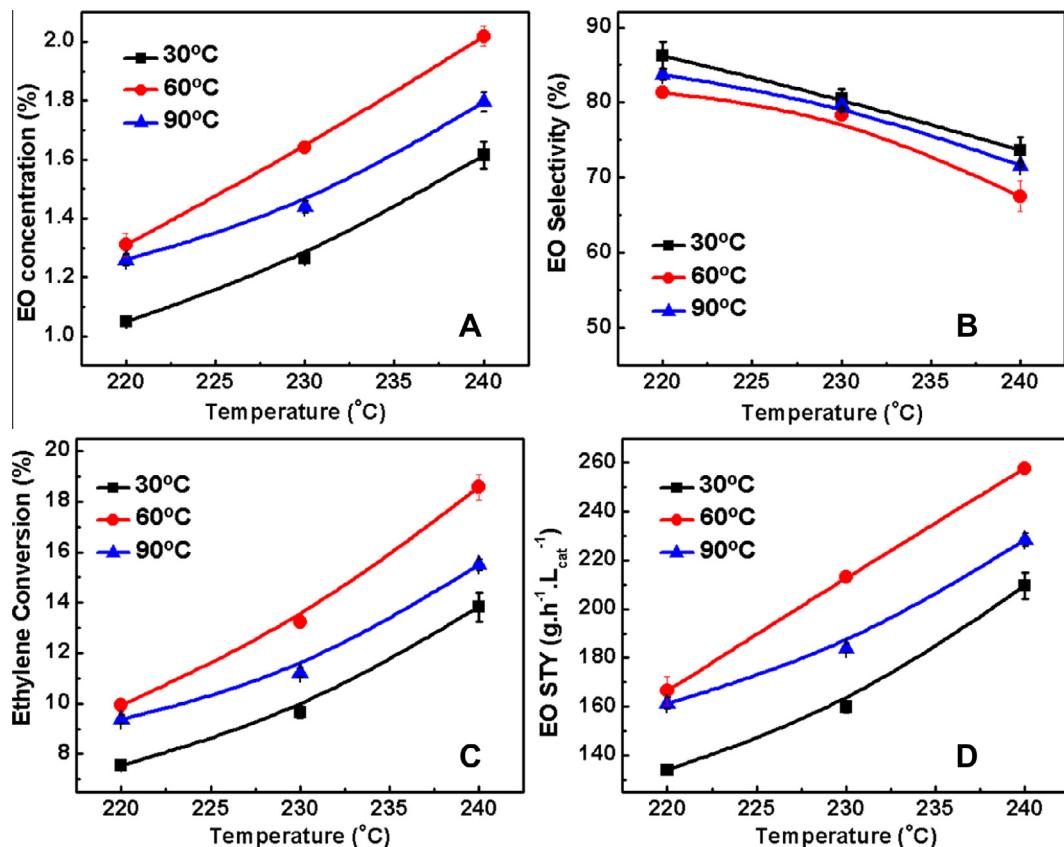


Fig. 1. Epoxidation of ethylene over $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ prepared with different bioreduction temperatures. (Reaction conditions: feed gas $V(\text{C}_2\text{H}_4):V(\text{O}_2):V(\text{CO}_2):V(\text{N}_2) = 15:7:5:73$, reaction pressure = 2 MPa, GHSV = 7000 $\text{mL h}^{-1} \text{mL}_{\text{cat}}^{-1}$).

cined in N_2 at required temperature. For the Cs-promoted catalysts, the $\alpha\text{-Al}_2\text{O}_3$ support was treated with cesium nitrate solution at room temperature, and dried in vacuum. The Cs-treated $\alpha\text{-Al}_2\text{O}_3$ support was used to prepare the catalyst in the same procedure as mentioned above. The catalysts with different Cs contents can be obtained by treating $\alpha\text{-Al}_2\text{O}_3$ with different concentration of cesium nitrate solution. The obtained Ag catalysts are denoted as $x\text{Ag}/\alpha\text{-Al}_2\text{O}_3\text{-yCs-z}$, where x is the calculated weight percent of Ag in the catalysts, y is the Cs contents in the catalysts, and z is the calcination temperature.

2.5. Characterization of the catalysts

Scanning electron microscopy (SEM) images of the samples were taken on a Hitachi S-4800 microscope. Size distribution of the resulting Ag NPs was estimated through the previous method [31]. X-ray powder diffraction (XRD) experiments were conducted on a Panalytical X'pert PRO diffractometer (PANalytical BV, Netherlands) with monochromatized CuK α radiation at a voltage of 40 kV and a current of 30 mA. For O_2 -TPD measurements, the sample was pretreated under an He flow of 30 mL/min at 250 °C for 1 h, then cooled to 170 °C and switching O_2 (30 mL/min) to the sample. After 1 h in O_2 , the sample was cooled to room temperature and He (30 mL/min) was used to remove O_2 in gas phase. O_2 desorption process was recorded in the He flow by raising the temperature at a rate of 10 °C min $^{-1}$.

2.6. Catalytic activity tests

The catalytic tests were carried out in a vertical fixed-bed stainless-steel reactor. The gas feed composition was 15% C_2H_4

(99.999%), 7% O_2 (99.999%), 5% CO_2 (99.999%) and balanced with N_2 (99.999%) at 2 MPa total pressure. 0.5 mL catalyst was loaded into the reactor and the space velocity was 7000 $\text{mL h}^{-1} \text{mL}_{\text{cat}}^{-1}$. The reaction products were analyzed online by a gas chromatograph equipped with a thermal conductivity detector (TCD), using a Porapak Q packed column (2 mm × 3 m), and a flame ionization detector (FID), using a $\beta\text{-}\beta\text{-oxydipropionitrile}$ packed column (2 mm × 1.5 m).

3. Results and discussion

3.1. Influence of bioreduction temperature

The influence of bioreduction temperature on the catalytic performance of the $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts was investigated. Different catalysts were prepared by reducing the silver-ethylenediamine complex impregnated on $\alpha\text{-Al}_2\text{O}_3$ support at 30, 60 and 90 °C, respectively. And the catalytic performance of ethylene epoxidation over $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ with different bioreduction temperatures is shown in Fig. 1. As shown in Fig. 1, when the bioreduction temperature is 30 °C, EO concentration increases from 1.05 to 1.61% with the catalytic reaction temperature changing from 220 to 240 °C. When the bioreduction was conducted at 60 °C, 2.02% of EO concentration was achieved at 240 °C. As 90 °C is chosen for preparation, the performance of the corresponding catalyst decreased slightly compared to that prepared at 60 °C. The catalyst prepared at 30 °C exhibited the highest selectivity (Fig. 1B), while considering EO concentration, 60 °C was the optimal bioreduction temperature to achieve the highest EO yield (Fig. 1D).

XRD is used to characterize the $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ prepared at different bioreduction temperatures in Fig. 2. Curve a in Fig. 2 shows the

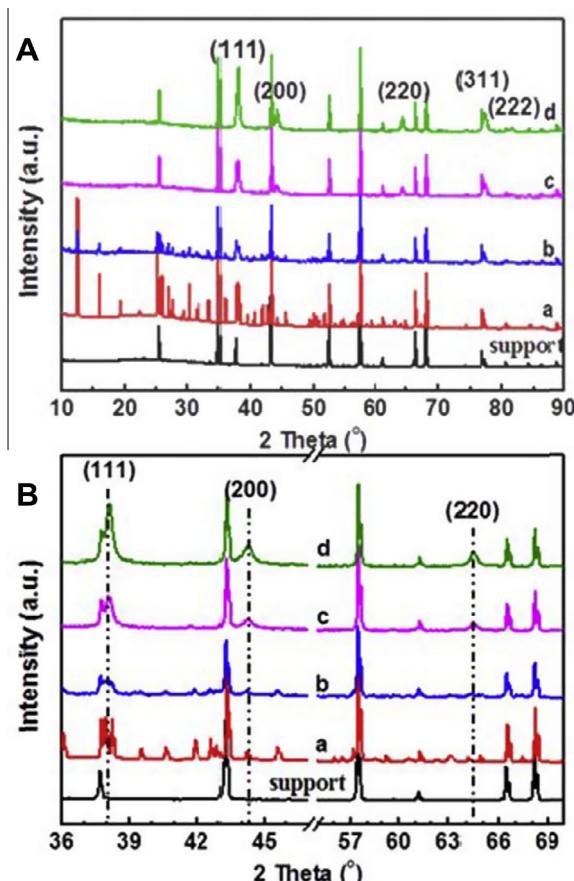


Fig. 2. XRD patterns of $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ prepared with different bioreduction temperatures. (a) without bioreduction; (b) 30 °C; (c) 60 °C; (d) 90 °C.

diffraction peaks of the silver–ethylenediamine complex impregnated on $\alpha\text{-Al}_2\text{O}_3$ support without further bioreduction and a series of peaks related to the Ag precursor appeared comparing to the $\alpha\text{-Al}_2\text{O}_3$ support. With increasing bioreduction temperature, XRD peaks related to the Ag precursor decreased while peaks assignable to metallic Ag became stronger. Peaks related to the Ag precursor completely disappeared when the bioreduction was carried out at 60 °C and only peaks attributed to metallic Ag was detected on the support. Further increasing the bioreduction temperature to 90 °C, the Ag peaks became sharper, suggesting the formation of larger Ag particles.

FTIR spectroscopy was used to analyze the $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ prepared at different bioreduction temperatures. As shown in Fig. 3, after impregnated with Ag precursor, new bands at 3317, 3263, 1615, 1309, 1000 and 770 cm^{-1} arose comparing with the IR spectrum of the $\alpha\text{-Al}_2\text{O}_3$ support. Among the bands, those at 3317 cm^{-1} and 3263 cm^{-1} can be assigned to the stretching vibration of N–H. And the band at 1615 cm^{-1} can be attributed to the scissoring vibration of NH₂ while that at 1309 cm^{-1} can be assigned to the vibration of CH₂. In addition, the bands at 770 and 1000 cm^{-1} can be assignable to the stretching vibration of Ag–C after Ag complexing with organic ligand. By reducing the Ag precursor at 30 °C (curve b in Fig. 3), the above-mentioned peaks were weak. However, if further increasing the bioreduction temperature to 60 or 90 °C, the bands related to the Ag precursors disappeared. From the above results, it can be concluded that the bioreduction of Ag precursors was influenced by the temperature and 60 °C was the optimal bioreduction temperature, which was selected for the catalyst preparation.

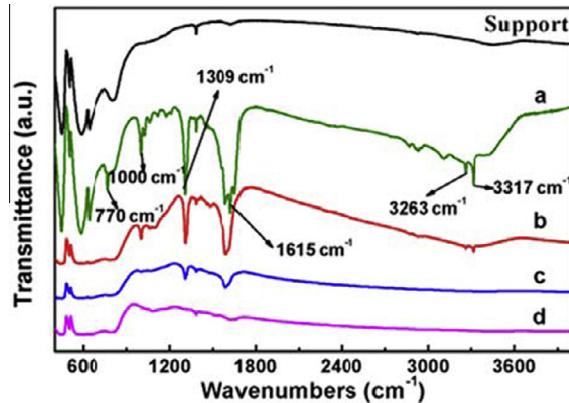


Fig. 3. FTIR spectra of $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ prepared with different bioreduction temperatures. (a) without bioreduction; (b) 30 °C; (c) 60 °C; (d) 90 °C.

3.2. Influence of CC extract concentration

The influence of CC extract concentration on the catalytic performance of $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts with Ag loading of 15% was studied. All the catalysts shown in Table 1 are prepared at 60 °C with 15 wt.% Ag loading and calcined at 600 °C for 1 h in N₂. In the absence of biomass, only 0.63% EO concentration and 20.67% EO selectivity were obtained at higher reaction temperature, i.e. 250 °C. It can be seen that not only the EO concentration and selectivity were significantly enhanced, but also the initiation temperature effectively decreased by using CC extract. With the increase of the CC extract concentration from 0.01 to 0.15 g·mL⁻¹, the corresponding initiation temperature decreased from 240 °C to 200 °C. However, it increased a little with further increasing the CC extract concentration. The lowest initiation temperature 200 °C was found on the catalysts prepared with 0.10 and 0.15 g·mL⁻¹ CC extract. And much better catalytic activity was obtained at 0.15 g·mL⁻¹. When the biomass concentration was higher than 0.15 g·mL⁻¹, the epoxidation performance exhibited a downward trend. EO concentration was an important index in practical industrial process.

Table 1
Effect of concentration of CC extract on ethylene epoxidation over $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts.

CC concentration (g·mL ⁻¹)	Reaction temperature (°C)	EO concentration (%)	EO selectivity (%)	EO space time yield (g h ⁻¹ L _{cat} ⁻¹)
0	250	0.63 ± 0.09	20.67 ± 2.19	43.77 ± 9.73
0.01	240	1.00 ± 0.07	86.73 ± 2.39	140.71 ± 8.77
	260	1.24 ± 0.04	73.71 ± 0.33	171.95 ± 5.09
0.05	220	0.94 ± 0.02	92.13 ± 1.13	122.85 ± 2.69
	240	0.97 ± 0.02	88.91 ± 3.59	125.33 ± 2.64
	250	1.28 ± 0.01	79.60 ± 0.16	165.94 ± 0.87
0.10	200	0.90 ± 0.02	94.04 ± 1.45	116.23 ± 3.14
	210	1.00 ± 0.01	91.85 ± 0.89	130.14 ± 2.30
	220	1.11 ± 0.01	87.76 ± 2.47	142.91 ± 2.22
	230	1.28 ± 0.02	85.35 ± 0.61	163.09 ± 1.03
0.15	200	1.02 ± 0.00	88.67 ± 0.44	134.51 ± 0.54
	210	1.25 ± 0.01	85.31 ± 0.74	165.42 ± 0.22
	220	1.68 ± 0.01	79.63 ± 0.31	221.12 ± 3.50
0.20	210	0.92 ± 0.01	97.43 ± 0.85	118.75 ± 1.74
	220	0.99 ± 0.01	94.33 ± 0.44	126.09 ± 2.63
	230	1.11 ± 0.01	93.48 ± 1.00	146.38 ± 1.53
	240	1.19 ± 0.03	88.11 ± 1.02	153.01 ± 1.16
0.25	210	0.89 ± 0.01	95.14 ± 1.43	114.60 ± 1.57
	220	1.00 ± 0.01	93.24 ± 0.21	130.94 ± 0.62
	230	1.13 ± 0.01	88.67 ± 2.52	146.21 ± 2.17
	240	1.18 ± 0.01	87.27 ± 2.90	153.91 ± 2.83

Reaction conditions: feed gas $V(\text{C}_2\text{H}_4):V(\text{O}_2):V(\text{CO}_2):V(\text{N}_2) = 15:7:5:73$, reaction pressure = 2 MPa, GHSV = 7000 ml h⁻¹ mL_{cat}⁻¹.

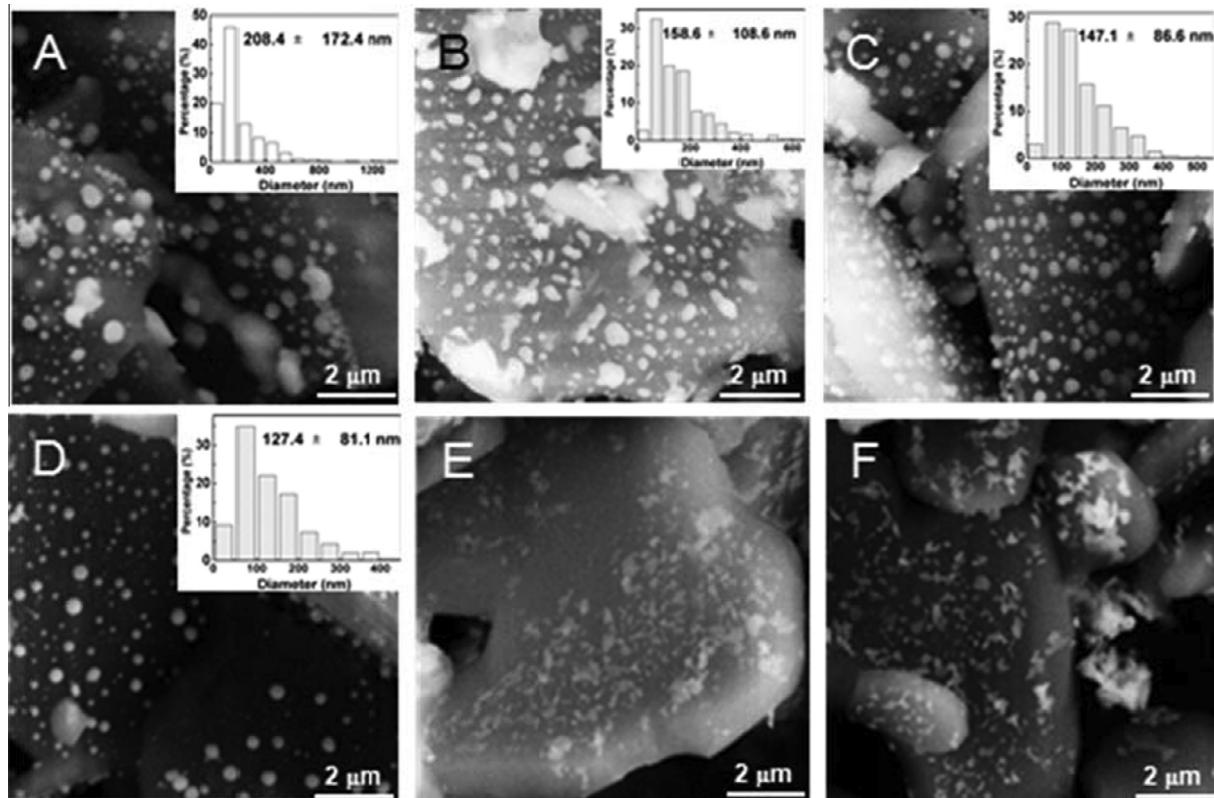


Fig. 4. SEM images and size distributions (insets) of $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ prepared with different concentrations of CC extract: (A) 0, (B) 0.05, (C) 0.10, (D) 0.15, (E) 0.20, (F) 0.25 g mL^{-1} .

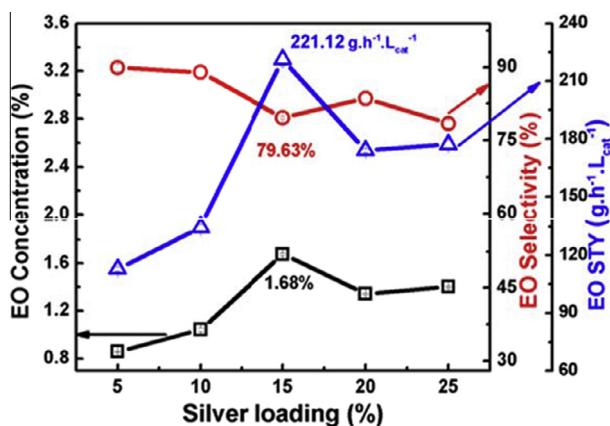


Fig. 5. Epoxidation of ethylene over $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts with different silver loadings at 220°C .

The highest EO concentration (1.68%) was achieved at 220°C , giving rise to the highest EO space time yield (STY) of $221.12 \text{ g.h}^{-1}\text{L}^{-1}\text{cat}^{-1}$.

SEM is used to further characterize the catalysts prepared from different CC extract concentration. As shown in Fig. 4, when no CC extract is used, large AgNPs with mean diameter of $208.4 \pm 172.4 \text{ nm}$ are observed (Fig. 4A). After CC extract was introduced, size of the AgNPs on the support decreased. When 0.15 g.mL^{-1} CC extract was used, it was found that spherical AgNPs with mean diameter of $127.4 \pm 81.1 \text{ nm}$ were well dispersed on the support (Fig. 4D). While, when 0.20 (Fig. 4E) and 0.25 g.mL^{-1} (Fig. 4F) CC extract were used, thin sheets with obvious agglomeration instead of spherical AgNPs were obtained on the support. Therefore, CC extract concentrations in the catalyst preparation

process were closely associated with the morphology and size of AgNPs on the support. And 0.15 g.mL^{-1} was the optimal concentration for the catalyst preparation.

3.3. Influence of silver loading

Epoxidation of ethylene over $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalysts with different silver loadings at 220°C is shown in Fig. 5. For the catalysts with 5 Ag and 10% loading, higher EO selectivity than 85% was achieved, while the EO concentrations on both are lower than 1.2%. The EO concentration increases as the increasing of Ag loading till it reached around 15% and then decreased as the further increase of Ag loading. As shown in Fig. 5, 15Ag/ $\alpha\text{-Al}_2\text{O}_3$ exhibiting the best catalytic performance. With a lower Ag loading, the concentration of active center might be insufficient, leading to the low catalytic activity. While excessive Ag loading might give rise to the sintering of AgNPs, which also led to the decrease of catalytic performance. SEM images in Fig. S1 (Supplementary information, SI) show that obvious agglomeration occurred on the catalysts with 20% and 25% Ag loading.

3.4. Influence of calcining temperature

As a common but important procedure in catalyst preparation, calcination can be adopted to improve the catalyst performance by enhancing the interaction between metal and support. For the biosynthesized catalyst, calcination was an essential way to expose the reactive center by removing the residual biomolecule on the catalyst. And it was found that the residual biomolecules on the metal NPs can prevent them from sintering or agglomerating [16]. Influence of calcination temperature in N_2 atmosphere on ethylene epoxidation over $\text{Ag}/\alpha\text{-Al}_2\text{O}_3$ catalyst was investigated.

Table 2

Effect of calcination pretreatment temperature under N₂ on ethylene epoxidation over Ag/α-Al₂O₃ catalysts.

Calcination temperature (°C)	Reaction temperature (°C)	EO concentration (%)	EO selectivity (%)	EO space time yield (g h ⁻¹ L _{cat} ⁻¹)
Without calcination	230	0.72 ± 0.01	95.51 ± 1.73	100.21 ± 0.58
	240	0.82 ± 0.01	86.04 ± 0.32	112.55 ± 0.50
	250	1.41 ± 0.01	79.11 ± 0.71	195.63 ± 0.85
	260	2.22 ± 0.08	62.04 ± 1.82	300.35 ± 10.88
	200	0.81 ± 0.01	92.98 ± 2.12	105.98 ± 1.45
	210	0.89 ± 0.01	88.36 ± 0.37	115.67 ± 0.83
	220	1.04 ± 0.01	82.16 ± 1.06	135.18 ± 0.47
	230	1.27 ± 0.01	74.96 ± 0.19	164.74 ± 3.31
	240	1.60 ± 0.01	65.12 ± 0.79	205.34 ± 1.73
	200	0.75 ± 0.02	95.82 ± 1.25	99.00 ± 2.20
200	210	0.96 ± 0.01	86.42 ± 1.14	125.98 ± 1.74
	220	1.16 ± 0.03	84.22 ± 1.63	152.66 ± 4.29
	230	1.39 ± 0.01	80.28 ± 1.06	183.51 ± 0.94
	200	0.81 ± 0.02	96.60 ± 2.67	109.30 ± 2.62
	210	0.97 ± 0.01	89.12 ± 1.04	129.14 ± 2.01
300	220	1.17 ± 0.01	88.91 ± 1.32	159.56 ± 2.59
	230	1.41 ± 0.01	84.73 ± 0.22	194.09 ± 1.55
	200	0.86 ± 0.02	94.89 ± 2.36	114.02 ± 2.04
	210	0.98 ± 0.01	88.09 ± 0.87	129.83 ± 1.63
400	220	1.20 ± 0.02	85.48 ± 1.05	160.45 ± 3.24
	230	1.54 ± 0.03	80.75 ± 0.76	200.34 ± 2.58
	200	0.92 ± 0.01	93.24 ± 3.08	120.77 ± 2.43
	210	1.10 ± 0.01	88.58 ± 2.72	142.80 ± 2.83
500	220	1.43 ± 0.02	86.10 ± 1.52	187.77 ± 4.82
	230	1.87 ± 0.02	75.43 ± 1.41	241.85 ± 3.89
	200	0.78 ± 0.01	94.65 ± 1.42	103.48 ± 1.52
	210	0.85 ± 0.00	90.36 ± 0.36	112.78 ± 0.09
600	220	0.96 ± 0.02	84.16 ± 1.53	126.17 ± 2.35
	230	1.14 ± 0.01	78.56 ± 0.89	149.19 ± 0.77
	200	1.40 ± 0.01	70.16 ± 0.10	183.99 ± 0.73
	210	0.83 ± 0.02	82.37 ± 1.05	111.00 ± 2.91
700	220	0.91 ± 0.01	72.62 ± 0.78	123.90 ± 1.06
	230	1.01 ± 0.01	55.80 ± 1.45	136.37 ± 0.82
	200			

Reaction conditions: feed gas V(C₂H₄):V(O₂):V(CO₂):V(N₂) = 15:7:5:73, reaction pressure = 2 MPa, GHSV = 7000 ml h⁻¹ mL_{cat}⁻¹.

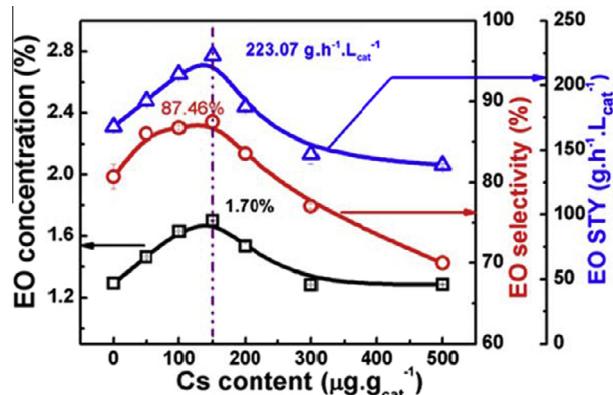


Fig. 6. Epoxidation of ethylene over Ag/α-Al₂O₃ catalysts with different Cs contents at 200 °C.

All catalysts in Table 2 were prepared at 60 °C, 0.15 g·mL⁻¹ CC extract and with 15 wt.% Ag loading. It can be seen that without calcination, the initiation temperature of the biosynthesized catalyst was 230 °C showing poor activity for the ethylene epoxidation. After calcination between 200–700 °C, the initiation temperature of the catalysts decreased to 200 °C. After calcination at 800 °C, the initiation temperature is up to 240 °C. These results indicate that the reaction temperature can be effectively lowered by appropriate calcination. Moreover, the catalytic performance was also influenced by the calcination temperature. For example, at the same reaction temperature of 220 °C, EO selectivity was close to or higher than 80% for the catalysts calcined at different temperatures (except 800 °C). The EO concentration at 220 °C increased

Table 3
Epoxidation of ethylene over biosynthesized Ag/α-Al₂O₃ catalysts and the industrial catalyst YS-7.

Catalyst	15Ag/αAl ₂ O ₃ -150Cs	YS-7
Reaction temperature (°C)	190	200
EO concentration (%)	1.37	1.34
EO selectivity (%)	89.61	80.60
EO space time yield (g h ⁻¹ L _{cat} ⁻¹)	180.42	166.24

Reaction conditions: feed gas V(C₂H₄):V(O₂):V(CO₂):V(N₂) = 15:7:5:73, reaction pressure = 2 MPa, GHSV = 7000 mL h⁻¹ mL_{cat}⁻¹.

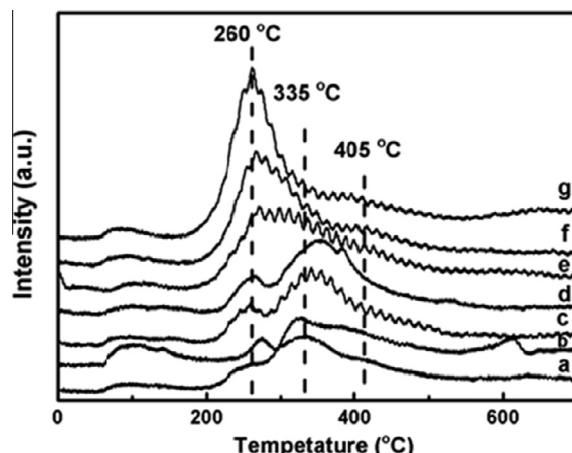


Fig. 7. O₂-TPD profiles of Ag/α-Al₂O₃ with different Cs contents; Cs content from (a) to (g) is 0, 50, 100, 150, 200, 300, 500 μg g_{cat}⁻¹, respectively.

from 1.04% to 1.68% with increasing calcination temperature from 200 to 400 °C, and then decreased to 0.96% at 700 °C. While no EO was detected for catalyst calcined at 800 °C at the reaction temperature of 220 °C. Therefore, the best calcination temperature was 600 °C.

3.5. Influence of Cs promoter

As the most common promoter, Cs plays an important role on EO selectivity in ethylene epoxidation [33]. In this work, Cs was introduced by impregnating the α -Al₂O₃ support with CsNO₃ prior to the bioreduction. The epoxidation performance of Ag/ α -Al₂O₃

catalysts with Ag loading of 15% and Cs contents of 0–500 $\mu\text{g g}_{\text{cat}}^{-1}$ was tested at 200 °C. The catalytic performance of these catalysts is presented in Fig. 6. It can be seen that both EO concentrations and EO selectivity increased with the Cs contents from 0 to 150 $\mu\text{g g}_{\text{cat}}^{-1}$, and then decreased with further increasing the Cs contents from 150 to 500 $\mu\text{g g}_{\text{cat}}^{-1}$. The catalyst 15Ag/ α -Al₂O₃-150Cs with Cs contents of 150 $\mu\text{g g}_{\text{cat}}^{-1}$ gave the highest EO concentrations of 1.70%, EO selectivity of 87.46% and EO space time yield (STY) of 223.07 $\text{g h}^{-1} \text{L}_{\text{cat}}^{-1}$. From the above discussion, it can be seen that the catalytic performance of Ag/ α -Al₂O₃ catalysts was strongly affected by Cs contents. Comparing with the catalyst 15Ag/ α -Al₂O₃-600 without Cs addition in Table 2, although the EO STY is similar, EO selectivity is 12% higher with comparable EO concentration on 15Ag/ α -Al₂O₃-150Cs. And more importantly, the reaction temperature decreased by 20 °C, which could greatly reduce energy consumption. Comparative study was carried out between the biosynthesized catalyst 15Ag/ α -Al₂O₃-150Cs and industrial catalyst YS-7 from Yanshan petrochemical company in the same reaction system. The catalytic performance of the two catalysts is presented in Table 3. At the same EO concentration of ~1.35%, 15Ag/ α -Al₂O₃-150Cs exhibited the EO selectivity of 89.61% which was 9% higher than that of YS-7 catalyst, and the reaction temperature was 9 °C lower than that of YS-7 catalyst. Therefore, the performance of the bioreduction catalyst 15Ag/ α -Al₂O₃-150Cs was superior to that of YS-7 catalyst.

O₂-TPD results of the Ag/ α -Al₂O₃ catalysts with different Cs contents are presented in Fig. 7. The nonpromoted catalyst had three peaks in the temperature of 200–500 °C. The peak at 260 °C was due to the desorption of nucleophilic oxygen species located in the regular silver surface [34], and the peak at 335 °C could be

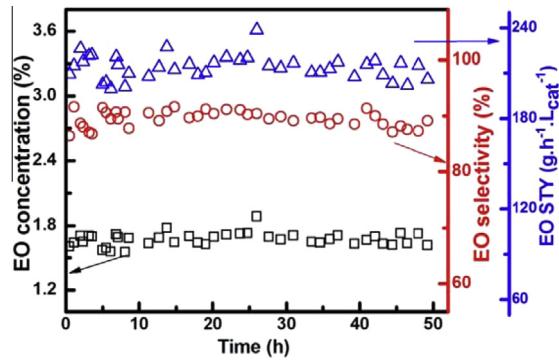


Fig. 8. Stability of 15Ag/ α -Al₂O₃-150Cs catalyst for ethylene epoxidation for 50 h at 200 °C; □ EO concentration (%); ○ EO selectivity (%); △ EO STY ($\text{g h}^{-1} \text{L}_{\text{cat}}^{-1}$).

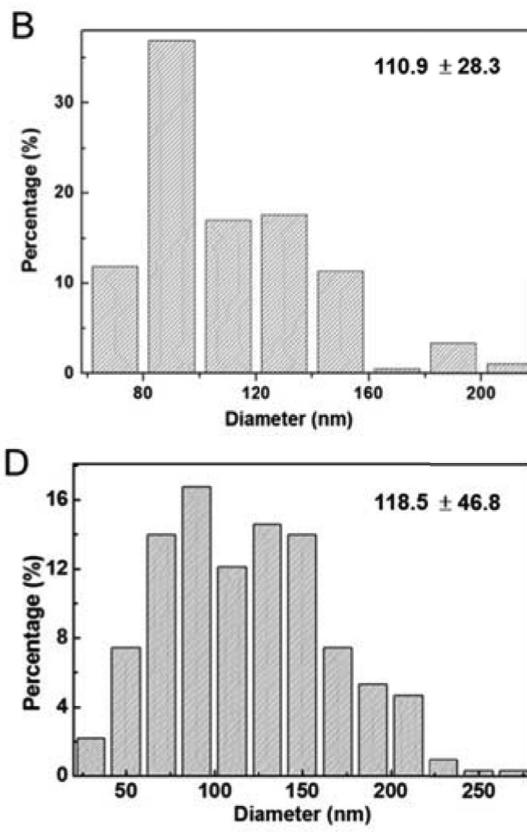
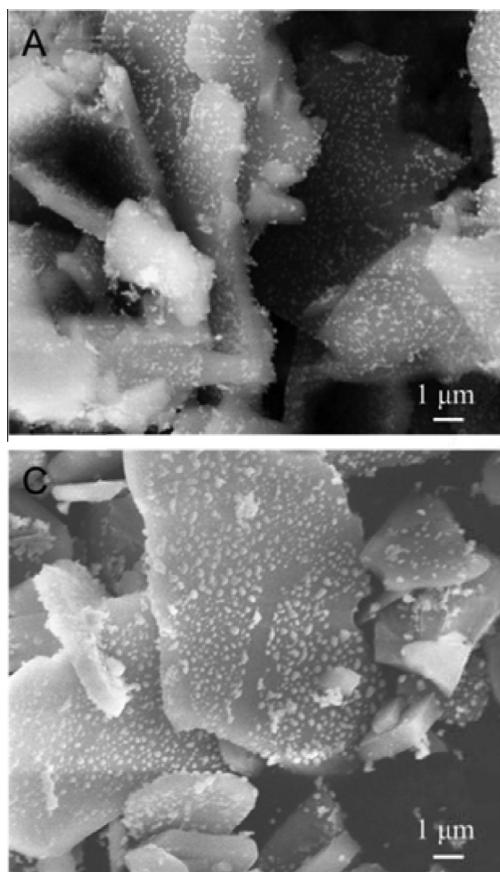


Fig. 9. SEM characterization of the optimum catalyst (15Ag/ α -Al₂O₃-150Cs) before (A) and after (C) the stability test. (B) and (D) is the corresponding size analysis of Ag nanoparticles on the catalysts.

attributed to the desorption of electrophilic oxygen species located in the silver crystalline defects where epoxidizing oxygen species are located [35]. The peak at 405 °C was associated with oxygen species from subsurface [12]. Increasing the Cs contents from 0 to 500 µg g_{cat}⁻¹, the peak at 260 °C was gradually enhanced, however, the peak at 335 °C increased firstly when the Cs contents increased from 0 to 150 µg g_{cat}⁻¹ and then decreased when the Cs contents were 200–500 µg g_{cat}⁻¹. When the Cs content was less than 150 µg g_{cat}⁻¹, Cs addition caused a significant increase in both the electrophilic oxygen species and nucleophilic oxygen species compared with the nonpromoted catalyst, and increased the electron density of adsorbed oxygen species, inhibiting EO ring-opening [36–40]. When the concentration of Cs was higher than 150 µg g_{cat}⁻¹, the catalytic performance of the Ag catalysts decreased. It is because that high concentration of nucleophilic oxygen species is unfavorable to ethylene epoxidation, resulting in complete ethylene oxidation [41–44].

3.6. Stability of the Cs promoted Ag/α-Al₂O₃ catalyst

The optimum catalyst (15Ag/α-Al₂O₃-150Cs) is used for a long-time reaction test to evaluate the stability of the catalyst prepared by the bioreduction method. As shown in Fig. 8, the specific activity on stream is ideal and stable in 50 h, with the EO concentration of 1.60–1.70%, the EO selectivity is higher than 85% and the EO STY is about 200 g·h⁻¹ L_{cat}⁻¹.

Fig. 9 shows the SEM characterization of the optimum catalyst (15Ag/α-Al₂O₃-150Cs) before and after the stability test. After a long-time reaction test on stream, the size of the Ag nanoparticles increased a little, and the Ag nanoparticles maintained well dispersion on the support. It had been reported that plant biomass still remained on the surface of the calcined catalyst, and the protective effect of the biomolecules on catalysts surface has been proved by the previous studies [28–30]. The high catalytic stability of the 15Ag/α-Al₂O₃-150Cs catalyst might be due to the existence of residual bimolecular on the catalysts preventing Ag NPs from agglomeration.

4. Conclusion

In summary, we have fabricated the Ag/α-Al₂O₃ catalysts by the impregnation–bioreduction method for ethylene epoxidation with O₂. The preparation process was thoroughly investigated and the optimal preparing conditions of the Ag catalysts were identified as follow: bioreduction temperature 60 °C, silver loading 15%, concentration of CC extract 0.15 g mL⁻¹, calcination temperature 600 °C. It was found that the catalytic performance of Ag/α-Al₂O₃ catalysts can be strongly affected by Cs contents. Cs promoter can enhance the Ag electropositivity benefit for the adsorption of oxygen species. The best Cs addition amount was 150 µg g_{cat}⁻¹. The optimized catalyst 15Ag/α-Al₂O₃-150Cs led to the EO concentrations of 1.70%, EO selectivity of 87.46% and EO STY of 223.07 g h⁻¹ L_{cat}⁻¹ at 200 °C, which was superior to the industrial YS-7 catalyst from Yanshan petrochemical company. In addition, stability test showed there was no significant decrease in both the activity and the selectivity during 50 h. The high catalytic stability of the catalysts was due to the existence of residual biomolecules on the catalysts preventing Ag NPs from agglomeration.

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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.cej.2015.08.082>.

References

- [1] A. Chongtertoonskul, J.W. Schwank, S. Chavadej, Effects of oxide supports on ethylene epoxidation activity over Ag-based catalysts, *J. Mol. Catal. A: Chem.* 358 (2012) 58–66.
- [2] J. Lacson, Ethylene Oxide, Chemical Economics Handbook, SRI International, Menlo Park, Calif., 2003.
- [3] M. Ghanta, B. Subramaniam, H.-J. Lee, D.H. Busch, Highly selective homogeneous ethylene epoxidation in gas (ethylene)-expanded liquid: transport and kinetic studies, *AIChE J.* 59 (2013) 180–187.
- [4] W.J. Yan, A. Ramanathan, M. Ghanta, B. Subramaniam, Towards highly selective ethylene epoxidation catalysts using hydrogen peroxide and tungsten- or niobium-incorporated mesoporous silicate (KIT-6), *Catal. Sci. Technol.* 4 (2014) 4433–4439.
- [5] T. Sreethawong, T. Suwannabart, S. Chavadej, Ethylene epoxidation in low-temperature AC corona discharge over Ag catalyst: effect of promoter, *Chem. Eng. J.* 155 (2009) 396–403.
- [6] T.E. Lefort, Process for the production of ethylene oxide, French Patent 729952, 1931.
- [7] H. Takada, M. Shima, Silver catalyst for production of ethylene oxide, method for production thereof, and method for production of ethylene oxide, U.S. Patent 6103916 (2000-8-15).
- [8] M.A. Pena, D.M. Carr, K.L. Yeung, A. Varma, Ethylene epoxidation in a catalytic packed-bed membrane reactor, *Chem. Eng. Sci.* 53 (1998) 3821–3834.
- [9] M.O. Özbek, R.A. van Santen, The mechanism of ethylene epoxidation catalysis, *Catal. Lett.* 143 (2013) 131–141.
- [10] B.A. Rokicki, C. Verrier, Method for preparing an epoxidation catalyst, U.S. Patent 8546297 (2013-10-1).
- [11] 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* 244 (2003) 59–70.
- [12] M.C.N.A. de Carvalho, F.B. Passos, M. Schmal, Study of the active phase of silver catalysts for ethylene epoxidation, *J. Catal.* 248 (2007) 124–129.
- [13] J.C. Dellamorte, J. Lauterbach, M.A. Barreau, Rhodium promotion of Ag and Cu–Ag bimetallic catalysts for ethylene epoxidation, *Catal. Today* 120 (2007) 182–185.
- [14] P. Christopher, S. Linic, Engineering selectivity in heterogeneous catalysis: Ag nanowires as selective ethylene epoxidation catalysts, *J. Am. Chem. Soc.* 130 (2008) 11264–11265.
- [15] X.L. Jing, H.X. Wang, H.M. Chen, J.L. Huang, Q.B. Li, D.H. Sun, Biosynthesized Ag/α-Al₂O₃ catalyst for ethylene epoxidation: the influence of silver precursors, *RSC Adv.* 4 (2014) 27597–27603.
- [16] D.H. Sun, H.X. Wang, G.L. Zhang, J.L. Huang, Q.B. Li, Preparation of Ag/α-Al₂O₃ for ethylene epoxidation through thermal decomposition assisted by extract of *Cinnamomum camphora*, *RSC Adv.* 3 (2013) 20732–20737.
- [17] 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/CsRe/α-Al₂O₃ high-selectivity, ethylene epoxidation catalysts, *J. Catal.* 322 (2015) 14–23.
- [18] N. Rizkalla, Process for preparing silver catalyst, U.S. Patent 6184175, (2001-2-6).
- [19] D.M. Minahan, G.B. Hoflund, W.S. Epling, D.W. Schoenfeld, Study of Cs-promoted, α-alumina-supported silver, ethylene epoxidation catalysts: III and nonpromoted catalysts, *J. Catal.* 168 (1997) 393–399.
- [20] W.S. Epling, G.B. Hoflund, D.M. Minahan, Study of Cs-promoted, α-alumina-supported silver, ethylene-epoxidation catalysts, *J. Catal.* 171 (1997) 490–497.
- [21] M.O. Özbek, I. Önal, R. Van Santen, Ethylene epoxidation catalyzed by chlorine-promoted silver oxide, *J. Phys. Condensed Matter: Inst. Phys. J.* 23 (2011). 404202–404202.
- [22] J.C. Dellamorte, J. Lauterbach, M.A. Barreau, Promoter-induced morphological changes of Ag catalysts for ethylene epoxidation, *Ind. Eng. Chem. Res.* 48 (2009) 5943–5953.
- [23] S. Iravani, Green synthesis of metal nanoparticles using plants, *Green Chem.* 13 (2011) 2638–2650.
- [24] J.L. Huang, L.Q. Lin, D.H. Sun, H.M. Chen, D.P. Yang, Q.B. Li, Bio-inspired synthesis of metal nanomaterials and applications, *Chem. Soc. Rev.* (2015), <http://dx.doi.org/10.1039/C5CS00133A>.
- [25] Y. Ma, Y.Q. Huang, Y.W. Cheng, L.J. Wang, X. Li, Selective liquid-phase hydrogenation of maleic anhydride to succinic anhydride on biosynthesized Ru-based catalysts, *Catal. Commun.* 57 (2014) 40–44.
- [26] W.B. Liang, T.L. Church, A.T. Harris, Biogenic synthesis of photocatalytically active Ag/TiO₂ and Au/TiO₂ composites, *Green Chem.* 14 (2012) 968–975.
- [27] A.R. Vilchis-Nestor, M. Avalos-Borja, S.A. Gómez, J.A. Hernández, A. Olivas, T.A. Zepeda, Alternative bio-reduction synthesis method for the preparation of Au (AgAu)/SiO₂–Al₂O₃ catalysts: Oxidation and hydrogenation of CO, *Appl. Catal. B* 90 (2009) 64–73.
- [28] G.W. Zhan, M.M. Du, J.L. Huang, Q.B. Li, Green synthesis of Au/TS-1 catalysts via two novel modes and their surprising performance for propylene epoxidation, *Catal. Commun.* 12 (2011) 830–833.

- [29] G.W. Zhan, M.M. Du, D.H. Sun, J.L. Huang, X. Yang, Y. Ma, A.-R. Ibrahim, Q.B. Li, Vapor-phase propylene epoxidation with H₂/O₂ over bioreduction Au/TS-1 catalysts: synthesis, characterization, and optimization, *Ind. Eng. Chem. Res.* 50 (2011) 9019–9026.
- [30] M.M. Du, G.W. Zhan, X. Yang, H.X. Wang, W.S. Lin, Y. Zhou, J. Zhu, L.Q. Lin, J.L. Huang, D.H. Sun, L.S. Jia, Q.B. Li, Ionic liquid-enhanced immobilization of biosynthesized Au nanoparticles on TS-1 toward efficient catalysts for propylene epoxidation, *J. Catal.* 283 (2011) 192–201.
- [31] J.L. Huang, C. Liu, D.H. Sun, Y.L. Hong, M.M. Du, T. Odoom-Wubah, W.P. Fang, Q. B. Li, Biosynthesized gold nanoparticles supported over TS-1 toward efficient catalyst for epoxidation of styrene, *Chem. Eng. J.* 235 (2014) 215–223.
- [32] Y.L. Hong, X.L. Jing, J.L. Huang, D.H. Sun, T. Odoom-Wubah, F. Yang, M.M. Du, Q. B. Li, Biosynthesized bimetallic Au–Pd nanoparticles supported on TiO₂ for solvent-free oxidation of benzyl alcohol, *ACS Sustain. Chem. Eng.* 2 (2014) 1752–1759.
- [33] M.O. Özbek, I. Önal, R.A. van Santen, Chlorine and caesium promotion of silver ethylene epoxidation catalysts, *ChemCatChem* 5 (2013) 443–451.
- [34] V.I. Bukhtiyarov, I.P. Prosvirin, R.I. Kvon, B.S. Bal'zhinimaev, E.A. Podgornov, XPS and TPD studies of Cs–O complexes on Ag surfaces: single crystal versus supported catalysts, *Appl. Surf. Sci.* 115 (1997) 135–143.
- [35] B.S. Bal'zhinimaev, Ethylene epoxidation over silver catalysts, *Kinet. Catal.* 40 (1999) 795–810.
- [36] 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, isomerisation, and combustion of ethylene oxide on Ag (111), *J. Catal.* 106 (1987) 54–64.
- [37] J.F. Deng, J. Yang, S. Zhang, X.H. Yuan, Promoting effects of Re and Cs on silver catalyst in ethylene epoxidation, *J. Catal.* 138 (1992) 395–399.
- [38] R.B. Grant, C.A.J. Harbach, R.M. Lambert, S.A. Tan, Alkali metal, chlorine and other promoters in the silver-catalysed selective oxidation of ethylene, *J. Chem. Soc., Faraday Transactions 1: Phys. Chem. Condensed Phases* 83 (1987) 2035–2046.
- [39] R.B. Grant, R.M. Lambert, Ethylene oxide isomerisation on single-crystal Ag (111) in atomically clean and Cs-modulated conditions, *J. Catal.* 93 (1985) 92–99.
- [40] N. Macleod, J.M. Keel, R.M. Lambert, The effects of catalyst aging under industrial conditions: ethylene oxide conversion over Ag–Cs/α-Al₂O₃ catalysts, *Catal. Lett.* 86 (2003) 51–56.
- [41] V.I. Bukhtiyarov, A.F. Carley, L.A. Dollard, M.W. Roberts, XPS study of oxygen adsorption on supported silver: effect of particle size, *Surf. Sci.* 381 (1997) L605–L608.
- [42] V.I. Bukhtiyarov, A.I. Boronin, V.I. Savchenko, Stages in the modification of a silver surface for catalysis of the partial oxidation of ethylene: I. Action of oxygen, *J. Catal.* 150 (1994) 262–267.
- [43] V.I. Bukhtiyarov, M. Hävecker, V.V. Kaichev, A. Knop-Gericke, R.W. Mayer, R. Schlögl, Atomic oxygen species on silver: photoelectron spectroscopy and x-ray absorption studies, *Phys. Rev. B* 67 (2003) 235422.
- [44] V.I. Bukhtiyarov, V.V. Kaichev, E.A. Podgornov, I.P. Prosvirin, XPS, UPS, TPD and TPR studies of oxygen species active in silver-catalysed ethylene epoxidation, *Catal. Lett.* 57 (1999) 233–239.