ORIGINAL PAPER

Effect of Preparation Conditions on Ag Catalysts for Ethylene Epoxidation

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Abstract The effect of calcination of silver catalysts supported on foamed monoliths was examined for the epoxidation of ethylene. Previous results suggested that calcination at 673 K for 3 h would give a maximum conversion. Further study revealed that calcination for >3 h reduced the catalyst surface area and therefore the conversion seen in reactor studies. This phenomenon has been attributed to sintering, with the migration of Ag from mesopores of the catalysts to macropore regions and the eventual formation of a Ag film covering the walls of the macropores. Studies of the metal loading showed that a tradeoff exists between metal loading and calcination time. Increasing the amount of silver can have a detrimental effect on catalysts calcined for 12 h, however the opposite trend, an increased conversion with higher loadings, was observed for catalysts calcined for 2 h. These results imply that the sintering of Ag can play a dramatic effect on catalyst design for optimum performance.

1 Introduction

The direct gas phase production of ethylene oxide (EO) over Ag catalysts has been an active research field since its discovery in the 1930s by Lefort [1]. Factors including the Ag precursor, particle size, support materials, and promoters have been shown to affect catalyst performance and lifetime. In particular, many studies have focused on how these factors affect the characteristics of supported Ag particles. Several precursors are available for Ag particle synthesis, including silver nitrate [2], silver lactate [3], and silver oxalate [4], to produce catalysts with different performance. In general, the effect of the Ag source is not completely understood. Sajkowski and Boudart have suggested that the epoxidation reaction is structure-insensitive, which would imply that there is little need to tune the Ag morphology [5]. However, several studies have shown that particle size does affect the catalyst performance [6–9]. Wu and Harriott reported that increasing the Ag particle size from 6 to 50 nm caused a 3-fold increase in the EO selectivity [6]. Goncharova et al. reported a 6-fold increase in the selectivity for 40 nm particles compared to 1.6 nm [10]. A corresponding increase in the rate was seen as well. Tsybulya et al. claimed that Ag particles with multiple grains are more active, and that further enhancement of the activity occurs as the quantity of intergrain boundaries increases [8]. The size of the grains was found to be greater for more active catalysts as well. However, ex situ characterization may not provide particle morphologies or size distributions representative of those under reaction conditions. For example, Ruckenstein and Lee observed that Ag particles changed shape upon the addition of ethylene [11]. Particle shapes shifted from spherical to ellipsoidal upon exposure to hydrocarbons. Shifts in Ag morphology to ellipsoidal particles and chain structures were also seen by Chimentao et al. for Ag nanoparticles synthesized via a polyol process for the oxidation of styrene [12].

One of the difficulties with studying particle size effects is the sintering of Ag on Al_2O_3. In fact, Verykios et al. used sintering to tune Ag particles for optimum ethylene epoxidation performance [9]. For such studies, the calcination

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and reduction conditions become increasingly important. A recent high throughput (HTE) design of experiments study from our lab focused on the calcination and reduction conditions of monolith-supported Ag catalysts. In that study, a maximum ethylene conversion was identified for catalysts calcined for 2–3 h at 673 K with a 12 h reduction in 20% H_2/He at 573 K [13]. Similar to the literature results presented above, it was postulated that sintering of the Ag affected the surface area and therefore the activity and selectivity. Here we present a more systematic study of the effects of preparation procedure, and in particular calcination, on the connections between morphology and activity of Ag catalysts for the production of EO.

2 Experimental Methods

Foam monoliths composed of 99.5% α-Al_2O_3, obtained from Vesuvius Hi-Tech Ceramics, were used as catalyst supports. The monoliths were 18 × 10 mm cylinders (diameter × length), with a nominal pore density of 45 pores per linear inch. The monoliths were immersed in a solution of silver nitrate and distilled water. These catalysts were then dried at 353 K, calcined at 673 K in an open air furnace, and reduced at 573 K under a flow of 20% H_2/He. Catalysts with nominal weight loadings varying from 0.5 to 20 wt% Ag were prepared by varying the concentration of silver nitrate and subsequently characterized through reactor studies, Scanning Electron Microscopy (SEM), and O_2 uptake measurements.

For reactor studies, the catalyst was placed under reaction conditions (100 sccm feed of 10 or 6% ethylene, 10% oxygen, balance nitrogen, at 540 K) and allowed to reach steady-state (typically 36–48 h) before temperature and/or reactant partial pressures were altered. After reaching steady-state, the temperature of each catalyst was changed as necessary to give 1.8% ethylene conversion. This allowed for comparison of the EO selectivities at fixed conversion for all catalysts. Testing was undertaken either in a single reactor apparatus, where effluents were analyzed and quantified using an HP6890 gas chromatograph with a flame ionization detector (FID) and thermal conductivity detector (TCD), or in a HTE reactor described in [13], with parallel analysis of the reaction products using FTIR spectroscopic imaging [14, 15].

In order to account for the possibility of mass transfer effects skewing the reactor studies the Thiele modulus was calculated for a range of pore sizes using the pre-exponential and activation energies for oxygen dissociation on Ag presented by Linic [16]. The modulus was found to be less than 1 in all cases. Two examples of which were moduli of 4E−4 and 4E−2, which were calculated for 1 and 100 μm pores, respectively. As is commonly known,

moduli less than 1 indicate a reaction limited process and therefore no mass transfer limitations were found for the reactor experiments.

Fresh and used catalysts were imaged using a JEOL 7400F SEM. To permit imaging of all parts of the catalyst, the monolith was cross-sectioned approximately half-way along its length with a low speed diamond wheel saw. Ag particle size distributions were determined from the SEM images using Image J processing software. All distributions were based on particles ranging from 0.1 to 20 μm in size within an 18 × 24 μm image.

O_2 uptake and temperature programmed desorption (TPD) experiments were conducted in vacuum at a base pressure of 10^{-9} torr. All catalysts were exposed to 10^{-6} torr O_2 for 1 h at 507 K. The catalyst was cooled in O_2 to 317 K, before the oxygen was pumped out and the catalyst further cooled to 307 K for 1 h to ensure a constant O_2 baseline. The TPD experiments were carried out with a ∼15 K/min ramp to 627 K followed by cooling to room temperature. A mass spectrometer (SRS RGA100) was used to quantify O_2 desorbed from the sample. Several cycles of O_2 uptake and TPD for each sample were required to reach a constant O_2 uptake; steady-state uptakes were used for calculations of active surface area based on the assumption of spherical particle shape.

3 Results and Discussion

As noted previously [13], from our statistical design of experiment study of calcination and reduction conditions, a maximum in ethylene conversion was found for catalysts calcined for 3 h at 673 K. A more complete HTE study of catalysts calcined for various times at 673 K is shown in Fig. 1. The maximum ethylene conversion was observed for catalysts calcined between 2 and 3 h. The EO selectivity remained constant, within experimental error, for all catalysts calcined for more than 2 h. Characterization of these catalysts using SEM was undertaken to further understand this phenomenon. Figure 2 shows a cross-section of a support impregnated with Ag. In addition to the macroscopic pores, sectioning of the monolith exposed the interior of the alumina structural elements. These were also porous; they contained mesoscopic pores of ca. 1 μm created from the packing of the primary Al_2O_3 particles. The porosity is particularly apparent in the higher magnification images in Fig. 3. We will refer to the characteristic regions in images of the sectioned monoliths as "macropore surface" and "structure region." We eschew terms such as "external" or "internal" surfaces to avoid confusion with the geometric description of the monolith. As shown in Fig. 3 for catalysts calcined for various times, 100–400 nm Ag particles were observed within the structure region,
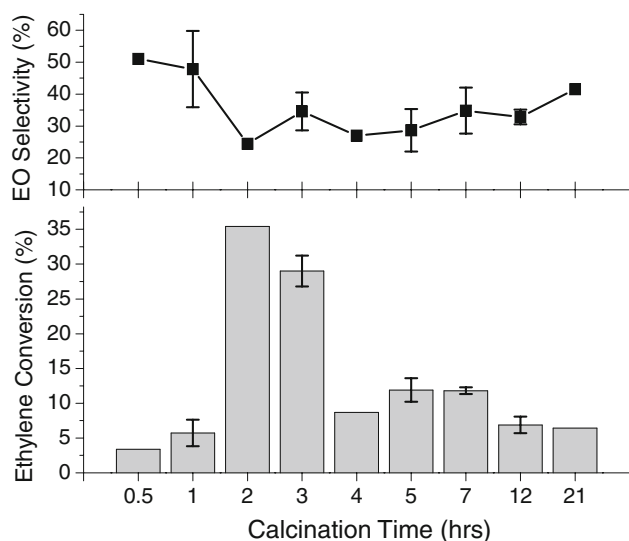
Fig. 1 Ethylene conversion (*bottom*) and EO selectivity (*top*) versus calcination time at 673 K. All catalysts had a nominal silver loading of 15% w/w
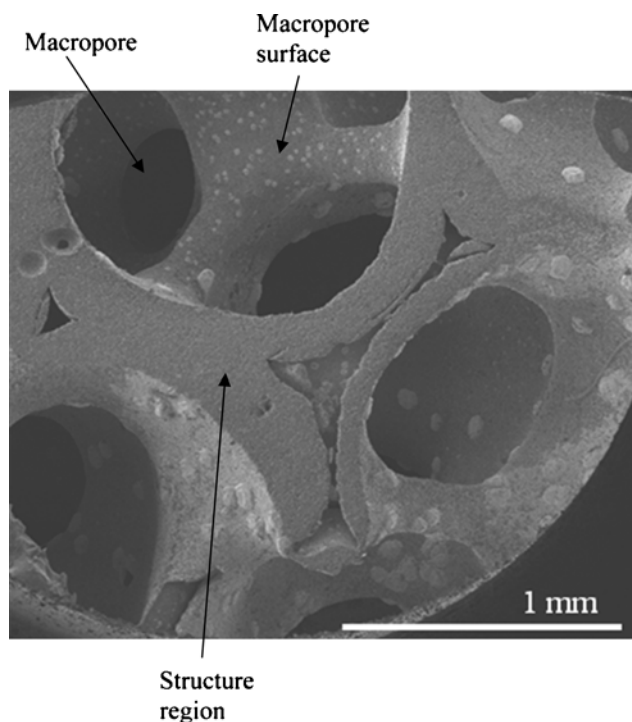

Fig. 2 SEM image of a representative Ag catalyst, showing the macropore, macropore surface, and alumina structure region exposed by sectioning the monolith

indicating that Ag particles were present in the mesopores. The macropore surface (Fig. 4) showed a markedly different morphology, with a much wider range of particle sizes for the various calcination times. The Ag particle size distributions for this region were bimodal, with peaks around ∼1 and 20 µm. Representative average particles

sizes and particle counts can versus calcination time can be found in Fig. 5. The statistics were performed on 18 × 24 µm images, restricting the majority of particles counted to the 1 µm particle size distribution. The average particle size changed significantly on the macropore surfaces as the calcinations time was increased. No appreciable changes were detected in the mesopores. Conversely, the number of particles decreased in both regions for catalysts calcined for >3 h. Therefore, sintering of the catalysts profoundly changed the amount of Ag present in the mesoscopic and macroscopic pores. Based on the migration shown by Ruckenstein and Lee [11], we believe that the agglomeration of particles on the macropore surface proceeds via a migration of the Ag from the mesopore region, creating the large Ag crystallites (almost a Ag sheet) seen in Fig. 4e. In general, smaller particles would be expected to account for the bulk of the active surface area and therefore a decrease in the number of small particles seen in the structure region is likely to be responsible for the lower ethylene conversions for longer calcinations.

The effect of Ag loading was also studied for catalysts calcined for both 2 and 12 h. As seen in Fig. 6, the 12 h calcined catalysts have a maximum in activity for a 1 wt% nominal loading. Increases in the loading actually led to an apparent decrease in the ethylene conversion. Catalysts calcined for 2 h behaved more consistently with expectations, in that as more Ag was added, the activity increased. Catalysts calcined for 2 h underwent less sintering, as mentioned previously, and instead presented large quantities of particles on the order of 1 µm. The particle size statistics for the catalysts calcined for 12 h, shown in Fig. 7, indicate that the particle size increased dramatically as the loading was increased. All catalysts mentioned were stable for more than 100 h after the induction period of 12–36 h to reach steady state, implying that temperatures greater than 540 K are needed for sintering on the time scale of days to occur.

O_2 uptake measurements were performed in order to determine the active surface area of each catalyst. Representative TPD spectra for catalysts with various Ag loadings calcined for 12 h are shown in Fig. 8. For all catalysts, a single peak at 535–545 K was observed. Single crystal studies on Ag(111) and Ag(110) have reported O_2 desorption temperatures of 579 K [17] and 590 K [18]. Busser et al. performed O_2 TPDs for supported catalysts with a peak temperature of 542 K for a 20 K/min ramp [19]. Atkins et al. [20] and Bal'zhinimaev [21] also presented spectra for supported catalysts, however both reported two peaks. Atkins et al. reported peak temperatures near 523 and 573 K, while Bal'zhinimaev observed peaks near 580 and 690 K. Based on comparison to XPS experiments, Bal'zhinimaev assigned the lower temperature peak to nucleophilic oxygen atoms on Ag terrace sites,
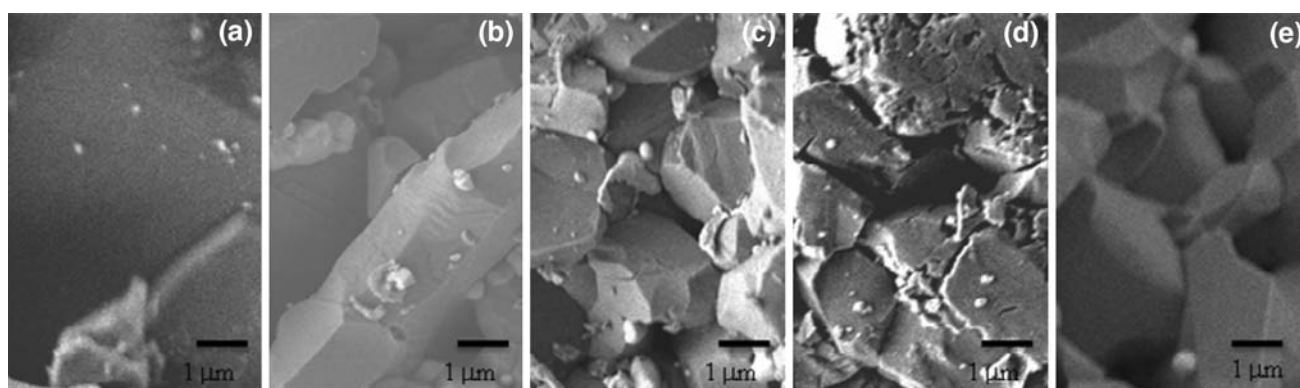
Fig. 3 SEM images of the structure region of 15% w/w Ag catalysts supported on α-Al$_2$O$_3$ after various calcination times. White particles are Ag, dark gray are Al$_2$O$_3$. **a** 0 h, (**b**) 1 h, (**c**) 2 h, (**d**) 4 h, (**e**) 12 h calcination
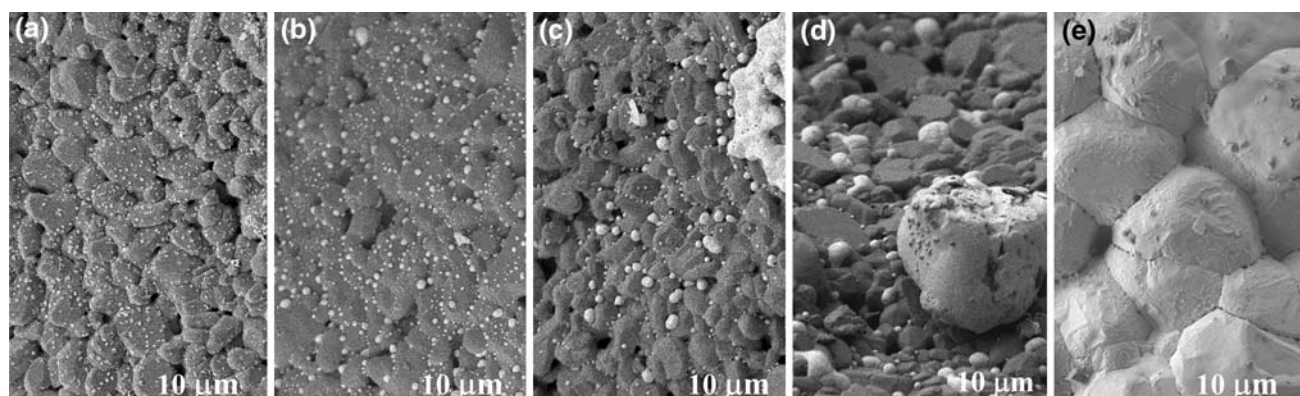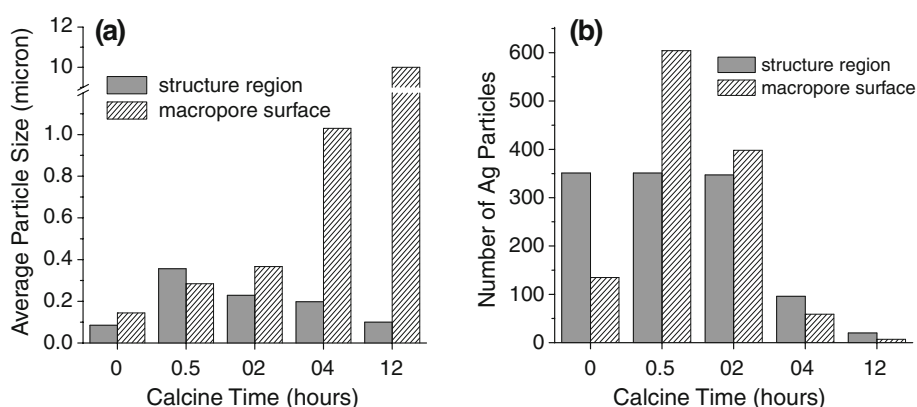

Fig. 4 SEM Images of macropore surfaces of 15% w/w Ag catalysts supported on α-Al$_2$O$_3$ after various calcination times. White particles are Ag, dark gray are Al$_2$O$_3$. **a** 0 h, (**b**) 0.5 h, (**c**) 2 h, (**d**) 4 h, (**e**) 12 h calcination

Fig. 5 a Particle size versus calcination time for both the structure and macropore surface regions of the Al$_2$O$_3$ monolith (**b**) Number of Ag particles in 18 × 24 mm SEM image for various calcination times

while the higher temperature peak was assigned to electophilic oxygen on defect or stepped regions. The peaks near 550 K in Fig. 8 indicate that a large amount of O$_2$ is present on Ag terrace sites. This agrees with the images from Figs. 3 and 4, which showed that the majority of the Ag was present as large Ag crystallites that would be expected to expose large terrace regions. The number of defects for these large particles should be small compared the 50 nm (or smaller) particles used in the studies by

Atkins and Bal'zhinimaev, possibly explaining the lack of a second peak. The turnover frequencies (TOF) obtained for catalysts calcined for 12 h are shown in Table 1, along with ethylene conversions obtained with these catalysts at 540 K. The TOF and conversion show opposite trends, where the TOF increases with increasing loading. Based on the results from Wu and Harriott, as well as Bukhtiyarov et al. [6, 7], and the SEM results of Fig. 7, this discrepancy between the TOFs and ethylene conversions can be
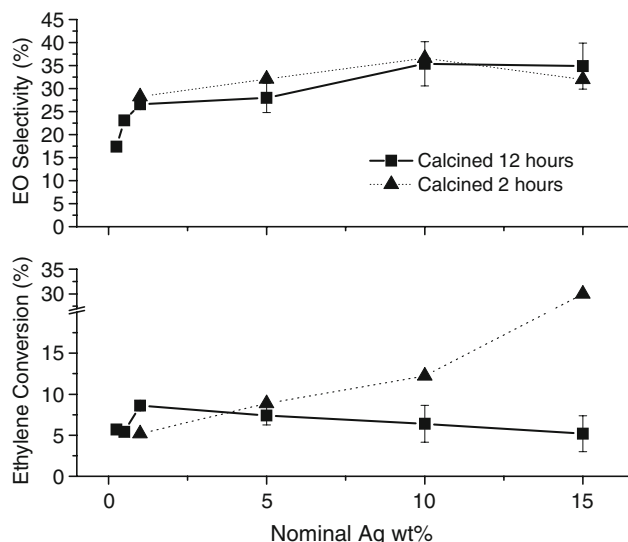
Fig. 6 Reactor results for Ag catalysts with nominal weight loadings from 0.25–20% w/w at 540 K with 10% v/v ethylene and 10% v/v oxygen

Fig. 8 Representative TPD spectra of catalysts loaded with 1–15% w/w of Ag

Fig. 7 Average particle size and frequency for Ag catalysts of varying nominal weight loadings in both the structure and macropore surface regions. Calcination time is 12 h
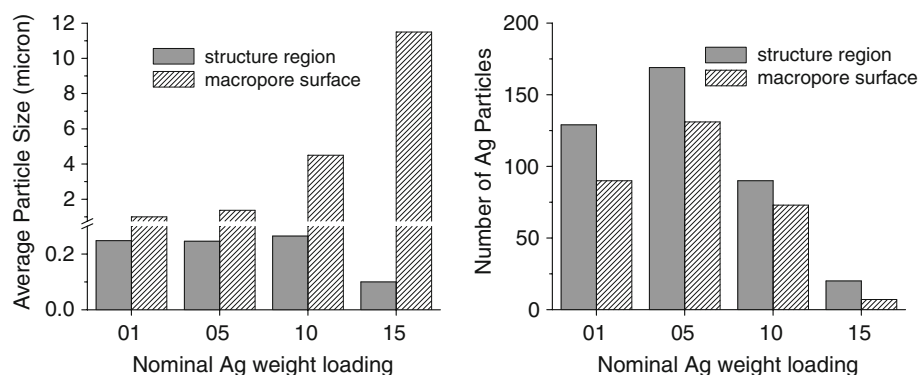

Table 1 Comparison between the ethylene conversion and TOF for Ag catalysts calcined at 673 K for 12 h

wt% Ag	Ethylene conversion (%)	TOF (s^{-1})	Surface area (m^2/g_{cat})
1	8.6	1.5E+03	3.89E−04
5	7.4	4.4E+03	1.13E−04
10	6.4	5.2E+03	7.45E−05
15	6.1	9.9E+03	3.78E−05

explained by the difference in particle distributions between the various loadings of Ag. Large loadings lead to more agglomeration and larger average particle size which has been shown to increase the TOF. Therefore, a tradeoff appears to exist between creating catalysts with high surface areas and high turnover frequencies. Based on the conversion results from Fig. 6, the optimum catalyst conversion can be attained near 1 wt% Ag loading. Catalysts with lower loadings will have a decreased particle size, increasing the surface area. However the increases in
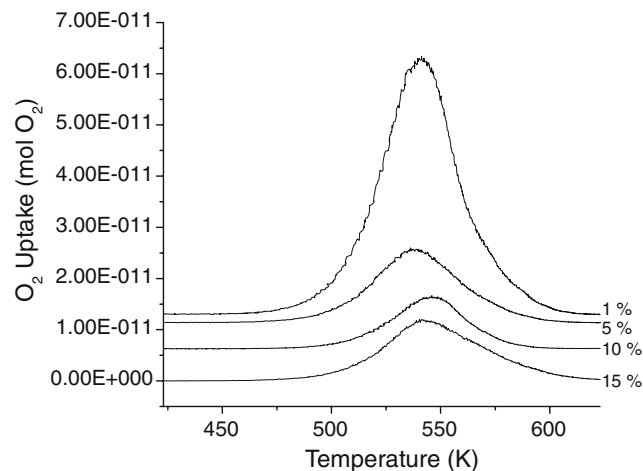
surface area are too small to overcome the decrease in turnover frequency for the smaller particles.

Also, the disparity in conversion trends between the catalysts calcined for 2 and 12 h can be explained by the difference in the particle size distributions for the different calcination times. By reducing sintering, the 2 h catalysts undergo increases in surface area while maintaining an almost constant particle size distribution eliminating the tradeoff seen for the 12 h calcined samples. Therefore, these catalysts show increases in conversion as more Ag is added and markedly higher conversions than the 12 h calcined counterparts.

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