Propene epoxidation over K-promoted Ag/$CaCO_3$ catalysts: the effect of metal particle size

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With increasing loading of potassium promoter, Ag/$CaCO_3$ catalysts exhibit a clear maximum in selectivity towards propene epoxide formation. This behavior correlates with changes in silver particle size distribution as revealed by HREM and XPS. Maximum selectivity and activity are achieved when the catalyst contains a large proportion of Ag particles whose size lies in the intermediate range 20–40 nm. Ag particles that are either much smaller or much larger than this are less selective towards epoxidation. The mechanistic implications of these findings are discussed and comparison is made with the corresponding properties of Ag/α-alumina catalysts normally used for ethene epoxidation.

KEY WORDS: propene; epoxidation; silver; potassium; $CaCO_3$; morphology; particle size; HREM; XPS.

1. Introduction

The heterogeneous selective oxidation of ethene to the epoxide over Ag/α-alumina catalysts is a much-studied process and the basis of a well-developed large-scale technology. The reaction mechanism is relatively well understood [1] as is the mode of action of certain key promoters including chlorine [2], alkalis [3], and NO_x [4,5]. Optimally-promoted catalysts deliver selectivities approaching 90% and a recent concise review is provided by Serafin *et al.* [6]. The consensus view is that in this case the crucial epoxidizing species are oxygen ad-atoms in an appropriate valence state which renders them effective for electrophilic attack on the adsorbed alkene. In marked contrast, propene epoxidation over Ag/α-alumina typically yields PO selectivities in the order of only a few percent.

As a result, efficient heterogeneously catalyzed epoxidation of propene *by gaseous oxygen* remains an important technological goal. Such a process is desirable because propene epoxide is a strategically important and versatile chemical intermediate whose manufacture currently employs either the old chlorohydrin process or a newer homogenous route that involves co-production of styrene. The former is environmentally unfriendly because it generates large amounts of halogenated waste; the latter involves use of expensive hydroperoxides as the oxidizing agent. It has been plausibly proposed [7–11] that the very low selectivities encountered with propene epoxidation are due to the ease with which an allylic hydrogen atom may be stripped from the molecule, a process that would immediately preclude epoxidation and result in combustion.

Recently, the heterogeneously-catalysed direct epoxidation of propene by oxygen has received increased attention in both academic and industrial laboratories. This interest has been stimulated by the findings of Haruta and his co-workers [12], who showed that certain Au/titania catalysts yield almost 100% selectivity towards propene epoxide, albeit at very low conversion, when co-fed with hydrogen, oxygen and propene. The interpretation of these findings is still the subject of debate. On the other hand, in the industrial arena, ARCO have reported promising propene epoxide selectivities when using K-promoted Ag/$CaCO_3$ catalysts [13]. At first sight, this suggests that the $CaCO_3$ support must somehow play an important role. Very recently, we carried out a comparative study of electrochemically-promoted Ag-catalyzed propene and ethene epoxidation [14]. In the course of this work we examined the properties of three support materials, namely α-alumina, K-β'' alumina, and $CaCO_3$. It was shown that the apparently beneficial effects of $CaCO_3$ as the support for Ag propene epoxidation catalysts are *not* due to low activity of $CaCO_3$ toward further conversion of the epoxide product (isomerization and combustion). Therefore the puzzle remains—why should alkali-promoted Ag/$CaCO_3$ be substantially more selective towards propene epoxidation than Ag/α-alumina? The present paper reports on an attempt to address this issue.

2. Experimental methods

2.1. Catalyst preparation

Unpromoted and K-promoted catalysts were prepared by mixing the metal precursor solution and the

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support to form a slurry as described in [13] rather than by the more usual incipient wetness impregnation procedures generally used for preparing Ag-based ethene epoxidation catalysts. 69.8 mmol of ethene diamine (Lancaster Synthesis, 99%*)* was mixed with an equivalent amount of distilled water, followed by slow addition of 46.7 mmol of oxalic acid (Aldrich, 99.5%) which was allowed to dissolve completely. 31.4 mmol of Ag(I) oxide was then slowly added and allowed to dissolve while keeping the temperature below 313 K. After stirring for 1 h, 24 mmol of ethanolamine (BDH, 99.5%) and, for the promoted catalysts, the appropriate amount of potassium carbonate (Breckland Scientific Synthesis, 99.5%) were added, with stirring continued for another hour. Finally, 10 ml of distilled water was added, followed by 61.5 mmol of calcium carbonate (Breckland Scientific Synthesis, 99%). The slurry was then stirred for another 4 h, dried at 383 K for 1 h, and calcined in air at 632 K for 3 h. Four $CaCO_3$-supported Ag catalysts were prepared thus. In each case the Ag loading was 45% w/w with potassium loadings of zero (catalyst C1), 1.7% (C2), 2.5% (C3), and 4.2% (C4) w/w. The Ag loading mimics that described in the patent literature [13].

2.2 Catalyst testing

Testing was carried out in a single-pass, fixed-bed, tubular 4 mm diameter stainless steel microreactor of conventional design. Gas mixtures were delivered by means of mass flow controllers (Bronkhorst Hi-Tec), with reactor inlet and outlet analyses being performed by means of quadrupole mass spectrometry and gas chromatography (HysepN and molecular sieve 5 Å columns). The catalyst sample (300 mg, ground and sieved to 250–355 μm) was held in position by glass wool plugs and its temperature measured by an embedded K-type thermocouple. The reaction gases were 20% C_2H_4/He, 20% C_3H_6/He and 20% O_2/He (BOC 99.998%) and these were used without further purification. The total flow rate in all experiments was 25 STP ml min^{-1} corresponding to a space velocity of $\sim$1750 h^{-1}, with alkene conversion being $<$10% in all cases.

2.3. High resolution electron microscopy

Specimens were prepared by fine grinding of catalysts C1–C4 in acetone followed by ultrasonic treatment to produce a suspension. A drop of suspension was then placed on a holey carbon gold grid and the acetone allowed to evaporate. The resulting specimens were examined by high resolution electron microscopy (HREM) (JEOL 3011, 300 kV) and energy dispersive X-ray spectroscopy (EDS). For each catalyst, two separate samples were examined. For each sample, images were viewed at low magnification to confirm that the distribution of metal particles was essentially uniform. Twenty high resolution (20–500k) images were then acquired from different parts of the sample in order obtain a valid description of the Ag particle size distribution and particle morphology. Figures 2(a) to (d) show representative HREM images obtained in this way from samples of the used catalysts C1–C4.

2.4. X-ray photoelectron spectroscopy

XPS data were acquired in a VG ADES 400 UHV spectrometer system. Catalyst samples were mounted using a method free from organic contamination by pressing a small amount of the material between two discs of pure aluminum. Separating the latter then gave two specimens consisting of a thin film of catalyst powder adhering to the aluminum. XP spectra were acquired with Mg K_α radiation and quoted binding energies (BEs) are referred to the C 1s emission at 284 eV. As will become apparent, it was necessary to extract from the data the relative intensities of two different contributions to the Ag $3d_{5/2,3/2}$ emission. This was achieved by first subtracting a Shirley-type background and then fitting the residual with two pairs of Gaussians (one for each doublet), all with the same half-width.

3. Results

3.1. Catalyst testing

Catalysts C1–C4 were tested for propene epoxidation at atmospheric pressure with a 1 : 2 feed composition [14,15] composed of 6.8 K Pa propene and 13.6 K Pa oxygen. Under all conditions the only observed products were propene oxide, carbon dioxide and water. All four catalysts exhibited stable performance immediately on start-up and maintained this performance for the duration of the experiments. Surveys carried out over the temperature range 453–553 K showed a shallow selectivity maximum at 483 K. This was therefore used as the temperature for comparative testing.

Figure 1 shows the effect of varying potassium loading on both propene oxide selectivity and propene conversion at 483 K. It is clear that alkali exerts a pronounced effect on catalyst performance, with both activity and selectivity passing through a maximum at catalyst C2. The un-promoted catalyst (C1) gave the lowest selectivity (3.7%) whereas catalyst C2 containing 1.7% K was best of all, delivering 15.2% propene epoxide at a propene conversion of $\sim$6%. Higher K loadings caused both activity and selectivity to decrease.

Figure 2(a) shows a representative image obtained from catalyst C1 (un-promoted). EDS confirmed that the large $\sim$70 nm particle in the centre of the frame was silver: note the well-developed facets. This was the most common particle size observed in this sample:

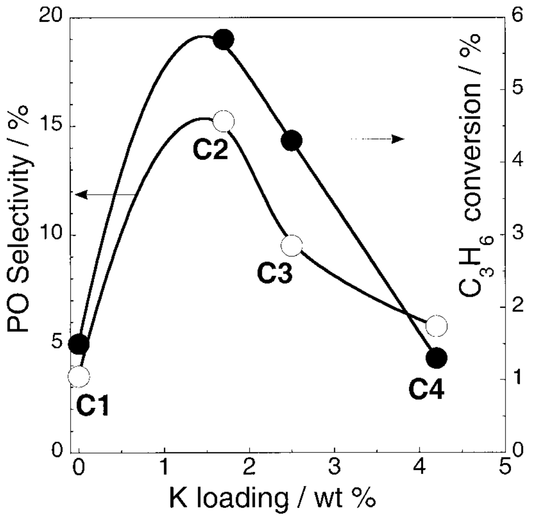
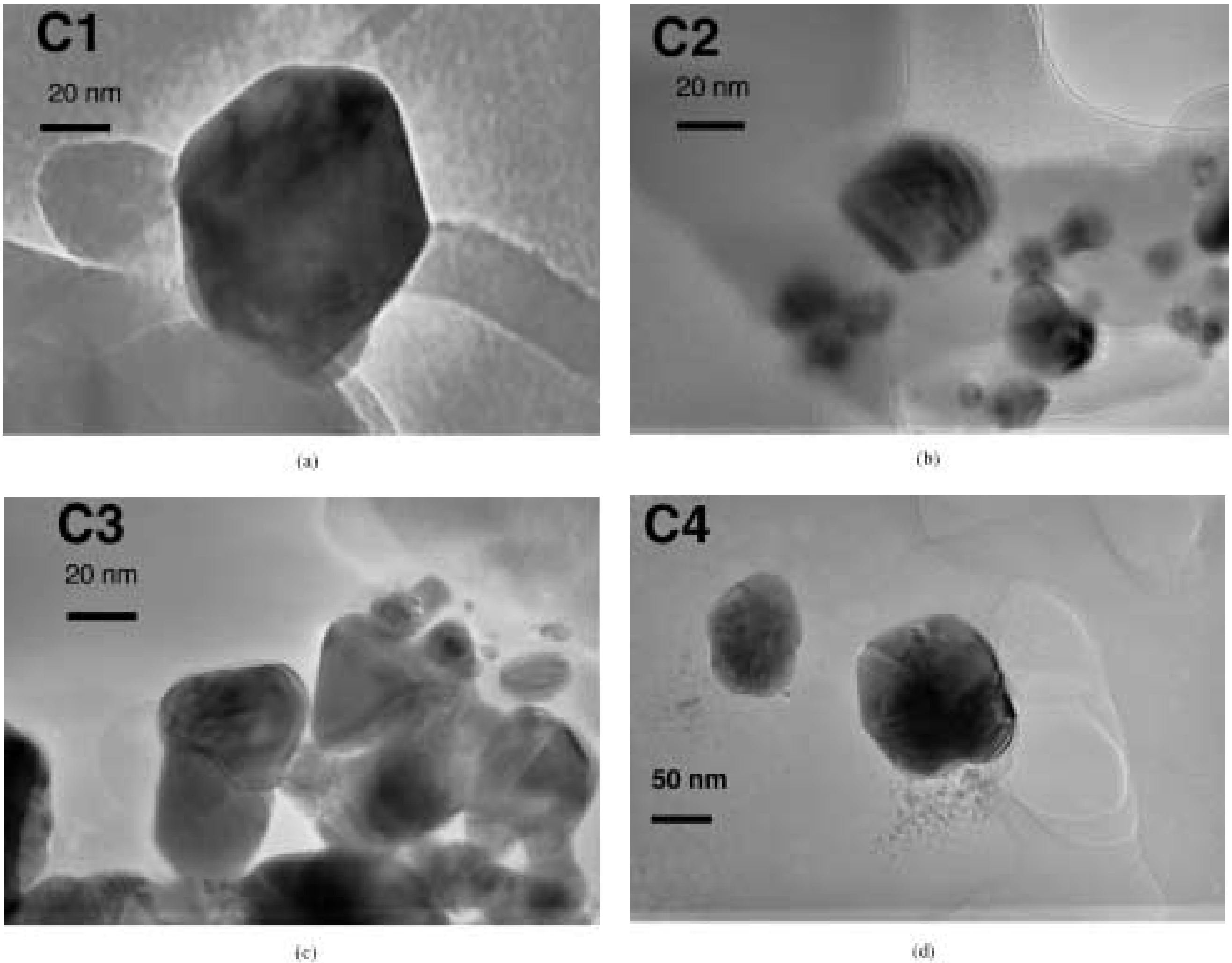


Figure 1. Effect of varying potassium loading on propene oxide selectivity and propene conversion at 483 K.

some larger particles were also detected along with a significant number of very small particles (~4 nm). The best catalyst (C2, 1.7% K) was characterized by Ag particles whose dimensions were in the range 20–40 nm; in addition, very few Ag crystallites were detected that were either much larger or much smaller than these (figure 2(b)). Increased K loading (catalyst C3, 2.5% K) resulted in a dominant Ag particle size of ~20–40 nm (figure 2(c)), but in this case there was extensive agglomeration of the individual metal crystallites; in some areas, numbers of very small Ag particles (~5 nm) were also visible. At the highest K loading (catalyst C4, 4.2% K) an apparently bimodal distribution of particle sizes was found (figure 2(d)). Images showed two distinctly different groups of Ag particles: very small crystallites (<5 nm) and very large crystallites (>100 nm). The small and large silver particles were sometimes found in close association, as exemplified by the large central feature in figure 2(d); the effect is also visible, though less pronounced, in the case of the smaller Ag particle seen on the left-hand side of figure 2(d).



(a) (b) (c) (d)

Figure 2. (a), (b), (c), (d) are representative HREM images obtained from catalysts C1, C2, C3, C4 containing, respectively, 0.0, 1.7, 2.5, 4.2 w/w% K. Note different magnifications.

3.2. X-ray photoelectron spectroscopy

The XP spectra of metal particles on insulating supports are subject to a number of complicating effects, some of which are intractable. One important issue concerns the effect of metal particle size on measured core level BEs. Such size-dependent phenomena have often been discussed in terms of either initial-state or final-state effects, although the subject remains controversial. However, as Barr points out [16], these authors seldom consider effects of metal particle charging which are necessarily present to a varying, and generally unknown, degree. The problem has been examined and discussed comprehensively by Barr [16,17] who considered in detail the various phenomena, including that of size-dependent differential charging of the metal particles. The underlying physics leads one to conclude that in general very small metal particles (~5 nm) should exhibit an apparently increased BE due to reduced screening of the photo-excited core hole [16,17]. Barr showed that this expectation is indeed borne out in the case of Pt/catalysts.

Figure 3 shows XP spectra of the Ag 3d region taken from catalysts C1–C4. It is apparent in every case that not one but two Ag $3d_{3/2,5/2}$ doublets appear. In the light of the above remarks, the component corresponding to the lower Ag $3d_{5/2}$ BE of 368 eV is ascribed to relatively large silver particles; the other, at the higher BE of 371 eV, is ascribed to nanoscopic Ag particles (smaller than ~5 nm) characterized by limited core-hole screening. Thus we may use these two components of the Ag 3d emission as an indication of the relative populations of very small and larger Ag particles. Figure 4 shows the relative intensities of these two components as a function of K loading. Also shown in figure 4 is the ratio of the Ag 3d/Ca 2p integrated XP intensities as a function of K loading. This latter quantity provides a measure of the silver surface area. These XPS data usefully complement the HREM results because they provide spatially averaged information as opposed to the detailed "snapshot" view derived from the microscopy. The correlation between the reactor, microscopy and spectroscopy data is discussed below.

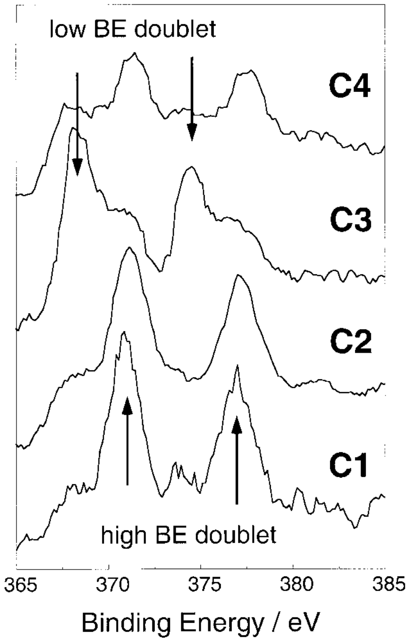


Figure 3. Ag 3d XP spectra obtained from catalysts C1, C2, C3, C4.

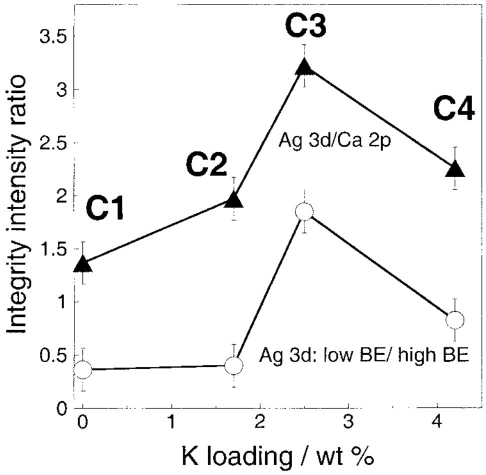


Figure 4. Relative intensities of low BE/high BE Ag $3d_{5/2}$ components (larger particles/very small particles) as a function of K content. Also shown is the ratio of the Ag 3d/Ca 2p integrated XP intensities as a function of K content.

4. Discussion

The reactor data clearly show that selectivity towards epoxide formation passes through a maximum with increasing K loading, while the conversion follows a similar trend. Both observations are in good accord with a recent study of propene epoxidation over Ag films electrochemically promoted (EP) by K [14]. Since the EP data refer unambiguously to K-induced changes in the catalytic chemistry of the Ag film, it seems reasonable to suppose that the behavior found here is at least partly due to the effect of the potassium promoter on the Ag component of the catalyst, not least because we have already shown [14] that $CaCO_3$ is ineffective for the further conversion of propene epoxide to unwanted products. In other words the beneficial effects of K are unlikely to be due to chemical modification of the support chemistry, *e.g.* by neutralizing acid sites. How might K favorably affect the Ag chemistry? Our EP results [14] suggested that in the case of propene a K-superoxy or peroxy species might also be an active epoxidizing agent. The coverage of such species should initially increase with K loading and then decline again, perhaps according to

$$KO_2 \rightarrow K_2O_2 \rightarrow K_2O$$

in line with the well-known chemistry of bulk potassium oxides [18]. Such behavior would tend to produce a selectivity maximum. However, we note that there are no reports of comparable behavior in the case of alkali-promoted Ag/α-alumina catalyst which (a) are very poor for propene epoxidation and (b) are dominated very large Ag particles ($>$150 nm) [19].

Thus the above picture is unlikely to contain the whole story because it ignores the obvious changes in particle Ag size distribution that occur as the K loading is increased.

A comparison of the reactor and HREM data (figures 1 and 2) shows that selectivity is highest at the point where HREM shows that the catalyst contains many 20–40 nm Ag particles (C2). Consistent with this, XPS shows that in going from C1 (HREM indicates that the larger Ag particles are predominantly $\sim$70 nm) to C2 there is a measurable increase in overall Ag surface area and no detectable change in the relative amounts of very small and larger particles. The increase in selectivity between C1 and C2 must therefore be associated with the reduction in size of the larger particles to 20–40 nm. Next, consider catalyst C3. HREM shows that it is characterized by agglomerates of individual $\sim$20–40 nm particles, substantial quantities of intermediate particles ($>$10 nm) and some very small particles. This morphology is associated with a decrease in selectivity and XPS confirms that the number of “fully screened” Ag particles ($>$5 nm) has increased—the low BE/high BE ratio increases. The implication is that the agglomerates and the intermediate and very small particles have an adverse effect on selectivity. Finally, at C4, we achieve the lowest selectivity of any promoted catalyst. HREM shows numerous very large particles and some very small particles: again, the implication is that neither of these provides good selectivity.

The trends in propene conversion may also be understood in the light of the HREM and XPS results. The increase from C1 to C2 is mainly due to the increased contribution to the active metal area, which both techniques confirm: 70 nm are replaced by 20–40 nm particles and the Ag 3d total intensity increases. Between C2 and C3 the Ag surface area increases (appearance of very small particles) but the conversion falls, implying that the very small particles are less active. Between C3 and C4 a relatively large drop in conversion occurs and the XPS and HREM data suggest that this is mainly associated with an increase in the proportion of very large Ag particles and a loss of active metal area.

The HREM results and the XPS data reveal that epoxidation selectivity is highest when the catalyst contains a large proportion of 20–40 nm Ag particles. Increasing the proportion of particles that are substantially larger or smaller than these adversely affects selectivity. It thus appears that there is an optimum particle size at which propene epoxide selectivity is maximized. It is possible to offer an (admittedly speculative) explanation for this effect of Ag particle size, as indicated below.

The overall selectivity of propene epoxidation is controlled by the interplay of the primary chemistry (propene → epoxide *versus* CO_2) and the secondary chemistry (propene epoxide → desorption *versus* further conversion, ultimately to CO_2). Oxygen adatoms on low index planes of Ag particles should be in the most electrophilic state, thus favouring alkene epoxidation over combustion [1]. However, low index planes should also adsorb propene epoxide (an electron donor) most strongly, favoring further conversion at the expense of product desorption. Thus changing the ratio of high index to low index planes exposed by an Ag catalyst should result in two opposing effects on selectivity and such an effect could provide a basis for qualitatively rationalizing our observation of an optimum Ag particle size. However, implicit in this explanation is the assumption that particle morphology is size-dependent. Inspection of all the HREM images, unfortunately, permits no definitive conclusion concerning this point. It is also possible that specific chemical effects of the K promoter are at work, for example (i) modification of the metal/support interaction thus stabilizing certain facets of Ag, or (ii) preferential adsorption of the promoter at certain facets of Ag.

A comparison between the present case and ethene and propene epoxidation over Ag/α-alumina is instructive. At steady state, Ag/α-alumina catalysts are dominated by very large silver particles ($>$150 nm; [20]) while exhibiting good selectivity towards ethene epoxidation but very poor selectivity towards propene epoxidation. Furthermore, it is claimed [21] that decreasing the Ag particle size decreases ethene epoxide selectivity—in contrast to the opposite behavior found here. The evidence seems to suggest that in regard to overall selectivity it is the primary chemistry that matters most with ethene while the secondary chemistry is more important with propene. This tentative conclusion is of course dependent on the validity of a particular reaction model. What does seem clear is that ethene and propene epoxidations behave differently toward changes in Ag particle size and that K-promoted $CaCO_3$ is a good support in propene epoxidation because it favors the formation of relatively small Ag particles.

5. Conclusions

1. Ag/$CaCO_3$ catalysts exhibit a maximum in selectivity towards propene epoxidation as the amount of potassium promoter is increased.
2. There is a correlation between potassium loading and Ag particle size: particles in the intermediate size range 20–40 nm are the most selective catalysts. Ag particles that are either much larger or much smaller than this are less selective.

Acknowledgment

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