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Ag-Catalysed Epoxidation of Propene and Ethene: An Investigation Using Electrochemical Promotion of the Effects of Alkali, NO_X, and Chlorine

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The Ag-catalysed epoxidation of propene and ethene have been studied using an electrochemical promotion method involving supply or removal of potassium from the surface of the working catalyst. The two systems respond in very different ways to the addition of K, NO, Cl, and combinations of these modifiers, pointing to important differences in reaction mechanisms. The results suggest that in the case of propene epoxidation adsorbed alkali superoxides or peroxides may act as epoxidising agents, in addition to or instead of O_a. Control experiments with $CaCO_3$, K-$\beta''Al_2O_3$, and a Ag/K-$\beta''Al_2O_3$ dispersed catalyst strongly suggest that support effects do not play a critically important part in determining the commonly observed low selectivity of propene epoxidation. Further conversion of propene epoxide is not an issue: the problem resides in the primary chemistry and probably hinges on the presence of allylic hydrogen atoms in the alkene. Postreaction X-ray photoelectron spectroscopy data suggest that the state of oxygenation of the Ag subsurface region is likely to be significant in determining the very different selectivities observed in ethene and propene epoxidation.

Key Words: **propene; ethene; epoxidation; potassium; NO_x; chlorine; electrochemical promotion; XPS.**

INTRODUCTION

The heterogeneous selective oxidation of ethene to ethene oxide (EO) is a mature technology based on Ag/α-alumina as the catalyst with O_2 as the oxidant. The molecular mechanisms involved in EO catalysis over Ag are relatively well understood (1); the same is true of the mode of action of various promoters, including chlorine (2), alkalis (3), and NO_x (4, 5), whose use can result in EO selectivities approaching 90%. The subject has been extensively reviewed and Ref. (6) provides a concise account of the key scientific and technical issues. Most authors now agree that the crucial epoxidising species in EO catalysis are oxygen adatoms in an appropriate valence state (partly controlled by promoter species) that renders them effective for electrophilic attack on the C=C function. However, it is still possible to find recently published papers in which adsorbed dioxygen is posited as the epoxidising agent (7).

On the other hand propene epoxidation over Ag/α-alumina is notably unsuccessful, yielding propene epoxide (PO) selectivities in the order of only a few percent. As a result, efficient heterogeneous selective oxidation of propene to PO is a key technological goal that remains to be realised. PO is a strategically important and versatile chemical intermediate whose manufacture accounts for ~10% of total European usage of propene. Two-thirds of this PO production is consumed in the manufacture of polyether polyols, with the rest being converted to propene glycols, glycol ethers, and other materials that have a wide range of applications. Current technology employs either (i) the old chlorohydrin process, environmentally unfriendly because it involves the use of chlorine, or (ii) a newer homogenous route that involves coproduction of PO and styrene. It has been proposed, and seems to be generally agreed, that the difficulty with propene epoxidation resides in the ease with which an allylic hydrogen atom may be stripped from the molecule, a process that presumably shuts off the epoxidation channel and results in combustion.

Recently (5), we used electrochemical promotion (EP) to investigate Ag-catalysed ethene epoxidation in the presence of, variously, chlorine, potassium, and NO_x. The results shed further light on the role of promoters, especially K and NO_x, in the overall process. Here, we report the results of an EP study of propene oxidation over Ag undertaken in an attempt to address basic mechanistic issues. New data for ethene epoxidation are also presented for purposes of comparison. A merit of the EP approach is that we may be certain that the observed alkali-induced effects reflect changes in the surface chemistry of only the Ag: alteration of support properties is not an issue. It is found that the responses of PO selectivity to K, K + NO, Cl, and K + Cl are very different, even opposite, to those exhibited in the case of EO catalysis: the implications of this are discussed.

The EP phenomenon was discovered by Vayenas and coworkers, who subsequently developed the methodology and laid down the basis for interpreting the effect (8, 9). The technique entails electrochemical pumping of ions from a solid electrolyte to the surface of a porous, catalytically active metal film with which it is in contact. It thus provides

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a unique means of varying promoter levels at the metal surface under reaction conditions by simply changing the potential of the catalyst film measured with respect to a reference electrode. In the present case the solid electrolyte is K-β'' alumina, a K^+ conductor, upon which the porous thin film Ag catalyst is deposited. Decreasing the catalyst potential results in K being pumped to the Ag surface to a level determined by the set potential; increasing the catalyst potential has the opposite effect. The chemical state (carbonate, nitrate, ...) of the electropumped K at the Ag surface, as with any conventionally supplied promoter, is determined by the reactive gas atmosphere (10, 11).

EXPERIMENTAL METHODS

Preparation and Use of EP Sample

The EP reactor, analysis system, and electrochemical technique have been described in detail elsewhere (12). Specific features relevant to the present case are summarised here. The silver catalyst consisted of a porous continuous thin film (ca. 1 μm) ($\sim$25-cm^2 geometrical area) deposited by DC sputtering in an Ar atmosphere on the outer face of a K-$\beta''Al_2O_3$ cylinder (5 cm × 10 mm) (Ionotec). Au reference and counterelectrodes were deposited on the inner face of the solid electrolyte cylinder, also by DC sputtering. Electrical contact with the electrodes was achieved by means of 0.5-mm diameter Au wires and the whole assembly was suspended in a quartz, atmospheric pressure well-mixed reactor ($\sim$35 cm^3). All three electrodes were exposed to the reactant gas mixture and the system behaved as a single-pellet, continuous stirred-tank reactor (13). The reactor, electrical connections, and analytical procedures have been described in detail previously [12] and are essentially the same as those used by Vayenas *et al.* (8, 9). Inlet and exit gas analysis was carried out using a combination of online gas chromatography (GC Shimadzu 14B equipped with a TCD and molecular sieve 5A and Haysep N columns) and quadrupole mass spectrometry.

Reactants were fed by mixing 20% O_2 in He (MG gas) and either 20% C_3H_6 in He or 30% C_2H_4 in He (BOC gases) with pure helium by means of electronic mass-flow controllers (Brooks 5850 TR). Gaseous dichloroethane (DCE) and NO are effective selectivity promoters in ethene epoxidation and their effects were therefore investigated here. DCE (20 ppm; Messer) and 300 ppm NO in He (BOC) were supplied to the reactor to achieve concentrations in the 0- to 60-ppm range. EP experiments were carried out in a well-mixed atmospheric pressure reactor with total flow rates in the range 1.0×10^{-5} mol^{-1}–3.4×10^{-5} mol^{-1}. Reactant conversion was restricted to <5% in order to avoid mass-transfer limitations, i.e., the system was operated differentially. The dispersed materials were tested in a single-pass microreactor, also operated at atmospheric pressure and with conversions <5%.

Preparation and Characterisation of Supported Catalysts

Reports in the patent literature describe Ag catalysts supported on $CaCO_3$ which deliver propene epoxide (PO) selectivities in the range 50–60% (14): this is much higher than commonly found for Ag/α-alumina. To investigate whether effects due to the support (e.g., further conversion of PO) could be of importance in the present case, we carried out a limited number of experiments on propene oxidation and PO oxidation using conventional dispersed catalysts consisting of Ag particles supported on K-$\beta''Al_2O_3$ powder. We also examined the reactivity of K-$\beta''Al_2O_3$ and $CaCO_3$ towards PO conversion.

The Ag/K-$\beta''Al_2O_3$ catalyst was prepared as follows. K-$\beta''Al_2O_3$ (355-μm mesh) was impregnated with a 16 wt% $AgNO_3$ aqueous solution. This was allowed to dry overnight in air followed by calcination in N_2 at 573 K for 4 h. During testing, the catalyst was run in the reaction mixture at 523 K for 24 h, by which time conversion and PO selectivity were constant. The K-$\beta''Al_2O_3$ and $CaCO_3$control samples were similarly pretreated. BET total surface areas were determined using a Micromeritics Gemini 2360 surface area analyser after degassing samples in N_2 for 2 h at 473 K. The Ag metal surface area of the supported catalysts was determined by N_2O titration at 473 K (15). Appreciable Ag sintering of the Ag/K-$\beta''Al_2O_3$ catalyst occurred with use, the observed characteristics being similar to those of conventional Ag/α-alumina catalysts (16). Relevant data are summarised in Table 1.

The surface area of the EP sputter-deposited Ag thin-film sample was estimated by means of a calibration experiment in which propene epoxidation was studied with a clean silver foil after oxidation/reduction pretreatments with oxygen/hydrogen (100 STP ml/min) at 523 K for 3 h, followed by reaction gas (propene : oxygen = 1 : 2, 523 K) for 15 h. At this point the Ag foil gave the same PO selectivity as that observed under open circuit conditions for the EP sample. In thus estimating the Ag surface area of the EP sample, the surface roughness of the Ag foil was not taken into consideration; therefore the value quoted in Table 1 is a lower limit.

TABLE 1

Surface Area Measurements

Determinant	Surface area
BET	
K-$\beta''Al_2O_3$	2.0 m^2/g
α-alumina	2.7 m^2/g (for comparison)
Ag metal	
Ag/K-β''-alumina (postreaction)	108 cm^2/g
Ag/α-alumina (postreaction)	100 cm^2/g
EP thin-film sample	250 cm^2

Pre- and Postreaction XPS Measurements

X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG ADES 400 UHV spectrometer using Mg K_α radiation at an analyser pass energy of 50 eV. Quoted binding energies (BEs) are referenced to the Ag $3d_{5/2}$ emission (368.1eV) from the clean sample. The polycrystalline Ag sample (15 × 20 × 0.5 mm) was attached to a ceramic block containing an embedded Ni–Cr filament that permitted heating to ~700 K both in vacuum and in the reaction cell (volume, 100 cc) that was attached to the spectrometer chamber. Sample cleaning was achieved by Ar^+ sputtering (5 keV, 20 mkA, 30 min, 300–600 K) after which there was no detectable contamination of the Ag surface by C, O, S, P. The reaction cell, isolated from the analysis chamber by a gate valve, allowed exposure of the sample to flowing reaction gas mixture at atmospheric pressure at a specified temperature, thus mimicking conditions in the catalytic reactor. Gas mixtures were delivered using mass-flow controllers; after gas exposure of the sample for the chosen period of time, the cell was evacuated to $\sim 1 \times 10^{-9}$ mbar prior to transferring the sample to the analysis chamber, where XP spectra were acquired at room temperature.

RESULTS

Reactor Data for EP Samples

All experiments were carried out at 523 K with an inlet partial pressure ratio $P_{O2} : P_P$ of 2 : 1, in accord with the findings of Lu and Zuo in regard to the optimum gas composition for maximum selectivity (17). At this temperature the unpromoted, electrochemically cleaned Ag sample (V_{WR} = +500 mV; (18)) exhibited a selectivity of only ~0.25% towards PO production, with the only detectable products being propene epoxide, carbon dioxide, and water.

Effect of Potassium on Activity and PO Selectivity

Starting with the electrochemically cleaned sample (V_{WR} = +500 mV), electropumping of potassium to the Ag surface increased both PO selectivity and activity (Fig. 1). With increasing K coverage the selectivity increased by a full order of magnitude, from 0.25 to 2.5%, before declining again to virtually zero. As is apparent from Fig. 1, the overall activity (in effect, the CO_2 rate) followed the same trend, passing through a maximum at a somewhat higher K loading (+300 mV) than the selectivity (+350 mV). This behaviour was fully reversible: on pumping K away from the Ag surface (by increasing V_{WR}) the activity and selectivity curves retraced the original path, with both parameters eventually reaching their original clean surface values. Among other things, this shows that under our conditions there was no irreversible trapping of CO_2 as alkali carbonate. For purposes of comparison, corresponding data for ethene epoxidation taken from Ref. (5) are shown in Fig. 2.

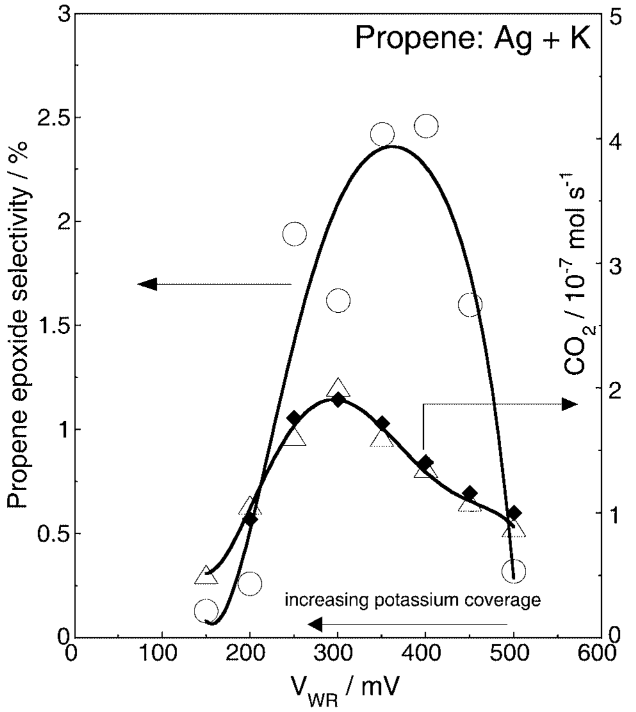

FIG. 1. Effect of potassium on PO selectivity and CO_2 production. (○) Propene epoxide selectivity; (△) CO_2 moles, increasing K coverage; (◆) CO_2, decreasing K coverage. Conditions: $P_{O2} : P_P = 2 : 1$, $T_R = 523$ K, $F_t = 15$ ml min^{-1}.

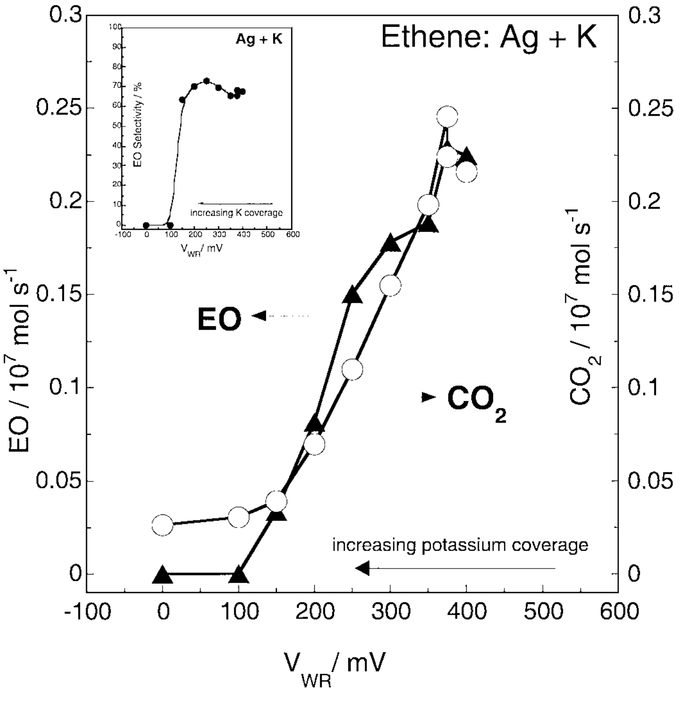

FIG. 2. Effect of potassium on ethene epoxide and CO_2 production. (○) CO_2 moles, (●) EO moles. Conditions: $P_{O2} : P_E = 1 : 2.5$, $T_R = 518$ K, $F_t = 50$ ml min^{-1}.

Note that in the case of ethene, addition of alkali to the surface strongly suppressed both activity and selectivity. Here, too, the effects of electropumping were fully reversible—increasing the catalyst potential caused the system to retrace the original path, ultimately restoring clean surface behaviour.

Effect of Potassium and NO on Activity and PO Selectivity

Addition of parts per million levels of gaseous NO in the presence of alkali enhances the selectivity of Ag catalysts towards *ethene* epoxide formation. This has been demonstrated with both single-crystal (19) and EP samples (5). Accordingly, the effects of K + NO on propene epoxidation were studied. Figures 3 and 4 depict the effect of pumping potassium to the Ag surface for five different levels of NO concentration in the range 0–60 ppm. On the clean surface ($V_{WR} = +500$ mV), parts per million levels of NO had no effect: neither activity nor selectivity was measurably affected. The same behaviour was found in the case of ethene epoxidation (5, 19). However, as potassium was pumped to the Ag surface in the presence of NO, *both activity and PO selectivity decreased* (Figs. 3 and 4, respectively), with the magnitude of this effect increasing with increasing NO concentration. As before, these effects of K + NO were completely reversible with catalyst potential. Once again, this behaviour stands in complete contrast to that observed in ethene epoxidation (5), where this combination of promoters led to a marked improvement in selectivity.

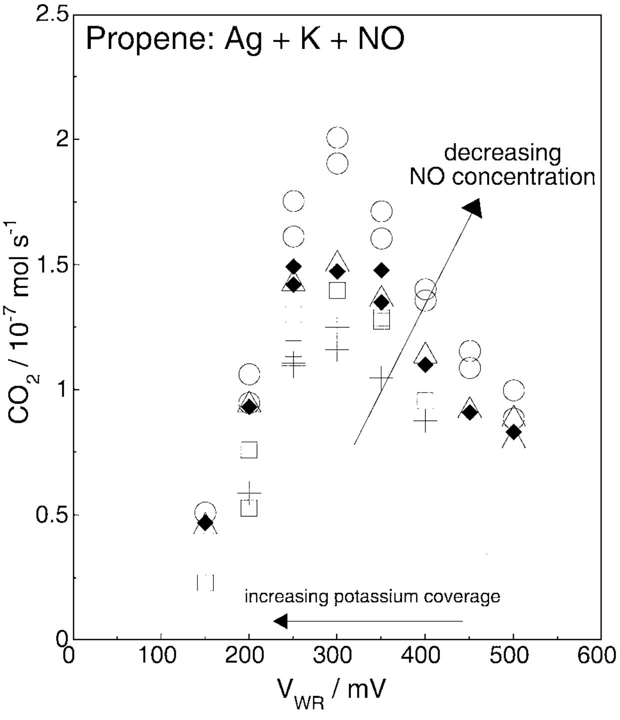

FIG. 3. Effect of potassium and parts per million levels of NO on CO_2 production in propene epoxidation reaction. (○) 0 ppm NO, (△) 10 ppm NO, (◆) 20 ppm NO, (□) 40 ppm NO, 60 (+) ppm NO. Conditions: $P_{O2} : P_P = 2:1$, $T_R = 523$ K, $F_t = 15$ ml min^{-1}.

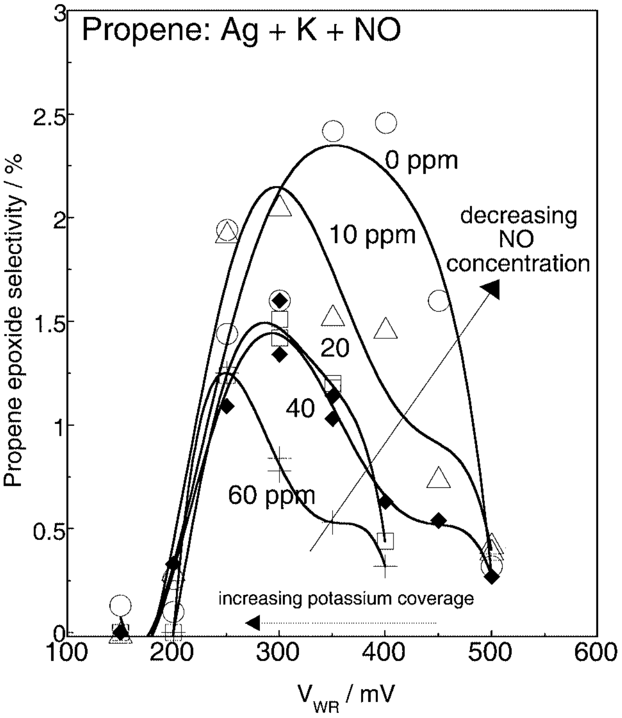

FIG. 4. Effect of potassium and parts per million levels of NO on PO selectivity. (○) 0 ppm NO, (△) 10 ppm NO, (◆) 20 ppm NO, (□) 40 ppm NO, 60 (+) ppm NO. Conditions: $P_{O2} : P_P = 2:1$, $T_R = 523$ K, $F_t = 15$ ml min^{-1}.

Propene and Ethene: Effect of Potassium and Chlorine on Activity and Epoxide Selectivity

Chlorine (added by means of parts per million levels of DCE) is an extremely important selectivity promoter in ethene epoxidation, both in the presence and in the absence of alkalis. Therefore we studied the effect of parts per million levels of DCE on the epoxidation of both propene and ethene. It is apparent from Fig. 5 that addition of 1.5 ppm DCE to the clean Ag surface had little effect on PO selectivity: a small increase was observed (see open *versus* filled symbols at 450 mV). At the same time, an appreciable decrease in activity occurred (open triangles *versus* filled triangle). Subsequent electrochemical pumping of K to the catalyst surface in the presence of DCE caused a monotonic decline in PO selectivity which eventually reached zero at 150 mV. This was accompanied by a shallow maximum in the activity profile. On reversing the potential, in contrast with the results above, an irreversible partial poisoning was observed. For example, at 300 mV the selectivity and activity recovered to ∼50 and ∼84%, respectively, of the values found on the forward potential sweep. Increasing the DCE concentration to 2.5 ppm led to the same general behaviour, but with more pronounced irreversible poisoning.

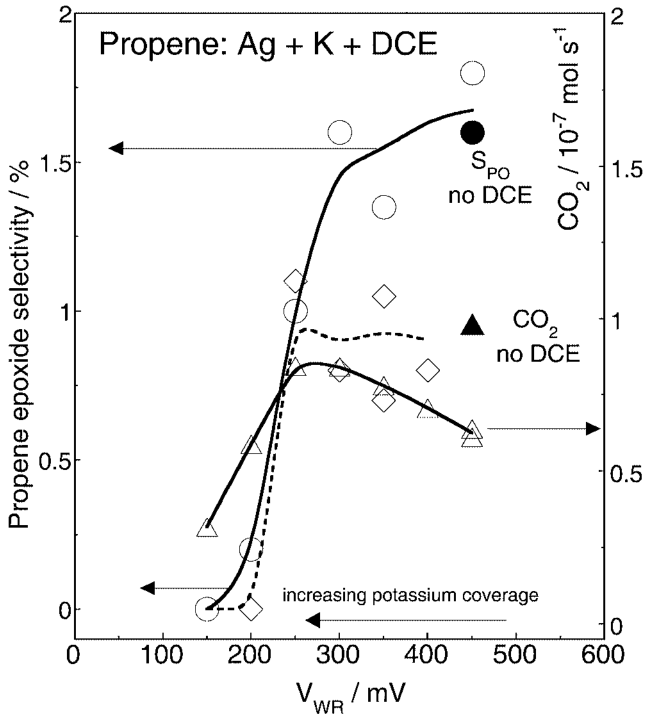

FIG. 5. Effect of potassium and DCE (1.5 ppm) on CO_2 production and PO selectivity. (○) PO selectivity in the direction of increasing K coverage, (◇) PO selectivity reverting catalyst potential, (△) CO_2 moles. Conditions: $P_{O2} : P_P = 2:1$, $T_R = 523$ K, $F_t = 15$ ml min^{-1}.

Analogous measurements carried out for *ethene* epoxidation showed almost exactly the opposite behaviour (Fig. 6). First, addition of DCE to the clean Ag surface substantially *increased* ethene epoxide selectivity from 50 to 76%. This is of course just what is found with conventional Ag/α-alumina catalysts during ethene epoxidation. Second, subsequent electropumping of K resulted in further *increase* in EO selectivity to 85%. Third, DCE caused a very large decrease in activity, exacerbated by addition of K. Fourth, the effects on selectivity and activity were reversible with catalyst potential.

Reactor Data for Supported Catalysts

Propene epoxidation and PO oxidation. A conventional dispersed catalyst consisting of Ag supported on K-$\beta''Al_2O_3$ powder was studied in order to determine whether the EP data contain any artefacts peculiar to this type of sample and method of measurement. Experiments were carried out at the same temperature (523 K) and gas composition ($P_{O2} : P_P = 2:1$) as for the EP measurements. The K-$\beta''Al_2O_3$ catalyst exhibited a selectivity of ~0.5% towards PO production, which is comparable to that shown by the electrochemically cleaned EP sample (~0.25%) at the same level of conversion (<5%). Furthermore the turnover frequencies (TOFs) of the EP catalyst (0.3) and of the Ag/K-$\beta''Al_2O_3$ (0.8) were comparable.

Propene oxide oxidation. In order to investigate whether the low selectivity of Ag/K-$\beta''Al_2O_3$ catalysts (both EP and dispersed) is dominated by PO burning on the support, we studied PO oxidation over K-$\beta''Al_2O_3$ and CaCO3 and with the Ag/K-$\beta''Al_2O_3$ dispersed catalyst. The propene epoxide (0.1–0.7 kPa) and oxygen (7.5–18.5 kPa) partial pressures were varied so as to encompass the range of gas compositions that the Ag/K-$\beta''Al_2O_3$ catalysts were subjected to under *propene* oxidation conditions. Similarly, the temperature (523 K) and space velocity were the same as those used for the propene oxidation measurements. In order to make comparisons between the different samples, the reactor data were normalised with respect to the corresponding surface area using the values shown in Table 1. These results showed clearly that the K-$\beta''Al_2O_3$ support was very inactive towards PO oxidation: negligible CO_2 was observed under all conditions studied. In contrast, both $CaCO_3$ and the Ag/K-$\beta''Al_2O_3$ catalyst were active towards the further conversion of PO. $CaCO_3$ yielded mainly isomerisation products (propionaldehyde and acetone) and some CO_2. Ag/K-$\beta''Al_2O_3$ gave only CO_2.

Postreaction XPS results for ethene and propene oxidation. Akimoto *et al.* speculated that the oxidation state of the Ag surface may be critically important in explaining the very different selectivities achievable with ethene and propene (20). Therefore, we carried out postreaction XPS

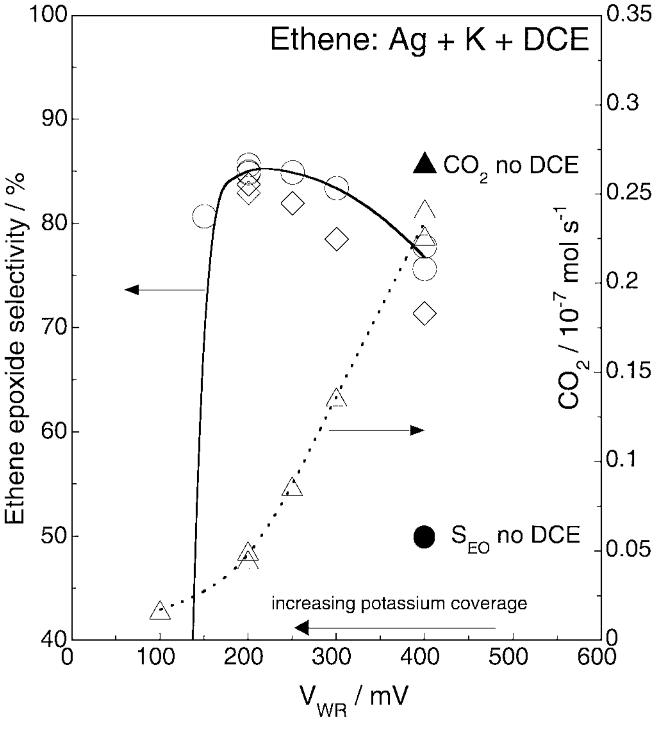

FIG. 6. Effect of potassium and DCE (1.5 ppm) on CO_2 production and EO selectivity. (○) EO selectivity, (◇) EO selectivity reverting catalyst potential, (△) CO_2 moles. Conditions: $P_{O2} : P_P = 1:2.5$, $T_R = 518$ K, $F_t = 50$ ml min^{-1}.

analysis of the surface of an Ag foil (of the same type as that used for the surface area calibration), as follows. Using the reaction cell, the initially clean Ag sample (XPS) was exposed to reaction gas mixtures containing oxygen and either ethene or propene at 550 K, using the same gas compositions as those used in the respective reactor studies. In both cases, postreaction XP Ag 3d, Ag LMM (Auger) O 1s and C 1s spectra were acquired after 10 and 60 min reaction time. The measured Ag Auger parameter (21) was exactly the same for the clean metal surface and after 60 min of ethene or propene oxidation (726.2 ± 0.2 eV). This is an indication that neither reaction resulted in formation of an oxidelike layer at the catalyst surface (Auger parameter of $Ag_2O = 724.3$ eV (21)).

Figure 7 shows postreaction O 1s spectra acquired after exposure to either ethene or propene oxidation conditions. Spectrum 1 was acquired after a 10-min reaction in *ethene*: oxygen and exhibits three features: in this case, as in all subsequent cases, the fitting routine employed Gaussian functions with fixed parameters. The most important features are the strong component at 530.9, which may be reliably assigned (22) to oxygen adatoms (O_a) and the distinct feature at 529.5 due to subsurface oxygen (22), shown as a broken line in Fig. 7. The 533-eV component is ascribed to oxygen-containing carbonaceous residues (23). Spectrum 2 was obtained after a further 50 min under reaction conditions (spectra recorded after longer reaction times confirmed that spectrum 2 corresponded to the steady state). Here, the O_a emission still dominates, and although the relative amount of subsurface oxygen has been somewhat reduced, *it is still clearly present*.

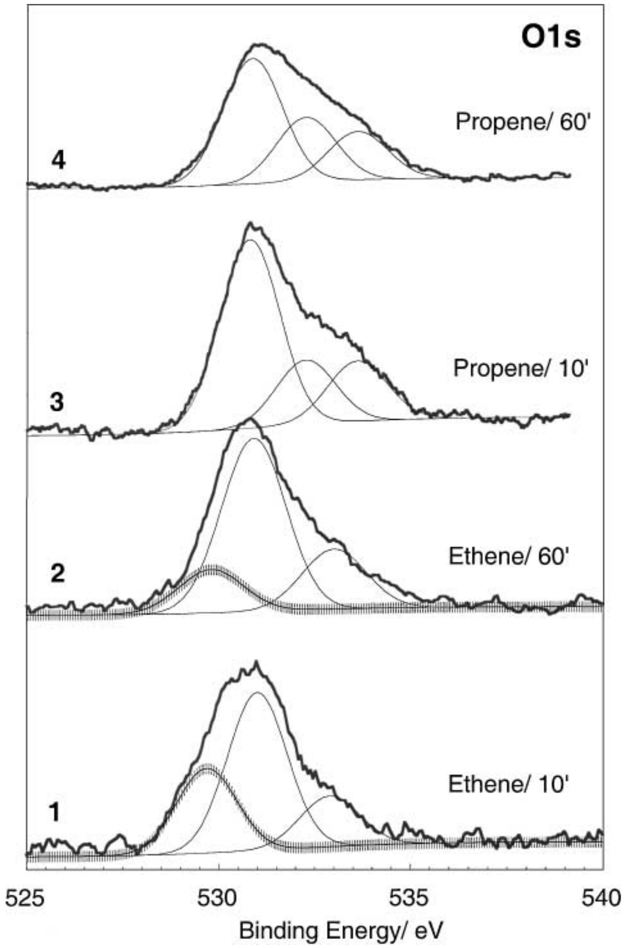

FIG. 7. O 1s postreaction XP spectra after exposure to ethene : oxygen (spectra 1, 2) and propene : oxygen (spectra 3, 4) at 550 K and 1 bar for 10 and 60 min.

The *propene* : oxygen postreaction spectra differ from the *ethene* : oxygen spectra in an important respect: with propene the amount of dissolved oxygen is far less—in effect below the detection limit (spectra 3 and 4, 10- and 60-min reactions, respectively). These spectra also exhibit two peaks (532.3 and 533.6 eV), which we again ascribe to oxygen-containing carbonaceous residues, but differing in oxygen content from those produced during ethene oxidation (23). The assignment is not unreasonable, given the more pronounced tendency of propene to deposit carbon residues, probably polymeric in origin, on the surface of the working Ag catalyst, as noted by others (24–26). Without doubt, however, the most important observation relates to the very low level of dissolved oxygen: in propene oxidation, at steady state, there is far less dissolved oxygen than in the case of ethene oxidation.

For completeness, the corresponding C 1s spectra are shown in Fig. 8, although the relatively poor signal/noise ratio in spectra 1–3, which reflects the relatively low coverage by carbonaceous species, precludes close interpretation. Spectra 1 and 2 were obtained after 10- and 60-min reactions in ethene : oxygen, and spectra 3 and 4 after 10- and 60-min reactions in propene : oxygen. Emission around 284.5, present in spectra 1, 2, and 4, is ascribed as usual to elemental carbon (23). That at higher BEs (286–288 eV) is due to hydrocarbonaceous (CH_x) and oxygen-containing hydrocarbonaceous residues (CH_xO_y): the higher the BE the higher the oxygen content (23). A comparison of the steady-state spectra 3 and 4 shows that propene oxidation does indeed lead to higher coverage of the surface by carbonaceous residues, as inferred by others on the basis of reactor data (24–26), and that the oxygen content of these residues is higher than in the case of ethene.

DISCUSSION

In common with most other studies on both supported and unsupported Ag catalysts (24–30) we observe low selectivities towards PO formation. The control experiments with dispersed materials strongly suggest that the high PO selectivities reported in the ARCO patents (14) are not the result of the $CaCO_3$ support being especially inert towards the further conversion of PO. In addition, they demonstrate

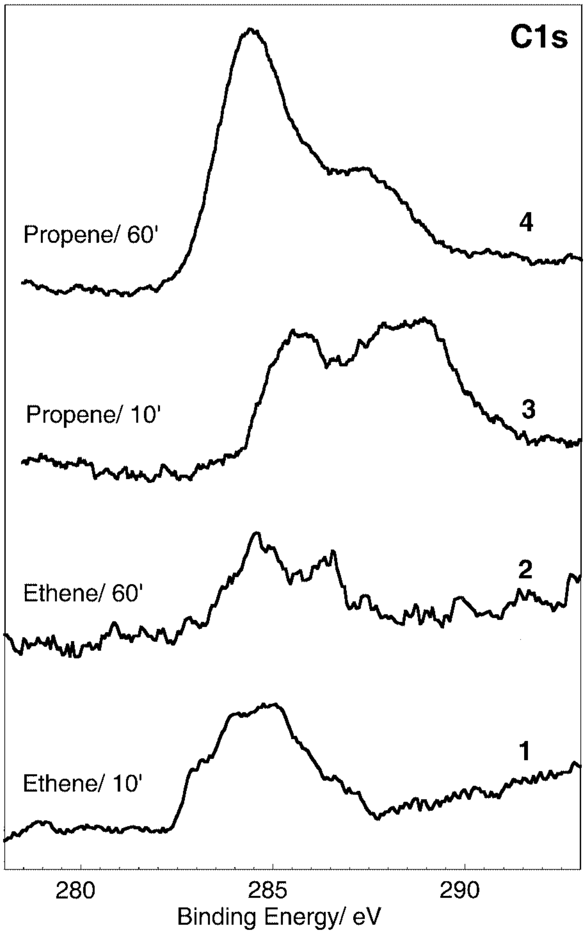

FIG. 8. C 1s postreaction XP spectra after exposure to ethene : oxygen (spectra 1, 2) and propene : oxygen (spectra 3, 4) at 550 K and 1 bar for 10 and 60 min.

that K-$\beta''Al_2O_3$ is inert towards PO, so that our EP results do reflect the intrinsic catalytic behaviour of Ag, undistorted by any effects due to the solid electrolyte support. Moreover, the comparable TOFs observed under similar conditions for the EP and dispersed Ag/K-$\beta''Al_2O_3$ samples indicate that the catalytic properties of the polycrystalline Ag thin film are essentially the same as those of supported silver particles. We may therefore suppose that inferences drawn from the EP data are relevant to the behaviour of supported silver catalysts.

The most striking feature of the present EP results is the very different response of propene epoxidation to added K, K + NO, and K + Cl, compared to ethene epoxidation. In simple terms, K alone is bad for EO, good for PO; K + NO is good for EO, bad for PO; Cl alone is good for EO, indifferent for PO; K + Cl is good for EO, bad for PO. We take as our starting point the generally agreed view that oxygen adatoms on the Ag surface are responsible for both epoxidation and combustion of *ethene*, and that dioxygen species, though present, are merely spectators (1). In ethene epoxidation the adverse effect of alkali on EO selectivity may be rationalised in terms of increased alkene burning (1): alkali renders O_a more nucleophilic, favouring C–H scission at the expense of O-insertion into the C=C bond. In complete contrast with this, K alone strongly promotes both activity and selectivity of PO formation. This implies that K generates a surface oxo species other than O_a that is effective for propene epoxidation, though ineffective for ethene epoxidation. Obvious candidate species are alkali peroxy or superoxy compounds, and indeed it was demonstrated many years ago that alkali superoxide monolayers grown from alkali + oxygen are stable on the Ag{111} (31) and Ag{100} (32) surfaces. The fact that PO selectivity passes through a maximum with increasing K loading is noteworthy. This is at least consistent with the participation of a superoxy or peroxy reactant, the coverage of which initially increases with K loading, then declines again at sufficiently high K loading as the composition of the alkali oxide changes, perhaps according to

$$KO_2 \rightarrow K_2O_2 \rightarrow K_2O,$$

with K_2O being ineffective for epoxidation. Note that this order of evolution with available ambient oxygen of the proposed alkali surface species is in line with the well-known oxide chemistry of bulk potassium oxides (33).

Note that we do not exclude the possibility that O_a may also contribute to the epoxidation of propene. Its low efficiency for PO formation may very well be due to the relative ease of abstraction of the allylic hydrogen, a plausible hypothesis that receives support from a number of investigations, including theoretical studies, of the epoxidation of propene and higher alkenes (20, 26, 29, 32, 34–36). As we see below, another factor may also act to decrease the effectiveness of O_a in propene epoxidation. Given the above circumstantial evidence, what is the likelihood that some type of adsorbed dioxo species participates in propene epoxidation?

In earlier discussions of propene epoxidation (25, 26, 28, 30) it has generally been assumed that the molecular mechanism is analogous to that for ethene epoxidation and that the same oxygen surface species is active in both cases. Given the consensus that now exists regarding (i) the role of O_a as the epoxidant for ethene and (ii) the relative ease of allylic hydrogen abstraction by O_a in the case of propene, we consider evidence in addition to that presented here in favour of the possibility that a dioxo species may participate in propene epoxidation, in addition to O_a. An interesting pointer comes from the work of Geenen *et al.* They studied ethene and propene oxidation over Ag and Ag/Au catalysts (26), although it must be emphasised that the interpretation of some of their data which follows is ours, not theirs. First we note that isolated Ag sites such as those present at the surface of an Ag/Au alloy do not favour dissociative chemisorption of oxygen to yield O_a.

On the other hand, they should be capable of adsorbing a dioxygen species. Geenen *et al.* found that Au strongly suppressed selectivity towards EO formation while promoting acrolein formation; no PO was detected. Acrolein formation (which competes with PO formation) was plausibly ascribed to an electrophilic attack on propene by a dioxygen species adsorbed at isolated Ag sites. Thus alloying with Au favours partial oxidation of propene via $O_{2(a)}$ and strongly disfavours partial oxidation of ethene via O_a.

Very recently, Lange de Oliveira *et al.* reported on Ag/TiO$_2$ catalysts that are highly selective (90%) for propene epoxidation, albeit at very low conversion (0.4%), when co-fed with propene, oxygen, *and hydrogen* (37). In this respect, the findings of Lange de Oliveira *et al.* closely resemble those of Haruta and his coworkers (38), who worked with Au/TiO$_2$ catalysts and who also co-fed with propene, oxygen, *and hydrogen.* These two pieces of work suggest at least the possibility that these related and unusual systems work by means of *in situ* hydrogen peroxide generation. Again, this points to the possible involvement in propene epoxidation of an adsorbed peroxo species. This discussion does of course beg the question of why $O_{2(a)}$ should be effective for propene epoxidation and not ethene epoxidation. The latter would appear to be an established fact: $O_{2(a)}$ is a spectator species in ethene epoxidation. Further work is required to establish beyond doubt whether or not $O_{2(a)}$ plays a role in propene epoxidation in addition to or instead of O_a.

PO and EO selectivity respond in opposite ways to K promotion in the presence of NO. There is good evidence that under such conditions surface alkali nitrates are formed (10) and that they participate in oxygen transfer to terminal alkenes that do not contain allylic hydrogen (39), including ethene itself (40), thereby enhancing epoxidation selectivity. However, with propene, K + NO actually *decreases* PO selectivity. Two possible causes are (i) alkali nitrate formation, which competes with alkali superoxide formation, the latter being considered desirable for PO formation, and (ii) the possibility that alkali nitrate may actually be an unselective oxidant for propene.

Next we consider the response of propene and ethene epoxidation to the presence of chlorine and potassium. Cl alone strongly promotes EO selectivity by decreasing the valence charge on O_a, rendering it more electrophilic, thus favouring epoxidation (1). Cl has relatively little effect on PO selectivity because allylic hydrogen stripping by O_a, which leads to combustion, is so strongly favoured in this case. Addition of K increases further the selectivity for EO formation, possibly due to its influence on the secondary chemistry (by promoting EO desorption) and/or by promoting Cl adsorption (this would also account for the strongly decreasing activity; Fig. 6). Again, why does PO catalysis behave so differently? Here, selectivity actually decreases on addition of K (Fig. 5). It is possible that this is due to excessive formation of potassium chloride at the expense of the less stable superoxo or peroxo compounds. KCl formation would also be consistent with the irreversible partial poisoning of selectivity and activity that is observed in the case of propene oxidation. Related to this, White and coworkers (41) found that relatively low coverages of preadsorbed chlorine ($\theta \sim 0.1$) actually enhance ethene uptake on Ag{111}, whereas propene uptake was always inhibited. As a result, residual levels of Cl might be expected to exert a much stronger poisoning effect on reactions involving adsorption of propene as compared to ethene.

The postreaction XPS data provide a valuable indication of the state of the Ag surface and immediate subsurface region (sampling depth, ~3 nm) under reaction conditions. Recall that these experiments were prompted by the interesting speculative interpretation advanced by Akimoto *et al.* (20) based on their comparative study of the oxidation of ethene, propene, and higher alkenes. Their argument hinges on the supposition that the state of oxidation of the Ag surface plays a critical role. In particular, they suggest that under reaction conditions the Ag surface is significantly more oxidised in the case of ethene than in the case of propene. They go on to ascribe different chemical behaviour to alkene molecules adsorbed on $Ag^{\delta+}$ and Ag^0 sites, but this is peripheral for present purposes. The key question is this: is it actually the case that the oxidation state of the Ag surface is substantially different in the two cases? As far as we are aware, the present work represents the first attempt to address this issue directly.

As already noted, the measured Auger parameters show that there is no gross difference in oxidation state of the Ag surface and near-surface region between the cases of ethene and propene oxidation. It is also clear that in the case of ethene the apparent steady-state O_a population of the surface is significantly greater than in the case of propene. This is unsurprising, given that the C 1s spectra show a higher concentration of carbonaceous residues in the case of propene. What is most interesting, and possibly very important, is the substantially higher concentration of dissolved oxygen that is clearly present in the case of ethene. Note that this explanation is consistent with results obtained by Stoukides and Vayenas (29) for Ag-catalysed propyene oxidation under electrochemical promotion, but with yttria-stabilised zirconia as the solid electrolyte (an oxygen ion conductor). They found a small increase in PO selectivity when oxygen was pumped *to* the Ag catalyst film: this could have resulted in an increase in the amount of subsurface oxygen.

Long ago (1), using an Ag{111} model catalyst, we showed that selectivity towards ethene epoxide formation depended critically on building up an appreciable content of subsurface oxygen. We rationalised this in the same terms as those we used to explain the very specific selectivity promotion induced by chlorine (as opposed to Br, I, S, . . . , all of which merely poison the system). Briefly, the argument is as follows. Epoxidation depends on O_a acting as an electrophile; the higher the electronic charge density on O_a, the more nucleophilic its behaviour, favouring H-abstraction, leading to alkene combustion, at the expense of epoxidation. Adsorbed chlorine reduces the valence charge density on O_a, improving its electrophilicity, thus favouring epoxidation; and chlorine works because its electronegativity is comparable to that of oxygen. Dissolved oxygen, located just below the surface, works in exactly the same way as adsorbed chlorine. It withdraws valence charge from O_a, rendering it a better electrophile, favouring epoxidation.

We now have a possible explanation for the much lower epoxidation selectivity found with propene. In this case, the low concentration of dissolved oxygen renders O_a a relatively poor electrophile, favouring combustion at the expense of epoxidation. Worse, this tendency is exacerbated because of the ease of allylic hydrogen abstraction. Why is the concentration of dissolved oxygen less with propene? In a general sense, this is probably connected with the fact that propene is a more effective reducing agent than is ethene. This may serve to inhibit surface-to-subsurface transport of O atoms or even to abstract subsurface oxygen.

In summary, our results suggest that two phenomena, previously not considered, are of significance to an understanding of Ag-catalysed propene epoxidation. First, an effective epoxidising agent other than O_a is induced by alkali—possibly a peroxo or superoxo species. Second, the epoxidation efficiency of O_a is itself strongly impaired by the low concentration of subsurface oxygen. In addition, it appears that whereas alkali nitrates benefit selectivity in the case of ethene epoxidation, the opposite is true with propene. This is an additional indication that different alkali-induced auxiliary selective oxidants may operate in the two cases—nitrate with ethene and peroxo or superoxo with propene.

CONCLUSIONS

1. Ag-catalysed propene epoxidation and ethene epoxidation respond in very different ways to the addition of K, NO, Cl, and combinations of these modifiers. In some instances the two systems exhibit exactly the opposite behaviour, signalling important differences in reaction mechanisms.

2. The results suggest that in the case of propene epoxidation some oxo species other than O_a (or in addition to O_a) may also be involved in the selective oxidation channel. Peroxy or superoxy species present as adsorbed alkali superoxides or peroxides are plausible candidate compounds.

3. Control experiments with support materials and a dispersed catalyst strongly suggest that support effects do not play a critically important part in determining the observed low selectivity of propene epoxidation. Further conversion of PO is not an issue: the problem resides in the primary chemistry and probably hinges on the presence of allylic hydrogen atoms in the alkene.

4. Postreaction XPS data suggest that the state of oxygenation of the subsurface region may also be important in determining the very different selectivities observed in ethene and propene epoxidation.

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