Triply-promoted ethene epoxidation: NO_x promotion of the Ag-catalysed reaction in the presence of alkali and chlorine under electrochemical control

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Potassium, electrochemically supplied from K β''-alumina to a silver thin film catalyst in the presence of ppm levels of NO_x, strongly promotes the selectivity of ethene epoxidation. However, in the absence of gaseous NO_x, alkali catastrophically suppresses both activity and selectivity. Addition of surface chlorine via ppm levels of ethylene dichloride further enhances the promotional effect of alkali + NO yielding the highest selectivity of all. The minimum necessary and sufficient conditions for the appearance of NO_x promotion are submonolayer quantities of alkali on the metal surface, and ppm levels of gaseous NO_x.

Keywords: ethene, epoxidation, silver, promotion, potassium, NO_x

1. Introduction

Heterogeneously catalysed alkene epoxidation is of great interest from both academic and technological points of view. Ethene epoxidation, for which Ag is an apparently unique catalyst, is a strategically important large-scale industrial process. As a result, elucidation of the mechanism of Ag-catalysed epoxidation has attracted a great deal of academic research and many key features of the reaction may be regarded as well understood. Gaseous and solid state promoters play a vital role in ethene epoxidation catalysis. In practice, adsorbed chlorine, usually supplied by addition of ppm levels of gaseous dichloroethane (DCE), is always used as a promoter. Additionally, alkalis are almost always added as co-promoters in commercial catalysts where they influence both the metal chemistry and the support chemistry. The mode of action of adsorbed chlorine and alkali [1] promoters has been elucidated and a recent review of progress in the field is provided by [2].

In the 1980s, a series of patents appeared [3–6] in which it was claimed that addition of ppm levels of NO_x or NO_x precursors to the feedstream led to selectivities even higher than those delivered by doubly-promoted Ag (Cl, alkali). However, the mechanism of NO_x promotion remains to be elucidated. A key question is the following. Does NO_x act by enhancing "conventional" Ag epoxidation catalysis or does it open up a new highly selective reaction channel that runs in parallel with this chemistry? Here, we address these issues by making use of electrochemical promotion (EP), a technique that allows control of alkali promoter levels on the surface of a working catalyst.

Electrochemical promotion provides a unique means for *in situ* control of catalyst performance [7]. Reference [7] provides a detailed account of the phenomenology and outlines a theoretical basis in terms of which the EP effect may be interpreted. The method entails electrochemical pumping of ions from a solid electrolyte to the surface of a porous, catalytically active metal film: the resulting changes in work function of the catalyst alter the adsorption enthalpies of adsorbed species and the activation energies of reactions involving these species. The electrochemically induced changes in catalyst potential measured with respect to a reference electrode (ΔV_{WR}) are related to $\Delta\phi$, the change in catalyst work function [8]. Thus controlling V_{WR} provides control of the concentration of spilt-over promoter species on the catalyst surface.

Karavasilis et al. investigated EP by Na of ethene epoxidation over Ag, all data being acquired in the presence of gaseous dichloroethane [9]. No results were reported for the effect of Na in the absence of surface chloriding. That is, they investigated the catalytic system used in current industrial practice and whose behaviour is relatively well understood, as indicated above. Our objective here is to shed light on the ultraselective epoxidation catalysis that can be induced in the presence of gaseous NO. In particular, we seek to answer the question "what are the minimum necessary conditions for this phenomenon to appear?"

We have therefore investigated electrochemically promoted Ag thin film catalysts supplied with potassium from a K β''-alumina electro-active support to investigate the origin of NO_x promotion of ethene epoxide formation. The EP technique has been used to study the effects of K, Cl, NO separately and in combination. It is demonstrated that the minimum necessary and sufficient conditions for NO_x pro-

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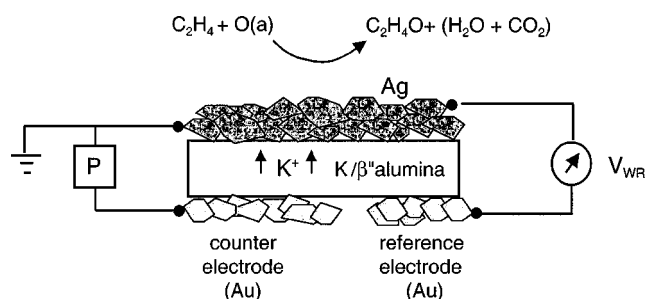* To whom correspondence should be addressed.

Figure 1. Schematic of EP catalyst sample. P denotes the potentiostat.

motion are adsorbed alkali on the metal surface and ppm levels of gaseous NO_x in the reactant feedstream. This leads to very substantial selectivity enhancement without appreciable loss of activity. Finally, the triply-promoted system (alkali + NO_x + chlorine) is investigated.

2. Experimental

The EP reactor, analysis system and electrochemical technique have been described in detail elsewhere [10]. Specific features relevant to the present case are summarised here. The silver catalyst consisted of a porous continuous thin film ($\sim$12 cm^2 geometric area) deposited by DC sputtering in an Ar atmosphere on one face of a K β''-Al$_2$O$_3$ wafer. Au reference and counter electrodes were deposited on the other face of the solid electrolyte wafer, also by sputtering. Electrical contact with these electrodes was achieved by means of 0.5 mm diameter Au wires, which also served to suspend the Ag/K β''-Al$_2$O$_3$/Au sample in a quartz, atmospheric pressure well-mixed reactor ($\sim$45 cm^3). All three electrodes were exposed to the reactant gas mixture and the system behaved as a single pellet, continuous stirred tank reactor [11]. A schematic drawing of the experimental arrangement is shown in figure 1. Inlet and exit gas analysis was carried out by a combination of on-line gas chromatography and on-line mass spectrometry. Reactants were 20% O_2/He (MG Gas) and 30% ethene/He (BOC Gases) diluted in ultrapure He (99.996%) and fed to the reactor by mass flow controllers (Brooks 5850 TR). The gaseous promoters, dichloroethane (DCE) and NO (20 and 300 ppm in He, respectively, Messer, BOC Gases) were supplied to the reactor so as to achieve controlled concentrations in the 1–5 ppm range. The total flow rate was kept constant in all experiments at 3.4×10^{-5} mol/s (50 cm^3 (STP)/min), at a total pressure of 1 atm in every case. Reactant conversion was restricted to <5% in order to avoid mass transfer limitations, i.e., the system was operated differentially and behaved as a well-mixed reactor in the flow regime employed.

3. Results and discussion

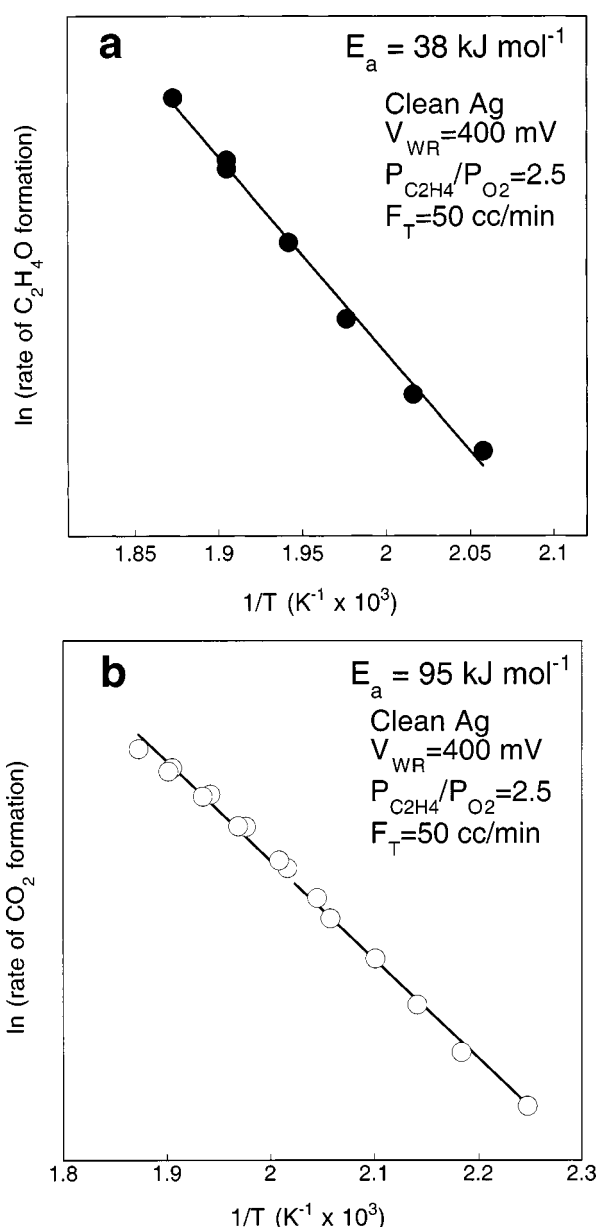Under all conditions, the only detectable products were ethene epoxide, carbon dioxide and water. At 245 °C with

Figure 2. Activation energies for production of (a) ethene epoxide and (b) CO$_2$.

$P_{C_2H_4} : P_{O_2} = 2.5$ the clean Ag sample exhibited a selectivity of $\sim$55% towards ethene oxide (EO) formation, comparable to that achieved with unpromoted dispersed Ag/α-alumina catalysts [12]. The activation energies (figure 2 (a) and (b)) for EO and CO$_2$ formation on the clean Ag surface (38 and 95 kJ/mol, respectively) were in good accord with those obtained with single crystal model catalysts (45 ± 5 [13] and 97 kJ/mol [14], respectively).

Starting with the electrochemically cleaned surface ($V_{WR} = 400$ mV), electro-pumping of K to the Ag surface strongly *decreased* both activity and selectivity, both indices collapsing at $V_{WR} \approx 200$ mV ($\Theta_K \approx 0.02$), as shown in figure 3 (a) and (b). Note that the alkali-induced loss of selectivity is entirely consistent with the well-known selectivity-enhancing effect of chlorine. This
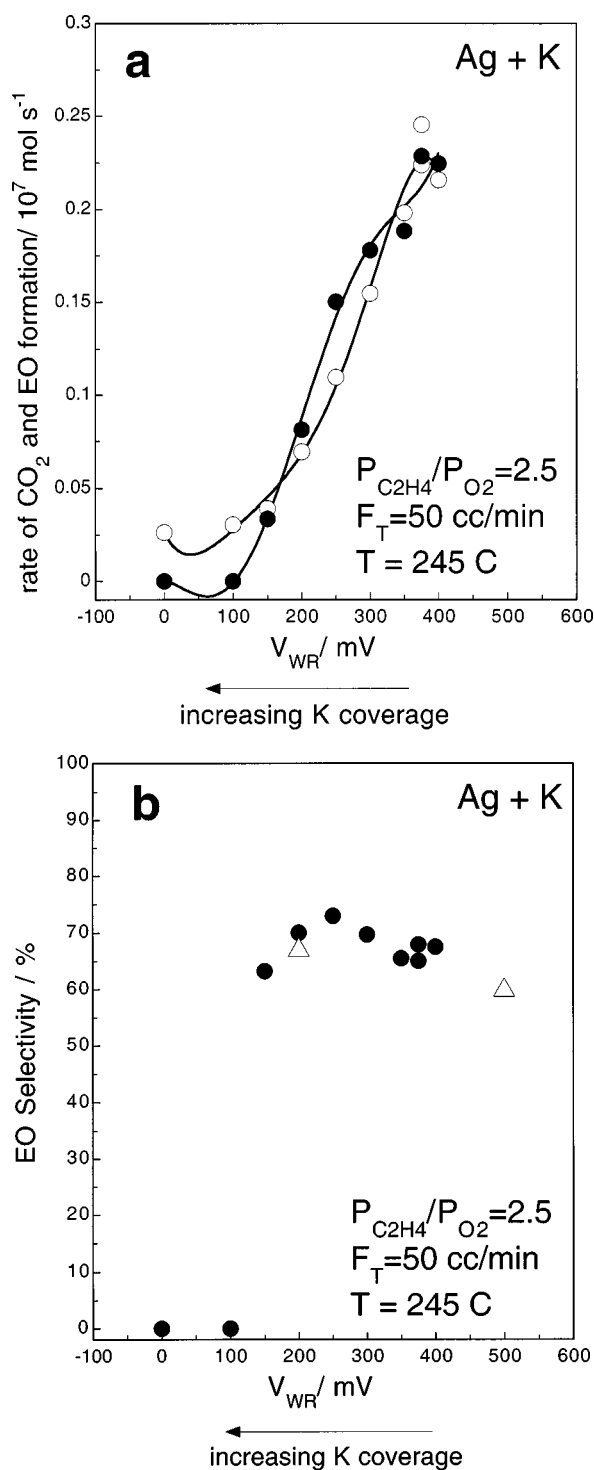
Figure 3. Effect of electro-pumped K on (a) activity (($\circ$) CO_2; ($\bullet$) epoxide) and (b) selectivity. ($\triangle$) Data in (b) obtained by reversing V_{WR} after the catalyst had been poisoned at $V_{WR} = 0$ mV.

that block active sites. Our earlier XPS and XANES study of the EP of Pt-catalysed propene oxidation [15] suggests that in the present case poisoning is probably due to coverage of the Ag surface by potassium carbonate. In the present case, increasing the catalyst potential to 400 mV, thus pumping K away from the Ag surface, electrochemically destroyed the poisoning surface compound, restoring initial performance. This reversibility is demonstrated by the ($\triangle$) data points in figure 3(b) which were obtained by reversing V_{WR} after the catalyst had been poisoned at $V_{WR} = 0$ mV.

In the absence of K, ppm levels of NO had no effect whatever on the reaction: neither activity nor selectivity were measurably affected. However, in the presence of electro-pumped K, addition of NO induced a dramatic change in behaviour. For example, with 5.5 ppm NO in the feed gas, K pumping to the Ag surface led to a pronounced *increase* in selectivity (figure 4(a)) from $\sim$50% on clean Ag to a maximum value of 75%, followed by a gradual decrease to 70% as the K loading is increased further. It is important to note that the effect of K + NO in strongly promoting selectivity is not merely due to a decrease in conversion induced by these promoters. Thus when the maximum selectivity was achieved at a sodium loading corresponding to 250 mV (figure 4(a)), conversion had decreased by only 5% with respect to the clean, unpromoted Ag surface. The behaviour under electrochemical promotion was fully reversible: as the catalyst potential was increased from -100 mV, thus pumping K away from the Ag surface, clean surface behaviour was recovered at $V_{WR} = 400$ mV (see ($\triangle$) data points in figure 4(a)).

Figure 4(b) shows the results of carrying out K pumping in the presence of both 5.5 ppm NO and 1.5 ppm dichloroethane, where the latter acts to deposit Cl on the metal surface. Addition of DCE in the absence of K and NO raises the EO selectivity from 52% ($\square$) to 76% (∇). Addition of 5.5 ppm NO and pumping of some K to the Ag surface ($\bullet$) raises the selectivity still further, to 83%, *and this high value is sustained* as more K is pumped to the surface. What is the range of alkali coverage encompassed by these measurements? This can be determined only by detailed XPS and work function measurements. Such measurements have been carried out for Cu thin film surfaces electropumped with alkali in a manner exactly analogous to that used here. Those findings [16] indicate that at the most negative catalyst potential employed here (-400 mV) the potassium coverage is in the order $\sim$5% of a monolayer.

For the optimally promoted catalyst, the EO activity is $\sim$59% that of clean Ag. This stands in contrast to the behaviour observed for the doubly-promoted systems K + NO (figure 4) and K + Cl (not shown) where high levels of K lead to a collapse of both activity and selectivity.

Our most significant finding is that the minimum necessary and sufficient conditions for the appearance of NO_x promotion of ethene epoxidation are (i) ppm levels of NO in the reactant feed, and (ii) adsorbed alkali *on the Ag surface*. That is, our technique allows us to exclude the possibility
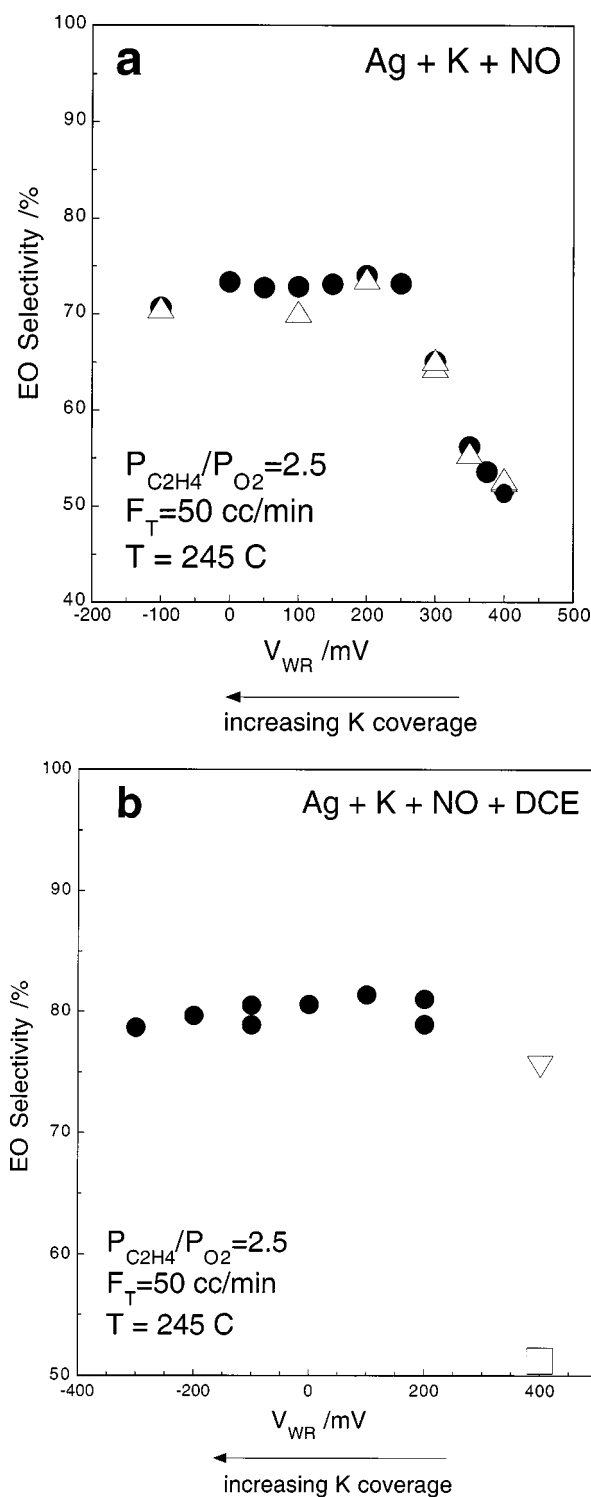
behaviour demonstrates the expected opposite effects of electropositive and electronegative promoters in decreasing and increasing, respectively, the electrophilicity of oxygen adatoms. The higher the electrophilicity, the higher the selectivity towards epoxidation [13]. It is likely that the eventual catastrophic poisoning of activity is due to the accumulation of catalytically inert alkali surface compounds

Figure 4. Effect of K pumping on selectivity for (a) doubly-promoted and (b) triply-promoted Ag. In (a), ($\triangle$) data points demonstrate reversibility upon increasing catalyst potential back to 400 mV.

that NO_x promotion involves effects due to the support. Earlier studies of K-doped Ag/alumina dispersed catalysts carried out under ultrahigh vacuum demonstrated that dosing such materials with NO resulted in the formation of adsorbed alkali nitrate [17]. The present results strongly suggest that such surface oxyanions could be directly in-

volved in alkene epoxidation via a cycle such as
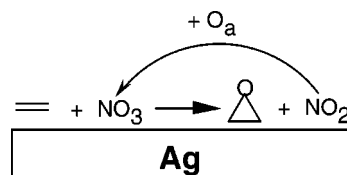
where oxygen transfer to the alkene could either be direct or mediated by the metal surface.

Our results also indicate that triply-promoted Ag delivers a higher selectivity than any of the doubly-promoted systems, K + NO, NO + Cl and K + Cl and that this selectivity is rather insensitive to the alkali loading. It is apparent that there are significant synergistic effects between the three promoters and it seems at least possible that competition between KCl formation and KNO_3 formation plays a part. Adsorbed alkali halides are known to form when Ag surfaces are exposed to K + chlorine [18]. Spectroscopic work is in progress in order to determine the chemical identity of the surface species involved and the role they play in oxygen transfer to adsorbed alkenes.

4. Conclusions

(1) In the absence of other promoters, K alone serves only to poison both the activity and selectivity of Ag in the epoxidation of ethene.

(2) In the presence of ppm levels of gaseous NO, the situation is transformed: supply of alkali to the catalyst strongly promotes selectivity. The minimum necessary and sufficient conditions for the appearance of this phenomenon are ppm levels of gaseous NO and submonolayer quantities of alkali on the silver surface.

(3) Addition of chlorine to the catalyst surface enhances NO + alkali promotion. The triply-promoted system exhibits the highest selectivity of all.

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