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Halogen-induced selectivity in heterogeneous epoxidation is an electronic effect—fluorine, chlorine, bromine and iodine in the Ag-catalysed selective oxidation of ethene

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Selectivity promotion in the Ag-catalysed heterogeneous epoxidation of ethene correlates with halogen electron affinity showing that it is an electronic phenomenon rather than a steric or geometrical effect.

Selectivity promotion by adsorbed chlorine is critically important in the Ag-catalysed heterogeneous partial oxidation of ethene to the epoxide, not least because the effect is vital to process economics in modern large-scale chemical technology. Adsorbed chlorine, supplied from the gas phase by continuous addition of ppm levels of chlorocarbons (*e.g.* $C_2H_4Cl_2$), raises epoxidation selectivity from ~40% to >70%.

The mechanism of ethene epoxidation remained a controversial issue for many years, virtually all discussion pivoting on the identity of the active oxygen species.[1,2] According to the view of Sachtler[3] and his school, initially supported by Campbell[4] and his co-workers, $O_2(a)$ is the epoxidant with O_a being responsible for ethene combustion. However, according to us,[5] *all* the catalytic chemistry is due to O_a, the valence charge state of this species determining reaction selectivity—oxygen insertion *versus* alkene combustion. (We showed that $O_2(a)$, though present, is merely a spectator.[5]) Lower valence charge density on O_a makes it a better electrophile, favouring electrophilic attack on adsorbed ethene and hence epoxidation. Conversely, higher valence charge density on O_a favours H-abstraction from ethene, and hence combustion. It is here that interpretation of the role of the chlorine promoter plays a key role.

According to the Sachtler hypothesis chlorine acts “geometrically”. It simply occupies surface sites, inhibiting the chemisorption of O_a more strongly than that of $O_2(a)$ because dissociative chemisorption of oxygen requires a larger ensemble of vacant Ag sites than does non-dissociative chemisorption.[6] On the other hand, our model calls for the chlorine promoter to act electronically, withdrawing valence charge from co-adsorbed O_a thus favouring epoxidation over combustion. For our mechanism to operate, the promoter atom’s affinity for valence electrons must be comparable with that of O, which is certainly true for chlorine.

So what about the effects of F, Br and I, never previously reported? Experiments with all four halogens should provide an acid test of reaction mechanism and lay the matter to rest, once and for all. According to the geometric or steric view, F, Br, I should act in a manner similar to Cl. At comparable halogen coverages, all three should increase epoxidation selectivity to about the same extent as chlorine. On the other hand, according to our electronic hypothesis, given the electron affinities of the halogens,[7] one might expect a clear selectivity maximum at chlorine (EA = 3.40, 3.61, 3.36, 3.06 eV for F, Cl, Br, I, respectively).

Here we report such a test. The results are unambiguous: under comparable conditions all four halogens do promote selectivity and there is indeed a clear maximum at chlorine. Thus the electronic nature of halogen promotion in heterogeneous alkene epoxidation in unequivocally established.

The Ag/α-Al_2O_3 catalysts were prepared by incipient wetness impregnation of 350 μm α-Al_2O_3 with a 16 wt.% $AgNO_3$ (Aldrich) aqueous solution followed by drying in air (8 h, 370 K) and air-calcination (4 h, 573 K). Reactions were carried out in a single-pass, fixed-bed quartz tubular reactor (id 4 mm) of conventional design. The reactant gases were 30% C_2H_4/He and 20% O_2/He (BOC gases, Messer, respectively, 99.998%) and were used without further purification. The feed gas mixture was delivered by means of mass flow controllers (MKS) with reactor inlet and outlet analyses being performed by mass spectrometry (MKS Spectra Products) and gas chromatography (Shimadzu 14B, HysepN and molecular sieve 5 Å columns). Catalyst samples were 500 mg, the total flow rate was 15 $cm^3\ min^{-1}$ (STP) (space velocity ~1450 h^{-1}) with ethene conversion being <10% in all cases. Halogen dosing followed technical practice: vapour phase injection of aliquots of halocarbon upstream of the catalyst using CH_2CHF (Fluorochem), CH_2Cl_2, C_2H_5Br, CH_3I (Aldrich). The resulting changes in catalyst performance (selectivity, ethene conversion) were then followed by mass spectrometry and gas chromatography. Testing was carried out at atmospheric pressure, 518 K, and with a feed composition of 18.6 kPa ethene and 7.5 kPa oxygen (balance helium). The only products ever observed were ethene epoxide, CO_2, and H_2O. X-Ray photoelectron spectroscopy (XPS) measurements were performed in a VG ADES 400 UHV spectrometer using Mg Kα radiation.

The un-promoted catalysts were pre-conditioned by running in the reaction mixture for 20 h at 518 K at which point ethene conversion and epoxide selectivity attained steady values. At this stage the conditioned, un-promoted catalysts exhibited epoxide selectivities in the range 35–38%. Pure α-Al_2O_3 control samples were similarly pre-treated for use in control experiments with the various halocarbons.

Successive injections of halocarbon were then applied, and at each stage the activity and epoxide selectivity were measured. Results were reproduced with two different catalyst samples in each case. Note that single crystal measurements on Ag(111)—the dominant surface structure on large silver particles such as ours—show that Cl,[8] Br[9] and I[10] adatoms are homogeneously distributed and develop the same series of structures with increasing halogen coverage.

Fig. 1a–d show the effects of the four halogens on relative activity, expressed as ethene conversion (to epoxide + CO_2) relative to that exhibited by the un-promoted catalyst. As expected, in every case, over-dosing poisons the catalyst as active sites are increasingly blocked by adsorbed halogen atoms. The effect of a given number of pulses varies with the identity of the halocarbon, presumably reflecting different C–X bond strengths and hence different probabilities for deposition of X per incident molecule of halocarbon. For reasons that will become apparent, Fig. 1a shows an “infinity point” (△) obtained after a large number of CH_2CHF doses.

Our principal interest is the effect on *selectivity*: the corresponding results are shown in Fig. 2a–d. Where error bars are not shown, the error in each point is smaller than the plotting symbol used. It is apparent that adsorption of all four halogens led to significant enhancement of selectivity. It is equally clear that chlorine is the most powerful promoter, delivering 82% epoxide selectivity at pulse number 4, at which point much of the original activity has been retained. (Even after pulse 3, the selectivity is 79% with 59% of the original activity retained). In

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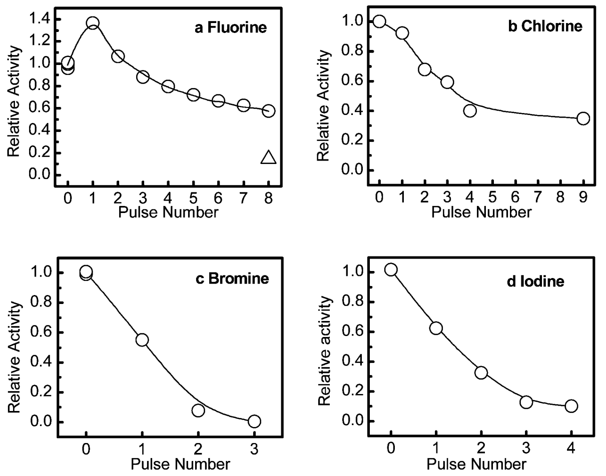

Fig. 1 Effect of the four halogens on catalyst activity.

contrast, the other three halogens are markedly inferior, delivering maximum selectivities in the range 42–55%, and, unlike chlorine, only at the expense of very substantial decreases in activity. Even at very high F coverages, at which point catalytic activity is heavily suppressed, fluorine promotion yields only 60% selectivity (▲, Fig. 2a).

In order to compare like with like so as to obtain a reliable measure of the relative efficiency of promotion, we may proceed as follows. Halogen adatoms have two effects. First, they enhance selectivity, by whatever means. Second, they reduce activity by diminishing the number of bare Ag sites. At our low levels of overall ethene conversion ($< 10\%$) the activity should be directly related to the number of available Ag sites. Therefore, by comparing epoxide selectivities at some fixed level of ethene conversion, say 50% of initial activity, we are dealing with comparable coverages of halogen atoms in each case. The relevant data are illustrated in Fig. 3a which shows the crucial like-with-like comparison—selectivity enhancement at the 50% of initial activity point where the surface concentration of halogen should be approximately the same in the four cases. The strong maximum at chlorine is striking. Had we chosen to make the comparison at 20% of initial ethene conversion the superiority of Cl would appear even more pronounced. Clearly, the promoting effect per halogen adatom is greatest for chlorine.

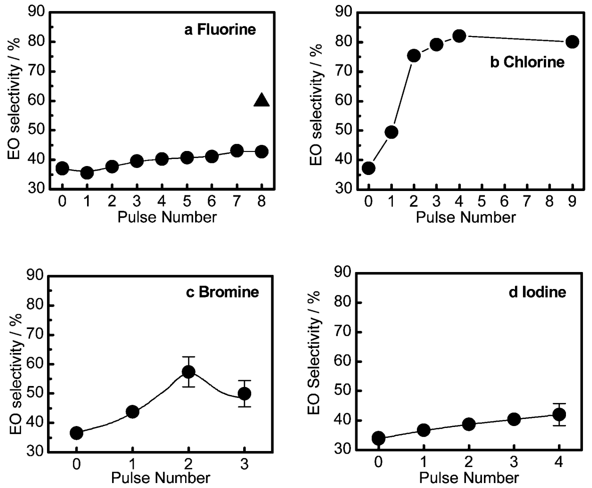

Fig. 2 Effect of the four halogens on selectivity.

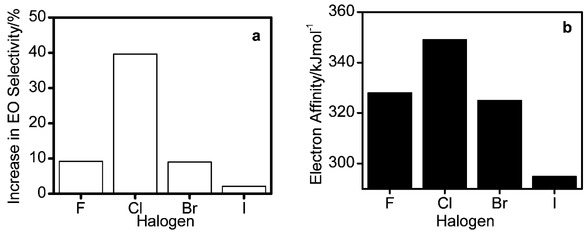

Fig. 3 a) EO selectivity enhancement at 50% reactant conversion for each halogen. b) Electron affinities of the halogens.

XPS measurements provide control data and useful additional insight into the catalytic behaviour. Due to limitations imposed by photoionisation cross sections,[11] only F 1s and I 3d were measurable. These data showed that the pure alumina support (which exhibited no measurable catalytic activity) did not pick up halogen under halocarbon treatment. They also showed that when the activity had dropped by 50% the estimated halogen fractional surface coverage (for fluorine and iodine) was indeed ~0.5. Therefore we are justified in interpreting the catalytic behaviour in terms of halogen-induced effects on the surface chemistry of silver, unperturbed by any effects due to the α-Al_2O_3 support.

Thus we see that although all four halogens act to enhance selectivity, chlorine is much more effective than the other three. Under conditions of comparable halogen surface coverage, chlorine induces a large increase in selectivity whereas F, Br and I yield only modest improvements. This behaviour correlates with the electron affinities of the halogens, Fig. 3b, which show a maximum at chlorine. Our findings constitutes strong evidence that halogen promotion of ethene epoxidation is overwhelmingly due to an electronic effect, and that steric or geometric factors are of minor or insignificant importance. Valence charge withdrawal from O_a by co-adsorbed halogen enhances its electrophilicity and hence its effectiveness as an epoxidising agent.

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Notes and references

1 J. G. Serafin, A. C. Liu and S. R. Seyedmonir, *J. Mol. Catal. A*, 1998, **131**, 157–168.
2 R. A. Van Santen and H. P. C. E. Kuipers, *Adv. Catal.*, 1987, **265**, 35.
3 W. M. H. Sachtler, *Catal. Rev.*, 1970, **4**, 27.
4 C. T. Campbell and M. T. Paffett, *Surf. Sci.*, 1984, **139**, 396–416.
5 R. B. Grant and R. M. Lambert, *J. Catal.*, 1985, **92**, 364–375.
6 C. T. Campbell and B. E. Koel, *J. Catal.*, 1985, **92**, 272–283.
7 *CRC Handbook of Chemistry and Physics*, 82nd edn., CRC Press, Boca Raton, FL, 2001, p. , 975.
8 P. J. Goddard and R. M. Lambert, *Surf. Sci.*, 1977, **67**, 180–194.
9 P. J. Goddard, K. Schwaha; and R. M. Lambert, *Surf. Sci.*, 1978, **71**, 351–363.
10 U. Bardi, *Surf. Sci.*, 1983, **128**, 145.
11 C. D. Wagner, W. M. Riggs, L. E. Davies and J. F. Moulder, *Handbook of X-ray Photoelectron Spectroscopy*, ed. G. E. Muilenberg, Perkin Elmer Corporation, Eden Prairie, MN, 1978, p. , 188.