Two-dimensional oxide catalysts: propene oxidation on $FeSbO_4$

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$FeSbO_4$ catalysts used for selective propene oxidation/ammoxidation have been examined using a combination of XPS and TPD before and after ammonia reduction. These data indicate that the surface has a thin "skin" which is enriched in antimony oxide. This "skin" is shown to be important for selective oxidation. This two-dimensional oxide covering can be reduced to metallic antimony after only low pressure treatment in ammonia and the metallic layer can be desorbed upon heating above 600 K. The remaining surface is then covered with an Fe-rich layer which is not so easily reduced, and which is of lower selectivity in partial oxidation to acrolein.

Keywords: propene; ammonia; selective oxidation; ammoxidation; $FeSbO_4$; TPD; XPS; surface enrichment; antimony oxide reduction

1. Introduction

Oxide materials are widely applied in catalysis, not usually for their activity, which is low compared with metals, but for their selectivity in yielding intermediate products of oxidation. In the case of propene oxidation/ammoxidation, a variety of oxides can be used to selectively yield acrolein/acrylonitrile and minimise combustion, namely bismuth molybdates [1,2], and uranium [3], tin [4] and iron [5] antimonates. The work we are reporting here concerns studies of the surface properties of $FeSbO_4$, which forms a rutile type structure.

Although there is relatively little work in the literature on $FeSbO_4$ (especially compared with bismuth molybdate), this material is an excellent one for selective oxidation/ammoxidation, and, with a multiplicity of other additives, is a patented catalyst/process [6]. Studies by Yamazoe [9] and Teller et al. [10], which showed that the surface of this catalyst is enriched in Sb, were supported also by ourselves in a previous publication [7], among others [8]. In this paper we have utilised temperature programmed desorption and X-ray photoelectron spectroscopy to reveal more detail about the relationship between the surface composition and selectivity/reactivity of the catalyst. In this paper we will show:

(i) that a layer with unique properties is formed;
(ii) that this layer is highly reducible in ammonia to form antimony metal (Sb^0);
(iii) that after Sb^0 desorption an Fe-rich layer is left;
(iv) that the Sb-rich "skin" is essential to the selective properties of the catalyst.

2. Experimental

The catalyst preparation has been reported elsewhere [9]; in brief it can be described as a slurry impregnation followed by high temperature (900°C) calcination to give inter-diffusion of the cations. The structure so formed is of a rutile type arrangement (fig. 1) [11] containing Fe^{3+} and Sb^{5+} cations with no metal or oxygen deficiency in the bulk [10]. The XPS was carried out using a VSW system with a 100 mm radius hemispherical analyser and Al K_α photons. The sample was

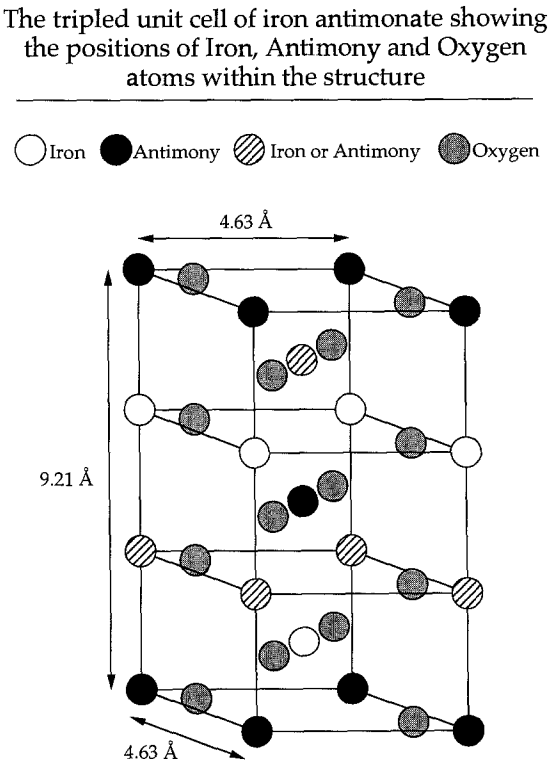

Fig. 1. Structure of $FeSbO_4$ as proposed by Berry et al. [11] utilising vacuum calcination conditions. Others [10] proposed a more random arrangement of Fe and Sb atoms when calcined in air, as most catalysts are, including that used in this study.

mounted in a vacuum system on a stainless steel mesh with a chromel–alumel thermocouple attached, and this was mounted on an x–y–z rotational manipulator. The spectra were referenced to the Au 4f at 83.9 eV and C 1s 284.8 eV (Al K_α) lines as standard. TPD was carried out by radiative heating from the sample from a tungsten filament heater situated close to the rear of the sample. The weight of the catalyst used was typically 0.2 g. The XPS background subtraction method utilised was a Proctor/Hercules modified Shirley integration [12].

3. Results and discussion

XPS of the fresh catalyst after heating in situ in the vacuum system is shown in fig. 2 and shows very large Sb 3d peaks and small Fe 2p peaks, even though the relative cross sections (at 4.47 and 2.67 respectively [13]) for these two transitions are similar. The integral difference is, however, much lower, due to the width of the Fe peaks and the presence of multiple states/satellite structure [14,15]. The escape depths for antimony and iron electrons is also very similar as demonstrated in ref. [16]. The integral ratio is 3.5 : 1 (Sb 3d : Fe 2p), which allowing for cross section/escape depth corrections yields a near surface atomic ratio of approximately 2 : 1 (Sb : Fe). It must be noted that the O 1s peak coincides with the Sb $3d_{5/2}$ peak and so the ratio of Sb $3d_{5/2}$ to Sb $3d_{3/2}$ is greater than the expected 3 : 2. Previous X-ray diffraction spectra indicate that the bulk of this material is predominantly a rutile type structure [7]. Neutron diffraction results also demonstrate that the Fe/Sb ratio in the bulk is essentially 1 [10]. This spectrum is similar following annealing

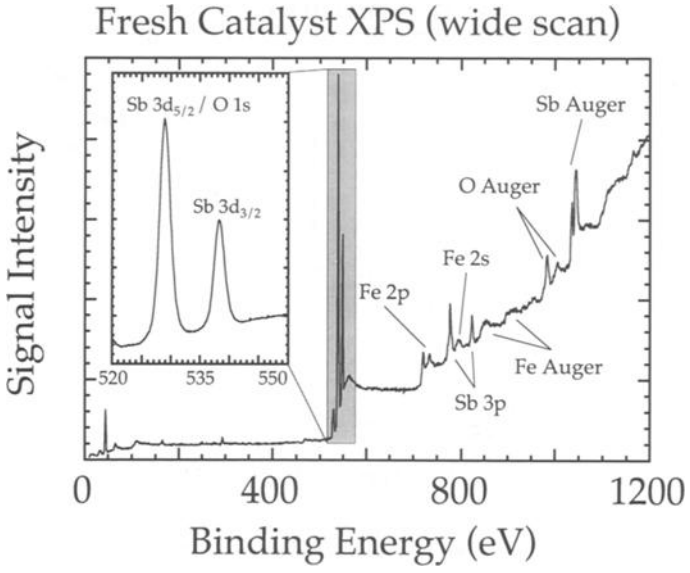

Fig. 2. XPS spectra of fresh $FeSbO_4$ catalyst (after heating to 820 K in vacuum).

up to 800 K and stable to repeated oxygen and propene treatments. However, after only a mild treatment in ammonia the surface layer can be completely reduced, as shown in figs. 3 and 4. It is difficult to separate Sb^{3+} and Sb^{5+} in unmonochromated XPS because the shift of Sb core levels is very small at ~0.3 eV [17,18]. However, after ammonia treatment the Sb peak was shifted by 2.0 eV to lower binding energy, an effect which could only be produced by formation of Sb^0 metal. This is confirmed by TPD (fig. 5) which shows Sb desorption with a peak at 690 K. Following Sb desorption the XPS spectrum is now different from that of the fresh sample with the Sb : Fe atomic ratio now being 1 : 2.6, that is, Fe is much more dominant in the spectrum. Referring to fig. 4, the oxygen content of the surface layers has also changed from that in the fresh catalyst due to the surface iron enrichment since after reduction and Sb desorption the O : Sb atomic ratio has increased to 4 : 1.

Our conclusion from the XPS is that we have a catalyst with a "skin" oxide of different structure and composition from the bulk, presumably produced during the high temperature air calcination step which is part of the preparation procedure. We propose the structure shown in fig. 6, which has a skin enriched in Sb over the $FeSbO_4$ core. The relative XPS Sb : Fe intensities are consistent with a model in which the top two surface layers are composed entirely of antimony oxide followed by a gradual return to the bulk composition (using values for the cross sections and escape depths published elsewhere [16]). Therefore the antimony enrichment in this "skin" is greater than that proposed by Aso [9], who stated that the surface

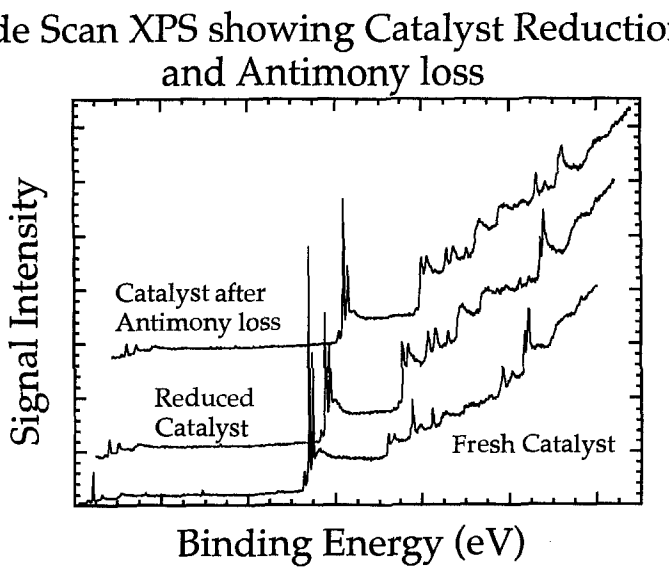

Fig. 3. XPS spectra of the fresh catalyst, the catalyst after reduction in 1.5×10^{-4} Torr of ammonia at 550 K for 20 min, and after subsequent heating to 820 K, followed by cooling. The three spectra are offset vertically and horizontally for clarity.

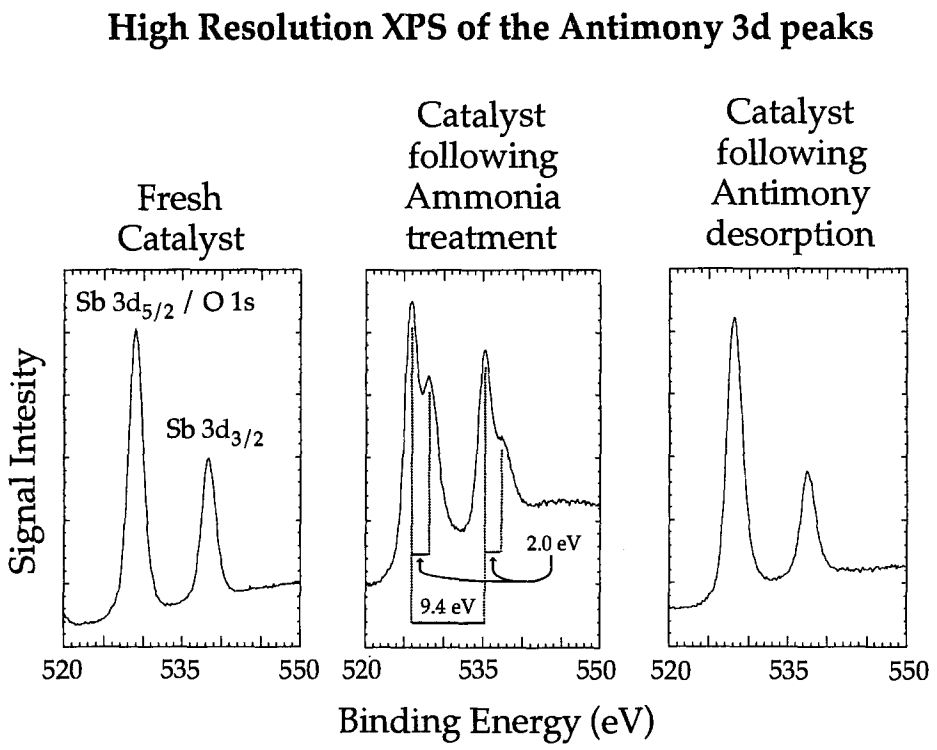

Fig. 4. Sb 3d XPS spectra for the catalyst as shown in fig. 3.

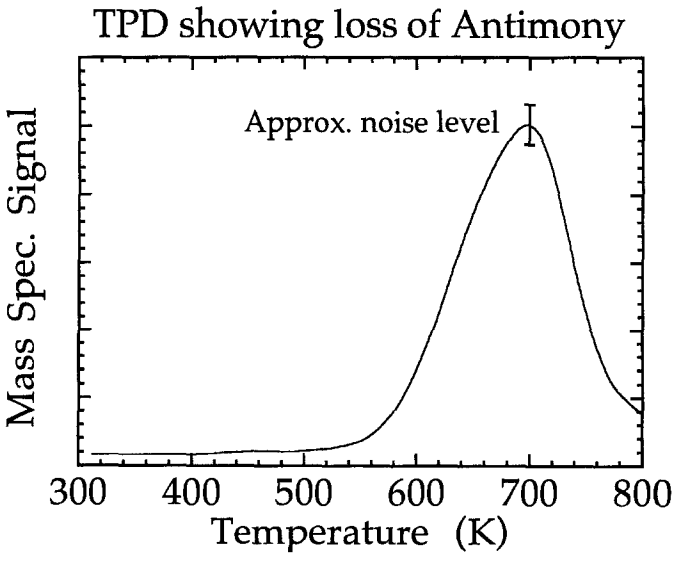

Fig. 5. Temperature programmed desorption spectra at 121 amu for Sb desorption from the ammonia reduced catalyst.

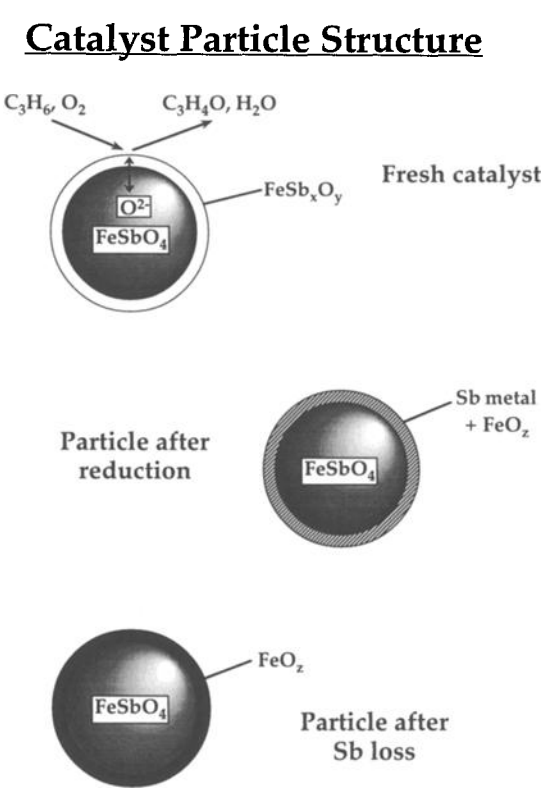

Fig. 6. Schematic diagrams of the structure of $FeSbO_4$ catalysts after different treatments. Each is proposed to consist of a thin "skin" with an $FeSbO_4$ core. Before reduction the skin is strongly enriched in Sb oxide, after reduction it is coated with Sb metal, which after thermal desorption leaves an iron oxide rich skin. The nature of this surface is crucial for the selectivity in propene (amm)oxidation.

(~6 Å) was of a composition close to $FeSb_2O_6$, and Teller et al. [10], who proposed that small individual Sb_2O_4 crystallites covered the $FeSbO_4$ surface. The real situation is more likely to be one of a concentration gradient of Fe from severe, probably complete, depletion in the top layer to a bulk ratio in the core of 1 : 1. It is interesting to speculate as to why this enriched surface "skin" is formed. One explanation could be that during calcination Sb^{3+} is formed (which, having a lone pair of electrons, does not favour octahedral co-ordination) and may migrate to the surface of the $FeSbO_4$ lattice. Note, however, there is no evidence, by XRD, for the formation of bulk phases of Sb^{3+} oxides of β-Sb_2O_4. A second explanation could be that the preferred exterior atomic plane of $FeSbO_4$ during calcination is one in which the surface unit consists of predominantly antimony and oxygen atoms (fig. 1), that is, an all-antimony outer layer is combined with a second layer which is also completely substituted by Sb. For instance, referring to fig. 1 between the top layer and the second layer, labelled as Fe or Sb, could be all Sb. Of course, at a fundamental level

the driving force for this structure must be thermodynamic, that is, the Sb oxide is of lower surface energy than either iron oxide or $FeSbO_4$.

The presence of this skin oxide has great significance for the catalysis, as evidenced by the TPD spectra shown in fig. 7. The unreduced catalyst is, as expected from previous work [7], a good selective oxidation catalyst yielding large amounts of acrolein in an experiment in which only propene is dosed onto the surface. Initially the propene is completely burned to CO_2 and H_2O [7], but after several such propene doses/TPD cycles the reaction becomes more selective towards partial oxidation and ammoxidation. Though propene adsorption, to form a stably bound intermediate, results in a decrease in the formal oxidation state of antimony from Sb^{5+} to Sb^{3+} the catalyst behaves reproducibly. The XPS spectrum confirms that there was no change in the surface which was indistinguishable from that of the fresh catalyst shown in fig. 2. The desorption integrated acrolein selectivity in experiments such as that in fig. 7 was approximately 32%. It can be seen that the instantaneous selectivity is high on the low temperature side of the desorption peak. However, after ammonia reduction and removal of "metallic" antimony (that is a catalyst with an XPS spectrum like that in fig. 3), subsequent propene dosing yields a somewhat different desorption profile, showing decreased total acrolein yield and selectivity (17%) and much reduced acrolein selectivity at any particular temperature (fig. 8). This catalyst, which is now richer in iron in the surface region, is also not such a selective ammoxidation catalyst, showing decreased acrylonitrile and much increased CO_2 yield in an experiment in which ammonia

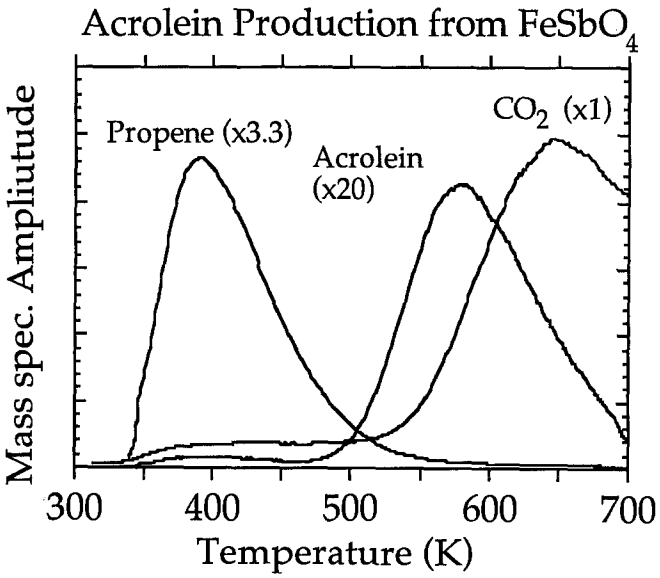

Fig. 7. Products during TPD after dosing 4.5 Torr s of propene onto the fresh catalyst after five propene treatments. These curves are actually traces of 41 amu for propene, 56 amu for acrolein and 44 amu for CO_2.

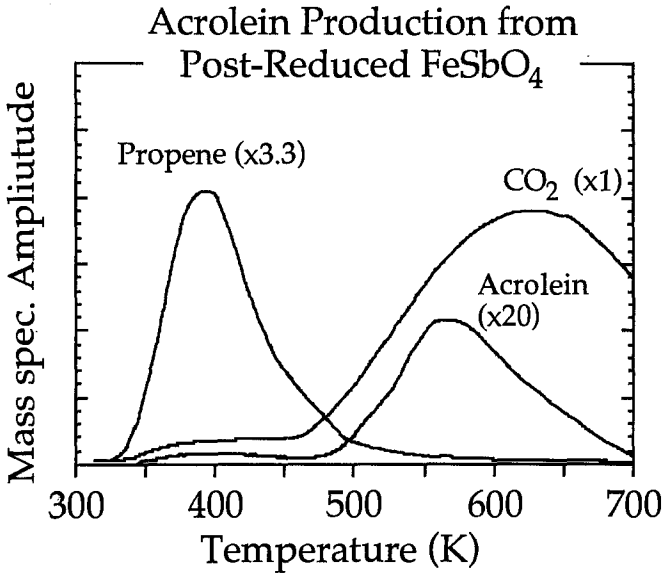

Fig. 8. As for fig. 7, except for the catalyst after NH_3 reduction and Sb desorption, which has an iron oxide rich coating.

and propene are sequentially dosed. The skin oxide left after reduction and Sb desorption may be close to Fe_2O_3 (fig. 6), which has been shown to be a low selectivity material [9]. Furthermore, we have previously found evidence of haematite formation (by XRD) in post-micro reactor $FeSbO_4$ catalysts. If the surface were coated in Fe_2O_3 then this layer would be approximately three layers thick to give the XPS ratio seen.

It must be noted that the $FeSbO_4$ sample used is not a commercial ammoxidation catalyst, the latter having other additives, such as W, Te and other components. Most importantly, the commercial catalyst has a different bulk Fe : Sb ratio and it is supported. The Fe : Sb ratio in industrial catalysts is closer to 1 : 2 [5,6], presumably to avoid the kind of haematite formation seen here. This will be tested in further experiments in our laboratory and we will report a more detailed study of this system in the near future, with a more thorough investigation of the properties of components of the system such as Sb^{5+}, Sb^{3+} and Fe^{3+}. Nevertheless, these data have some relevance to the commercial catalytic samples. In particular, it is likely that the shell and core model of fig. 6 will still apply in higher Sb-loaded catalysts, since $FeSbO_4$ is still the only Fe containing material identified by XRD.

We should note that such a "skin" model may be common to many types of oxide catalyst and a similar type of model has been used to describe the reactivity of Bi–Mo acrolein synthesis catalysts by Moro-oka et al. [19].

There may well be a "dual" function associated with the structure in fig. 6. It could be that the underlying $FeSbO_4$ structure acts as a template for a particular morphology of the Sb-rich surface layer. It could be also that the $FeSbO_4$ core pro-

vides a source of extra oxygen mobility to allow faster oxygen/defect exchange with the surface, since defects are known to play an important role in the chemistry of such metal oxide catalysts, improving adsorptivity and selectivity [9,10,20].

In conclusion it has been shown that:

(i) $FeSbO_4$ catalysts have an Sb-enriched coating.

(ii) The Sb component of this skin oxide is readily reduced to Sb metal.

(iii) When Sb^0 is removed it leaves an Fe-rich layer which is much less selective to the partially oxidised product.

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