

FORMATION OF AN Sb-ENRICHED SURFACE LAYER ON $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_4$ CATALYST
STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY

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The surface analyses of $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_4$ catalysts by XPS showed that the surface of FeSbO_4 grains was enriched in Sb content at the bulk compositions $\text{Sb/Fe} > 1$. The surface layer, which was considered to be responsible for the selective propene oxidation, had an estimated composition $\text{Sb/Fe} \approx 2$, suggesting a surface compound like FeSb_2O_6 .

The mixed oxide catalyst $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_4$ is a well-known catalyst for the allylic oxidation of olefins¹⁾. In the actually prepared catalysts with various compositions of Fe_2O_3 and Sb_2O_4 , there is only a mixed oxide phase, FeSbO_4 (atomic ratio $\text{Sb/Fe}=1$), detectable by X-ray diffraction analysis. Interestingly, however, the selectivity of allylic oxidation can be much improved when the ratio Sb/Fe exceeds unity where FeSbO_4 and Sb_2O_4 phases coexist. Considering that Sb_2O_4 itself is not catalytically active, a certain type of promoting effect between FeSbO_4 and Sb_2O_4 is thus suggested. Although some proposals²⁻⁵⁾ have been made concerning the above phenomenon, none of them are far from being established. In our previous study on propene oxidation over the $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_4$ catalyst⁶⁾, it was demonstrated that the properties of surface oxygen of the catalyst were modified in favor of the selective acrolein formation when Sb_2O_4 was added in excess of FeSbO_4 composition. This suggests that a particular surface layer may be formed on the surface of FeSbO_4 grains in the presence of excess Sb_2O_4 . To prove this suggestion, we have carried out the surface analyses of the catalysts by using a X-ray photoelectron spectroscopic (XPS) technique. In this letter, we report some evidence for the surface layer formation of the $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_4$ catalyst.

The $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_4$ mixed oxide catalysts with the atomic ratio $\text{Sb/Fe} \approx 2$ were prepared by mixing an aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a water suspension of Sb_2O_3 . The resulting slurry was evaporated to dryness under stirring, and calcined at 900°C for 2 hr. Fe_2O_3 was obtained by thermal decomposition of ferric hydroxide precipitated from an aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with ammonia, followed by calcination at 600°C for 5 hr. Sb_2O_4 was prepared by oxidizing Sb_2O_3 in air at 600°C for 5 hr.

X-ray diffraction analyses revealed that only FeSbO_4 was formed in the catalyst with $\text{Sb/Fe}=1$, while either Fe_2O_3 or Sb_2O_4 was present together with FeSbO_4 in those of lower or higher Sb contents, respectively.

XPS spectra were recorded with VG ESCA3 MkII spectrometer using $\text{Al K}\alpha_{1,2}$ (1486.6 eV) or $\text{Mg K}\alpha_{1,2}$ (1253.6 eV) radiation under the vacuum of less than 10^{-8} Torr. Finely pulverized samples were used without further treatments. Sample charging, which was less than 1 eV, was corrected in determining binding energies (BE) by making references

to the Au $4f_{7/2}$ level (83.6 eV) of evaporated gold.

Figure 1 shows XPS spectra for three representative catalysts with Sb/Fe=0.8, 1, and 2. The signals of O $1s_{1/2}$ and Sb $3d_{5/2}$ overlap with each other at $BE=530.5 \pm 0.1$ eV, while those from Sb $3d_{3/2}$ ($BE=539.8 \pm 0.1$ eV) and Fe $2p_{3/2}$ (711.3 ± 0.3 eV) are free from such overlapping. By using the last two signals, we first examined the surface compositions of catalysts having various bulk compositions. For this purpose, the signal intensity ratio of Sb $3d_{3/2}$ to Fe $2p_{3/2}$, I_{Sb}/I_{Fe} , was measured from the peak area⁷⁾ for a series of catalysts. For comparison, the same measurements were also carried out for mechanical mixtures of Fe_2O_3 and Sb_2O_4 . The ratios thus measured are plotted versus the bulk Sb/Fe ratio in Fig. 2. For the mechanical mixtures, I_{Sb}/I_{Fe} is proportional to the bulk Sb/Fe ratio as expected. On the other hand, it is noted that the intensity ratio for the catalyst samples changes with the bulk Sb content in a very characteristic manner. In the lower Sb content region ($Sb/Fe < 1$), I_{Sb}/I_{Fe} almost coincides with that for the mechanical mixtures. However, I_{Sb}/I_{Fe} jumps stepwise by a certain value at $Sb/Fe=1$, above which it increases again steadily. The sudden increase of I_{Sb}/I_{Fe} at $Sb/Fe=1$ strongly suggests that the surface of $FeSbO_4$ grains is covered by a layer which is enriched in Sb content. The composition of the formed layer was estimated to be $Sb/Fe=1.8$, close to 2, from the step height of the increase at $Sb/Fe=1$ (see dotted arrow). Taking into account the fact that the intensity ratio exerts a parallel increase with that for the mechanical mixtures in the range of $Sb/Fe > 1$, the composition of the Sb enriched surface layer is considered to remain unaltered with increasing the bulk Sb content. According to separate SIMS experiments, the surface layer was estimated to be less than 6 Å thick.

In accordance with the surface layer formation mentioned above, it was found that there was a subtle but significant change in the shape of Fe $2p_{3/2}$ spectra.

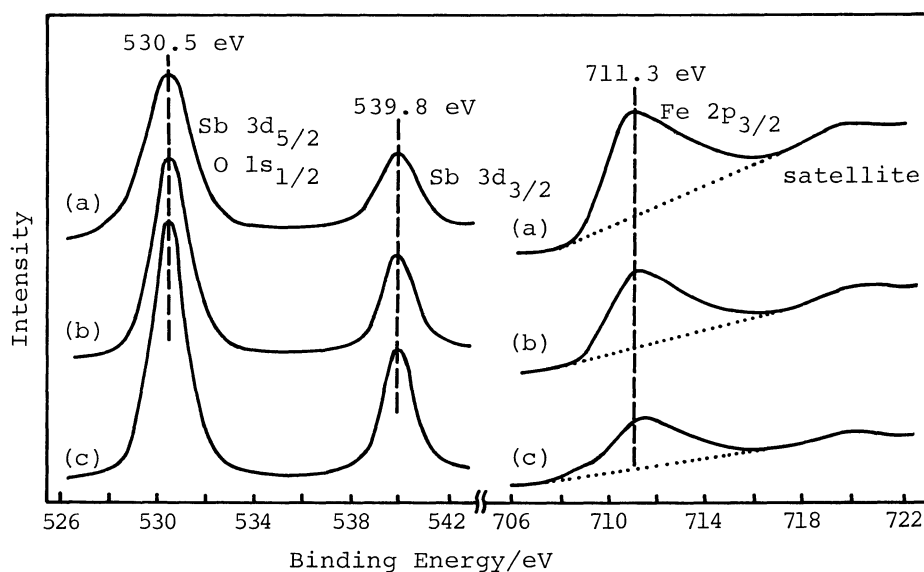


Fig.1. XPS spectra of Fe_2O_3 - Sb_2O_4 catalysts. Catalyst composition, (a) $Sb/Fe=0.8$; (b) $Sb/Fe=1$; (c) $Sb/Fe=2$.

The change, though not clear in Fig. 1, could be made clear by repeating the scanning 50 times as shown in Fig. 3. Whilst a single peak was observed at $BE=711.3 \pm 0.3$ eV for catalysts with $Sb/Fe \leq 1$, a shoulder did appear at $BE=709.2 \pm 0.3$ eV for Sb rich samples ($Sb/Fe > 1$) as typically shown in Fig. 3(c). According to the BE values reported by Brundle et al.⁸⁾, the peak and shoulder can be assigned to Fe(III) and Fe(II), respectively. The appearance of Fe(II) ions supports that the catalyst surface is modified in the Sb rich region. As for the spectra of Sb $3d_{3/2}$ level, there was no detectable change over all mixed oxide catalysts examined. However, the binding energy (539.8 ± 0.1 eV) was found to be 0.3 eV higher than that of Sb_2O_4 (539.5 ± 0.1 eV). The latter value was also obtained with Sb_2O_3 , being assigned to Sb(III). Orchard and Thornton⁹⁾ have reported that, while Sb_2O_4 is a mixed valence oxide of Sb(III) and Sb(V), the surface of Sb_2O_4 was composed of only one oxidation state of Sb(III) when the sample was prepared without special precautions. At the same time, they have estimated a binding energy shift of 0.6 eV between Sb(III) and Sb(V) by the deconvolution of a single Sb $3d_{3/2}$ spectrum from the Sb_2O_4 sample reoxidized within a UHV chamber. Thus the observed shift of 0.3 eV in our catalysts suggests the co-existence of Sb(III) and Sb(V) on the catalyst surface, possibly the surface of $FeSbO_4$ grains.

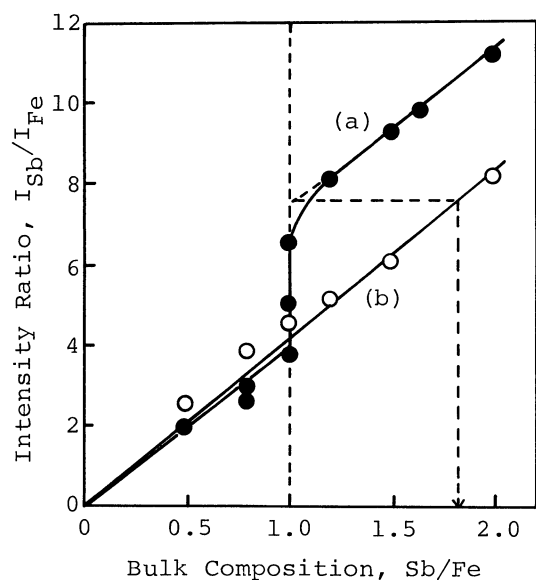


Fig.2. Correlation between the XPS intensity ratio and the bulk composition for (a) catalyst samples and (b) mechanical mixtures of Fe_2O_3 and Sb_2O_4 .

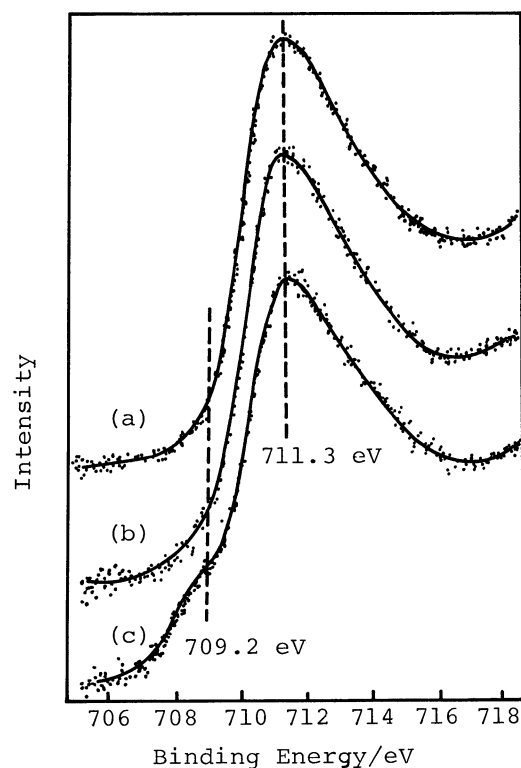


Fig.3. XPS spectra of Fe $2p_{3/2}$ level for Fe_2O_3 - Sb_2O_4 catalysts. Catalyst composition, (a) $Sb/Fe=0.8$; (b) $Sb/Fe=1$; (c) $Sb/Fe=2$.

As demonstrated above, the surface analysis by XPS has provided evidence that the Sb enriched layer is formed on the surface of FeSbO_4 grains at the bulk Sb/Fe ratio >1 . The layer was estimated to have a Sb/Fe ratio close to 2. In this connection, notable is that a compound FeSb_2O_6 (Sb/Fe=2), which has trirutile structure¹⁰⁾ similar to the rutile structure of FeSbO_4 ¹¹⁾, has been reported to form under certain conditions. It is thus suggested that the Sb enriched layer is composed of FeSb_2O_6 or something like that. This suggestion is supported by the fact that Fe(II) is detected in the Sb-enriched surface, since FeSb_2O_6 is formally described as $\text{Fe}^{\text{II}}\text{Sb}_2\text{O}_6^{\text{V}}$ (an alternative is $\text{Fe}^{\text{III}}\text{Sb}_{0.5}^{\text{III}}\text{Sb}_{1.5}^{\text{V}}\text{O}_6$) while FeSbO_4 as $\text{Fe}^{\text{III}}\text{Sb}^{\text{V}}\text{O}_4$ ^{10,12)}.

The formation of the Sb enriched surface layer is deeply associated with the catalytic properties of Fe_2O_3 - Sb_2O_4 system. Previously⁶⁾, we showed that, in the propene oxidation, the selectivity to the acrolein formation was markedly improved with increasing Sb content beyond Sb/Fe=1 (FeSbO_4) mainly as a result of marked depression of CO_2 formation. This effect of excess Sb was shown to be combined with a change in the properties of surface oxygen; i.e., while FeSbO_4 contains two types of surface oxygen which are active for the CO_2 formation and for the acrolein formation, respectively, the former type is selectively depressed over the catalysts with Sb/Fe >1 . On the basis of the results of the present XPS study, we conclude that such a modification of surface oxygen is ascribable to the formation of the Sb enriched surface layer, possibly FeSb_2O_6 , on the FeSbO_4 grains.

References and Note

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