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OXYGEN ADSORPTION SITES OF Fe_2O_3-Sb_2O_4 CATALYST DETERMINED BY SECONDARY ION MASS SPECTROMETRY-^{18}O TRACER METHOD

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In an attempt to determine oxygen adsorption sites of the Fe_2O_3-Sb_2O_4 catalysts, SIMS measurements of the catalysts were performed after $^{18}O_2$ preadsorption (SIMS-^{18}O tracer method). It was clearly shown that the adsorbed oxygen was accommodated by the surface Sb ions.

Mixed metal oxides such as Fe_2O_3-Sb_2O_4 and Bi_2O_3-MoO_3 are active catalysts for the selective oxidation of olefins$^{1)}$. During catalytic oxidation, adsorbed oxygen and/or lattice oxygen of catalysts are consumed repeatedly by attacking reactant molecules, followed by continuous supply from gas phase through the mediation of metal ions of the catalyst surface. In other words, oxygen must be activated prior to the reaction. Thus in a multi-component oxide catalyst, it is important to discern which metal ions are responsible for the adsorption or activation of oxygen. Although this has been a difficult task because of the lack of adequate physicochemical techniques, a potential method for this purpose may be provided by secondary ion mass spectrometry if an adequate use of ^{18}O tracer is combined (SIMS-^{18}O tracer method). SIMS is a sensitive surface analytical technique endowed with an advantage of distinguishing the isotopes of an element$^{2)}$. Usually the secondary ions ejected from metal oxides include considerable amounts of cluster ions $MeO_x^{\pm}$ (Me = metal atom), the metal-oxygen bonds of which have been reserved during the sputtering process. Therefore, if oxygen adsorption on a mixed oxide takes place on one component metal ion in preference to others, the SIMS spectrum after $^{18}O_2$ adsorption would show a preferential accumulation of ^{18}O in the corresponding cluster ions. In this letter, we have applied the SIMS-^{18}O tracer method to the Fe_2O_3-Sb_2O_4 mixed oxide. Our previous study$^{3)}$ has clearly shown that in this catalyst system only surface oxygen is active for the catalytic oxidation of propene. The present study aims at discriminating which metal ions, Fe or Sb ions, accommodate the active surface oxygen.

Three Fe_2O_3-Sb_2O_4 catalysts were used. Catalyst I($FeSbO_4$) and catalyst II with atomic ratios Sb/Fe = 1 and 2, respectively, were prepared from $Fe(NO_3)_3\cdot 9H_2O$ and Sb_2O_3 followed by calcination at 900°C for 2 hr, as described in detail elsewhere$^{3)}$. The third, Sb-impregnated $FeSbO_4$, was prepared by impregnating catalyst I($FeSbO_4$) with antimonic acid solution to a measured amount of 21 µmol Sb/m^2-$FeSbO_4$ (equiva-

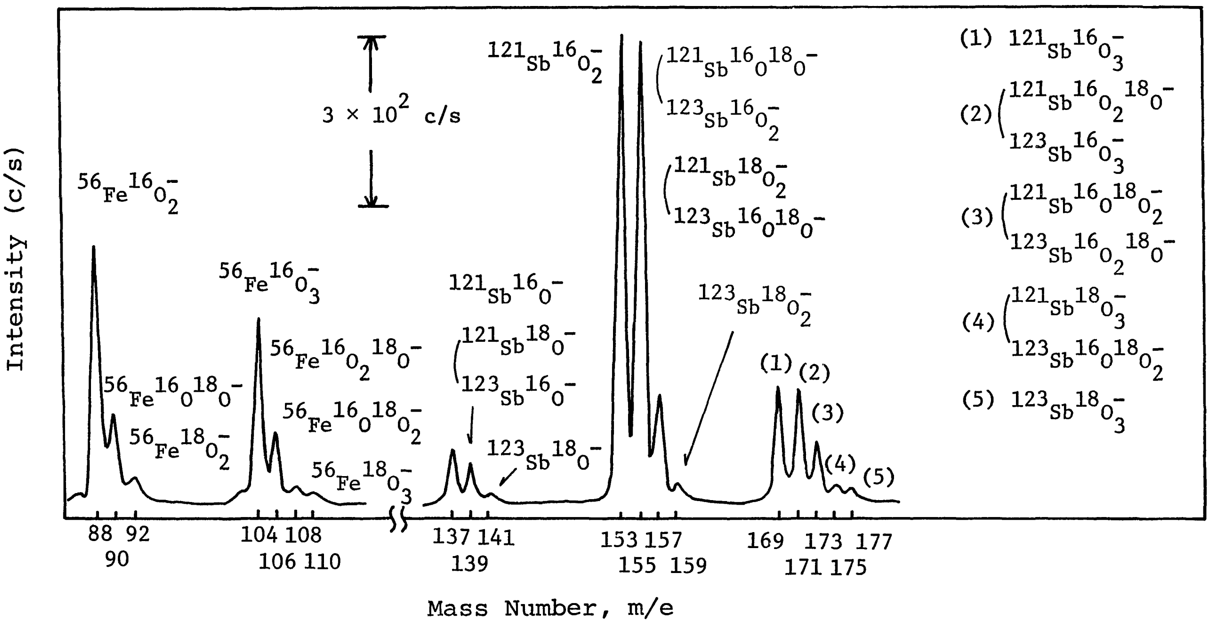

Fig.1 SIMS spectrum of catalyst I (Sb/Fe=1) preadsorbed with $^{18}O_2$.

lent to surface coverage 1.5), followed by calcining at 800°C for 2 hr. X-Ray diffraction analyses detected only $FeSbO_4$ in catalyst I and Sb-impregnated $FeSbO_4$ while both Sb_2O_4 and $FeSbO_4$ were detected in catalyst II.

Finely pulverized samples were, after being suspended in water, applied and dried on SIMS sample holders for the subsequent $^{18}O_2$ adsorption and SIMS experiments. The oxygen adsorption was carried out in a separate apparatus. After evacuation at 700°C for 15 min, the catalyst samples were exposed to 100 torr of $^{18}O_2$ (99.1 atomic %) either (A) at 400°C for 15 min followed by cooling (10°C/min) to room temperature(RT), or (B) at a selected temperature of 400°C, 500°C, or 600°C for various periods (t_{ads} = 1 ~ 60 min) followed by quenching to RT.

SIMS spectra were recorded on a VG ESCA 3 equipped with an Ar ion gun (VG AG 5) and a quadrupole mass spectrometer (VG Q8, mass range m/e = 1 ~ 300). A primary Ar^+ beam of 4 keV energy, 5 nA current, and 1 mm spot size was used. The sputtering rate was estimated to be about 1 Å/min for our catalyst samples. Among various secondary ions, the negative ion species, FeO_x^- (FeO_2^- and FeO_3^-) and SbO_x^- (SbO, SbO_2^-, and SbO_3^-), were repeatedly measured in the course of sputtering.

Figure 1 shows an example of SIMS spectrum obtained for catalyst I after $^{18}O_2$ preadsorption by procedure(A). The observed peaks are assigned to the indicated negative secondary ions from their mass numbers (m/e). The ^{18}O tracer is contained in both FeO_x^- and SbO_x^- and this was also the case for catalyst II and Sb-impregnated $FeSbO_4$. In order to know the ^{18}O distribution quantitatively, the atomic fraction of ^{18}O in each cluster ion MeO_x^- was calculated from the observed SIMS peak heights4) As a result, it was found that the ^{18}O fractions not only were different for FeO_x^- and SbO_x^- but also changed with sputtering time (t_s). Figure 2 shows the ^{18}O fraction of each cluster ion ejected from the three catalyst samples as a function of t_s. Obviously the fractions were highest at t_s=0 and decreased with t_s approaching each other gradually. It is noted that, at $t_s=0$, the SbO_x^- species always have higher ^{18}O fractions than the FeO_x^- species do. This indicates that the ^{18}O tracer is accommodated by the surface Sb ion more preferentially than by the surface Fe ion. However, the observed disparity in ^{18}O fraction between FeO_x^- and SbO_x^- can not be a direct measure for the site preference of adsorbed oxygen, because it has possibly been affected by the isotopic mixing of ^{18}O with lattice ^{16}O. The decrease of ^{18}O fraction with t_s, commonly observed for all cluster ions, is quite natural since the ^{18}O tracer should be localized in the surface region of catalyst grains, but the phenomenon is rather complicated because of the peripheral effect appearing in the sputtering process.

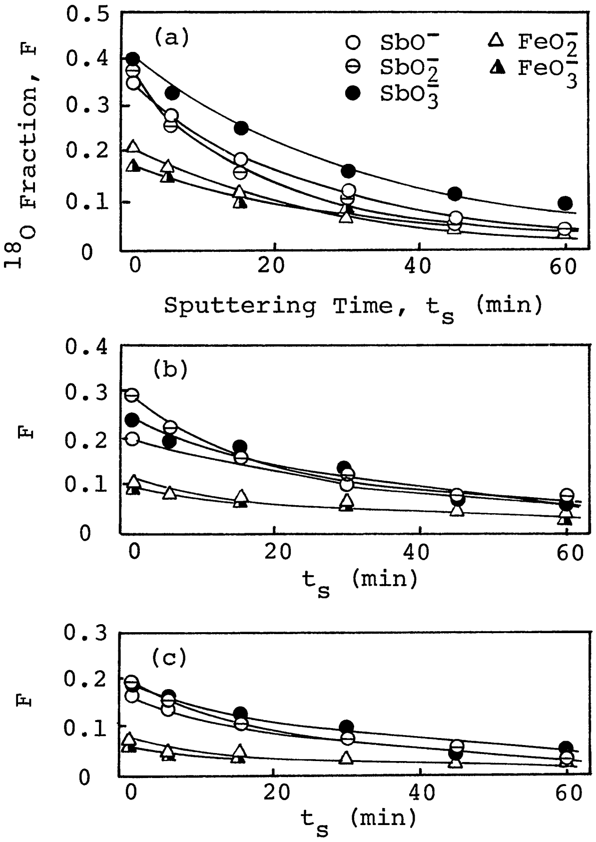

Fig.2 Change of ^{18}O atomic fraction in secondary ions with sputtering time. (a) catalyst-I (b) catalyst-II (c) Sb-impregnated $FeSbO_4$.

In order to check the effect of isotopic mixing, $^{18}O_2$ adsorption was carried out for Sb-impregnated $FeSbO_4$ by procedure (B) with varying adsorption temperature (400°C ~ 600°C) and time (t_{ads} = 1 ~ 60 min). The results of SIMS measurements at $t_s=0$ are summarized in Fig. 3. In this case, the disparity in ^{18}O fraction between FeO_x^- species and SbO_x^- species is expressed by the following ratio, R,

$$R = \sum_x (F_{SbO_x^-}) \ / \ \sum_x (F_{FeO_x^-})$$

where $F_{SbO_x^-}$ and $F_{FeO_x^-}$ are the ^{18}O atomic fractions in SbO_x^- and FeO_x^-, respectively. It is seen that R decreases with an increase in t_{ads} as well as in adsorption temperature, revealing that the isotopic mixing in fact takes place and increases at higher temperatures and longer t_{ads}. Taking into account the effect of such isotopic mixing, it is concluded that the oxygen coming from gas phase is adsorbed almost exclusively on the surface Sb ion.

It is notable that the surface Sb ions act as active sites for oxygen adsorption in any of the three catalysts. Preveously we reported[3)] that, concerning the superior selectivity of catalyst II over catalyst I for the formation of acrolein in the propene oxidation, the addition of Sb in excess of Sb/Fe = 1 ($FeSbO_4$) had an effect to change the properties of surface oxygen in favor of the acrolein formation. Further the XPS study[5)] showed that such modification of surface oxygen was associated with the formation of an Sb-enriched surface layer, probably a surface compound $FeSb_2O_6$, on the $FeSbO_4$ grains. On the basis of these results, the present SIMS-^{18}O tracer study indicates that there is no distinction between the Sb-enriched layer and $FeSbO_4$ as far as the role of surface Sb ions as the oxygen adsorption sites is concerned. However, this by no means implies that both surfaces have similar activities of oxygen. Rather, the properties of surface oxygen, even though bonded to Sb ions, can be different for $FeSb_2O_6$ and $FeSbO_4$ due to the difference in the circumstances surrounding the Sb ions; at the $FeSb_2O_6$ surface an Sb ion should be adjacent to more Sb ions and fewer Fe ions than it is at the $FeSbO_4$ surface. We assume that such a situation of $FeSb_2O_6$ surface is relevant to the suppression of the activity of the surface oxygen and the resulting superiority in selective acrolein formation.

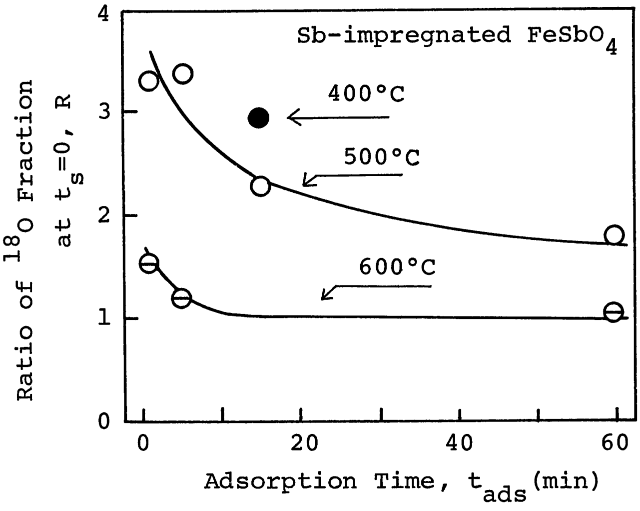

Fig.3 Effect of isotopic mixing on the ratio of ^{18}O atomic fraction at t_s=0.

As demonstrated above, the SIMS-^{18}O tracer method has an potentiality to identify the active sites for oxygen uptake in mixed metal oxide catalyst. The application of this method is in progress for other mixed systems such as Bi_2O_3-MoO_3 and SnO_2-Sb_2O_4.

References and Note

1) D.J. Hucknall, "Selective Oxidation of Hydrocarbons" Academic Press, New York, 1974.

2) H.W. Werner, Surface Sci., 47, 301 (1975).

3) I. Aso, S. Furukawa, N. Yamazoe, and T. Seiyama, J. Catalysis, 64, 29 (1980).

4) The ^{18}O atomic fraction in SbO_x^- ($F_{SbO_x^-}$) was estimated from the peak heights of respective mass numbers ($h_{m/e}$) and the relative isotopic abundance of Sb (N_{Sb}). For example, F_{SbO^-} was calculated by

$$F_{SbO^-} = [(h_{139} - N_{Sb} \cdot h_{137}) + h_{141}] / (h_{137} + h_{139} + h_{141})$$

where $N_{Sb} = {}^{123}Sb/{}^{121}Sb = 42.7/56.3$. In the case of $F_{FeO_x^-}$, however, only ^{56}Fe (92%) was taken into account because of relatively small abundance of ^{54}Fe (6%), ^{57}Fe (2%), and ^{58}Fe (0.3%).

5) I. Aso, T. Amamoto, N. Yamazoe, and T. Seiyama, Chem. Lett., 1980, 365.

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