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SURFACE COMPOSITIONS AND ACTIVITIES OF CATALYSTS STUDIED WITH X-RAY PHOTOELECTRON SPECTROSCOPY: sec-BUTANOL CONVERSIONS ON SnO_2-MoO_3 BINARY OXIDE CATALYSTS

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The surface compositions of SnO_2-MoO_3 catalysts were determined using XPS and compared with the activities for sec-butanol. Surface enrichment of MoO_3 occurred in the composition range of Mo/Mo+Sn < ca. 0.6, while SnO_2 was enriched in the other catalysts. The activities were understood better in terms of the surface composition of the catalyst.

It is well known that the surface composition of an alloy is usually different from the bulk one (1-3) and that the catalytic activity depends on the surface composition of the alloy (4). However, only a little attension has so far been paid to multi-component oxide catalysts. Very recently, Cimino and his co-workers (5) have investigated ZnO-MgO system and found the enrichment of ZnO in the surface, as expected from theoretical considerations (3). There have been, however, no correlation reported between surface compositions and catalytic activities of binary oxide catalysts, although the catalytic behavior are supposed to be understood better on the basis of such correlations. In this letter, we report some results on the surface compositions and catalytic activities of SnO_2-MoO_3 catalysts for the dehydration and dehydrogenation of sec-butanol using X-ray photoelectron spectroscopic (XPS) techniques. SnO_2-MoO_3 catalysts show excellent performances for the acetone formation from propylene (6-8) and for the selective oxidation of methanol (9).

SnO_2-MoO_3 catalysts having various compositions were prepared by calcining mechanically mixed component oxides at 550°C for 5 h. SnO_2 was prepared by precipitating stanous hydroxide from $SnCl_2$ solution with aqueous ammonia solution, followed by filtration, washing, drying, and calcining at 600°C for 8 h. MoO_3 was prepared by decomposing ammonium paramolybdate at 500°C for 5 h in air. The BET surface areas of the catalysts were 1.5 ± 0.5 m^2/g.

XPS spectra of the catalysts were measured on a Hitachi 507 photoelectron spectrometer using Al $K\alpha_{1,2}$ radiation. The surface compositions of the catalysts were determined using the XPS area intensities of the Sn $3d_{5/2}$ and Mo 3d levels for the catalysts. Calibration curves providing atomic ratios from XPS intensity ratios were obtained by measuring the XPS intensity ratios for mechanically mixed composite oxides with appropriate compositions. The precisions of the atomic ratios thus obtained were ±5%. The binding energies were corrected by using contaminant carbon as a standard (C 1s=285.0 eV). The effect of the contaminant carbon on the XPS intensity ratios were neglected here, since its amount was almost invariant among the catalysts and the samples used for the calibration.

The binding energies of Sn $3d_{5/2}$, Mo $3d_{5/2}$, and O 1s levels were 486.8, 233.1, and 531.0 eV, respectively, and the kinetic energy of Sn $M_4N_{4,5}N_{4,5}$ Auger level was 428.5 eV for the all catalysts after the calcination. The in situ treatments with H_2 (10 Torr) at 400°C caused the reductions of the catalysts, accompanied by the Mo enrichment in the catalyst surface. The resultant binding (kinetic) energies were; Mo $3d_{5/2}$: 229.9 eV, Sn $3d_{5/2}$: 486.3 eV, and Sn Auger: 431.0 eV, indicating the formations of SnO and MoO_2. The larger chemical shift (2.5 eV) was observed in the Sn Auger level than in the Sn $3d_{5/2}$ level (0.5 eV), as pointed out by Wagner and Biloen (10). However, although the in situ treatments with 10 Torr of sec-butanol produced MoO_2, the reduction of SnO_2 was not apparent at 300°C.

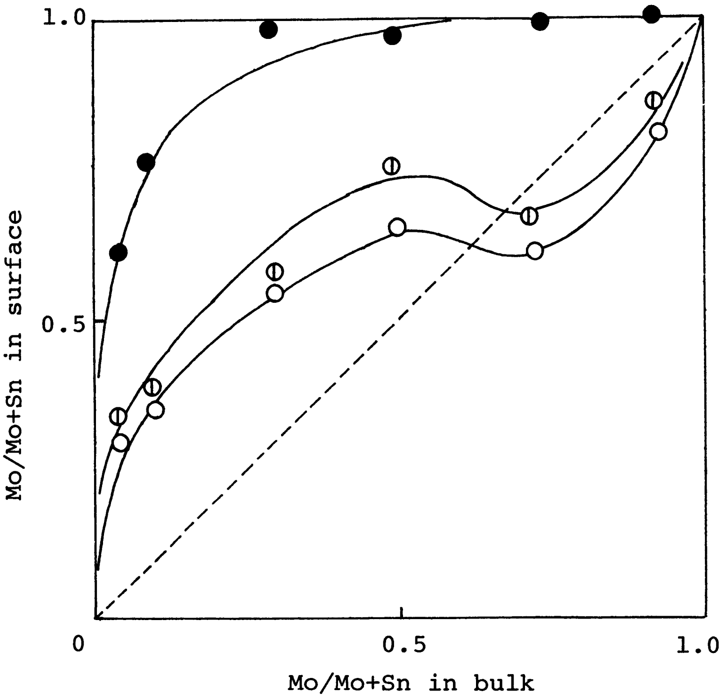

Fig.1 Correlations between surface and bulk compositions of the SnO_2-MoO_3 catalysts after calcination (○), reactions in the air stream (⦶), and reactions in the N_2 stream (●)

The surface composition of the SnO_2-MoO_3 catalysts are shown in Fig.1. It is obvious that the surface composition of the catalyst is considerably different from the bulk one and that MoO_3 is enriched in the surface of the catalyst having the bulk composition of Mo/Mo+Sn < ca. 0.6, while SnO_2 is segregated in the catalyst surface in the other composition range. The surface composition of the catalyst would be determined by the surface tensions of composite oxides (3) and also by the phase diagram of the binary oxide system (11,12). In the SnO_2-MoO_3 catalysts, unfortunately, both are not available and the equilibria in surface composition of the catalysts are not attained. However, the surface composition diagram in Fig.1 corresponds well to theoretical diagrams of metal alloys (13), including an inversed surface composition around 50-70% of Mo content in the bulk. It is noteworthy that the surface composition of the catalyst is not varied so much as the bulk one in the composition range of 30-70% Mo in the bulk.

The calcination temperature affected the surface composition of the catalyst. The calcination at 400°C for 5 h caused only slight differences between surface and bulk compositions, whereas the calcination at 600°C resulted in more surface enrichment of MoO_3 than the calcination at 550°C.

It will be interesting to compare the surface composition of the catalyst with the catalytic activity. The reactions of sec-butanol were carried out at 200°C using a conventional flow reactor in an air stream or in a N_2 stream. The conversions of

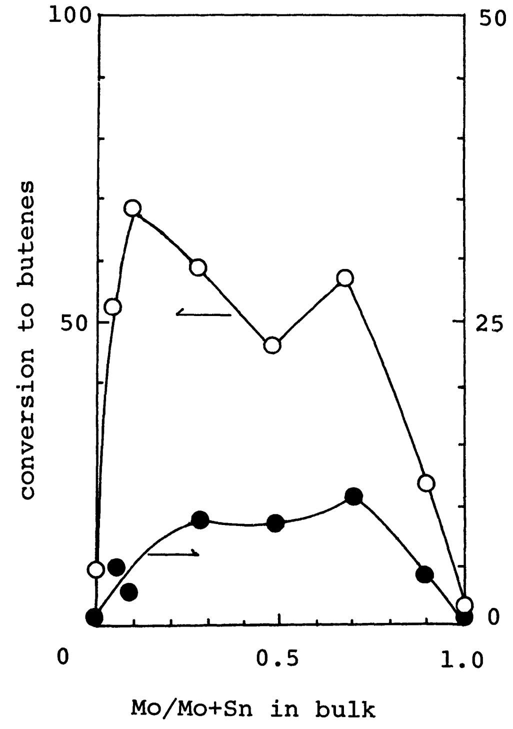

Fig.2 Dependences of conversions of sec-butanol to butenes (○) and to methylethylketone (●) on the bulk compositions of the SnO_2-MoO_3 catalysts

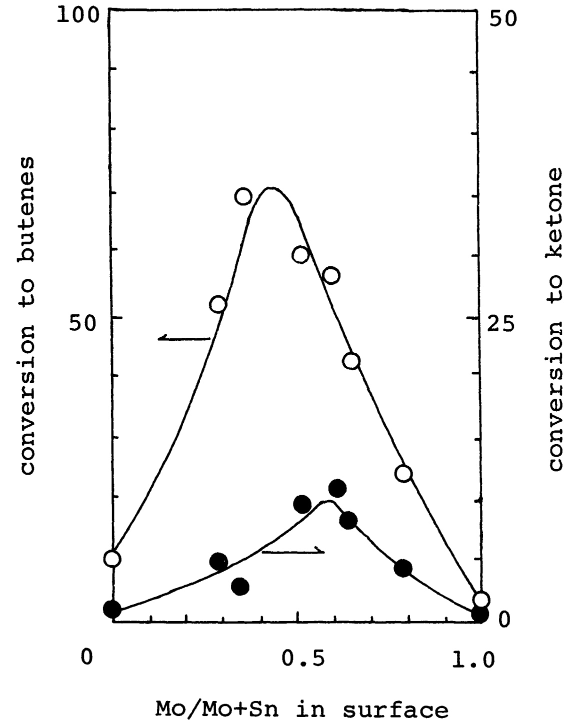

Fig.3 Dependences of conversions of sec-butanol to butenes (○) and to ketone (●) on the surface compositions of the SnO_2-MoO_3 catalysts

sec-butanol were measured after steady states were reached (2 h). The products were analyzed with glc. The reproducibilities of the conversions were ±3%.

The conversions of sec-butanol to butenes and methylethylketone in the air stream are plotted in Fig.2 as a function of the bulk composition of the catalyst. Two activity maxima were observed for the catalysts containing 10 and 70% Mo. It was found that the surface compositions of the catalysts were altered slightly after the reactions even in the air stream, although no apparent reduction of the catalyst was detected with XPS. The slight enrichment of MoO_3 were observed after the reaction as shown in Fig.1. The activities are plotted in Fig.3 as a function of the surface composition of the catalyst measured after the reaction in the air stream. Interestingly, only a single activity maximum was obtained for the dehydration of sec-butanol when the catalyst contained about 50% Mo in the surface. Therefore, it is concluded that two maxima observed in Fig.2 are resulted from the differences between surface and bulk compositions and that the maximum activity for the dehydration, that is, the maximum acidity is generated for the catalysts which contains similar amounts of MoO_3 and SnO_2 in the catalyst surface. The isomer distributions of butenes were almost invariant for the all catalysts; 1-butene: 20%, cis-2-butene: 50%, and trans-2-butene: 30%, suggesting the E-2 mechanism (14) for the dehydration of sec-butanol over the SnO_2-MoO_3 catalysts. As regard with the oxidative dehydrogenation of sec-butanol, the catalyst containing about 60% Mo in its surface showed the maximum activity.

Takita et. (8) and Ai (15) have reported single catalytic activity maxima for the isomerization of 1-butene, the oxidations of propylene and butadiene, and the dehydration and dehydrogenation of iso-propanol over SnO_2-MoO_3 catalysts. The discrepancies among the activity patterns are considered to be ascribed to the differencies in the preparation methods of catalysts, since the surface compositions of catalysts depend strongly on the preparation methods (16).

In the case of the reaction in the N_2 stream, the catalysts were reduced (MoO_2 was formed), accompanying the remarkable surface composition changes (16,17). As shown in Fig.1, considerable Mo enrichments were observed after the reaction. In the reductive conditions, the catalyst containing 96% Mo in its surface showed a maximum activity for the dehydration of sec-butanol, implying different synergistic effects among composite oxides for the resultant MoO_2-SnO_2 catalysts. The reduced catalysts exibited only very low activities for the dehydrogenation of sec-butanol.

In summary, it is clearly demonstrated that the determination of the surface composition of binary oxide catalyst is necessary to discuss the catalytic properties in detail.

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