Bull. Chem. Soc. Jpn., **53**, 1206—1209 (1980) [Vol. 53, No. 5

Surface Composition of SnO_2-ZrO_2 Binary Oxide Catalyst and Its Selectivity for C_3H_6-NO Reaction

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(Received June 12, 1979)

The relation between the composition of outermost surface layer on SnO_2–ZrO_2 binary oxide catalyst and catalytic selectivity in the C_3H_6–NO reaction has been investigated by XPS technique. The composition of outermost surface layer was estimated from a comparison of the intensity ratios of X-ray induced Auger peak or XPS peak of Sn to XPS peak of Zr. A superficial enrichment of Zr was observed in these catalysts calcined at 600 °C in the air, while surface enrichment of Sn took place during the course of evacuation at 450 °C. The catalytic selectivity for formation of acrylonitrile showed a maximum with the catalyst containing Sn and Zr in the same concentration at the outermost surface layer of catalyst.

Enrichment of one component of a binary alloy occurs when the alloy is prepared in the air or reactive gases.[1,2] Knowledge of the surface composition of a binary catalyst is necessary for the clarification of heterogeneous catalytic reactions. Only a little evidence of the difference in surface and bulk compositions in cases of multicomponent oxide catalysts has been obtained.[3–6]

Studies with some binary oxide catalysts were carried out by means of X-ray photoelectron spectroscopy (XPS) in order to show the considerable difference occuring in the surface composition from the bulk composition of binary oxide catalysts such as SnO_2–MoO_3 and CoO–MoO_3 binary systems.[7–9] Only a few studies have been made to elucidate the influence of surface composition of solid catalysts on catalytic activity or selectivity.[7]

In the present work, the relation between the surface composition of some SnO_2–ZrO_2 binary oxide catalysts and the catalytic activity or selectivity for the C_3H_6–NO reaction has been studied. Special attention was attached to the role of the outermost surface layer of catalysts on catalytic activity and selectivity.

Experimental

The SnO_2–ZrO_2 binary oxide catalysts were prepared by impregnation and coprecipitation. The impregnated catalysts were prepared as follows: Powder of SnO_2 or ZrO_2 as a support was immersed in aqueous solutions of $ZrO(NO_3)_2$, $ZrOCl_2$, or $SnCl_2$ respectively, followed by evaporation to dryness at 100 °C and calcination in the air at 600 °C for 8 h. The SnO_2/ZrO_2 catalyst represents the SnO_2 supported on ZrO_2, the ZrO_2/SnO_2 catalysts representing the ZrO_2 supported on SnO_2.

Coprecipitated SnO_2–ZrO_2 catalysts were prepared by precipitation at pH∼5 from a solution of $SnCl_2$ and $ZrO(NO_3)_2$ or $ZrOCl_2$ with dilute NH_4OH. The precipitates were washed, dried at 100 °C and then calcined in the air at 600 °C for 8 h. $SnCl_2\cdot 2H_2O$, $ZrO(NO_3)_2\cdot 2H_2O$, ZrO_2 (Nakarai Chemical Co.), $ZrOCl_2$, SnO_2, and a solution of NH_3 (Wako Pure Chem. Co.) were used.

Procedures

XPS spectra were measured on a Hitachi 507 photoelectron spectrometer equipped with a cylindrical mirror analyzer using Al $K\alpha_{1,2}$ radiation. The catalysts were mounted on a sample holder made of stainless steel. All binding energies were referred to the contaminant carbon [C 1s=285.0 eV]. The peak area intensities of Sn $3d_{5/2}$ and Zr 3d were used to obtain the Sn/Zr intensity ratio. The peak of Sn $3d_{5/2}$ (binding energy, *B.E.*, 486.6±0.2 eV) and Sn Auger (LMM, Kinetic energy; *K.E.*, 420 eV) were also used for obtaining information on depth profiles from the surface to the bulk of the catalysts. The surface compositions were determined by the intensity ratio Sn $3d_{5/2}$: Zr 3d or Sn Auger: Zr 3d using the calibration curve obtained by using mixtures of SnO_2 and ZrO_2 powder.

The reaction of C_3H_6–NO was studied over the SnO_2–ZrO_2 catalysts by using a reaction mixture, C_3H_6/NO=1/1, in a circulating system under 2.533×10^4 Pa (190 Torr) total pressure at 530 °C. Products were analyzed by GLC after 3 h.

Results and Discussion

Figure 1 shows the correlation between the content of Sn at the surface and that in bulk of SnO_2–ZrO_2 binary oxide catalysts prepared by coprecipitation.

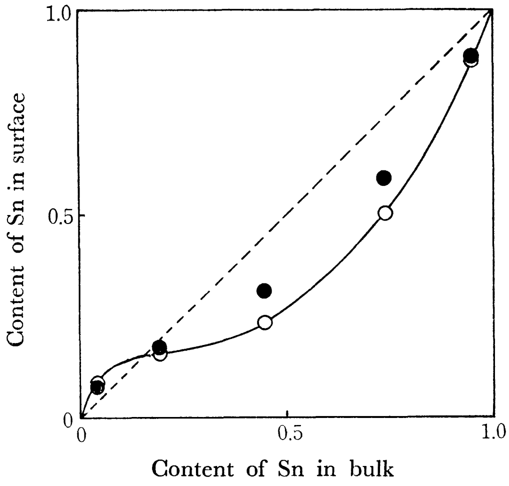

Fig. 1. Correlation between content of Sn in surface and that in bulk for coprecipitated SnO_2–ZrO_2 catalysts.
○: After calcination, ●: after evacuation at 450 °C for 2 h.

The value of surface composition was calculated from the intensity ratio of Sn Auger peak to Zr XPS peak, Zr 3d (*B.E.* 181.8±0.2 eV). The dotted straight line corresponds to the surface composition equal to bulk composition. A superficial enrichment of Zr was observed in these catalysts calcined in the air except for a small content of Sn ($\mathrm{Sn}/(\mathrm{Sn}+\mathrm{Zr})<0.15$ molar fraction). It is accepted that the surface is enriched by the constituent which has the lowest free energy under a surrounding gas. The surface enrichment of Zr during the course of preparation in the air would be due to the fact that the heat of formation of ZrO_2, 1079.5 kJ mol^{-1}, is larger than that of SnO_2, 574.9 kJ mol^{-1}. If the surface enrichment of Zr can be ascribed to the process in the formation of precipitate, the solubility product constant K_{sp} of $Sn(OH)_2$ should be smaller than that of $Zr(OH)_4$. However, the K_{sp} values of $Sn(OH)_2$[10)] and $Zr(OH)_4$[11)] are 1.8×10^{-15} and 8×10^{-52}, respectively, at 25 °C. The surface enrichment of Zr cannot be attributed to the difference of solubility in the formation of precipitates. A slight Sn enrichment was observed in the region less than 0.15 mole fraction of Sn in bulk. This might be due to the exclusion of Sn from the bulk of the catalyst by the crystallization of SnO_2. When evacuated at 450 °C for 2 h, the atomic intensity ratio $\mathrm{Sn}/(\mathrm{Sn}+\mathrm{Zr})$ increased (Fig. 1), indicating that surface enrichment of Sn occurs during the course of evacuation.

The correlations between the content of Sn in surface and that in bulk of SnO_2–ZrO_2 binary catalysts prepared by the impregnation methods are shown in Fig. 2. As expected, the surface enrichment of Sn and Zr was observed in the SnO_2/ZrO_2 and ZrO_2/SnO_2 catalysts, respectively. After evacuation at 450 °C for 2 h, the surface enrichment of Sn was observed in both catalysts.

The surface is enriched by the constituent which has the lowest surface free energy, the surface composition being correlated with the surface tension of solids. Oresbury *et al.*[3)] pointed out that the surface tension of metals can be estimated from the heat of vaporization and sublimation, the surface tension of metals increasing with increase in the heat of vaporization and sublimation. The heat of vaporization of metals is correlated with the melting point of metals, the melting point increasing with increase in the heat of vaporization (*cf.* Zr: 581.6 kJ mol^{-1}, Sn: 290.4 kJ mol^{-1}). This relation might be applied to binary oxide catalysts. In the case of SnO_2–ZrO_2 binary catalysts, the surface enrichment of Sn seems to be due to the fact that the melting point of SnO_2, 1127 °C, is lower than that of ZrO_2, 2700 °C.[12)] It might also be due to the fact that SnO_2 of the surface is reduced more easily than ZrO_2 since the heat of formation of SnO_2 is lower than that of ZrO_2.

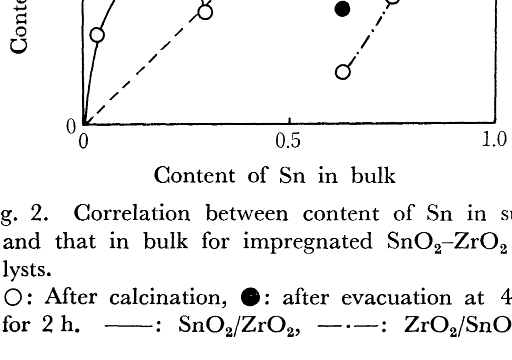

Fig. 2. Correlation between content of Sn in surface and that in bulk for impregnated SnO_2–ZrO_2 catalysts.
○: After calcination, ●: after evacuation at 450 °C for 2 h. ——: SnO_2/ZrO_2, —·—: ZrO_2/SnO_2.

It is necessary to estimate the composition of the outermost surface layer in relation to heterogeneous catalysis. The escape depth increases a great deal with increase in electron energy, characteristic of scattering length determined by electron-electron interactions.[13)] The values for the escape depth is evaluated by using samples consisting of homogeneous films having uniform thickness.[14)] The intensity, $I(d)$, of photoelectrons with a certain energy, expelled from a film of effective thickness d is given by $I(d)=I_\infty[1-\exp(-d/\lambda)]$, where λ is the electron escape depth in the film material and I_∞ the intensity of electrons expelled from a thick sample of the film material.

The energy dependence for the electron escape depth in the energy region of some kilovolts is expressed by the following relation obtained by Brundle,[13)]

$$\lambda(E) \propto E^n$$

where n is 0.5±0.1[15)] and E the kinetic energy, eV. Accordingly, the value of escape depth of the Sn Auger peak (kinetic energy: 420 eV) is *ca.* 8 Å, while the Sn XPS peak (kinetic energy: 1000 eV) is estimated to be *ca.* 12 Å. Thus, information on depth profiles is obtained from a comparison of both peak intensities.

A comparison of surface composition calculated from the intensity ratio of Sn Auger/Zr 3d to that of Sn 3d/Zr 3d is given in Fig. 3. The content of Sn obtained by using Sn Auger peak intensity is represented by r_1, and the content of Sn determined by Sn $3d_{5/2}$ by r_2. The surface layer in the impregnated and coprecipitated catalysts seems to be homogeneous. However, after evacuation at 450 °C, the surface enrichment of Sn is observed as shown in Figs. 1 and 2. The results indicate that the surface enrichment of Sn occurs in the surface layer of the SnO_2–ZrO_2 binary oxide catalysts during the course of evacuation at 450 °C.

In the presence of SnO_2–ZrO_2 catalysts, propylene reacts with NO to give $CH_2{=}CHCN$, CH_3CN, and CO_2. We have examined the relation between the composition of the outermost surface layer of the catalyst and the catalytic selectivity in this reaction (C_3H_6–NO).

Figure 4 shows the dependence of catalytic selectivity for the C_3H_6–NO reaction on the surface composition of the catalysts. In the catalysts prepared by both methods, the change in surface composition obtained from the intensity ratio Sn Auger/Zr 3d was not observed during contact with C_3H_6, NO, and

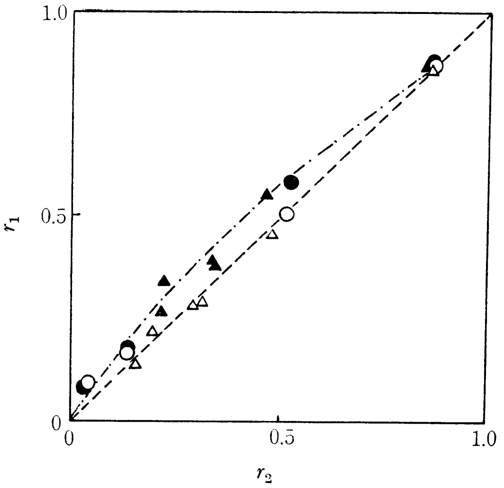

Fig. 3. Depth analysis of Sn in catalyst.
r_1: Content of Sn obtained by using Sn Auger intensity, r_2: content of Sn obtained by using Sn $3d_{5/2}$ intensity.
······, ○: Coprecipitated catalysts, ······, △: impregnated catalysts: SnO_2/ZrO_2 and ZrO_2/SnO_2. —·—, ●,▲: after evacuation at 450 °C for 2 h.

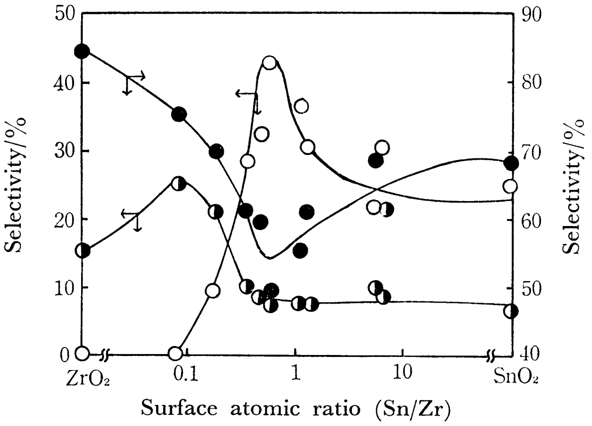

Fig. 4. Selectivity dependence of the reaction ($NO+C_3H_6$) on the surface composition of the catalyst. ○: CH_2=CHCN, ◑: CH_3CN, ●: CO_2.
Total pressure: 190 mmHg, Reaction mixtures: $C_3H_6/NO=1/1$ Reaction conditions: 530 °C for 3 h.

mixtures of C_3H_6 and NO. The selectivity for the formation of CH_2=CHCN becomes maximum at the atomic ratio, Sn/Zr=0.6, indicating that the catalytic selectivity is a function of surface composition of the catalyst irrespective of the method of preparation. The atomic ratios were estimated from the peak intensities of Sn Auger and Zr XPS, escape depths being 8 Å and 14 Å, respectively. The atomic ratio of Sn to that of Zr in the region near 3 Å from the outermost surface layer, $(\mathrm{Sn/Zr})_d$, was estimated by using the escape depths of Sn and Zr as follows.

$$(\mathrm{Sn/Zr})_d = f(I_{\mathrm{sn}}/I_{\mathrm{zr}})_d$$
$$= f(I_{\mathrm{sn}}/I_{\mathrm{zr}})_\infty[1-\exp(-d/\lambda_{\mathrm{sn}})]/[1-\exp(-d/\lambda_{\mathrm{zr}})]$$

where $d=3$ Å, $\lambda_{\mathrm{sn}}=8$ Å, $\lambda_{\mathrm{zr}}=14$ Å, and f is a constant. The value of atomic ratio in the region near 3 Å from outermost surface layer can thus be estimated by

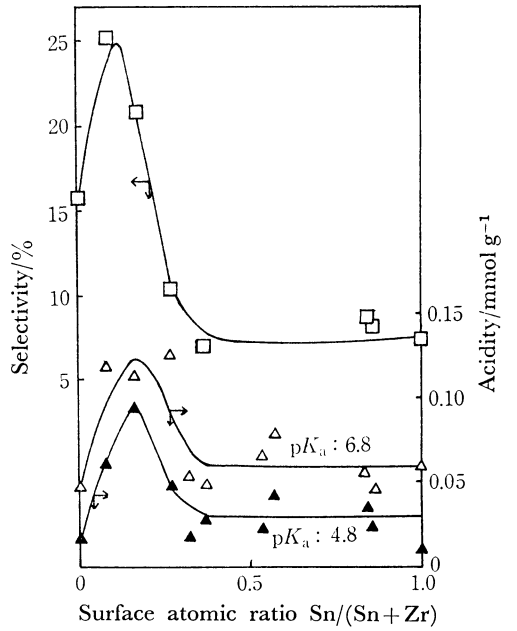

Fig. 5. Correlation between the selectivity for the formation CH_3CN as a function of the atomic ratio on the surface layer of the catalyst and its surface acidity.
□: Selectivity (%), △: pK_a: 6.8, ▲: pK_a: 4.8.

$(\mathrm{Sn/Zr})_{3\text{Å}}=0.96\simeq 1$.

This indicates that the catalytic selectivity for the formation of CH_2=CHCN becomes maximum with the same concentration of Sn and Zr of outermost surface layer on the catalyst.

On the other hand, the selectivity for the formation of CH_3CN becomes maximum near the atomic ratio 0.07 (Fig. 4). The results of acidity (amount of acid mmol/g) measured at pK_a=6.8 and 4.8 and the selectivity for formation of CH_3CN are shown in Fig. 5 as a function of the atomic ratio on the surface layer of the catalyst. The maximum selectivity agrees with that of acidity, indicating that the presence of acid sites on the surface of the catalysts results in the formation of CH_3CN produced by cracking reactions.

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