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The Surface Structure of the Oxidic Precursor of CoMo/γ-Al_2O_3 Hydrodesulfurization Catalysts

The hydrodesulfurization activity of molybdenum sulfide-based catalysts (supported or unsupported) is greatly promoted by the addition of a proper amount of cobalt (for a review, see (*1*)). For γ-Al_2O_3-supported catalysts, the maximum activity is obtained for an atomic proportion $r = Co/(Co + Mo) \simeq 0.3$. Much useful information has recently been gained from the use of advanced spectroscopic techniques (*2, 3*). For the most active CoMo/γ-Al_2O_3 samples ($r \simeq 0.3$), the major characteristics which are now well established are as follows: (i) in the oxidic precursor, molybdenum forms a mono- or multilayer tightly bound to the surface of γ-Al_2O_3 (*4*). This layer is sulfided into highly dispersed, small sized, MoS_2 crystallites during activation and catalytic working (*5*). (ii) When deposited together with or after molybdenum, cobalt tends to be associated with molybdenum, forming a Co–Mo double layer on the oxidic precursor samples (*2, 6*).

Knowledge of the atomic arrangement of Co and Mo within this double layer is a primary requisite for understanding the mutual role of Mo and Co for promoting activity. Up to now, this structure has remained poorly understood and it was not possible to decide between the various models which were proposed for describing the double layer (*7*). The study of such a surface structure requires a highly sensitive surface technique. The capabilities of XPS are too poor in this respect as the escape depth of the photoelectrons is larger than 1.5 nm, namely, several atomic layers. For this reason, an investigation has been undertaken using ion scattering spectrometry (ISS), which is known to provide a surface sensitivity limited to the *first atomic monolayer* of the surface while allowing depth profiling by gradual erosion of the successive layers. These measurements give striking evidence that the Co–Mo double layer is made of an oxidic molybdenum layer on top of an oxidic cobalt layer.

The oxidic precursor sample which has been investigated was prepared by successive deposition of Mo and Co on 160 $m^2\ g^{-1}$ γ-Al_2O_3 support in powder form. Mo was deposited by impregnation with ammonium paramolybdate solution, drying and calcination at 500°C for 24 hr. Co was then deposited by impregnation with cobalt nitrate solution followed by drying and calcination at 500°C for 24 hr. The weight content of the final calcined catalyst was 10.86% for molybdenum oxide (assumed as MoO_3) and 3.82% for cobalt oxide (assumed as Co_3O_4). This corresponds to an atomic proportion $r = 0.38$. After the final calcination the samples were finely ground in a mortar and slightly compressed in order to make self-supporting pellets to be introduced into the vacuum chamber of the spectrometer.

The measurements were performed on a 3 M Company model 535 BX instrument. The spectra were obtained with $^3He^+$ at 2 keV with a beam current of 200 nA. An area of about 2 × 2 mm^2 was rastered (mean current density 5 $\mu A\ cm^{-2}$) and a 50% gating of the signal was applied in order to analyze only the central part of the eroded area (*9*).

Spectra were repeatedly accumulated during 48 sec and stored on magnetic tape. Figure 1 presents such a typical spectrum. As shown in this figure, the peak intensities $I(O)$, $I(Al)$, $I(Co)$, and $I(Mo)$ were defined by performing the integration of the peaks over a background which was assumed to be linear. The overlapping of the Co and Mo peaks required deconvolution.

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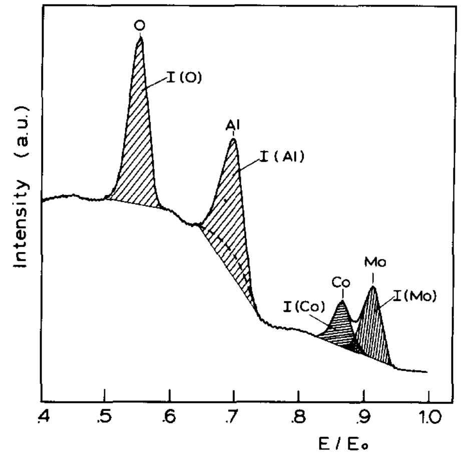

FIG. 1. ISS spectrum from CoMo/γ-Al_2O_3 catalyst.

As it was not possible to complete these time-consuming manual measurements on the hundreds of spectra stored, it was found sufficiently accurate to convert the peak heights directly into peak integrals by use of empirical factors (*10*). No attempt will be made here to interpret the evolution of the oxygen signal.

Figure 2 shows the variations with sputtering time of the ratios $I(\mathrm{Mo})/I(\mathrm{Al})$ (Fig. 2a), $I(\mathrm{Co})/I(\mathrm{Al})$ (Fig. 2b), and $I(\mathrm{Co})/I(\mathrm{Mo})$ (Fig. 2c). The experimental points are the mean values of the intensity ratios measured on 10 successive spectra (8 min erosion). The first spectrum recorded displays a very high molybdenum peak intensity but hardly any cobalt signal. $I(\mathrm{Mo})$ decreases then in an approximately exponential way, while $I(\mathrm{Co})$ increases up to a maximum followed by a monotonic decrease.

These results may be interpreted as indicating the presence of a molybdenum oxide surface layer, the erosion of which unveils progressively an underlying cobalt oxide layer. Concomitantly with the erosion of the surface layers initially exposed to the beam, the erosion of the Al_2O_3 carrier itself exposes to the ion beam some amount of fresh molybdenum oxide deposited near the mouth of the pores. A steady state is obtained when erosion and formation of freshly exposed surfaces match each other.

This interpretation may be checked by a fairly straightforward mathematical model, considering a surface double layer made of a molybdenum oxide layer on top of a cobalt oxide layer (*10*). We may assume that the sputtering yield k (defined as the fraction of atoms which are torn off per unit time) is the same for these two layers and that the erosion of each Mo atom exposes a constant proportion of underlying Co atoms to the analysis. Defining the product $k\epsilon$ as the ratio of the amount of fresh molybdenum oxide layer from the pores unveiled per unit time by the sputtering of the carrier, versus the molybdenum oxide content of the original surface, the change of the peak intensities may then be expressed as follows:

$$I(\mathrm{Mo}) \div \exp(-kt) + \delta$$

$$I(\mathrm{Co}) \div (kt - \delta)\exp(-kt) + \delta$$

where $\delta = \epsilon/(1 - \epsilon)$.

The full curve in Fig. 2c is the best fit of the $I(\mathrm{Co})/I(\mathrm{Mo})$ experimental points which can be derived from these latter expres-

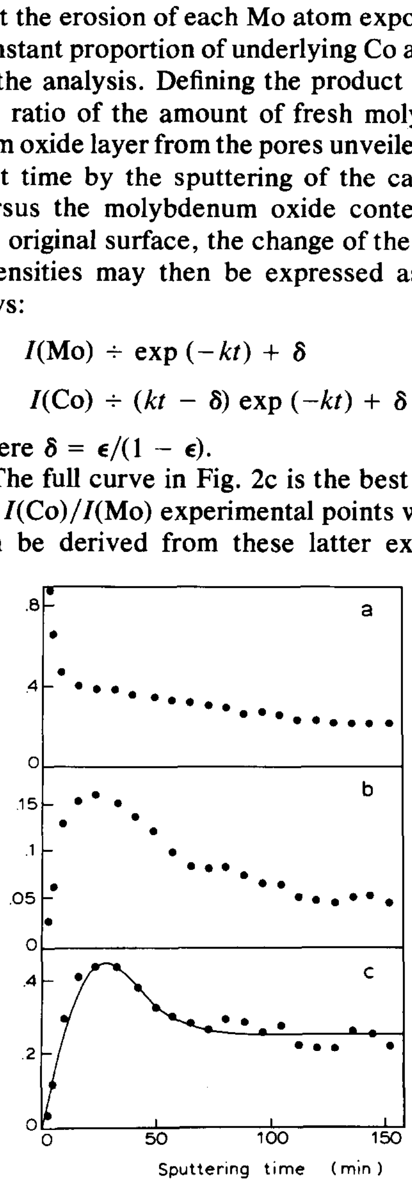

FIG. 2. Time dependence of the ISS intensity ratios $I(\mathrm{Mo})/I(\mathrm{Al})$ (a), $I(\mathrm{Co})/I(\mathrm{Al})$ (b), and $I(\mathrm{Co})/I(\mathrm{Mo})$ (c). The full curve has been drawn from a mathematical model of the erosion process (see text).

sions. The agreement is good. It corresponds to a sputtering yield $k = 1.7 \times 10^{-3}$ sec^{-1} and a ratio $k\epsilon = 1.2 \times 10^{-4}$ sec^{-1}. If the analyzed depth is equal to the thickness of the molybdenum oxide layer one may calculate that, with a current density of 5 μA cm^{-2}, such a k value implies a yield of 2×10^{-2} molecules of molybdenum oxide (assumed as MoO_3) per incident $^3He^+$ ion. Although we have no data about measurements of sputtering yield on such an oxide, it is noteworthy that this value compares favorably with the yield of 3.1×10^{-2} Mo atoms per incident ion which was measured experimentally by Bay *et al.* (*11*) for the erosion of molybdenum by 2 keV $^3He^+$ ions at 90° incidence. The $k\epsilon$ value can also be shown to be in accordance with reasonable expectations (*10*).

The numerical values obtained from this mathematical simulation give support to the picture of the "architecture" of the catalyst surface which has been proposed from the ISS depth profiles. However, owing to the number of hypotheses and the lack of precise data about sputtering yield and analyzed depth, it would be hazardous to attempt to extract from this simulation more details about the architecture of the surface. As concerns, for example, the thickness of the molybdenum oxide layer, the reasonable value of the sputtering yield obtained suggests a thickness of the same order as the analyzed depth. However, the formation of multilayered rafts cannot be excluded as the presence of an aluminum peak at the start of the ISS profiling indicates that some part of the Al_2O_3 surface remains uncovered although the amount of MoO_3 (10.83%) is sufficient for the formation of a complete monolayer coverage.

The ISS results indicate with a surprising clarity the structure of the Co–Mo double layer. The fact that practically no cobalt is exposed in the outer layers is particularly striking. This quite special architecture of the Co–Mo bilayer requires that during or after the second impregnation a rearrangement takes place, with Co diffusing below the Mo monolayer, toward the surface of Al_2O_3. A substantial part of it remains trapped at the interface between Al_2O_3 and the Mo monolayer. This special position of Co explains the ease with which some cobalt aluminate can form (*2*) by diffusion of cobalt atoms from the surface to the bulk of the support, as a reaction consecutive to the formation of the bilayer (*12*). It is striking to note that, paradoxically, the same surface structure cannot be formed by depositing cobalt before molybdenum in the pore volume impregnation method, presumably owing to the inability of cobalt to disperse in that case.

The use of ISS for the study of practical catalysts has already been suggested (*13, 14*). The present work confirms the extreme surface selectivity of the method and shows the fine information which can be obtained from the interpretation of depth profiling measurements at the scale of a few surface monolayers, even on such badly defined surfaces as those of highly porous catalyst supports. There is no doubt that careful measurements by ISS should bring new insight into the understanding of the structure of a large number of important catalytic systems.

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