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Structure of Hydrotreating Catalysts Revealed by Ion Scattering Spectrometry

INTRODUCTION

Although low-energy ion-scattering spectrometry (LEIS or ISS) has been known as a surface analytical technique for over a decade, its application to practical "real-world" catalyst systems has been limited. Shelef *et al.* first showed the promise of ISS toward catalyst studies in 1975 (*1*). Hercules and his co-workers combined XPS and ISS studies on alumina-supported Ni and Co hydrocracking catalysts (*2–4*).

In this decade, most of the surface studies of catalyst systems have thus far focused upon the Co- or Ni-promoted Mo(or W)/Al_2O_3 hydrodesulfurization catalysts. The goal of these studies has been to characterize the surface and/or active species and its surface dispersion and distribution within the first several layers of oxidic, reduced, and sulfided forms of the catalyst. ISS has been used in many of these studies.

For the Co/Mo/Al_2O_3 system, Delannay *et al.* used ISS intensity ratios to prove that the surface structure of the oxidic form consisted of a Co–Mo bilayer with an oxidic Co layer lying underneath an oxidic Mo layer (*5*). Chin and Hercules used ISS results to confirm the Co–Mo bilayer and to show the absence (or negligible concentration) of $CoMoO_4$ on the surface of the catalyst (*6*).

For the Ni/Mo/Al_2O_3 system, Knözinger and co-workers found that the Ni was distributed both within the surface Mo layer and also in the support; moreover, the relative dispersion of Ni within the surface layer depended upon the impregnation sequence (*7–9*). Another ISS study by Jeziorowski *et al.* showed that as calcination temperature increased, the Ni on the surface began to migrate into the support (*10*).

Little ISS work has been done on the Ni/W/Al_2O_3 system, although Salvati *et al.* observed that the Ni is distributed both in the surface oxidic W layer and within the support, and that the Ni/W ratio remained constant with sputtering time (*11*). No temperature effects were noted.

More about these and other systems such as nonpromoted Mo/Al_2O_3 and W/Al_2O_3 that have been studied by ISS can be found in a review article by Cocke and Horrell (*12*).

This paper reports ISS results in which the effects of varying calcination temperature upon relative surface dispersion and component location of the oxidic Co/Mo/Al_2O_3 and Ni/W/Al_2O_3 systems have been studied. Specifically, we report the breakdown of the CoMo bilayer and the formation of a highly dispersed surface Ni species at high calcination temperatures.

EXPERIMENTAL

The two catalysts, Co/Mo/γ-Al_2O_3 (3.5 wt% CoO, 14 wt% MoO_3) and Ni/W/γ-Al_2O_3 (6 wt% NiO, 19 wt% WO_3), were purchased from Strem Chemicals. The respective surface areas for the Co/Mo/Al_2O_3 and Ni/W/Al_2O_3 were 244 and 150 m^2/g. The physical forms were $\frac{1}{8}$- and $\frac{1}{16}$-in. cylindrical extrusions for the Co/Mo/Al_2O_3 and Ni/W/Al_2O_3 catalysts, respectively.

The catalysts were calcined in flowing air (47 cm^3/min) in a tube reactor at 300, 400, 500, 600, and 750°C for 1 h at each temperature.

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Ion scattering was done with a 3M Model 525 ISS/SIMS spectrometer equipped with a cylindrical mirror analyzer-integrated gun system. The samples were first pressed into thin wafers before mounting onto the sample holder. The UHV base pressure was 4 × 10^{-8} Torr; the analysis pressure when the chamber was backfilled was 6 × 10^{-5} Torr. $^3He^+$ ions of 2 keV at a current density of 1.25 × 10^{-6} A/cm^2 were used for analysis, and sputter profiling was accomplished using a 2 × 2-mm rastering of the beam. To neutralize any charging effects, an electron beam current of <1 mA was used to flood the sample.

RESULTS AND DISCUSSION

Some results are shown in Figs. 1–4. The X-axis for all plots is the log of the total sputtering time in seconds. The Y-axis represents ratios taken from peak height intensity measurements of ISS spectra.

In Fig. 1, for a calcination temperature of 600°C, the Mo dispersion on the surface, which is high initially, immediately decreases upon sputtering. Relative surface dispersion can be obtained from the first data point in the ISS depth profile. For a calcination temperature of 750°C (Fig. 1), it is seen that the Mo dispersion is about 2.5 times lower than for the 600°C calcination temperature. The question arises as to the cause of the loss in Mo dispersion. The answer perhaps lies in Fig. 2. At the 600°C calcination temperature, there initially is no surface Co present, but upon sputtering, there is a very sharp rise and then a steady decline in the Co distribution. This sharp rise in Co coincides nicely with the fall in Mo (Fig. 1, 600°C) upon sputtering. Note in Fig. 2 the dissimilarities between the 600°C calcination temperature and the 750°C calcination temperature. At 750°C, the rise in Co is not as sharp as that for 600°C, nor is the decline, and the profile maximum has shifted toward a deeper position. Upon heating then, the Co has migrated into the support (bulk); a spinel-type cobalt has probably formed at the higher temperature. This movement away from the surface may be related to the collapse of the Mo surface dispersion, which was high at 600°C due to the directly underlying Co layer. This is supported by the previous observation that Co aids Mo dispersion (*13*, *14*).

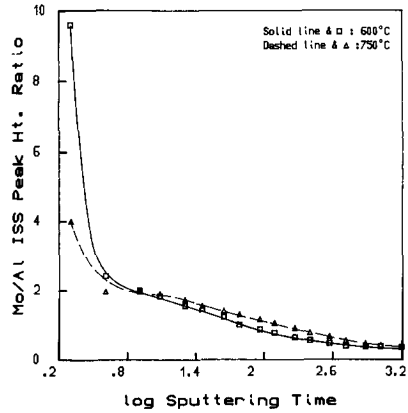

FIG. 1. ISS Mo/Al intensity ratio depth profile for calcination temperatures 600 and 750°C.

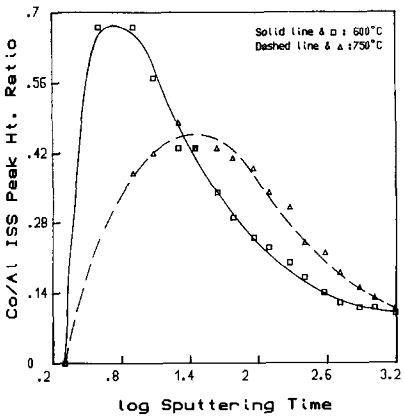

FIG. 2. ISS Co/Al intensity ratio depth profile for calcination temperatures 600 and 750°C.

The Ni/W/Al_2O_3 system (Figs. 3 and 4) appears to be much more complex than the Co/Mo/Al_2O_3 system. Figure 3 shows that although W is the predominant metal species on the surface, it is not at its highest dispersed state at a 600°C calcination temperature, and as sputtering continues, the W distribution within the first several atomic layers passes through a maximum

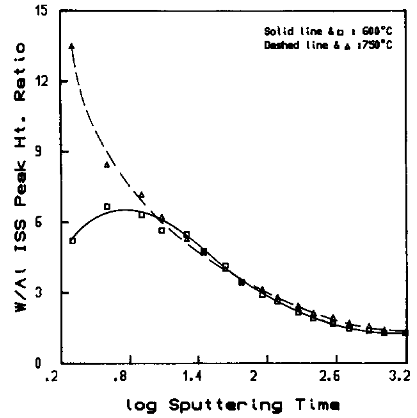

FIG. 3. ISS W/Al intensity ratio depth profile for calcination temperatures 600 and 750°C.

before decreasing. At a calcination temperature of 750°C, however, a highly dispersed surface W is seen, and its distribution steadily decreases upon sputtering. Figure 4 shows that at 600°C there is initially a very small amount of surface Ni, but as sputtering occurs, an underlying Ni layer appears and then decreases. A major change is seen for a calcination temperature of 750°C. At 750°C, a more highly dispersed (4.5 times more dispersed) Ni species on the surface in addition to the Ni layer beneath the surface is seen. Moreover, it appears that the underlying Ni species has migrated further into the support upon heating, as is indicated by the shift in profile maximum. Thus in going from 600 to 750°C, more surface W is produced. In addition, two forms of Ni, a surface species and a bulk form, are clearly formed. This bulk form is most likely a spinel-type nickel, which is known to form at high temperatures. The Ni species underlying the W species migrates into the support.

The apparent specific conclusions are as follows:

(1) For the Co/Mo/Al_2O_3 system, increasing the calcination temperature from 600 to 750°C causes the underlying Co layer to migrate into the support, and the subsequent breakdown of the Co–Mo bilayer and loss of Mo dispersion on the surface may be related to the loss of Co at the molybdenum oxide/alumina interface.

(2) For the Ni/W/Al_2O_3 system, increasing the calcination temperature from 600 to 750°C induces the formation of a well-dispersed W species and a well-dispersed Ni species on the surface, and causes the underlying Ni layer to migrate into the support.

The general conclusions are reached:

(1) Calcination temperature has a great influence upon the surface species and/or dispersion of the oxidic forms of promoted HDS catalysts.

(2) ISS is a viable analytical technique that can be used to follow dispersion and component location and migration in such catalysts and can monitor the surface effects of various treatments.

(3) ISS produces results which are difficult to obtain by any other surface technique. However, the observations made by using ISS need to be confirmed by complementary techniques such as STEM, LRS, and other surface probes.

More detailed ISS and related characterization studies involving calcination temperature and time, among other parameters, and their subsequent effects upon the structures of the oxidic, reduced, and sulfided forms

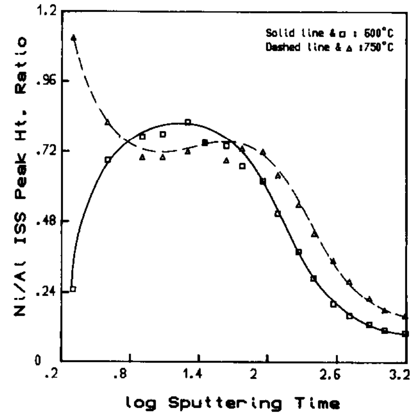

FIG. 4. ISS Ni/Al intensity ratio depth profile for calcination temperatures 600 and 750°C.

of the Co/Mo/Al_2O_3 and Ni/W/Al_2O_3 systems are currently underway.

ACKNOWLEDGMENT

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