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Working surface science model of CoMoS hydrodesulfurization catalysts

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Model catalysts, consisting of a conducting substrate with a thin SiO_2 or Al_2O_3 layer on top of which the active catalytic phase is deposited, were applied to study the sulfidation of Co–Mo catalysts and to test their catalytic behavior in the hydrodesulfurization of thiophene. CoMoS, the highly active cobalt promoted MoS_2 in which Co is thought to decorate the edges of MoS_2 slabs, can be synthesized by sulfiding nitrilotriacetic acid complexes of cobalt and molybdenum. These complexes are deposited on $SiO_2/Si(100)$ and $Al_2O_3/Si(100)$ model supports by spin coating. X-ray photoelectron spectroscopy measurements on these Co–Mo catalysts provide detailed insight into the mechanism of sulfidation. It appears that Mo is sulfided first and then the Co; this is imperative to form the CoMoS phase. Thiophene hydrodesulfurization studies of CoMoS model catalysts yield activities and product distributions consistent with those obtained from their high surface area counterparts, proving that these models are realistic. They offer, therefore, a great potential for fundamental surface science studies of catalytic phases and of adsorption, desorption, and reactions of gases as well. © *1997 American Vacuum Society.* [S0734-2101(97)57303-9]

I. INTRODUCTION

Hydrodesulfurization, the catalytic removal of sulfur from heavy oil fractions, is one of the most rapidly growing large scale applications of heterogeneous catalysis. It is carried out over sulfides of molybdenum or tungsten, and promoted with cobalt or nickel. Hydrodesulfurization (HDS) represents a number of different reactions, of which the reaction of thiophene with hydrogen to butadiene and H_2S is a good example:

$$C_4H_4S + 2H_2 \rightarrow C_4H_6 + H_2S.$$
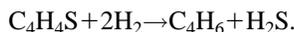
The butadiene product undergoes secondary reactions to butenes, butanes, and smaller hydrocarbons. Other commonly used model reactions for HDS involve the desulfurization of heavier molecules such as benzo and di-benzo thiophene. Catalysts promoted by Co or Ni are typically an order of magnitude more active than unpromoted MoS_2 is.[1,2]

Of the active catalyst combinations, the Co-promoted MoS_2 system is by far the best characterized. A structure advocated by Topsøe and co-workers in which cobalt atoms decorate the edges of MoS_2 slab particles, commonly referred to as the CoMoS structure (Fig. 1), has found widespread acceptance, with a wealth of spectroscopic and structural studies having yielded a detailed picture of this structure.[2–5] Nevertheless, many questions still exist as to the preparation of the CoMoS phase, for example, a molecular scale mechanism of the conversion of the oxidic Co and Mo precursors into sulfides. Also, little is known about the adsorption and reaction of gases on the edges of MoS_2, with or without promoters, where the catalytic activity resides. It is here that surface science offers excellent opportunities. The conventional single crystal approach, which works well for

metals, is, however, not very useful in the case of sulfides, as the catalytic activity is uniquely associated with defect sites at the edges of the MoS_2 slabs.

Model catalysts, consisting of a flat conducting substrate with a thin SiO_2 or Al_2O_3 layer on top of which the active catalytic phase is deposited, are the solution to this problem.[6] If the active phase is applied by impregnating a solution of the Mo and Co catalyst precursors, the model retains many of the properties of the high surface area supported catalysts used in industry. Impregnation of flat supports systems can successfully be mimicked by spin coating,[7] while the amount of material that is deposited can be accurately predicted.[8] Previous studies in our laboratory of the sulfidation of MoO_3 on 5 nm SiO_2 layers on Si(100) substrates have demonstrated the usefulness of this approach.[9–11]

In this article we study the preparation of CoMoS model catalysts on SiO_2 and Al_2O_3 thin film supports and we test the catalytic activity and selectivity of the models in the desulfurization of thiophene. The results show that it is very well possible to obtain realistic flat model analogs of the CoMoS system shown in Fig. 1, thus opening the way for new surface science studies of industrially relevant sulfidic HDS catalysts.

II. EXPERIMENT

Silica model supports are prepared by oxidizing a silicon wafer with (100) surface orientation and a diameter of 75 mm in air at 825 K for 24 h. The oxidized wafer is cleaned in a solution of concentrated ammonia [pro analyze (p.a.)] and hydrogen peroxide (p.a.) at 340 K for 10 min. In order to make it more similar to a high surface area silica, which contains hydroxyl groups, the surface is rehydroxylated by boiling in water for 5 min. Angle dependent x-ray photoelectron spectroscopy (XPS) experiments performed as explained in Refs. 12 and 13 indicate that the SiO_2 layer is
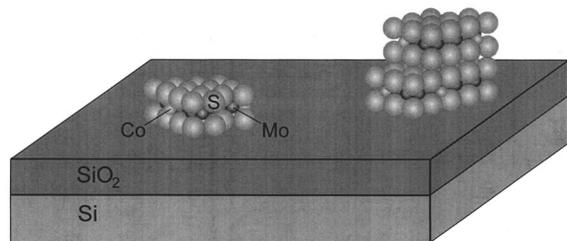
FIG. 1. Schematic representation of a CoMoS/SiO$_2$/Si(100) hydrodesulfurization model catalyst. MoS$_2$ forms a sandwich structure in which Co promoter atoms decorate the edges. The basal planes of MoS$_2$ are inactive. The support is a 3–5-nm-thick layer of SiO$_2$ on a Si(100) substrate, which is sufficiently conducting to prevent charging in photoelectron spectroscopy.

about 5 nm thick after oxidation. Some SiO$_2$ dissolves in the cleaning procedure resulting in an oxide layer of about 3 nm.

Alumina model supports are prepared by evaporating aluminum oxide on a silicon wafer with a native oxide layer. Prior to evaporation the wafer is cleaned in a HF solution. The evaporated alumina layer is approximately 5 nm thick.

Van Veen *et al.*[14] have demonstrated that the CoMoS phase (type II in Topsøe's terminology[2]) can be synthesized by sulfiding cobalt and molybdenum complexes of nitrilotriacetic acid (NTA). An aqueous solution of Co and Mo complexed with NTA and a Co/Mo ratio of 1/3 is applied to the model supports by spin coating at 2800 rpm according to a procedure described by Kuipers and co-workers.[7] A model describing the spin coating of dilute solutions[8] predicts that eventually a film of solution 1.7 μm in height will deposit on the model support. The concentration of Mo in the solution is 0.0034 M resulting in a loading of 3.6 Mo atoms/nm^2. This is the equivalent of a 12 wt % loading of Mo on a 250 m^2/g silica support, and is representative of the typical industrial catalyst.

The model catalysts are sulfided in a glass tube reactor with a mixture of 10% H$_2$S in H$_2$ at a flow rate of 60 ml/min while the catalyst is heated at a rate of 2 K/min to the desired temperature, and kept there for 30 min. After sulfidation, the catalyst is cooled under helium to room temperature. Next the reactor is closed and introduced into a nitrogen-filled glovebox, from which the sample can be transferred to a vessel for transport under nitrogen to the XPS spectrometer. XPS spectra are obtained with a VG Escalab 200 spectrometer equipped with an Al $K\alpha$ source and a hemispherical analyzer connected to a five-channel detector. Measurements are done at 20 eV pass energy. Correction of the binding energy is performed by using the C 1s peak at 284.7 eV as a reference.

The model catalysts are tested in thiophene HDS to monitor the activity and product distribution. First the model catalysts are sulfided at 675 K for 2 h as described above. Then a mixture of 4% thiophene in H$_2$ is passed through the reactor at a rate of 50 ml/min and at 675 K. After 3 min the reactor is closed and is then operated as a batch reactor. After the desired reaction time a sample is taken from the reactor with a valved syringe for gas chromatography (GC) analysis

of the reaction products. Blank runs of the empty reactor and of the model supports are also performed.

III. RESULTS AND DISCUSSION

As explained earlier, HDS catalysts are prepared by impregnation from solution of Co and Mo salts. Before they can be used in HDS, the oxidic phases have to be converted into sulfides. We shall first discuss the sulfidation of the oxidic CoMo model catalysts, and then their behavior in the catalytic desulfurization of thiophene.

A. Sulfidation of CoMo model catalysts

Figure 2 shows the Mo 3d XPS spectra of both the silica and alumina supported CoMo model catalysts after sulfidation in the H$_2$S/H$_2$ mixture at different temperatures. The spectra of the freshly prepared model catalysts reveal only Mo 3d peaks at a binding energy of 232.1 and 232.5 eV, respectively, corresponding to a Mo^{6+} species. At 350 K a shoulder develops around a binding energy of 230 eV for both model systems, indicating that Mo is already partially reduced. At 450 K the majority of the Mo is transformed to a species with a binding energy of 229.2 eV, indicating that Mo is mostly in an (oxy)sulfidic form. We refer to earlier XPS studies of MoO$_x$/SiO$_2$/Si(100) model catalysts[9,10] and of crystalline MoO$_3$ powders[15] for a detailed description of the changes in Mo XPS spectra during sulfidation. It is evident from Fig. 2 that molybdenum reacts to the sulfidic form between 350 and 450 K, whereas at 400 K the larger part of the Mo has already been converted to the sulfided state.

The XPS spectra of Fig. 3 indicate that sulfidation of cobalt proceeds more slowly than that of molybdenum. The Co 2p spectra of the freshly impregnated catalysts as well of those after treatment in H$_2$S/H$_2$ at 300–400 K show the pattern characteristic of oxidic cobalt, with a main peak between 781.5 and 781.9 eV and a shakeup feature at higher binding energies. The spectra after sulfidation at 500 K and higher show a binding energy for the Co 2p at 779.0 eV and are totally characteristic of sulfided cobalt,[16] whereas the catalysts sulfided at 450 K are in transition between the two states. Thus, for these systems, complete sulfidation of the cobalt takes temperatures between 450 and 500 K. This is in remarkable contrast to measurements on single component cobalt oxide reference catalysts, where complete sulfidation is observed around 400 K.[17]

The sulfidation of Co is apparently retarded by the NTA ligand to temperatures at which molybdenum is already in a fully sulfided state. These findings are in agreement with recent work of Medici and Prins[18] on NTA derived NiMoS catalysts and fit well into the picture of CoMoS and NiMoS in which the promoter atoms decorate the edges of MoS$_2$ particles.[3,19] The fact that sulfidation proceeds in a similar manner for the silica and alumina supported CoMo systems is in agreement with the notion that catalysts prepared from Co and Mo NTA complexes have negligible interaction with the support.[14]
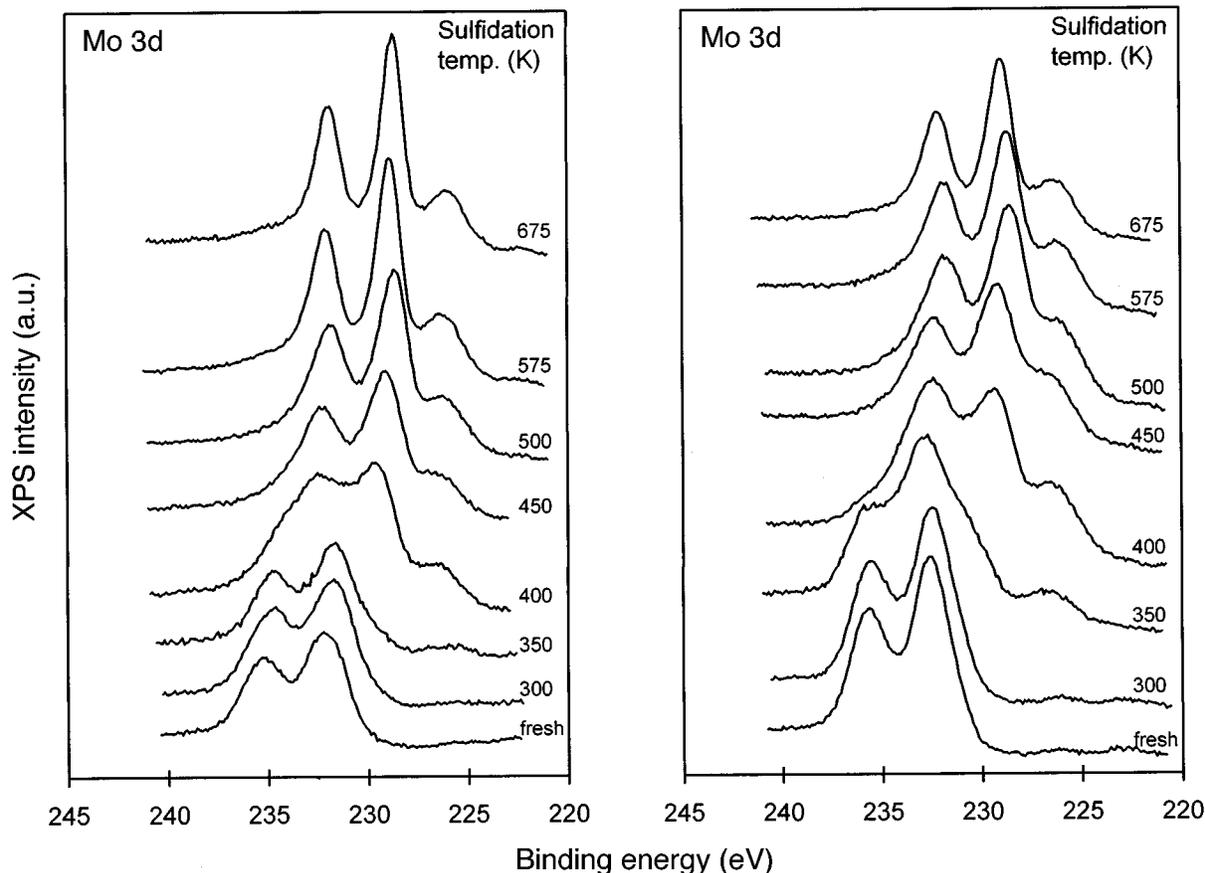
FIG. 2. Mo $3d$ XPS spectra of the CoMo/SiO$_2$/Si(100) and CoMo/Al$_2$O$_3$/Si(100) model catalysts as a function of sulfidation temperature.

B. Model CoMoS catalysts in thiophene hydrodesulfurization

Although the XPS results yield some good evidence that the CoMoS phase has formed, they do not actually prove the presence of CoMoS. As oxide-supported CoMoS catalysts are about an order of magnitude more active than unpromoted catalysts (or Co-containing catalysts in which Co is not associated with MoS$_2$ edges),[3] measuring the catalytic activity provides the most convincing test for the validity of the model system. To this end, batch thiophene HDS activity tests were performed with the model catalysts for different reaction times. The products formed are mainly butenes and C$_2$ and C$_3$ hydrocarbons. The total conversion of thiophene is plotted in Fig. 4 for both the model catalysts and for a blank experiment. In the blank experiment, the reactor is loaded with an oxidized and cleaned silicon wafer, in other words, a model support that was treated in the same way as the model supports used to prepare the model catalysts. This blank model support is also sulfided by the same procedure as used for the model catalysts. Figure 4 reveals that in the blank experiment some conversion of thiophene also occurs. This is thought to be due to thermal decomposition of the thiophene, which may or may not be assisted by the reactor wall. However, conversion of the Co and Mo loaded model catalysts is significantly higher, thus proving that these model catalysts are indeed active in HDS reactions. After 1 h

of batch reaction at 675 K the thiophene conversion is 1.6% (after subtraction of background conversion). Present in the reactor is a piece of model catalyst with a surface area of about 5 cm^2 and a Mo loading of 3.6×10^{14}/cm^2. This results in a pseudoturnover number per Mo atom of $\sim 10^{-2}$ s^{-1}, averaged over 1 h reaction time. This value agrees very well with turnover frequencies measured on alumina and silica supported CoMoS catalysts,[2] which fall in the range 1.10^{-3}–1.10^{-2} s^{-1} when expressed as conversion of thiophene per Mo atom. This implies that the dispersion of the CoMoS phase on the model catalysts is at least comparable to that on porous silica and alumina supported catalysts. The fact that the thiophene HDS activity is similar for CoMoS on both silica and alumina fully agrees with the earlier finding[14] that catalysts prepared via the NTA route exhibit minimal influence of the support on the activity.

The product distributions for both the silica and alumina supported model catalysts after 1 h of batch reaction are displayed in Fig. 5. The product distribution is independent of the reaction time and is similar on both supports. The ratios of the 1-butene, and *trans*- and *cis*-2-butene formed are in excellent agreement with those measured at low conversions on conventional, high surface area CoMoS catalysts prepared via the NTA method.[20] Since *n*-butane is formed through hydrogenation of butenes,[21] only a small amount is formed at low conversions.
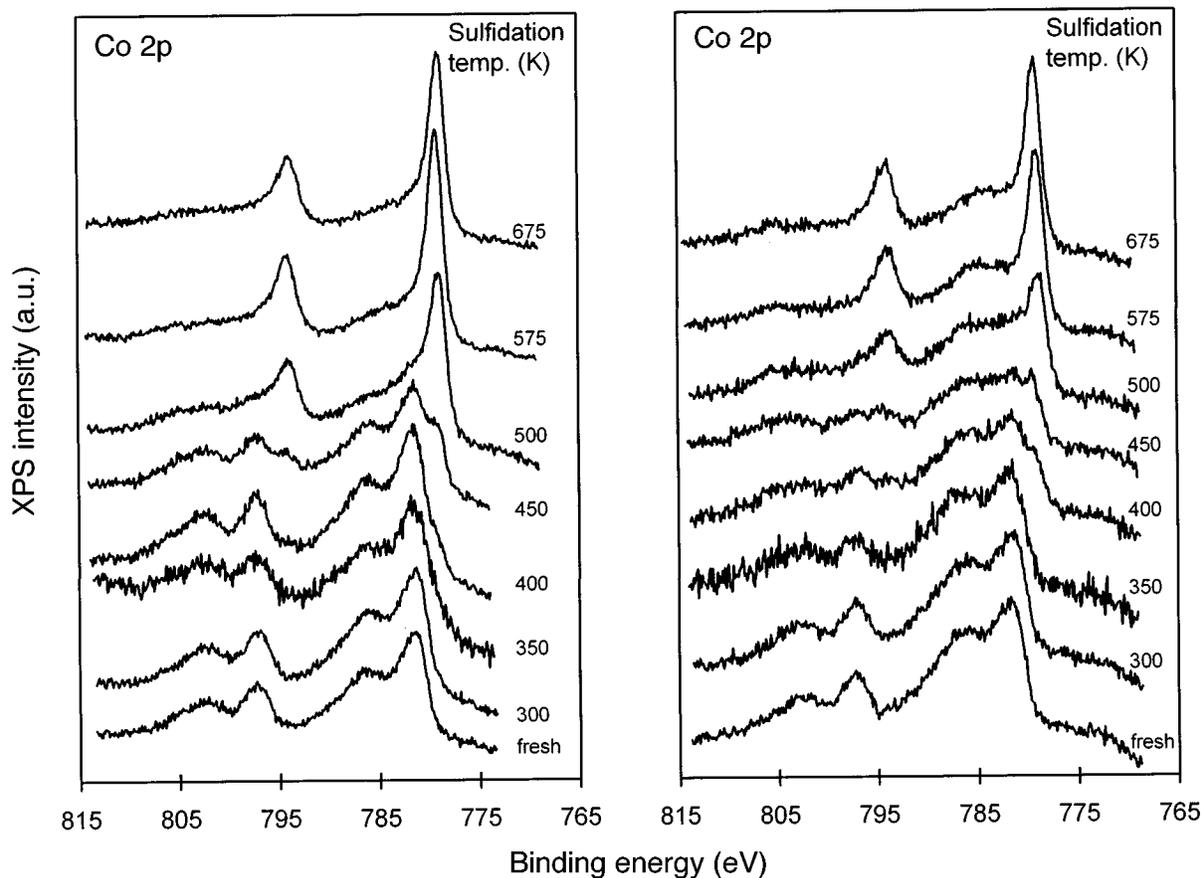
FIG. 3. Co $2p$ XPS spectra of the CoMo/SiO$_2$/Si(100) (left) and CoMo/Al$_2$O$_3$/Si(100) (right) model catalysts as a function of sulfidation temperature.

IV. CONCLUDING REMARKS

The results of this study show that we can prepare flat, conducting model catalysts for hydrodesulfurization reactions showing activities and product distributions that are in good agreement with those of conventional HDS catalysts supported on porous silica and alumina carriers. XPS spectra of CoMoS model catalysts prepared from nitrilotriacetic acid complexes as a precursor reveal that molybdenum is the first to form sulfidic species upon treatment in H$_2$/H$_2$S, whereas the sulfidation of cobalt is selectively retarded. Apparently the role of the NTA complex here is to form an environment for the cobalt that remains stable up to temperatures where MoS$_2$ has already formed so that the cobalt can end up at the
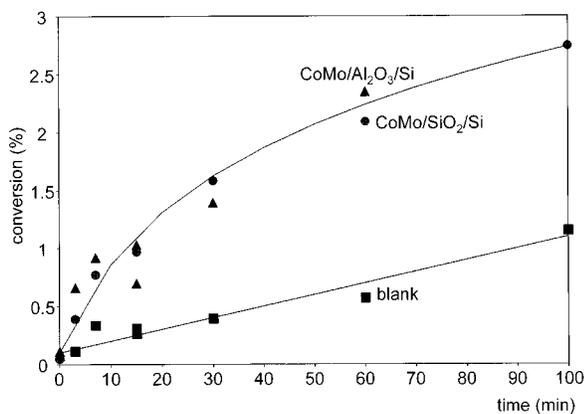

FIG. 4. Conversion of thiophene in HDS batch reactions at 675 K over the silica and alumina supported CoMoS model catalysts as a function of batch reaction time. (■) Conversion rates measured in the blank experiment. The silica (●) and alumina (▲) supported model catalysts exhibit similar conversion rates.
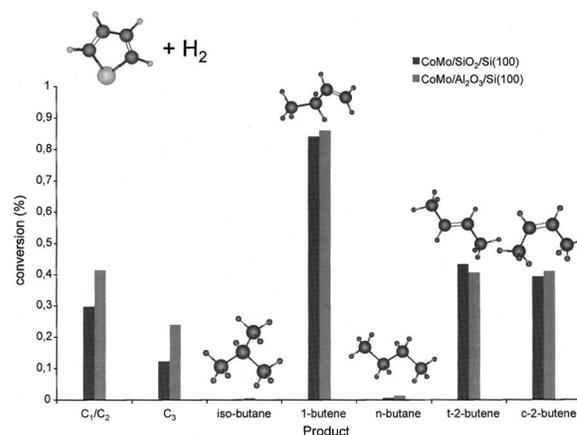

FIG. 5. Product distribution after 1 h of batch reaction for the silica and alumina supported CoMoS model catalysts in the hydrodesulfurization of thiophene.

edges of the preformed MoS$_2$. These model catalysts have the advantage that surface sensitive spectroscopies are applicable to their full potential to study properties of the catalytic surface. We intend to use this approach in the future for the study of adsorption and reaction of gases on sulfides by surface science techniques.

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