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Surface Science Models of a Working Cobalt-Promoted Molybdenum Sulfide Hydrodesulfurization Catalyst: Characterization and Reactivity

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Surface science models of silica- and alumina-supported CoMoS catalysts have been made by impregnating thin SiO$_2$ and Al$_2$O$_3$ films with a solution of nitrilotriacetic acid (NTA) complexes of cobalt and molybdenum. XPS spectra indicate that the order in which cobalt and molybdenum transfer to the sulfided state is reversed with respect to oxidic Co and Mo systems prepared by conventional methods, implying that NTA complexation retards the sulfidation of cobalt to temperatures where MoS$_2$ is already formed. Catalytic tests show that the CoMoS model catalysts exhibit activities for thiophene desulfurization and product distributions similar to those of their high surface area counterparts.

Introduction

Model catalysts, consisting of a conducting substrate with a thin SiO$_2$ or Al$_2$O$_3$ layer on top of which the active catalytic phase is deposited, are advantageous in studies of catalyst preparation and fundamental processes on the catalyst surface.$^1$ In this letter we apply this approach to supported CoMoS hydrodesulfurization (HDS) catalysts. Van Veen et al.$^2$ have demonstrated that CoMoS II (Topsøe’s terminology$^3$), the highly active cobalt-promoted MoS$_2$ in which cobalt is thought to decorate the edges of MoS$_2$ slabs,$^{4-8}$ can be synthesized by sulfiding cobalt and molybdenum complexes of nitrilotriacetic acid (NTA).

In order to check if the preparation of the CoMoS phase on these model catalysts was successful, we performed thiophene HDS experiments to determine the activity of the model catalysts. Spevak$^9$ and McIntyre$^{10}$ already examined the conversion of thiophene on model catalysts prepared by sputter-deposited layers of cobalt and molybdenum on oxidized aluminum substrates. The observed conversion, however, was hardly distinguishable from the conversion measured with an empty reactor. This might be due to the fact that models prepared in this way have very few MoS$_2$ edge sites, which are the seat of the HDS activity. In the following we will show that the model catalysts prepared from cobalt and molybdenum NTA complexes yield significant activities comparable to those of practical high surface area CoMoS catalysts.

Experimental Section

A silica model support is prepared by oxidizing a silicon wafer with (100) surface orientation and a diameter of 75 mm in air at 825 K for 24 h. After oxidation the wafer is cleaned in a solution of ammonia and hydrogen peroxide at 340 K for 10 min. The surface is rehydroxylated by boiling in water. Angle dependent XPS experiments done as explained in refs 11 and 12 indicate that the SiO$_2$ layer is about 5 nm thick after oxidation. During cleaning some SiO$_2$ dissolves, which results in an eventual oxide layer thickness of about 3 nm.

Alumina model supports are prepared by evaporating aluminum oxide on a silicon wafer with a native oxide layer. Prior

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Results and Discussion

Figure 1 shows the Mo 3d XPS spectra of the silica-supported CoMo model catalysts for different sulfidation temperatures. The spectra of the freshly prepared model catalysts reveal only Mo 3d peaks at a binding energy corresponding to a Mo$^{6+}$ species. At 350 K a shoulder develops at a binding energy of 229.5 eV, 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, which indicates that Mo is mostly in an (oxy)sulfidic form. For a detailed description of the changes in Mo XPS spectra during sulfidation we refer to earlier XPS studies of MoO$_x$/SiO$_2$/Si(100) model catalysts$^{15,16}$ and of crystalline MoO$_3$ powders.$^{17}$ The important point to note from Figure 1 is that sulfidation of Mo takes place between 350 and 450 K, while at 400 K the larger part of the Mo has already been converted to the sulfided state.

The XPS spectra of Figure 2 indicate that sulfidation of cobalt proceeds slower than that of molybdenum. The Co 2p spectra of the freshly impregnated catalyst as well as of those after treatment in H$_2$/H$_2$S at 300–400 K show the pattern characteristic of oxidic cobalt, with a main peak at 781.5 eV and a shake up feature at higher binding energies.$^{18}$ The spectra after sulfidation at 500 K and higher have the Co 2p at 779.0 eV and are fully characteristic of sulfided cobalt,$^{19}$ while the catalyst sulfided at 450 K is in the transition between the two states. Thus, complete sulfidation of the cobalt in the NTA complex 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 already at around 400 K.$^{8,20}$ Unfortunately, Co 2p binding energies give little information on the precise state of the Co and do not allow for further distinction between different sulfidic surroundings of the cobalt.$^{19}$

XPS spectra of the Al$_2$O$_3$/Si(100)-supported model catalysts (not shown) gave similar results. Again the sulfidation of molybdenum is completed before that of the cobalt. This is in agreement with the fact that these catalysts are prepared from Co and Mo NTA complexes, which are believed to have negligible interaction with the support.$^2$

Apparently, the sulfidation of Co is 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 Prins and co-workers$^{21,22}$ on NTA-derived NiMoS catalysts and fit well in the picture of CoMoS and NiMoS in which the promoter atoms decorate the edges of MoS$_2$ particles.$^7,23$

The presence of the CoMoS phase cannot be proven definitively by XPS. Therefore, we have done this indirectly by investigating the catalytic activity of the model systems for thiophene desulfurization and comparing it with the catalytic performance of their conventional counterparts. To this end, batch reactions have been performed for different reaction times after which the gas composition has been determined by GC analysis. The only products formed are butenes and C$_2$ and C$_3$ hydrocarbons. The total conversion of thiophene is plotted in Figure 3 for both the model catalysts and for a blank experiment. In the blank experiment, the reactor is loaded with an oxidized catalyst that has been previously treated in H$_2$/H$_2$S and then reoxidized in pure H$_2$. The results show that the CoMoS catalysts exhibit higher conversion rates than the CoMo/SiO$_2$/Si(100) catalysts.
and cleaned silicon wafer; this is a model support that was treated in the same way as the model supports used to prepare the model catalysts. Figure 3 reveals that in the blank experiment also some conversion of thiophene 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, the 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). In the reactor a piece of model catalyst present with a surface area of about 5 cm² and a Mo loading of 3.6 × 10⁻³/cm². This results in a pseudo turnover number per Mo atom of ~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, which fall in the range 1 to 10⁻¹ 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 that for catalysts prepared via the NTA route the influence of the support on the activity should be minimal.

The product distributions for both the silica- and alumina-supported model catalysts after 1 h of batch reaction are displayed in Figure 4. The product distribution is independent of the reaction time. The ratios of the formed 1-butene and trans- and cis-2-butene are far from thermodynamical equilibrium. This C₄ product distribution, however, is in excellent agreement with that measured at low conversions on conventional, high surface area CoMoS catalysts prepared via the NTA route. Since n-butane is formed through hydrogenation of butenes, only a small amount is formed at low conversions.

Summarizing, the results of this study show that we can prepare model catalysts for hydodesulfurization reactions that show activities and yield product distributions that are in good agreement with activities and products yielded by these catalysts supported on porous silica and alumina carriers. These model catalysts have the advantage that surface sensitive spectroscopies are applicable to their full potential to study properties of the catalytic surface. XPS spectra of CoMoS model catalysts prepared from NTA complexes as a precursor reveal that molybdnum is the first to form sulfidic species upon treatment in H₂/H₂S, whereas the sulfidation of cobalt is selectively retarded. Apparently the role of the NTA complex is here to form a relatively stable environment for the cobalt.

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References and Notes