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The Role of Cobalt and Nickel in Hydrodesulfurization: Promoters or Catalysts?

Even though sulfide catalysts have been successfully employed in large-scale hydrodesulfurization for decades, detailed models of catalyst structure and reaction mechanism have begun to emerge only in recent years. Among these are the monolayer models (*1*, *2*). Their starting point is the formation of a Mo- or W-containing monolayer in registry with the oxidic support γ-Al_2O_3. It is assumed that this structure remains preserved after reduction and sulfiding, except for partial replacement of oxygen by sulfur. Other models, like the pseudo-intercalation or decoration model (*3*, *4*), the defect structure model (*5*), and the contact synergism model (*6*) are all based on the assumption of complete conversion of the transition metal oxides into a structure containing Mo (or W) and Co (or Ni) sulfides. The latter is no longer related with the γ-Al_2O_3 carrier structure.

All theories attribute the hydrodesulfurization activity exclusively to Mo and W, whereas Co and Ni are regarded as promoters which enhance or preserve the activity of the Mo and W phase. The activity of sulfided CoO/γ-Al_2O_3 for thiophene hydrodesulfurization is indeed very poor compared to that of sulfided MoO_3/γ-Al_2O_3 (*7*).

Bachelier *et al.* (*8*) observed that both lowering the calcination temperature and raising the sulfiding temperature during preparation of NiO/γ-Al_2O_3 catalysts led to higher thiophene conversions. This indicates that the poor hydrodesulfurization activity of $CoO(NiO)/\gamma$-Al_2O_3 is at least partly due to the strong interaction between Co^{2+} or Ni^{2+} ions and the alumina support, as a result of which a considerable fraction of these cations is not accessible to the reactants. In accordance herewith cobalt was found to be substantially more active when supported on the less reactive SiO_2 carrier (*7*) and highly dispersed nickel in mordenite was reported to demonstrate outstanding performance for thiophene hydrodesulfurization (*9*). All this shows that, on carriers having weaker interaction with transition metal ions than alumina, cobalt and nickel may do more than just promote the activity of MoS_2 and WS_2. That cobalt and nickel have indeed the potential to be catalysts when present in a sulfide form can be inferred, directly or by extrapolation, from the results of thiophene hydrodesulfurization activity measurements reported by Delvaux *et al.* (*10*) and by Furimsky and Amberg (*11*), for unsupported mixed Mo- and Co-sulfides. These data suggest that per unit surface area Co_9S_8 is at least as active as MoS_2. In addition, Pratt *et al.* (*12*) have recently shown that unsupported nickel sulfide is as good a catalyst as molybdenum sulfide, and in fact has a somewhat lower activation energy.

To test the hypothesis that cobalt and nickel sulfide may act as catalysts in hydrodesulfurization we have prepared carbon-supported Co-, Ni-, Mo-, or W-containing samples. The carbon carrier chosen was Mekog carbon (*13*), which was treated in HCl in order to decrease the total metal content to 0.08 wt%. Its surface area and pore volume are 1002 $m^2\ g^{-1}$ and 2.5 ml g^{-1}, respectively.

Catalysts were prepared by pore volume impregnation of the dried (P_2O_5) support with aqueous solutions of ammonium heptamolybdate (Merck, min 99%), ammonium metatungstate (Koch-Light, 99.9%), cobalt nitrate (Merck, "for analysis"), and nickel nitrate (Merck, "for analysis"). The im-

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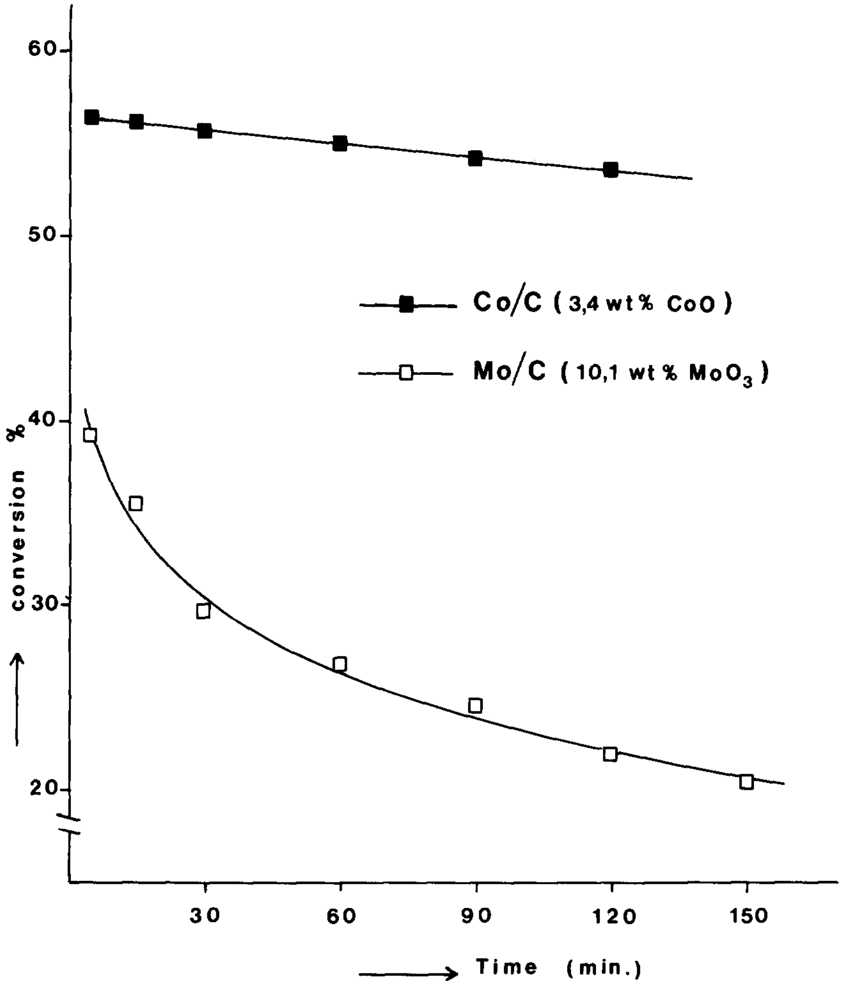

FIG. 1. Thiophene hydrodesulfurization as a function of run time.

pregnated samples were dried overnight in air at 383 K and stored above P_2O_5. Thiophene hydrodesulfurization activity measurements were carried out in a flow microreactor operating at atmospheric pressure (*7, 14*). Prior to the activity test the catalyst sample (0.2 g) was sulfided *in situ* in purified hydrogen containing 10 vol% H_2S (*7*). The flow rate was 60 $cm^3\ min^{-1}$, and the following temperature program was used: 10 min at 295 K, a linear increase from 295 to 673 K in 1 h, and 2 h at 673 K. After this sulfiding procedure the gas mixture was changed to purified hydrogen containing about 6 vol% thiophene (Merck, "for synthesis"). Thiophene conversions were subsequently measured at 673 K and a flow rate of 50 $cm^3\ min^{-1}$. Reaction rates [$r = -(F/W)\ln(1 - x)$] were calculated from conversions measured after the catalysts were allowed to stabilize for 2 h. The conversion (0.2–0.5%) observed for the pure support has always been corrected for.

Some of our experimental results are presented in Figs. 1 and 2. They show that sulfided Co/C and Ni/C are very active catalysts for thiophene hydrodesulfurization, as good (Ni) as or better (Co) than molybdenum and tungsten sulfides supported on carbon and much better than conventional Mo/γ-Al_2O_3 and W/γ-Al_2O_3 catalysts (*15*). These findings indicate that the

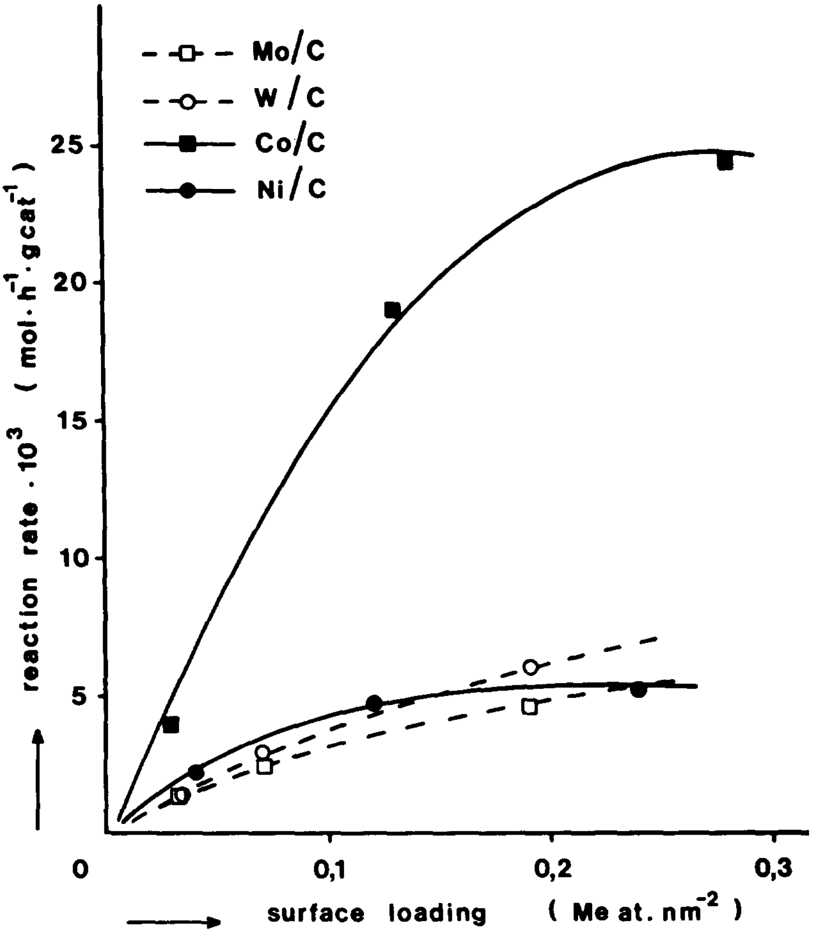

FIG. 2. Thiophene hydrodesulfurization as a function of surface loading.

present catalyst models (*1–6*), which regard Co and Ni only as promoters for the alumina-supported molybdenum and tungsten sulfide phases, may not do full justice to the role that Co and Ni actually play in these catalyst systems. At low concentrations the promoter function will very probably be dominating (*4*, *5*) but the idea that when present at higher concentrations Co and Ni act as catalysts deserves serious attention, even on γ-Al_2O_3. One may prove this idea by means of studies on alumina-supported cobalt and nickel sulfide catalysts prepared by routes which circumvent the calcination step in order to keep the majority of the Co^{2+} and Ni^{2+} ions at the support surface.

Accepting that cobalt and nickel sulfides are active catalysts for the hydrodesulfurization of thiophene, one might ask whether metal sulfides other than MoS_2 and WS_2 will also be active and whether, in addition, they have favorable catalytic properties for the removal of sulfur from other compounds as well as for typical denitrogenation and hydrogenation reactions. We have found rhenium sulfide to be very reactive for thiophene hydrodesulfurization (*16*), while others have recently reported that ruthenium and rhodium sulfides also are superior catalysts (*17*). Work is in progress to study the catalytic properties of various carbon-supported sulfides in a medium-high-pressure reactor using aromatic compounds with and without sulfur or nitrogen as reactants.

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