A Real Support Effect on the Activity of Fully Sulphided CoMoS for the Hydrodesulphurization of Thiophene

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It is shown that on Al_2O_3, SiO_2, and C, a fully sulphided CoMoS phase can be prepared with similar degrees of dispersion, and that the specific activity of this phase for the hydrodesulphurization of thiophene is higher when this phase is supported on carbon than when it is supported on alumina or silica.

The fact that the thiophene hydrodesulphurization (HDS) activity of sulphided CoMo/C catalysts is higher than that of their Al_2O_3-supported counterparts[1—3] is usually explained in terms of an electronic effect.[2—4] The essential difference between the two catalyst systems is, it is argued, that in the case of alumina Mo–O–Al linkages still remain (CoMoS type I in Topsøe's terminology[5]), while in the case of carbon the CoMo component is fully sulphided (CoMoS type II), which means that the interaction between active phase and support is only of the van der Waals type. That is, according to this line of thought, the catalysts have different activities essentially because they contain different active phases. To arrive at a full understanding of the 'support effect,' however, it would seem to be necessary to ascertain whether or not in the systems under discussion there exists a support effect in the strict sense of the expression, *viz.* whether or not for one and the same active phase at constant dispersion, the catalytic activity per site depends on the nature of the support. It is shown now that in fact the specific activity of CoMoS type II for thiophene HDS is significantly higher when the system is supported on carbon than when it is supported on SiO_2 or Al_2O_3.

As supports we employed KC 310 γ-Al_2O_3 (Shell, 250 $m^2 g^{-1}$), Shell SiO_2 spheres (265 $m^2 g^{-1}$), and Norit RX3 extra active carbon (1200 $m^2 g^{-1}$). Catalysts were prepared *via* pore-volume impregnation, using aqueous solutions containing the required amounts of Co and Mo (Co/Mo = 0.33 atom/atom), and an N-containing tetradentate organic ligand L (L/Mo = 1.2 mol/mol; in this paper L = nitrilotriacetic

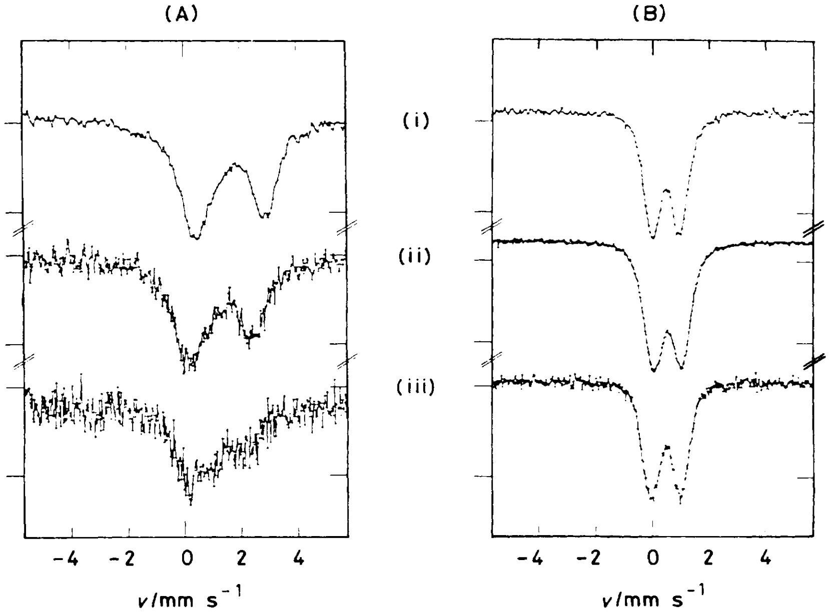

Figure 1. ^{57}Co emission Mössbauer spectra of CoMo supported on (i) Al_2O_3, (ii), SiO_2, and (iii) C. (A): Catalysts dried at 120 °C *in vacuo*; (B): Catalysts sulphided *in situ* at 350 °C in 1/9 v/v H_2S/H_2. Catalyst loadings (in %w): (i), 1.5 Co/7.8 Mo; (ii), 1.4 Co/7.5 Mo; (iii) 1.3 Co/6.7 Mo. Isomer shifts are given with respect to a source of ^{57}Co in metallic Rh; the absorber is $K_4Fe(CN)_6 \cdot 3H_2O$.

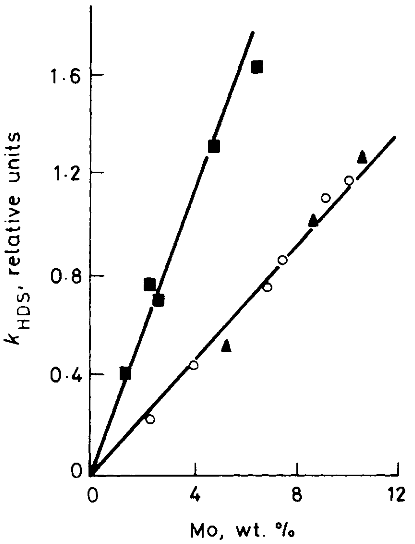

Figure 2. Thiophene HDS activity of CoMoS II *vs.* Mo loading, Co/Mo = 0.33 atom/atom. Supports: ○, γ-Al_2O_3; ▲, SiO_2; ■, C. Catalysts are presulphided at 350 °C in 1/9 v/v H_2S/H_2 for 1 h; test conditions, 0.2—0.3 g catalyst, H_2 flow rate 55 ml min^{-1}, [thiophene] = 6 vol %, T = 350 °C, P = 1 bar.

acid). The role of L is to complex with both Co and Mo, so that the precursor/support interaction is similar for all supports used here. That this is in fact the case is shown by the Mössbauer spectra in Figure 1(A), essentially the same species adsorbs in all three cases, and since the CoMoL/Al_2O_3 spectrum is quite different from that obtained when Al_2O_3 is impregnated with non-complexing solutions,[6,7] it can safely be assumed that the complex is still intact after drying.† Thus we can expect that the sulphiding behaviour of the catalysts is determined by the CoMoL complex, rather than a CoMo–support interactive phase, so that we will end up having the same phase (CoMoS type II) with approximately the same dispersion in all three catalyst systems. This expectation is borne out by the following findings: (i) the Mössbauer spectra depicted in Figure 1(B) clearly show that only CoMoS is present after sulphidation,‡ no Co_9S_8 or the phase present in Co/C preparations being detectable;[3] (ii) electron micrographs show a rather homogeneous dispersion in all cases with particle sizes of the order of 1 nm; *in situ* EDX measurements of the S/Mo ratio gave 2.0 ± 0.2 atom/atom, consistent with the CoMoS phase being fully sulphided, and (iii) the specific thiophene HDS activity§ of CoMoL/Al_2O_3 is about twice that of conventionally prepared CoMo/Al_2O_3 (*i.e.* containing CoMoS type I),[7] which tallies with the relative activities of Al_2O_3-supported CoMoS type I and II reported by Candia *et al.*[5]

Figure 2 shows the thiophene HDS activities, expressed as pseudo-first-order rate constants, of CoMoL supported on Al_2O_3, SiO_2, and C, as a function of Mo loading at fixed Co/Mo ratio. It is seen that, while a switch-over from Al_2O_3 to SiO_2 does not materially change the catalytic activity of CoMoS type II, the carbon support induces an appreciably higher activity. The exact difference between C and Al_2O_3 or SiO_2 depends on the test conditions, since thiophene conversion is influenced by product H_2S to different extents; in terms

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† It is equally evident, however, that the van der Waals interaction decreases in the order $Al_2O_3 > SiO_2 >$ C.

‡ In our experience, the Mössbauer parameters of phases I and II are not sufficiently different to allow an unequivocal phase identification.[7]

§ Specific activity = activity per Co in CoMoS. For a given preparation method, activity is linearly related to Co in CoMoS.[7]

of equation (1),[8] which describes well the results obtained in

$$-\frac{\ln(1-\chi_T)}{\chi_T} = \frac{(K_S - K_T)P^0}{1 + K_S P_T^0} + \frac{K_G P}{1 + K_S P^0} \times \frac{1}{\chi_T S_v} \quad (1)$$

experiments in which space velocity has been varied (χ_T = mole fraction of thiophene converted, P_T^0 = thiophene partial pressure, P = total pressure; K_S,K_T = adsorption equilibrium constants of H_2S and thiophene, respectively, K_G = global rate constant, and S_v = space velocity), the first term on the right-hand side equals about 0.9 for CoMo/C, and about 0.7 for CoMo/SiO_2 or Al_2O_3. The support effect is also apparent in the butane/butene ratio at constant conversion: it increases in the order $SiO_2 \lesssim Al_2O_3 < C$.

Thus, it appears that even when the active phase (CoMoS type II) and its dispersion are invariant, the support influences its specific activity, whether the effect of carbon is to be evaluated as positive, or that of silica and alumina as negative, in reference to the unsupported state, remains a matter for further study.

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