Solid State Synthesis and Activity of a Cu-containing Hydrodesulphurization Catalyst

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Metallic copper, believed to act as an electronic poison for hydrodesulphurization (HDS) catalysis, was combined *via* solid state reactions with elemental sulphur and molybdenum powders to synthesize a model catalyst that displayed high thiophene HDS activity, suggesting a predominantly structural, rather than electronic promoter effect in our solid state model catalyst system.

Transition metal sulphide catalysts based on MoS_2 and group VIII promoters play an important role in the removal of sulphur from petroleum feedstocks, and many theories have emerged over the years to explain the observed catalytic activity,[1—10] with much debate concerning the exact nature of the Group VIII promoter and Group VI metal interaction. Previous theoretical studies[11,12] predicted that Co and Ni should behave as electronic promoters, whereas Cu should act as a poison, effectively oxidizing the Mo. The poisoning effect of Cu was also demonstrated experimentally by studying the desulphurization of dibenzothiophene.[11,12]

Until now the methods used for the synthesis of hydrodesulphurization (HDS) catalysts, *e.g.* the comaceration,[6] homogeneous sulphide precipitation,[13] and coprecipitation methods,[14] and variations on these, gave materials which underwent phase changes during thermal pretreatment and presulphiding before becoming suitable catalysts for HDS. Consequently, the active catalysts are difficult to characterize. Farragher and Cossee[5] used a solid state synthesis procedure to form hydrogenation catalysts; however, their synthesis temperature was 1173 K and they did not investigate the HDS activity of their materials. The use of a solid state synthesis procedure similar to that reported earlier by Farragher and Cossee in their study of the hydrogenation activity of molybdenum and tungsten sulphides, has been used in this work to create model HDS catalysts. This procedure ensures that the resulting catalysts will be thermally stable at the temperatures used.

This paper reports on the relative importance of structural and electronic promoter effects by incorporating Cu, which should act as an electronic poison for HDS while possessing an ionic radius comparable to that of well known promoters. Previous work has shown that Co, Ni, or Fe containing bulk sulphides prepared by solid state synthesis have favourable HDS activities[15] and that the synthesis results in phases which are easier to characterize than catalysts produced by conventional means.[6,13,14]

The solid state catalyst was prepared from elemental copper, molybdenum (99.7%), and sulphur (99.999%) powders, heated under vacuum to 783 K for 12 h and then rapidly

Table 1.[a]

Catalyst		% Selectivity									
Catalyst	Turnover frequency/s^{-1}	C_2	$C_2=$	C_3	$C_3=$	$^iC_4$	$^nC_4$	$1C_4=$	$^iC_4=$ and $1,3C_4$	cC_4	tC_4
MoS_2	3.16×10^{-6}	0.0	12.8	6.7	38.2	0.0	0.0	15.7	8.3	12.6	5.8
$MoS_{1.95}$	2.22×10^{-5}	0.5	0.0	1.9	1.9	0.0	76.8	3.6	0.0	10.0	5.1
$Cu_{0.1}Mo_{0.95}S_2$	3.12×10^{-5}	0.1	0.1	0.7	0.0	0.2	57.3	10.0	0.0	20.5	10.6

[a] All data taken after 2 h on-stream, at atmospheric pressure and 573 K.

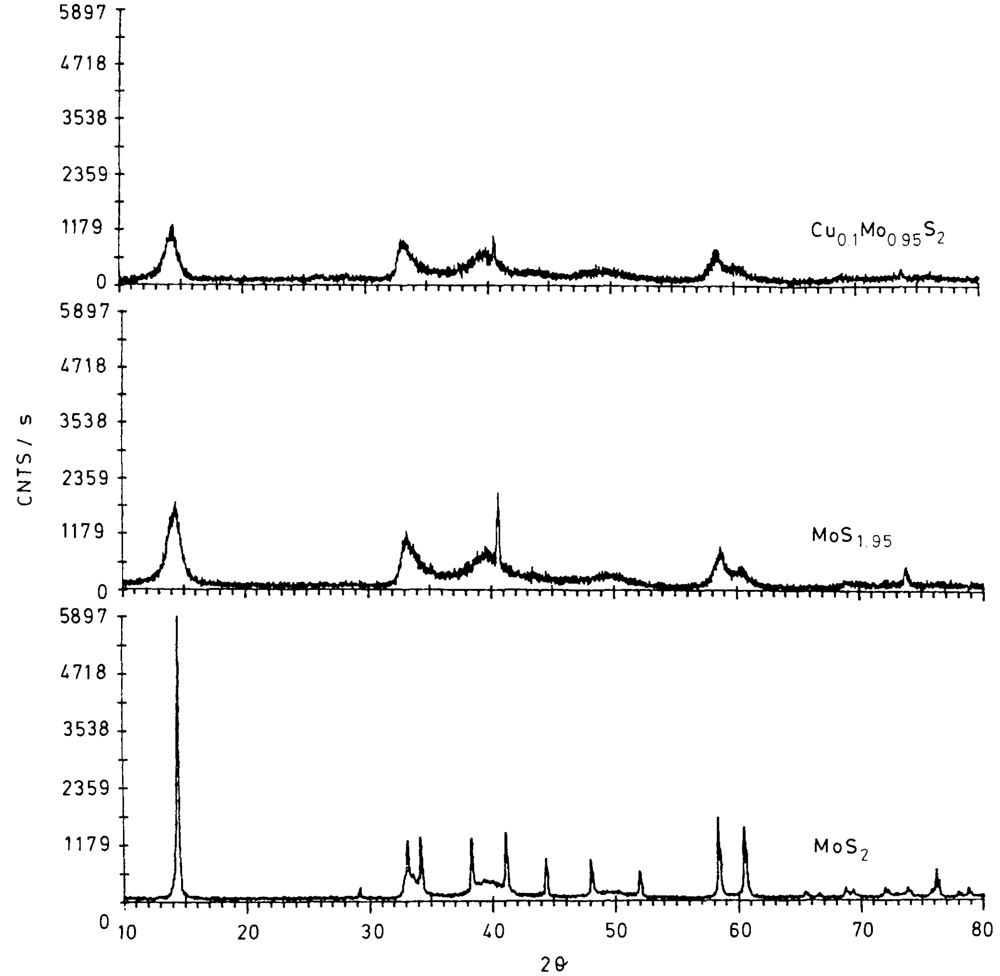

Figure 1. *X*-Ray diffraction patterns of the three catalytic materials.

quenched to give $Cu_{0.1}Mo_{0.95}S_2$ (based on the relative amounts of the powders used). Unpromoted MoS_2 and non-stoicheiometric $MoS_{1.95}$ were also prepared from a mixture of metallic molybdenum and elemental sulphur following the procedure mentioned above. Surface areas were determined using the Brunauer–Emmett–Teller (BET) method.

X-Ray diffraction patterns of the three samples are shown in Figure 1. The catalytic activity for the hydrodesulphurization of thiophene was measured in a continuous flow reactor. Catalyst pretreatment consisted of heating in He at 673 K. The feed stream contained thiophene (2.7 vol%), the balance being hydrogen. A flow rate of 10 ml min^{-1} and a pressure of 98.6 kPa were used in all catalytic runs. Product separation and analysis was done by gas chromatography.

The catalytic activity and selectivity of the samples after 2 h on-stream are displayed in Table 1. The turnover frequencies given are normalized on the basis of thiophene molecules converted per second per Mo atom in the catalyst. It can be seen that the introduction of Cu into the sample does not reduce the HDS activity of $Cu_{0.1}Mo_{0.95}S_2$ as compared to MoS_2. Instead, the activity of the Cu containing catalyst is significantly higher and similar to that of sulphur deficient $MoS_{1.95}$. The two more active catalysts, $MoS_{1.95}$ and $Cu_{0.1}Mo_{0.95}S_2$, not only had comparable activity, but also gave quite similar product distributions in the HDS of thiophene. On both catalysts, predominantly n-butane and H_2S were formed. The Cu sample favoured the production of *trans*-but-2-ene. Stoicheiometric MoS_2 did not produce any n-butane, but favoured the formation of propylene, along with significant amounts of ethylene and propane.

The increased activity cannot simply be attributed to surface area effects. The lack of correlation between HDS activity and surface area reported by other researchers[16,17] is also evident in these samples. Both MoS_2 (1 m^2 g^{-1}) and $Cu_{0.1}Mo_{0.95}S_2$ (3 m^2 g^{-1}) had low surface areas, while the $MoS_{1.95}$ surface area was an order of magnitude greater (20 m^2 g^{-1}). Therefore, the increased activity of $Cu_{0.1}Mo_{0.95}S_2$ has to be attributed to a promoting effect of some sort. Having ruled out on theoretical grounds[11,12] an electronic 'promotion' by Cu (which should lead to decreased HDS activities), we are left with a structural argument.

Comparing the activity of MoS_2 with that of sulphur deficient $MoS_{1.95}$, the presence of sulphur vacancies is beneficial for HDS activity. Evidence for the presence of sulphur vacancies and, consequently, increased structural disorder in $MoS_{1.95}$, comes from high resolution electron microscopy.[18] Stoicheiometric MoS_2 showed a highly crystalline and nearly defect free structure with long range order in the {1010} planes, which represent the crystallographic edges of the MoS_2 particles. In striking contrast, the edge planes of non-stoicheiometric $MoS_{1.95}$, and of the Cu sample, demonstrated a high concentration of defects, polycrystallinity, and roughening of the various layers. This disordered structure is presumably caused by the introduction of sulphur vacancies. From the strong similarity of high resolution electron micrographs and electron diffraction patterns of $MoS_{1.95}$ with those of $Cu_{0.1}Mo_{0.95}S_2$ we infer that one of the key roles of Cu is to facilitate the creation of sulphur vacancies in the molybdenum sulphide lattice. This could be accomplished through the formation of bulk copper sulphides during solid state synthesis, thereby depleting the synthesis mixture of sulphur needed for the formation of stoicheiometric MoS_2. A second possibility is the direct incorporation of Cu ions into the MoS_2 lattice. The latter scenario would require the creation of sulphur anionic vacancies for reasons of charge neutrality.

The sulphur deficient molybdenum disulphide and the Cu containing catalyst exhibited similar activity and selectivity quite different from that of the stoicheiometric MoS_2. These results cast some doubt on the view that in all cases Cu will have a poisoning effect in HDS catalysis.

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