JOURNAL OF CATALYSIS 71, 430–433 (1981)

Characterisation of Sulphided Co–Mo/Graphite Catalysts

The Co–Mo catalyst system has been widely studied in relation to hydrodesulphurisation (HDS) activity (*1*). Despite this attention a convincing relationship between structure and activity has yet to be established. It has become accepted, principally through studies by X-ray photoelectron spectroscopy (XPS, ESCA), that MoS_2 is formed in the sulphide state. In contrast, while the promoting effect of cobalt has been clearly demonstrated (*1, 2*), the exact nature of the cobalt species present in the activated catalyst and the mechanism of promotion are still in doubt, though several models have been proposed (*2, 3*). Recent ESCA studies (*4–8*) have failed to remove this uncertainty, since the presence of a cobalt sulphide (*7*) Co_9S_8 (*6*) and a reduced form of cobalt (*4, 5*) have been suggested.

In a study of a series of alumina- and carbon-supported Co–Mo catalysts, Brinen and Armstrong (*4*) concluded that the cobalt was present in the sulphided catalysts in a reduced form which was probably cobalt metal. This conclusion was based on the following evidence obtained by ESCA. The spin–orbit splitting of the 2*p* level (ΔE) in Co^{2+} is usually about 16 eV, whereas that of Co^0 is 15 eV. The sulphided form of both alumina- and carbon-supported catalysts showed a value for ΔE of 15.1 eV. In addition, the Co 2*p* peaks had no satellite structure and the S 2*p*/Mo 3*d* intensity ratio remained constant, irrespective of cobalt loading. In an earlier study, Okamoto *et al.* (*5*) also concluded that sulphided Co–Mo/Al_2O_3 catalysts contained Co^0 on the basis of the observed value of ΔE. In complete contrast, Declerck-Grimée *et al.* (*6*) concluded that while Co metal was formed during treatment of Co/γ-Al_2O_3 catalysts with H_2 or H_2S/H_2, Co_9S_8 was formed when Co–Mo/γ-Al_2O_3 catalysts were sulphided with H_2S/H_2. Other workers (*7*) have suggested the presence of a cobalt sulphide based on ESCA binding energies (b.e.), evidence rejected as unreliable by Brinen and Armstrong (*4*). They indicate that Co^0 and the sulphided Co–Mo catalysts differ in b.e. by less than 1 eV, while Okamoto *et al.* (*8*) report a 0.4-eV increase in b.e. when Co^0 is sulphided. Difficulties in achieving satisfactory reference levels and comparing b.e. of supported and unsupported species have been discussed by Dufresne *et al.* (*9*). It is clear from the above that the state of cobalt in sulphided catalysts cannot be identified uniquely by ESCA b.e. measurements. In an effort to overcome this difficulty, Okamoto *et al.* (*10*) examined the variation in S 2*p*, Mo 3*d*, and Co $2p_{3/2}$ intensity ratios as a function of cobalt loading in Co–Mo/γ-Al_2O_3 and concluded that the stoichiometry of the reduced form of cobalt was Co_9S_8. However, the use of another technique in conjunction with ESCA to characterise the nature of the cobalt species in sulphided catalysts would clearly be advantageous. Emission Mössbauer spectroscopy has been shown to be an important technique in this context (*11–13*).

The majority of previous studies have concentrated on unsupported or alumina-supported catalysts. However, carbon-supported catalysts, in particular graphitised-carbon supports, are reported to have high HDS and hydrogenation activity (*7*). Even though characterisation is not complicated by interaction of Co and Mo with the support in this case, the presence of Co^0 (*4*) and sulphided cobalt (*7*) has been claimed. In this note we report the results of a study of sulphided Co/graphite, Mo/graphite,

0021-9517/81/100430-04$02.00/0

and Co–Mo/graphite catalysts by ESCA and Mössbauer spectroscopy which yield a unique characterisation of the sulphided species.

Catalysts were prepared by stepwise impregnation to dryness using a high-purity, low-surface-area (0.3 m^2/g) graphite support. The graphite was first impregnated with cobalt nitrate, dried at 130°C in dry air for 16 hr and then calcined in a flow of dry air at 230°C for 16 hr. These samples were subsequently impregnated with ammonium paramolybdate, then dried and calcined under the same conditions. For comparison, catalysts containing Co or Mo only were made. Catalyst compositions were 1% Co, 6% Mo, and 1% Co–6% Mo by weight. Catalysts were sulphided in a flow of 10% H_2S/H_2 mixture at 400°C for 4 hr. For Mössbauer spectroscopy it was necessary to prepare the catalysts using cobalt nitrate labelled with ^{57}Co. The samples were sulphided under the above conditions in a special cell which allowed Mössbauer measurements to be performed on the catalysts in the sulphiding atmosphere. Mössbauer spectra were obtained at room temperature using the catalysts as a stationary source and $K_4Fe(CN)_6 \cdot 3H_2O$ as the moving absorber. Positive values of relative velocity refer to the source moving away from the absorber and are quoted relative to the centroid of the iron spectrum. ESCA measurements were made with a V.G. ESCA-3 spectrometer using Al$K\alpha$ radiation. All b.e. are referenced to C1*s* (graphite) = 284.3 eV (*14*) (equivalent to Al 2*p* = 74.5 eV, and Au $4f_{7/2}$ = 83.8 eV). Samples were cooled to room temperature under the sulphiding mixture, purged with nitrogen, and transferred rapidly to the spectrometer to minimise exposure to air. Sensitivity factors were determined to be S 2*p* : Mo 3*d* : Co $2p_{3/2}$ = 1 : 0.175 : 0.26 from $CoSO_4$, and ground mixtures of $Na_2MoO_4 \cdot 2H_2O$ and Na_2SO_4.

X-Ray photoelectron spectra showing S 2*p*, Mo 3*d*, and Co 2*p* levels for the sulphided catalysts are presented in Fig. 1. Measured b.e. and peak area ratios are given in Table 1 for MoS_2-cleaved crystal and the sulphided catalysts. The S 2*p* spectra from the catalysts show no evidence of sulphate formation, indicating minimal reoxidation on transfer from the reactor to the spectrometer. The Mo 3*d* spectra from Mo/graphite and Co–Mo/graphite catalysts are readily identified as MoS_2 (see

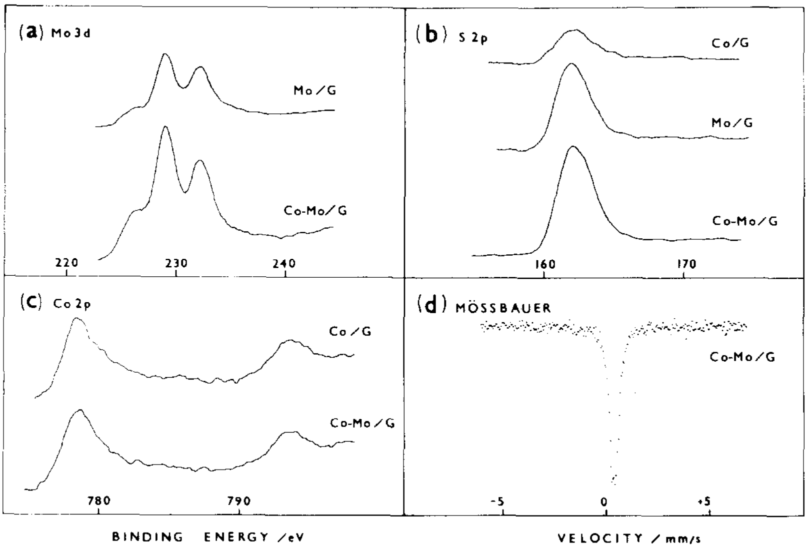

FIG. 1. ESCA and Mössbauer spectra of sulphided Co/graphite, Mo/graphite, and Co–Mo/graphite catalysts.

TABLE 1

ESCA Data for Sulphided Mo, Co, and Co–Mo/Graphite Catalysts

Compound or catalyst	Binding energies[a](eV)			Peak area ratio	
	Co $2p_{3/2}$	Mo $3d_{5/2}$	S $2p$	(S $2p$)/Mo $3d$)	(S $2p$)/(Co $2p_{3/2}$)
MoS_2 (crystal)	—	229.2	162.1[b]	0.37	—
Co/graphite	778.5	—	161.9	—	0.30
Mo/graphite	—	229.0	162.1	0.32	—
Co–Mo/graphite	778.7	229.0	162.1	0.44	1.05

[a] Reference level C 1*s* (graphite) = 284.3 eV.

[b] S $2p$ set at 162.1 eV.

Table 1) and indicate complete conversion to MoS_2 during sulphiding (a slight tailing of the Mo $3d_{3/2}$ peak from Mo/graphite may indicate fractionally less than complete conversion in this case). The Co $2p$ spectra from Co/graphite and Co–Mo/graphite are virtually identical and yield a Co $2p_{3/2}$ b.e. of 778.7 eV. This value is similar to that reported by other workers for sulphided Co–Mo catalysts on both Al_2O_3 and carbon when allowance has been made for the different reference levels (*4–7*). No strong satellites are associated with the Co $2p$ peaks (the slight tailing at higher b.e. may arise from slight reoxidation) and the value of ΔE is 15.1 eV for both catalysts. The Co/graphite catalyst yields a (S $2p$)/(Co $2p_{3/2}$) peak area ratio = 0.3, which may be compared to an estimated ratio of 0.23 for Co_9S_8 using a sensitivity factor determined from $CoSO_4$. Since the Co–Mo/graphite catalyst has a virtually identical Co $2p$ spectrum, we conclude that the same Co species is present in both cases. The Mössbauer spectrum of the sulphided Co–Mo/graphite catalyst is shown in Fig. 1d. It consists of a broad unresolved line with an isomer shift of 0.35 ± 0.01 mm/s, which may be identified as Co_9S_8 by comparison with published spectra (*15*). (Computer fitting shows the present spectrum to be consistent with the detailed Mössbauer parameters given in Ref. (*15*).) Thus, the sulphide state of the Co–Mo/graphite catalyst consists of a mixture of Co_9S_8 and MoS_2 with no evidence for any other species.

The peak area ratios obtained from the catalysts (Table 1) are consistent with the above conclusion. The (S $2p$)/(Mo $3d$) ratio should be independent of changes in dispersion of the Mo phase and give a reliable estimate of the stoichiometry of the surface, since the S $2p$ and Mo $3d$ photoelectrons have similar kinetic energies. The (S $2p$)/(Mo $3d$) ratio for a cleaved crystal of MoS_2 was 0.37 compared with 0.35 estimated from the sensitivity factors derived from mixtures of bulk compounds. A (S $2p$)/(Mo $3d$) ratio of 0.32 was obtained for the Mo/graphite catalyst, indicating complete sulphidation in agreement with the Mo $3d$ spectrum, Fig. 1. For the Co–Mo/graphite catalyst a (S $2p$)/(Mo $3d$) ratio of 0.44 was obtained. This value cannot give an accurate stoichiometry since it is influenced by the relative dispersion of the Co and Mo phases. Nevertheless, it is similar to the values of 0.39 calculated for Co_9S_8 and MoS_2 from the sensitivity factors and 0.45 using the data for MoS_2 and Co/graphite in Table 1.

In comparing the present ESCA results with those obtained previously from carbon-supported catalysts (*4*), we note that the Co $2p_{3/2}$ b.e., the value of ΔE, and the absence of Co $2p$ satellites are the same in both cases. However, this spectrum was interpreted previously as Co^0 (*4*), whereas the present Mössbauer results show conclusively that the ESCA spectrum from the Co–Mo/graphite catalyst arises from Co_9S_8. This suggests that the Co species present on the carbon-supported catalysts, and by implication the alumina-supported catalysts, in the previous work (*4*) could have been Co_9S_8. Brinen and Armstrong observed (S 2*p*)/(Mo 3*d*) ratios which were independent of Co loading (*4*). In contrast, the (S 2*p*)/(Mo 3*d*) ratio for the graphite-supported catalysts is increased when Co is present. However, for Co/Mo weight ratios of about 1 : 5 and less the expected changes in (S 2*p*)/(Mo 3*d*) caused by the presence of Co are quite small, and small changes in the degree of sulphiding of Mo are difficult to detect from the Mo 3*d* spectra. In addition, while the (S 2*p*)/(Mo 3*d*) ratio does not depend on the dispersion of the Mo phase, the contribution of the sulphur in the Co phase to this ratio would be affected by the relative dispersion of the two phases. Thus, the apparent lack of sensible variation in the (S 2*p*)/(Mo 3*d*) ratio with Co loading is not necessarily inconsistent with the presence of sulphided Co.

The present Mo/graphite and Co–Mo/graphite catalysts showed a significant activity for thiophene HDS measured under conditions previously described (*16*). A promoting effect of cobalt was indicated by the increase in thiophene conversion from 1.3% g^{-1} for Mo/graphite to 3.5% g^{-1} for Co–Mo/graphite. The present finding that the sulphided Co–Mo/graphite catalyst contains only Co_9S_8 and MoS_2 is consistent with the mechanism of promotion in these catalysts being similar to that proposed in the contact-synergy (*2*), remote-control or hydrogen spillover models (*17*).

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Received November 7, 1980; revised April 22, 1981

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