JOURNAL OF CATALYSIS **44**, 488–491 (1976)

NOTES

Surface Composition and Chemical Activity of a Sulfided CoMo Catalyst

We have studied the effect of various sulfiding conditions on the chemical state of molybdenum in a CoMo catalyst (3.6% wt CoO, 12.5% wt MoO_3 supported on $\frac{1}{16}$ in. γ-alumina extrudates) using ESCA (electron spectroscopy for chemical analysis). The same samples were also examined using a pulse microreactor so as to relate the catalytic activity of the catalyst to the molybdenum composition.

Samples from the same batch of catalyst were reacted in a small pilot plant under the conditions listed in Table 1. After sulfiding, the samples were withdrawn under nitrogen, crushed and ESCA spectra were measured as soon as possible to limit reoxidation and loss of sulfur from the surface which can occur if these precautions are not taken. Figure 1 shows the changes in the Mo(3*d*) spectra which took place on the fresh catalyst as the severity of the sulfiding increased. The spectra show the same changes found by other workers (*1*, *2*) and suggest the conversion of a state resembling that in supported MoO_3 (Mo^{6+} oxide) to a sulfide state similar to that in MoS_2 (Mo^{4+} sulfide). The binding energies of the Mo($3d_{3/2}$) peaks assuming C(1*s*) to be 284.5 eV were 235.9 eV (Mo^{6+} oxide) and 232.3 eV (Mo^{4+} sulfide) which are in satisfactory agreement with most values in the literature allowing for differences in binding energy standardization (*1–9*).

We attempted to extract further information from the spectra by computer deconvolution to gain an estimate of the

TABLE 1

Reaction of CoMo Catalysts and Interpretation of ESCA Spectra

Run no.	Conditions			Relative proportion of ESCA peak			
	Reactants	Temp (°C)	Pressure (bar)	Mo^{6+}–O	Mo^{4+}–O	Mo^{4+}–S	MoS_3
1	3% CS_2 in nC_7 under hydrogen	210	34.5	58	14	20	8
2	3% CS_2 in nC_7 under hydrogen	350	34.5	40	16	36	8
3	3% CS_2 in nC_7 under nitrogen, then H_2	350	34.5	25	10	47	18
4	H_2 alone then 3% CS_2 in nC_7 under H_2	350	34.5	40	24	22	14
5	ample from 1 in air,	350	1.0				
	then 3% CS_2 in nC_7 under H_2	180	34.5	54	11	20	15
Mo($3d_{3/2}$) mean binding energies (eV)[a]				235.9	233.8	232.3	231.1

[a] Calculated from peak kinetic energy assuming C(1*s*) = 284.5 eV on these samples.

relative proportions of states present. The computer optimization was based on the use of sulfur (2*s*) peaks due to sulfide and sulfate and peaks from MoS_2, MoS_3 (*10*) and MoO_3. The parameters used for these three sets of Mo(3*d*) spectra were derived by deconvolution of the signals from the model compounds themselves and were specified within ±0.5 eV relative binding energy. A fourth set of variable Mo(3*d*) peaks were then introduced which could be manipulated by the computer so as to get the best fit to the experimental data. The same set of Mo(3*d*) signals were used in the deconvolution of spectra from all 5 sulfided catalyst samples. S(2*s*) signals were calculated in each case from the S(2*p*) peaks measured separately.

We judged the reliability of the analysis by the degree of variation between the relative binding energies of the components used to achieve the best fit in each case. In particular, we wanted to see if the fourth set of peaks would be used consistently in each analysis and if the relative binding energy derived corresponded to the Mo(3*d*) signal from any known compound. We found that the average separation between MoO_3 and MoS_2 peaks in the calculations was 3.6 ± 0.05 eV (permitted a variation of 1 eV) and the average separation of MoO_3 and the fourth set of Mo (3*d*) peaks was 2.1 ± 0.5 eV (permitted a variation of 4 eV). Clearly the best solutions were obtained using a small variation of peak adjustment within the experimental errors for binding energy measurement (±0.5 eV).

Table 1 lists the peaks used in the analysis, their average binding energies and the proportion each contributes to the total Mo(3*d*) signal. It should be emphasized that these results do not provide evidence for the presence of the model compounds as such on the catalyst surface. The results are interpreted as showing that the catalyst contains molybdenum in combinations of oxidation state and ligand coordination similar to those found in the model compounds. The fourth set of variable peaks computed at 2.1 eV below MoO_3 is very similar to signals observed by Cimino and De Angelis (*7*) on reduced MoO_3/Al_2O_3 and $CoMo/Al_2O_3$ samples and attributed by them to a Mo^{4+} state. We follow these authors and attribute our fourth peak to Mo^{4+} oxide though we note that the Mo(3*d*) signals from MoO_2 itself have been confirmed at a binding energy more than 3.0 eV below MoO_3 (*6–8*) despite an early assignment only 2.1 eV below MoO_3 (*3*).

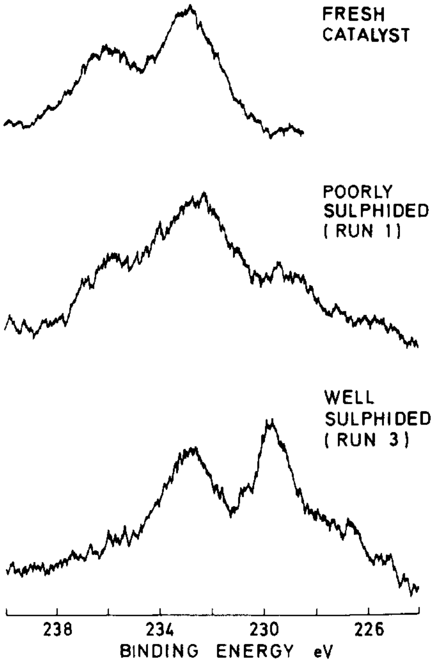

FIG. 1. Molybdenum (3*d*) ESCA signals from CoMo catalysts.

The results from the ESCA deconvolution show differences quite consistent with the sulfiding conditions used. The proportion of Mo^{4+} sulfide increased both with temperature of reaction and with the use of nitrogen instead of hydrogen during the initial sulfiding. Prereduction of the catalyst increased the level of the fourth peak, Mo^{4+} oxide, and apparently limited the extent of sulfiding. We therefore conclude that the activation procedure with a CoMo catalyst is important in determining the composition of the active surface.

We compared the activities of the five crushed samples examined by ESCA using a conventional atmospheric pressure pulse microreactor. Small volumes of CS_2 were injected into a hydrogen stream passing through a bed of crushed CoMo catalyst under conditions where there was complete conversion of CS_2 to methane. Methane was eluted gradually from the catalyst bed and the rate of elution could be measured by repetitive sampling and analysis with a flame ionization detector. The chromatograms obtained are illustrated in Fig. 2 and show that the rate of release of methane differed between samples sulfided in the different plant runs. The total amount of methane released in each case is the same.

It is important to note that when a methane pulse was injected over a catalyst sample, it was rapidly eluted. Further the release of methane could be suppressed by injection of a catalyst poison such as H_2S after the injection of CS_2. We therefore conclude that the rate of methane release was governed by the slow rate of methane formation under the experimental conditions.

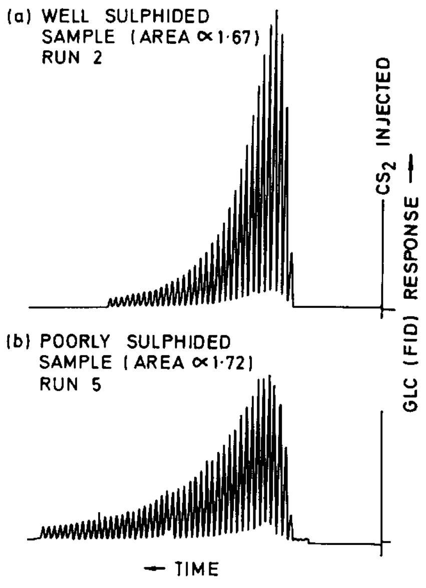

Fig. 2. Gas–liquid chromatography analysis of products released following pulse injection of CS_2 over samples of CoMo catalyst sulfided to different extents.

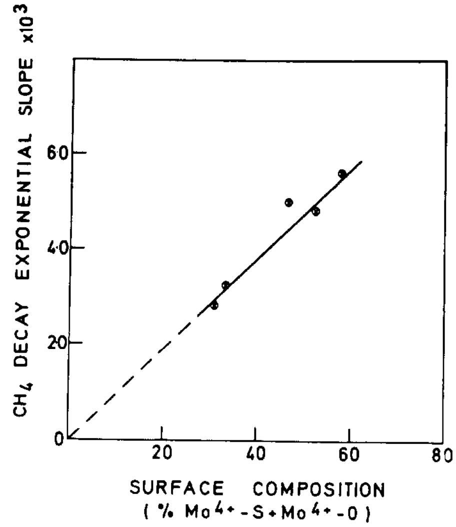

Fig. 3. Surface composition and rate of methane release.

The release of methane from the pulse experiments was exponential so that a first order rate constant could be calculated for each sample. This rate constant was compared with the proportions of the three molybdenum states formed on sulfiding in order to isolate the molybdenum states where reaction was occurring. Figure 3 shows the relation between the first order decay constant for methane release and the proportions of Mo^{4+} oxide and sulfide formed on the surface. There appears to be a direct relation over the range studied and the line can be extrapolated through the origin suggesting that the fresh catalyst is unable to hydrogenate CS_2 to methane. Experiments with fresh catalyst confirmed that this was the case although methane was detected at low levels after a brief sulfiding or reduction.

These results demonstrate a clear relation between the conditions used to sulfide a CoMo catalyst, the activity for hydrogenation of CS_2 and the proportion of Mo^{4+} oxide and sulfide states on the catalyst surface.

REFERENCES

1. Friedman, R. M., Declerck-Grimée, R. I., and Fripiat, J. J., *J. Electron Spectrosc. Related. Phenom.* **5**, 437 (1974).
2. Brinen, J. S., *J. Electron Spectrosc. Relat. Phenom.* **5**, 377 (1974).
3. Swartz, W. E., and Hercules, D. M., *Anal. Chem.* **43**, 1774 (1971).
4. Miller, A. W., Atkinson, W., Barber, M., and Swift, P., *J. Catal.* 22, 140 (1971).
5. Armour, A. W., Mitchell, P. C. H., Folkesson, B., and Larsson, R., *Proc. Int. Molybdenum Congr.*, Reading, September, *1973*.
6. Kim, K. S., Baitinger, W. E., Amy, J. W., and Winograd, N., *J. Electron Spectrosc. Relat. Phenom.* **5**, 351 (1974).
7. Cimino, A., and De Angelis, B. A., *J. Catal.* **36**, 11 (1975).
8. Lepage, F., Bailleif, P., and Bardolle, J., *C. R. Acad. Sci., Ser. C* 280, 1989 (1975).
9. Ratnasamy, P., *J. Catal.* **40**, 137 (1975).
10. Stevens, G. C., and Edmonds, T., *J. Catal.* **37**, 544 (1975).

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Received March 11, 1975; revised May 18, 1976