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**Citation for published version (APA):**

Craijé, M. W. J., Gerkema, E., Beer, de, V. H. J., & Kraan, van der, A. M. (1990). Stability of the so-called "Co-Mo-S" phase in a carbon-supported Co-Mo sulfide catalyst at very low Co/Mo ratio. *Hyperfine Interactions*, 57(1-4), 1795-1799. <https://doi.org/10.1007/BF02405724>

**DOI:**

[10.1007/BF02405724](https://doi.org/10.1007/BF02405724)

**Document status and date:**

Published: 01/01/1990

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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## STABILITY OF THE SO-CALLED “Co-Mo-S” PHASE IN A CARBON-SUPPORTED Co-Mo SULFIDE CATALYST AT VERY LOW Co/Mo RATIO

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Several aspects of the stability of the so-called “Co-Mo-S” phase in a fully sulfided Co(0.04)Mo(6.84)/C (wt%) catalyst have been examined by Mössbauer emission spectroscopy. The “Co-Mo-S” parameters turned out to be unchanged when the catalyst is exposed for 23 days to ambient air at room temperature. However, if this exposure to air is extended for over 100 days, the so-called “Co-Mo-S” phase was found to be oxidized to a high-spin  $\text{Fe}^{2+}$  phase which has no strong interaction with the “MoS<sub>2</sub>” particles. After resulfidation of the catalyst the so-called “Co-Mo-S” phase is formed again.

### 1. Introduction

Most commonly applied hydrotreating catalysts for removal of heteroatoms from crude oil consist of molybdenum disulfide or tungsten disulfide promoted by cobalt or nickel, deposited on a high area  $\gamma\text{-Al}_2\text{O}_3$  carrier. Using Mössbauer emission spectroscopy (MES) Topsøe and Clausen [1] and Clausen et al. [2] have demonstrated that the activity of sulfidic Co-Mo catalysts correlates with the presence of a so-called “Co-Mo-S” doublet in the MES spectrum of the active catalyst. However, Van der Kraan et al. [3,4] recently showed that the so-called “Co-Mo-S” doublet can also be observed in the MES spectra of carbon-supported Co-sulfide catalysts, that is in the absence of Mo-sulfide. Hence, the so-called “Co-Mo-S” spectrum is not unique for sulfided Co-Mo catalysts.

Candia et al. [5] proposed the existence of a so-called “Co-Mo-S” II phase with a similar Mössbauer spectrum as the “Co-Mo-S” I phase, but a much higher thiophene hydro-desulfurisation (HDS) activity. They reported a high thermal stability of the so-called “Co-Mo-S” II phase and predicted that this type of “Co-Mo-S” will be formed in carbon supported Co-Mo sulfide catalysts.

This paper describes the results of a MES study on the stability of the so-called “Co-Mo-S” II phase present in a Co-Mo/C catalyst.

## 2. Experimental

The catalyst was prepared by the incipient wetness method. The carrier used was an activated carbon (Norit RX3-Extra) with a surface area of  $1190 \text{ m}^2/\text{g}$  and a pore volume of  $1.0 \text{ cm}^3/\text{g}$ . The carrier was first impregnated with an aqueous solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (Merck, min 99.9%) after which the water was removed by drying in static air for 16 h at 383 K. Hereafter, the carrier was impregnated with an aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck p.a.) and subsequently dried in static air for 16 h at room temperature. The nitrate groups were removed by applying an additional treatment in a hydrogen flow. During this treatment the temperature of the catalyst was kept at 313, 353 and 393 K for 24 h at each temperature.

Sulfidation of the Co(0.04)Mo(6.84)/C catalyst (metal loadings in wt%) was carried out in a 10%  $\text{H}_2\text{S}/\text{H}_2$  gas mixture. Mössbauer spectra were recorded in-situ.

## 3. Results

Spectrum *a* in fig. 1 is recorded after the final sulfidation treatment at 673 K. The parameters of the observed doublet (table 1) are in good agreement with those of the so-called "Co-Mo-S" phase, [1].

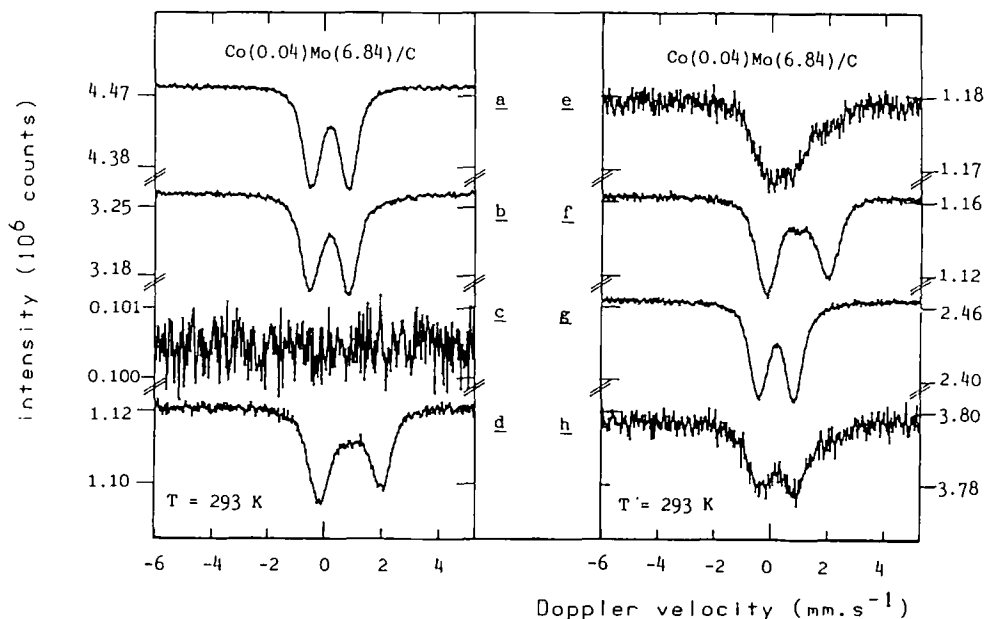


Fig. 1. Mössbauer emission spectra of Co(0.04)Mo(6.84)/C after various successive treatments. The explanation of the letters is given in table 1.

Spectra *b* and *c* are obtained after exposure of the sulfided catalyst to ambient air at room temperature for 23 days and 260 days, respectively. From the Mössbauer parameters it can be concluded that the catalyst is not affected by exposure to air for 23 days. Furthermore, it turns out that the resonant-absorption area of the spectrum is not significantly changed during these 23 days. However, after 260 days the resonant-absorption area has become zero.

The resonant-absorption area can be restored by linear heating of the catalyst in a (dry) argon flow upto 673 K in 1 h and keeping it at that temperature for 1 h, as is shown by spectrum *d*. However, from the strong decrease of resonant-absorption area shown in spectrum *e*, it follows that the resonant-absorption area is sensible towards exposure to ambient (wet) air at room temperature. Furthermore, the Mössbauer parameters indicate the presence of a high spin  $\text{Fe}^{2+}$  phase instead of the so-called “Co-Mo-S” phase after the argon treatment. The spectrum shows that the so-called “Co-Mo-S” phase is for over 80% converted into a high-spin  $\text{Fe}^{2+}$  phase.

The Mössbauer parameters of spectrum *f* show that after a second temperature treatment in argon (gradual heating upto 673 K in 1 h and holding at 673 K for 1 h), the resonant-absorption area has become much larger than after the first argon treatment. Furthermore, the resonant-absorption area is now found to decrease only slightly on exposure to air at room temperature.

Resulfidation of this sample via the same stepwise procedure as applied before, showed that the sulfidation takes place in the same way as found for the fresh catalyst (see spectrum *g*, recorded after the resulfidation upto 673 K). Exposing the resulfided catalyst to air at 293 K for one day does not result in a different spectrum. Even after exposing the resulfided catalyst to air for 90 days the spectrum is dominated by a “Co-Mo-S”-like doublet. However, in this case the resonant absorption area has decreased markedly and apparently it is not possible to see all the Co in the Mössbauer spectrum (see fig. *h*).

#### 4. Discussion

From the “Co-Mo-S”-like spectrum *b* it is clear that exposure of the fully sulfided catalyst to air at 293 K for 23 days has not influenced the Mössbauer parameters. This means that the “Co-Mo-S” phase is surprisingly stable in ambient air and that the chemical state of the Co present in this phase is not easily affected by oxygen or water at room temperature. However, the total resonant absorption area of the spectrum is found to decrease with time. This finally results in a complete disappearance of the Mössbauer spectrum as observed after 260 days exposure to ambient air. According to Viegers and Trooster [6] for ultra small particles the effective recoilfree fraction can be regarded as a product of two factors. The first one is the recoilfree fraction related to lattice vibrations within the particles in which the cobalt atoms are incorporated. The

Table 1

Mössbauer parameters belonging to the spectra presented in fig. 1. The isomer shift ( $IS$ ) is given relative to SNP. The resonant absorption areas ( $RA$ ) are not corrected for changes in the configuration.

| Fig.     | Treatment                    | $RA$<br>(a.u.) | "Co-Mo-S"      |                |          | high-spin $Fe^{2+}$ |                |            |
|----------|------------------------------|----------------|----------------|----------------|----------|---------------------|----------------|------------|
|          |                              |                | $IS$<br>(mm/s) | $QS$<br>(mm/s) | $A$<br>% | $IS$<br>(mm/s)      | $QS$<br>(mm/s) | $A$<br>(%) |
| <i>a</i> | H <sub>2</sub> S, 673 K, 1 h | 2.1            | 0.21           | 1.33           | 100      |                     |                |            |
| <i>b</i> | Air, 293 K, 23 d             | 2.4            | 0.20           | 1.39           | 100      |                     |                |            |
| <i>c</i> | Air, 293 K, 260 d            | 0.0            |                |                |          |                     |                |            |
| <i>d</i> | Ar, 673 K, 1 h               | 2.6            | 0.26           | 1.30           | 19 *     | 0.93                | 2.19           | 81         |
| <i>e</i> | Air, 293 K, 1 d              | 0.8            |                |                |          |                     |                |            |
| <i>f</i> | Ar, 673 K, 1 h               | 3.8            | 0.31           | 1.35           | 16 *     | 0.94                | 2.14           | 84         |
|          | Air, 293 K, 1 d              | 3.2            |                |                |          |                     |                |            |
| <i>g</i> | H <sub>2</sub> S, 673 K, 1 h | 2.7            | 0.21           | 1.25           | 100      |                     |                |            |
| <i>h</i> | Air, 293 K, 90 d             | 0.5            | 0.27           | 1.29           | 84       | 1.26                | 1.86           | 16         |

(Experimental uncertainties:  $IS = 0.05$  mm/s;  $QS = 0.05$  mm/s;  $A = 5\%$ .)

\* The attribution of this doublet to "Co-Mo-S" might be wrong, possibly the corresponding Co species is an oxidic 3+ phase. From the Mössbauer parameters it is not possible to decide on this.

second factor is related to vibrations of the catalyst particles as a whole. So, there are two possible explanations for the observed decrease in the resonant-absorption area. Either the chemical state of the catalyst has changed upon air exposure and a phase with a very low Debye temperature is formed, or the chemical state is not affected and the loss of recoil-free fraction is due to vibrations of the catalyst particles as a whole. The second explanation implies that the Co-containing catalyst particles have lost their contact with the support material. From the measurements presented in fig. 1 it cannot be decided which of these explanations is correct.

Direct evidence is found for the influence of water on the resonant-absorption area. The resonant-absorption area can be restored via a temperature treatment in dry argon resulting in the removal of adsorbed water from the catalyst (compare spectra *c* and *d*). Readsorption of water from ambient-air causes a significant decrease of the resonant-absorption area (compare spectra *d* and *e*).

Comparison of the resonant-absorption areas of spectra *d* and *f* (table 1) shows that the resonant-absorption area has increased markedly due to the second argon treatment. Furthermore, after this treatment the resonant-absorption area decreases only very slightly and probably slowly on exposure to air at room temperature, as is shown in table 1. At present, we have no clear explanation for these phenomena, which might be connected with the presence of the Co-containing catalyst particles in both the meso- and micro-pores of the carbon carrier.

After the argon treatments not only the resonant-absorption area turned out to be restored, but also the state of the Co appeared to be changed. From a measurement at 77 K on a similar catalyst sample, which had also lost its resonant-absorption area due to an ambient air exposure for a long time, it could be concluded that the chemical state of the Co was already changed as a result of this air exposure [7]. Although, it still has to be proven by means of measurements on one and the same catalyst sample, it is most likely that the high-spin  $\text{Fe}^{2+}$  phase observed after the argon treatments is similar to the one found to be present in the air exposed sample measured at 77 K. Following this suggestion, the observed loss of recoilfree fraction of the high-spin  $\text{Fe}^{2+}$  phase will be due to the adsorption of water, which enables this phase to vibrate relative to the "MoS<sub>2</sub>" particles.

Spectrum g shows that stepwise resulfidation of the sample treated in argon at 673 K and exposed to air brings the so-called "Co-Mo-S" spectrum back again. No contribution of Co<sub>9</sub>S<sub>8</sub>, which can be simulated by a doublet with  $QS = 0.26$  mm/s, is observed. If the adsorbed water would have caused sintering of the Co species, the formation of Co<sub>9</sub>S<sub>8</sub> upon sulfidation was to be expected. This suggests that we are dealing with well dispersed cobalt species in all the situations represented by the various Mössbauer spectra in fig. 1.

## 5. Conclusions

The main conclusion of these measurements is that the so-called "Co-Mo-S" phase in the Co(0.04)Mo(6.84)/C catalyst is very stable. Not only with respect to H<sub>2</sub>S/H<sub>2</sub> as reported by Candia et al. [5], but also under O<sub>2</sub> and H<sub>2</sub>O conditions at room temperature. It is not affected by exposure to air for long periods.

During exposure of the catalyst to ambient air the so-called "Co-Mo-S" phase slowly oxidizes to a high-spin  $\text{Fe}^{2+}$  phase which is most probably hygroscopic. The adsorbed water weakens the interaction between the Co-containing phase and the "MoS<sub>2</sub>" particles, which results in a decrease of the recoilfree fraction. Resulfidation leads to reappearance of the so-called "Co-Mo-S" phase.

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