

So-called "Co-Mo-S" phase observed in carbon-supported cobalt sulfide catalyst by Mössbauer emission spectroscopy

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So-Called “Co–Mo–S” Phase Observed in Carbon-Supported Cobalt Sulfide Catalyst by Mössbauer Emission Spectroscopy



A.M. VAN DER KRAAN*, M.W.J. CRAJÉ, E. GERKEMA and W.L.T.M. RAMSELAAR

Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft (The Netherlands)

and

V.H.J. DE BEER

Laboratory for Inorganic Chemistry and Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

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The demands for non polluting fuels and more efficient utilization of fossil fuel resources have made hydrotreating catalysts an important research area. These catalysts typically consist of alumina-supported molybdenum or tungsten sulfide promoted by cobalt or nickel. Efforts towards the clarification of the structure and the related hydrodesulfurization (HDS) activity of these complex catalyst systems resulted in different structural models in which the role and chemical state of the cobalt or nickel promoter ions in the sulfided catalysts remained much debated [1–3]. However, with the help of in-situ techniques such as Mössbauer spectroscopy, qualitative and quantitative information about the location of the cobalt promoter ions and their relevance for HDS activity has been obtained [2,4–10].

Clausen et al. [4] were the first to study the nature of the cobalt phases present in a working CoMo HDS catalyst by means of Mössbauer emission spectroscopy (MES). Later, Topsøe et al. [5,6] and Mørup et al. [7] showed that cobalt may be present in several different types of phases. It was observed that the HDS activity was governed almost completely by the presence of one of the cobalt phases, the so-called “Co–Mo–S” phase [8]. The Mössbauer parameters such as isomer shift (IS) and quadrupole splitting (QS) for this phase did not match those of any known cobalt sulfide and cobalt molybdenum sulfide compound. This phase was only observed in the presence of cobalt, molybdenum and sulfur and it was found to consist of cobalt ions at the edges of molybdenum disulfide crystallites [2,9,10]. Candia et al. [11,12] studied the effect of sulfiding temperature on HDS activity and structure of CoMo/Al₂O₃

catalysts and proposed the existence of a low- and high-temperature form of "Co-Mo-S" (denoted type I and type II, respectively). They suggested that high-temperature sulfiding results in the (partial) elimination of Mo-O-Al linkages, causing a transformation of the low-temperature type I to the more active high-temperature type II "Co-Mo-S" phase.

In sulfided carbon-supported CoMo catalysts, even at low-temperature sulfiding, only the more active type II "Co-Mo-S" phase is thought to be formed because in these catalyst systems strong bonds between the "Co-Mo-S" phase and the support (via oxygen ligands) are absent [13,14]. This idea is supported by the finding that the effective Debye temperature of the carbon-supported "Co-Mo-S" phase is lower than for the alumina-supported phase [12]. The interaction between the "Co-Mo-S" phase and the support material is thus indeed stronger for alumina-supported catalysts than for carbon-supported ones. Apart from the difference in intrinsic activity between the type I and type II "Co-Mo-S" phases, Van Veen et al. [13] have reported that even when the active phase is invariant ("Co-Mo-S" type II) the carbon support induces an appreciably higher activity.

Vissers et al. [14] reported an activity for optimally dispersed pure cobalt sulfide supported on activated carbon which is nearly as high as that observed for CoMo/C catalysts. They therefore ascribed the activity of the sulfided CoMo/C catalysts completely to the cobalt sites and suggested that the role of molybdenum disulfide in these catalysts is mainly to function as a support for optimally dispersed cobalt ions.

The cobalt species in "Co-Mo-S" phase are currently defined by a MES spectrum, consisting of a quadrupole doublet, which is only observed in sulfided catalysts containing both cobalt and molybdenum. Only ^{57}Co -MES measurements would enable us to check whether or not cobalt species with the same "Co-Mo-S" MES parameters can be formed in the absence of molybdenum sulfide: for instance, in the very active cobalt sulfide phase supported on a carbon carrier. Two carbon-supported catalysts, one (Co(0.04)/C) containing only 0.04 wt.-% carbon and the other (Co(0.04)Mo(6.84)/C) containing also 6.84 wt.-% molybdenum, were therefore characterized using the ^{57}Co -MES technique after being sulfided in-situ at various temperatures. Both catalysts were prepared by pore volume impregnation of an activated carbon (Norit RX3-Extra; surface area, 1190 m²/g; pore volume 1.0 cm³/g). The Co(0.04)/C catalyst was prepared using an aqueous solution of Co(NO₃)₂·6H₂O (Merck, "for analysis"). In the Co(0.04)Mo(6.84)/C catalyst, molybdenum was introduced first by impregnation with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (Merck, min. 99.9%) followed by an intermediate drying in static air at 383 K for 16 h and cobalt was introduced as described above. After the last impregnation step both catalysts were dried in flowing air (100 cm³/min) for 16 h at 293 K. Prior to the sulfidation, the samples were subjected to an additional treatment in a hydrogen flow (flow-rate 50 cm³/min) and kept under an hy-

drogen atmosphere. During this treatment the sample was kept at 313, 353 and 393 K for 24 h at each temperature. Sulfiding was also carried out in-situ, in a 10 mol-% hydrogen sulfide in hydrogen gas mixture at a flow-rate of 60 cm³/min. During the sulfiding procedure the following temperature program was applied: linear increase to the desired maximum sulfidation temperature in 1 h, holding at this temperature for 1 h and cooling (in the hydrogen sulfide-hydrogen flow) to 293 K.

Mössbauer experiments were carried out in-situ at 293 K using a constant velocity spectrometer in a vertical position, with a moving single-line absorber of K₄Fe(CN)₆·3H₂O enriched in ⁵⁷Fe. Isomer shifts with respect to a source of ⁵⁷Co in rhodium were observed and positive velocities corresponded to the absorber moving away from the source.

In Fig. 1 the room temperature Mössbauer spectra of Co(0.04)/C sulfided at 473 K and Co(0.04)Mo(6.84)/C sulfided at 673 K are shown. It is obvious that both spectra consist exclusively of a quadrupole doublet and that these doublets are identical (IS = 0.22 mm/s; QS = 1.33 mm/s). This observed quadrupole doublet is similar to the doublet which is ascribed by Topsøe et al. [6] to the so-called "Co-Mo-S" phase. However, as the Co(0.04)/C catalyst did not contain molybdenum, these results prove that the formation of a cobalt species like the one present in the so-called "Co-Mo-S" phase does not necessarily require the presence of molybdenum disulfide. This implies that, from a fundamental point of view, this special type of cobalt species should not be referred to as "Co-Mo-S".

The above results strongly support the postulation by Vissers et al. [14] that the so-called promoter effect in sulfided CoMo catalysts can be explained completely by the exceptionally high catalytic activity of cobalt sites and that the

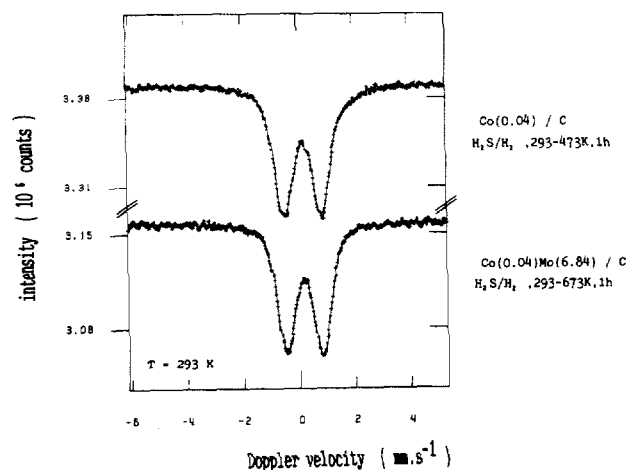


Fig. 1. In-situ Mössbauer emission spectra of sulfided Co(0.04)/C and Co(0.04)Mo(6.84)/C catalysts at 293 K.

role of molybdenum disulfide in these catalysts is mainly to function as a support for optimally dispersed cobalt ions. It is important to mention in this respect also the results recently obtained by Bouwens et al. [15] via characterization of a Co(4.1)/C and a Co(1.5)Mo(7.7)/C catalyst by means of extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES). They found that as a result of sulfidation similar cobalt phases are formed in these catalysts: i.e., in both cases a high sulfur coordination of the cobalt atoms was observed.

Characterization of carbon-supported cobalt sulfide and cobalt molybdenum sulfide catalysts by means of the ^{57}Co -MES technique seems a very promising approach in studies on the role of cobalt in commercial cobalt molybdenum sulfide catalysts. In our further research we will study parameters such as cobalt content, type of carrier and sulfiding conditions.

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