THE STRUCTURE OF THE COBALT SULFIDE PHASE IN CARBON-SUPPORTED Co AND Co–Mo SULFIDE CATALYSTS AS STUDIED BY EXAFS AND XANES

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An X-ray absorption spectroscopy study has been carried out on a sulfided Co/C and a Co–Mo/C catalyst, consisting of a fully sulfided Co–Mo–S phase. By comparing the EXAFS and XANES spectra of the catalysts with those of pure Co_9S_8 and CoS_2 reference compounds, it is shown that the cobalt ions in the Co–Mo–S phase have an octahedral-like sulfur coordination while the cobalt ions in the Co/C catalyst have a larger fraction of octahedral cobalt than Co_9S_8.

The role of the promoter Co and Ni ions in sulfided Co(Ni)–Mo hydrodesulfurization (HDS) catalysts is a subject of great interest and numerous studies have been devoted to it. By the use of Mössbauer Emission Spectroscopy, Topsøe and coworkers showed that the cobalt atoms are situated at MoS_2 crystallite edges in a so-called "Co–Mo–S" structure and that this structure governs almost completely the HDS activity [1–2]. Nevertheless, the exact structure of this phase or more precisely the location of the cobalt promoter is still an open question. Furthermore, the high specific activity of the Co–Mo–S structure is not understood. A different model was postulated by Duchet et al. [3] and by Vissers et al. [4] who observed a high activity for pure cobalt sulfide supported on activated carbon and hence explained the activity of a sulfided Co–Mo/C catalyst completely by the very high activity of the cobalt sites. Recently, Ledoux et al. [5] used solid state [59]Co NMR in a study of silica- and carbon-supported cobalt sulfide catalysts. In this study the authors showed that the promotion effect of cobalt was correlated with the concentration of cobalt sites with distorted tetrahedral symmetry, stabilized by so-called "rapid octahedral" cobalt atoms acting as a glue between the tetrahedral cobalt sites and the MoS_2 phase. The active tetrahedral cobalt sites could, according to the authors, also be stabilized

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without the presence of molybdenum by the small pores of the carbon support, confirming in this way the work of Vissers et al. [4]. The "rapid octahedral" cobalt atoms could not be related to the HDS activity [5]. Lately, however, Ledoux et al. proposed that these "rapid octahedral" cobalt atoms could be the origin of very active sites [6]. In this proposal the theory of Harris and Chianelli [7] was invoked. According to this theory, an electron transfer takes place from the "rapid octahedral" cobalt to the molybdenum ion, resulting in a strong activation of the three sulfur ions sandwiched between them.

In the present work we applied the EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near-Edge Structure) techniques to study the structure of the cobalt sulfide phase in a sulfided Co/C and a Co–Mo/C catalyst. The carbon support used was a Norit RX3-extra, activated carbon ($S_{BET} = 1190$ m$^2 \cdot$ g^{-1}, pore volume = 1.0 cm$^3 \cdot$ g^{-1}). The Co/C (4.1 wt% Co) catalyst was prepared by aqueous pore volume impregnation with a solution of cobalt nitrate (Merck p.a.), while the promoted catalyst (1.5 wt% Co, 7.7 wt% Mo) was obtained from Dr. J.A.R. van Veen. The latter catalyst was prepared in a special way, to ensure a maximum amount of the Co–Mo–S phase [8]. Mössbauer spectroscopy of this promoted catalyst clearly showed that only the Co–Mo–S phase was present after sulfiding [8] and furthermore that this Co–Mo–S is probably a Co–Mo–S type II phase, meaning a minor influence of active phase-support interaction [8,9]. The X-ray absorption measurements were carried out on freshly in situ sulfided catalysts at liquid nitrogen temperature at the SRS in Daresbury (EXAFS station 9.2). The sulfidation was carried out in a 10% H$_2$S in H$_2$ flow, flow rate 60 ml $\cdot$ min^{-1} under atmospheric pressure, the temperature was increased linearly from 293 to 673 K (8.5 K $\cdot$ min^{-1} for Co/C, 2 K $\cdot$ min^{-1} for Co–Mo/C) and kept constant at 673 K for 2 h (Co/C) or 1 h (Co–Mo/C).

In this article a comparison is made between the X-ray absorption spectra at the Co K-edge of the catalysts and those of pure Co$_9$S$_8$ and CoS$_2$ reference compounds. Co$_9$S$_8$ was prepared by heating Co$_3$O$_4$ at 773 K in a gas stream of H$_2$S (10%) in H$_2$ for 24 h. The precursor Co$_3$O$_4$ was prepared by heating Co(NO$_3$)$_2 \cdot$ 6H$_2$O (Merck p.a.) in air at 873 K for 48 h. CoS$_2$ was prepared according to Morris et al. [10]. The purity of the Co$_9$S$_8$ and CoS$_2$ compounds was checked by means of X-ray diffraction. In bulk Co$_9$S$_8$ 8 cobalt atoms are tetrahedrally coordinated and 1 cobalt is octahedrally coordinated by sulfur. The Co–S coordination distance is in the range of 2.13 to 2.39 Å. The CoS$_2$ structure consists of only octahedrally coordinated cobalt atoms.

In fig. 1 The Fourier-transformed EXAFS data of Co$_9$S$_8$, Co/C and Co–Mo/C are shown. The imaginary part of the Fourier-transform exhibits two peaks, the first one (at low R-value) can be ascribed to Co–S coordinations, the second one (at higher R-value) to the first Co–Co coordination (in Co$_9$S$_8$: $R_{Co-Co} = 2.50$ Å). It is obvious in this figure that the Co–S peak amplitude increases in the order: Co$_9$S$_8$ < Co/C < Co–Mo/C. Data-analysis (including the influence of

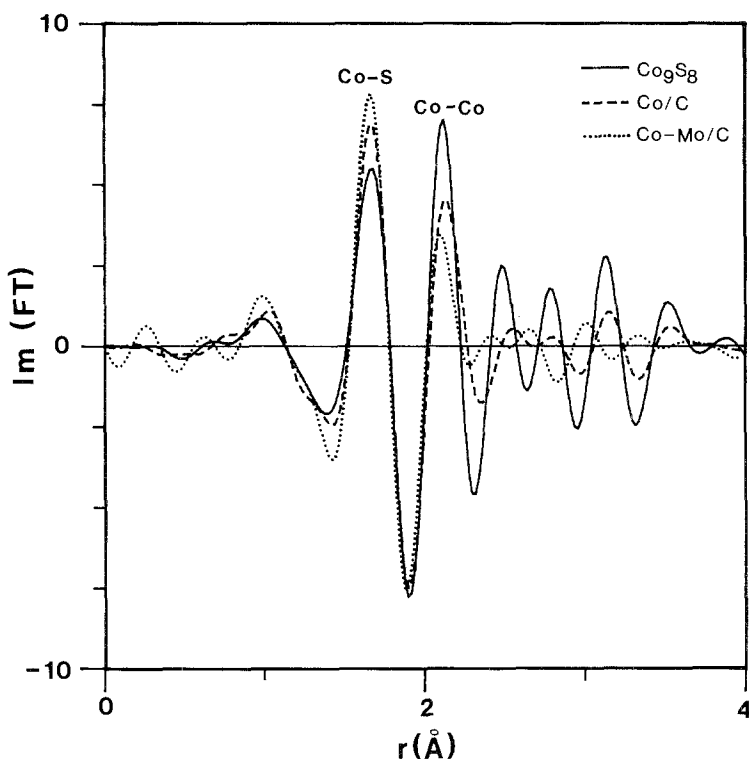Fig. 1. Imaginary k^3-weighed Fourier-transforms ($\Delta k = 3.0$–10.9 Å^{-1}) of the EXAFS data of Co_9S_8, Co/C and Co–Mo/C.

Debye–Waller factors) reveals that the Co–S coordination number increases in the same order [11]. From these spectral characteristics it is immediately clear that the cobalt ions in the catalysts have a higher sulfur coordination than those in Co_9S_8 and furthermore, that this phenomenon is more pronounced when cobalt is present in a Co–Mo–S structure. Supplementary information on the cobalt coordination can be derived from the XANES region. The near-edge structure of the samples is shown in fig. 2. The spectra all show a weak absorption peak near threshold which has been identified as a $1s \rightarrow 3d$ transition [12,13]. This transition has been observed to be more intense in tetrahedral than in octahedral coordination of the absorbing atom [12], hence, it can be used as a measure of the coordination of the cobalt atoms. It can be seen in fig. 2 that the $1s \rightarrow 3d$ transition is most intense for Co_9S_8 (consisting of 89% tetrahedral and 11% octahedral cobalt), whereas in CoS_2 (consisting of 100% octahedral cobalt) its intensity is very small. The sulfided Co/C catalyst shows an intensity between that of Co_9S_8 and CoS_2 suggesting a higher percentage of octahedral cobalt as present in Co_9S_8. Very remarkably, the Co–Mo/C catalyst shows a very small intensity, comparable to the CoS_2 compound, indicating that the cobalt ions in the Co–Mo–S phase have an octahedral-like sulfur coordination. The $1s \rightarrow 3d$
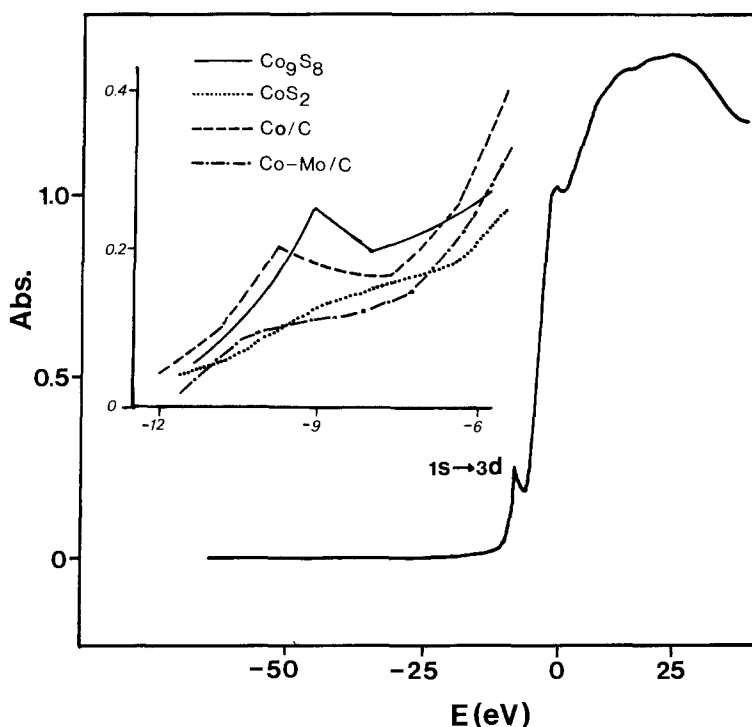
Fig. 2. XANES spectrum of Co_9S_8. The expanded inset shows the $1s \rightarrow 3d$ transition of Co_9S_8, CoS_2, Co/C and Co–Mo/C.

near-edge feature is thus in complete agreement with the EXAFS spectra shown in fig. 1.

In view of our results, the proposal of Ledoux et al. of tetrahedral cobalt sites being responsible for the high HDS activity of cobalt-promoted molybdenum sulfide catalyst [5] must be rejected since we observe an octahedral-like coordination in the catalyst with the highest activity, the promoted catalyst. On the other hand, the other proposal of Ledoux et al. [6] that the "rapid octahedral" cobalt atoms might be the origin of very active sites, corresponds quite closely to our findings. From the observation that the structure of the cobalt sulfide phase in the Co/C catalyst is not a specific Co_9S_8 phase, as expected from thermodynamical considerations, it seems that the carbon carrier can modify the active cobalt sites.

This idea is not only in agreement with the theory of Ledoux et al. [5] but also with the work of Burch and Collins [14], who discussed the possible interaction between the nickel sulfide phase and an alumina, silica and carbon carrier material. The latter authors proposed that a metal sulfide – support interaction may alter the morphology or composition of the nickel sulfide phase. Finally, our findings are in line with the theory of Vissers et al. [4] that the cobalt phase in sulfided Co–Mo catalysts is the actual active phase. According to our EXAFS

and XANES observations, the morphology of the cobalt phase in sulfided Co/C corresponds closely to that in a Co–Mo/C catalyst: in both catalysts a high sulfur coordination of the cobalt atoms is present. In this respect it is also relevant to note that Vissers et al. [4] observed atomic S-to-Co ratios of 1.3 to 1.5 in XPS measurements on sulfided Co/C catalysts, which values are much larger than the theoretical value of 0.89 for Co_9S_8.

Acknowledgements

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