An EXAFS study on the so-called "Co-Mo-S" phase in Co/C and CoMo/c, compared with a Mössbauer emission spectroscopy study

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.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

An EXAFS Study on the So-Called "Co–Mo–S" Phase in Co/C and CoMo/C, Compared with a Mössbauer Emission Spectroscopy Study

Menno W. J. Crajé,[†] Stefan P. A. Louwers,[‡] Vincent H. J. de Beer,[§] Roel Prins,[‡] and Adri M. van der Kraan*,[†]

Interfacultair Reactor Instituut, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands, Technisch-Chemisches Laboratorium, ETH Zentrum, 8092 Zürich, Switzerland, and Schuit Catalysis Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands (Received: November 1, 1991; In Final Form: March 2, 1992)

EXAFS measurements were performed on four sulfided catalysts with the same composition as their [57]Co-containing counterparts which were previously characterized by Mössbauer emission spectroscopy. It was shown that the Co species in Co(373)/C catalysts with a "Co–Mo–S"-like Mössbauer emission spectrum after sulfidation at 373 K is similar to the species with the Co–Mo–S spectrum in CoMo/C catalysts. In both cases the Co atoms are present in a very highly dispersed Co species. In the catalyst without Mo this sulfidic Co species strongly sinters during sulfidation at 673 K, resulting in a Co_9S_8-type phase. In the CoMo/C catalyst, the Mo hinders sintering of the Co species.

Introduction

Many characterization studies of hydrotreating catalysts have been performed to explain the observed synergetic behavior of Co and Mo in commercial sulfided $CoMo/Al_2O_3$ catalysts. Various models were proposed[1-4] but only the so-called "Co–Mo–S" structural model of Topsøe et al.[5] can explain many, but not all of the observed features of CoMo catalysts. Characterization studies by Mössbauer emission spectroscopy (MES) combined with thiophene hydrodesulfurization (HDS) activity measurements[6] formed the basis for this model. It is assumed that a Co + Mo + S containing phase with a characteristic MES spectrum is responsible for the observed synergy between Co and Mo. Additional information about the nature of Co–Mo–S has been presented by the Topsøe group by combining MES results with those obtained from other techniques.[7-9] However, the most recent MES results on a sulfided Co/C catalyst, presented by Topsøe et al.,[9] appeared to be in conflict with the results recently reported by Crajé et al.[10]

An interesting observation was made by Vissers et al.[11] who noticed that the intrinsic (per site) thiophene HDS activity of optimally dispersed cobalt–sulfide on a carbon support without Mo is equal to that of Co–Mo–S in CoMo/C catalysts. This suggested that cobalt sulfide could act as a catalyst, as was proposed earlier by de Beer et al.[12] and Duchet et al.[13] A MES study of CoMo/C and Co/C catalysts has been performed by van der Kraan et al.[14] They treated their catalysts in such a way that intermediate phases, which appear and disappear during the sulfidation process, could also be studied by MES. It turned out that the MES spectrum which according to Topsøe et al.[5] is characteristic for the so-called Co–Mo–S species can be observed as an intermediate during the sulfidation of Co/C catalysts (without Mo). Further MES studies at 4.2 K by Crajé et al.[10] proved that this intermediate cannot be distinguished from the so-called Co–Mo–S species in CoMo/C catalysts. Van der Kraan et al.[14] used the term "so-called Co–Mo–S" for the species which gives rise to this MES spectrum. If the so-called Co–Mo–S species in sulfided Co/C turns out to be exactly the same as that in sulfided CoMo/C, this would be a strong indication that the thiophene HDS activity is related to a cobalt-sulfide species and not to a mixed CoMo sulfide species. However, although MES is a technique sensitive to the local environment of the Mössbauer nucleus, in particular when used at various temperatures as done by Crajé et al.,[10] the possibility always remains that the observed MES spectra of the two catalysts with and without Mo are accidentally equal.

In order to solve this problem, the MES studies were complemented by another spectroscopic technique that can probe the local environment of the atoms of a catalyst under in situ conditions, which is important because the surface of the catalyst is in dynamic equilibrium with its gaseous environment. Extended X-ray absorption fine structure (EXAFS) is such a technique and therefore EXAFS measurements were performed on samples which were selected on the basis of the results of previous MES measurements carried out at room temperature.[15] In those studies a Co–Mo–S doublet was observed in a Co/C catalyst which had been sulfided at 300 K.[15] Sulfidation at 373 K did not affect this Co–Mo–S doublet, but sulfidation at elevated temperatures (673 K) made it disappear from the MES spectrum and led to the formation of a Co_9S_8-type species. In a CoMo/C catalyst a Co–Mo–S species with the same MES parameters as in the Co/C catalyst was observed after sulfidation up to 373 K. After sulfidation at 673 K the CoMo/C catalyst still showed a Co–Mo–S doublet, although the quadrupole splitting (QS) had decreased slightly. In summary, when sulfided at 373 K the Co/C and the CoMo/C catalysts showed the same MES spectrum, while after sulfidation at 673 K different MES spectra were observed. In the latter case the Co/C catalyst is characterized by a spectrum indicating a Co_9S_8-type species, while the CoMo/C catalyst is characterized by a Co–Mo–S spectrum with a smaller QS than observed for this catalyst sulfided at 373 K.

The aim of the present EXAFS study was to obtain detailed information on the local structure around the Co atoms in these Co/C and CoMo/C catalysts. In particular, it was to be elucidated whether the two so-called Co–Mo–S species characterized by the same MES spectra after sulfidation of the catalysts at 373 K exhibit similar EXAFS features as well. Also, it was hoped to find a relation between the QS observed by MES and the local surrounding of the Co as determined by means of EXAFS.

Experimental Section

Catalyst Preparation. The two catalysts were prepared by pore volume impregnation with aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (Merck, min. 99.9%) and $Co(NO_3)_2\cdot6H_2O$ (Merck, p.a.).[15] An activated carbon (Norit RX3-extra) with a BET area of 1197 m^2/g and a pore volume of 1.0 mL/g was used as carrier. The CoMo/C catalyst was prepared by a two-step procedure in which the Mo phase was introduced first followed by drying in static air at 383 K for 16 h. After Co introduction, both catalysts were left in ambient air at 293 K for 16 h. To remove residual nitrate ions, the catalysts were subjected to an additional treatment in a H_2 gas flow (flow rate 50 mL/min). During this treatment the temperature was kept at 313, 353, and 393 K for 24 h at each temperature. As analyzed by means of atomic absorption spectroscopy, the Co/C catalyst contains 2.45 wt % Co and the CoMo/C catalyst 2.25 wt % Co and 6.84 wt % Mo.

The dried catalysts were pressed into self-supporting wafers. Since this is difficult in the case of activated carbon, Lonza High

Surface Area Graphite (HSAG-13) was mixed with the CoMo/C and Co/C particles, to serve as a matrix. This HSAG can very easily be pressed into wafers and it is sufficiently inert to avoid changes in the catalyst. The thickness of the wafers was chosen such that the absorption μx, was about 2.5 to give an optimal signal-to-noise ratio in the EXAFS spectra. The sulfidation of the samples was carried out in a flow of 10% H_2S/H_2 (flow rate 60 mL/min, atmospheric pressure) in an EXAFS cell.[16] The temperature was increased from room temperature to the final temperature (373 or 673 K) in 1 h. It was kept at this level for 1 h, after which the sample was cooled down to room temperature in the 10% H_2S/H_2 gas mixture. In the text the following notation will be used: Co(373)/C and CoMo(373)/C for catalysts sulfided at 373 K, Co(673)/C and CoMo(673)/C for catalysts sulfided at 673 K. The cell was purged with He for 30 min at room temperature after which it was closed and transferred into a glovebox filled with N_2. One of the valves of the cell was replaced by a blind flange, so that the cell could fit in the beam line, because on the EXAFS station used the primary beam line is passing just along the sample table. So the measurements were performed under N_2 atmosphere.

EXAFS Measurements. The EXAFS measurements were carried out at EXAFS station 7.1 of the Synchrotron Radiation Source in Daresbury (U.K.). The storage ring was operated at 2.0 GeV, the ring current was in the range 100–200 mA and Si(111) monochromator crystals were used. The monochromator was detuned to 50% intensity to remove higher harmonics in the X-ray beam. The experiments were performed on the Co K edge. Four or five scans were recorded for each sample, which were averaged in the data analysis procedure.

The EXAFS function in k space was obtained from the X-ray absorption spectra by subtracting a Victoreen curve which is fitted to the pre-edge region, followed by a cubic spline background removal.[17] Normalization was done by division by the apparent edge height, which is obtained by back extrapolation of the background. The EXAFS function could be used up to a wave vector of about 12.50 $Å^{-1}$. At this k value the EXAFS function was disturbed by the Ni K-absorption edge, originating from Ni impurities in the Be windows of the EXAFS cell. The EXAFS functions (=spectra) were Fourier transformed (FT) over the largest possible k range to obtain the FT spectra. The limits of the k range were chosen in nodes of the EXAFS function to minimize cutoff effects.

For the analysis of the spectra phase shifts and backscattering amplitudes from reference compounds were used. The same references as the ones used by Bouwens et al.[18] were applied; the Co^{2+}–S^- coordination in CoS_2 for the Co–S EXAFS signals, the Ni^{2+}–Ni^{2+} coordination in NiO for the Co–Co EXAFS signal and the Ni^{2+}–Mo^{6+} coordination in $((C_6H_5)_4P)_2Ni(MoS_4)_2$ for the Co–Mo EXAFS signal. The use of a Ni absorber instead of Co is justified since Teo and Lee[19] showed that phase shifts of nearest neighbors in the periodic system hardly differ.

The data analysis has been carried out by inverse Fourier transformation (FT^{-1}) over a certain R range and subsequent fitting of the isolated EXAFS function (=FT^{-1} spectrum) in k space. By such an inverse Fourier transformation most of the noise can be removed from the spectrum. For the back transformation the R-range limits were chosen in minima of the absolute value of the FT spectrum to minimize cutoff effects. Also for this reason the range for Fourier transformation of an isolated EXAFS function to R space was decreased by 0.5 $Å^{-1}$ at each side. A fit was regarded acceptable when the similarity in k^1- and in k^3- weighted spectra in k space was good, while only then the coordination number and the Debye–Waller factor can be determined unambiguously. Furthermore, the similarity in R space had to be good for both the absolute value and the imaginary part of the function.

Results

EXAFS Measurements. In Figure 1 the k^3 weighted spectra of the four catalysts are presented pairwise. In Figure 2 the absolute value and imaginary part of the corresponding FT spectra

TABLE I: FT and FT^{-1} Ranges Applied for the Fourier Transformation of the Spectra

catalyst	FT range, $Å^{-1}$	FT^{-1} range, Å
Co(373)	3.15–12.50	0.78–3.50
Co(673)	3.23–12.49	0.68–2.85
CoMo(373)	3.06–12.45	0.74–3.14
CoMo(673)	3.20–12.54	0.76–3.21

are presented. The ranges over which the spectra have been Fourier transformed are presented in Table I.

From Figures 1 and 2 the following qualitative remarks can be made. First of all it is clear that the signal-to-noise ratio (S/N) for all four spectra is very high. This is confirmed by a comparison with EXAFS results published previously. The spectra published by Clausen et al.[20–22] have rather poor S/N ratios. Although the S/N ratio in the spectra presented by Bouwens et al.[23] is already much better, only their most recent spectra[18] have a S/N ratio comparable to the present spectra. A comparison of the k^1- and k^3-weighted spectra in k-space shows that the spectra of the Co(373)/C and CoMo(373)/C catalysts are quite similar, although significant differences are observed above $k = 10$ $Å^{-1}$ in the k^3-weighted spectra (Figure 1). As high-Z scatterers are emphasized by k^3-weighting, this indicates that Co is coordinated by a high-Z scatterer in the CoMo(373)/C catalyst. It is clear that the spectra of the Co(673)/C and the CoMo(673)/C catalyst differ from the spectra of the catalysts sulfided at 373 K. Not only does the amplitude decrease more rapidly, but also the phase is shifted. Furthermore, the spectra of the Co(673)/C and the CoMo(673)/C catalysts differ from each other. The FT spectra shown in Figure 2 provide some insight in the structure of the examined catalysts. First of all, in none of the FT spectra significant contributions are observed beyond 4 Å. This indicates that the ordering around the Co atoms is restricted to 4 Å, and points to a high dispersion of the Co-containing phases in all samples. In addition, it is clear that the main contribution in the FT spectra of the Co(373)/C and CoMo(373)/C catalyst is a peak at about 1.8 Å and that the peak heights are almost the same. The FT spectra of the Co(373)/C and the CoMo(373)/C catalysts also look rather similar at higher R values. The FT spectrum of the CoMo(673)/C catalyst shows a significantly lower main peak and that of the Co(673)/C catalyst a still lower one. Also the main peaks of these catalysts are shifted to lower R values with decreasing peak height. Furthermore, the FT spectra of the Co(673)/C and the CoMo(673)/C catalysts differ at higher R value as well.

Additional information concerning the Co environment can be obtained from an analysis of the EXAFS spectra. In the FT spectrum of the Co(373)/C catalyst the main peak was isolated by inverse Fourier transformation over the range 0.78–2.56 Å. The resulting FT^{-1} spectrum in k space was fitted with a single Co–S(1) contribution. A very good fit could be obtained of the k^1- and k^3-weighted spectra in k space and R space. In addition, an attempt was made to fit the same isolated FT^{-1} spectrum with a Co–S(1) as well as a Co–Co(1) coordination, because Bouwens et al.[18] needed such a Co–Co coordination at 2.50 Å (which is the first Co–Co contribution of Co_9S_8[27]) to obtain a good fit. However, the quality of the fit did not improve. Hence, it can be concluded that the main peak in the FT spectrum of the Co(373)/C catalyst arises from one Co–S coordination only.

The higher shell contributions could not be isolated easily, so in order to analyze higher shell contributions, the original FT spectrum in R space was inverse Fourier transformed over the range 0.78–3.50 Å and a multiple shell fit was performed. Several possible solutions were investigated. First a fit with a Co–S(1) contribution at 2.25 Å and a Co–Co(1) contribution at about 3.30 Å was tried, since these distances correspond to the main peaks in the absolute part of the FT. Although the difference spectrum (the calculated Co–S(1) and Co–Co(1) contributions subtracted from the overall EXAFS spectrum) indicated that there might be a second Co–Co(2) contribution around 2.6 Å or a Co–S(2) contribution at 3.10 Å, a satisfactory fit could not be obtained by adding one of these contributions. However, fitting the
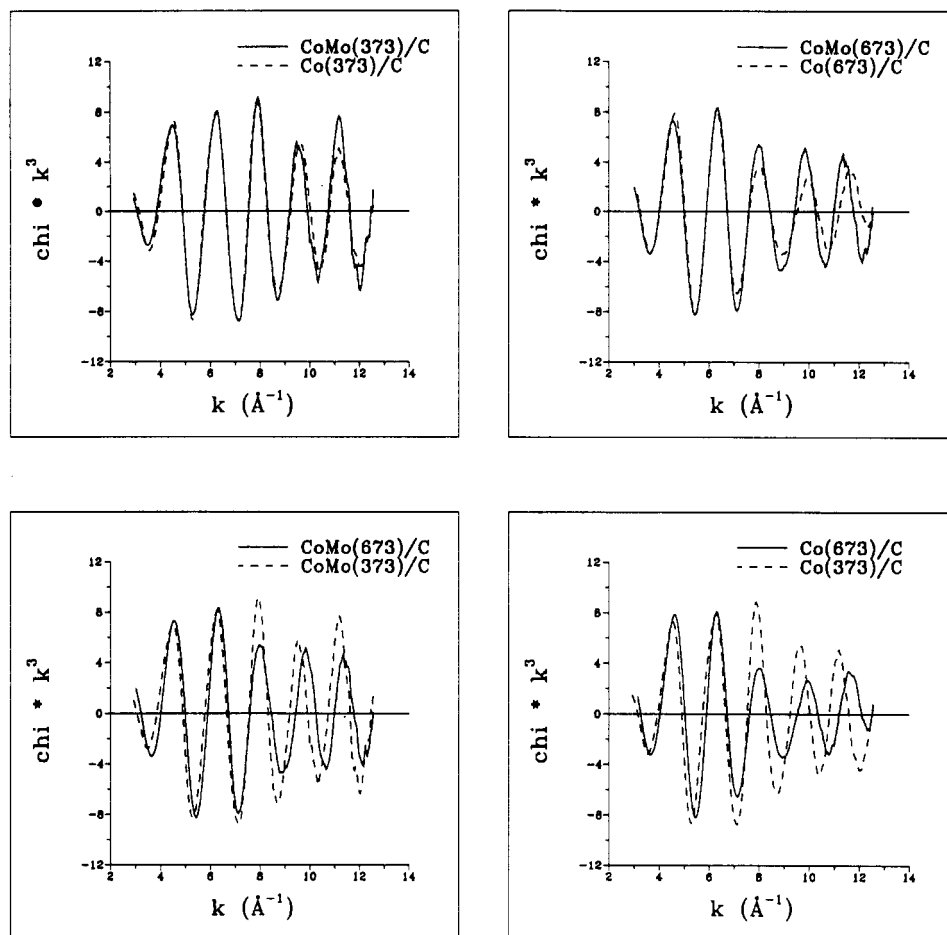
Figure 1. k^3-weighted spectra of the four samples, presented pairwise.

TABLE II: EXAFS Parameters of Co(2.45)/C and Co(2.25)Mo(6.84)/C after Sulfidation at 373 and 673 K[a]

catalyst	N	R, Å	$\Delta\sigma^2$, Å^2	ΔE_0, eV	N	R, Å	$\Delta\sigma^2$, Å^2	ΔE_0, eV	N	R, Å	$\Delta\sigma^2$, Å^2	ΔE_0, eV
			Co–S(1)				Co–Co(1)				Co–S(2)	
Co(373)/C	6.0	2.25	0.0013	−0.9	0.8	2.9	0.0070	13.1	4.0	3.4	0.0075	4.6
Co(673)/C	3.6	2.20	0.0003	−1.8	2.7	2.5	0.0058	5.7	0.7	2.8	0.0068	−7.5
			Co–S(1)				Co–Co(1)				Co–Co(2)	
CoMo(373)/C	5.5	2.26	0.0004	−2.3	1.2	2.9	0.0080	−6.6	1.6	3.2	0.0089	−2.7
			Co–S(1)				Co–Co(1)				Co–Mo(1)	
CoMo(673)/C	5.1	2.22	0.0011	−2.4	0.6	2.6	0.0030	−0.1	0.8	2.8	0.0051	−9.1
			Co–S(1)				Co–Co(1)				Co–Co(2)	
Co$_9$S$_8$[b]	4.2	2.22			3.0	2.51			6.0	3.51		

[a] The coordination number is represented by N, the coordination distance by R. $\Delta\sigma^2$ is the difference between the Debye–Waller factors of the coordination to be analyzed and the corresponding coordination in the reference compound. ΔE_0 represents the difference between the inner potentials of sample and reference compound. The values for Co$_9$S$_8$ are adopted from Rajamani et al.[27] Coordination numbers have been corrected for the photoelectron mean free path (λ) dependency, assuming that $\lambda = 5$ Å for a Co atom. [b] The Co–S(1) coordination number in Co$_9$S$_8$ ($N = 4.8$) as reported by Bouwens et al.[23] has to be corrected into $N = 4.3$. (V. H. J. de Beer and R. Prins).

spectrum with a Co–S(1) contribution at 2.25 Å and a Co–S(2) contribution at 3.4 Å gave a reasonable fit. A very good fit in the k^1- and k^3-weighted spectra in k space and in the absolute value and imaginary parts of the FT spectrum in R space was obtained when adding an additional Co–Co(1) contribution at 2.9 Å. The resulting parameters are listed in Table II and a comparison between the k^3-weighted spectra in k space and the absolute value and imaginary part of the FT spectrum in R space is given in Figures 3 and 4.

For the other three catalysts it was less easy to isolate the main Co–S(1) peak, due to interference with other contributions. Therefore, these FT spectra were inverse Fourier transformed over a large R range, followed by a multiple shell fitting procedure. Because the FT spectrum of the CoMo(373)/C catalyst looks rather similar to the one of the Co(373)/C catalyst, the FT^{-1} spectrum was first fitted with Co–S(1) and Co–S(2) contributions

at 2.26 and 3.5 Å and one Co–Co(1) contribution at about 2.9 Å. Although several attempts were made (other starting parameters, constraining certain parameters, etc.), no satisfactory fit could be achieved. As the similarity of the FT spectra in R space of the Co(373)/C and CoMo(373)/C catalysts at higher R values is not as good as at lower R values, it was assumed that the third contribution might be different. Therefore, a Co–S(1) contribution at 2.26 Å and a Co–Co(1) contribution at 2.9 Å were subtracted from the isolated FT^{-1} spectrum. The difference signal showed that the third contribution most likely is a Co–Co(2) contribution at about 3.20 Å. Such a Co–Co(2) contribution is in agreement with the observation that the difference in the k^3-weighted spectra indicates the presence of a high-Z scatterer in the CoMo(373)/C catalyst. At low k values the spectra are dominated by the Co–S(1) contribution, but at higher k values the Co–Co contribution(s) dominate(s). A very good fit could
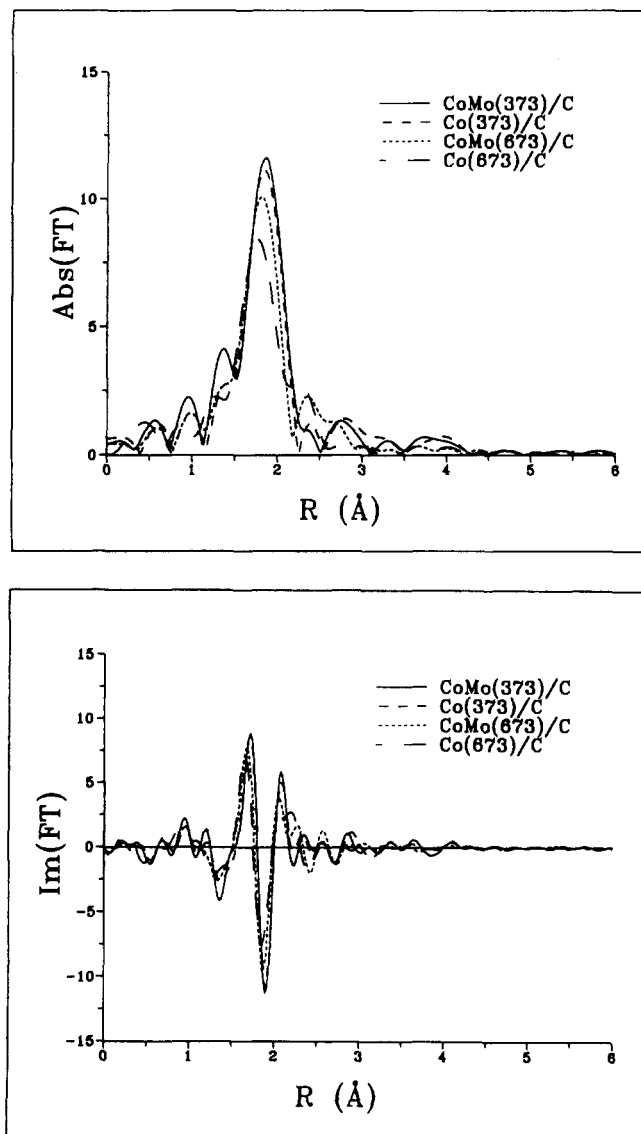
Figure 2. Absolute value and imaginary part of the FT spectra of the k^3-weighted EXAFS functions of the four samples. The spectra have not been phase- and amplitude-corrected.

be obtained for both k^1- and k^3-weighted spectra in k space and FT spectra in R space. The parameters obtained are included in Table II, and in Figures 3 and 4 a comparison between the experimental data and the fit is given.

The relative contributions of the higher shells in both catalysts are small and the uncertainties, especially in the coordination numbers N, are therefore rather large, possibly up to 50%. On the other hand, the Co-S(1) parameters are much more reliable since the Co-S(1) contribution dominates in the spectra.

It should be noticed that the Co-S(1) coordination numbers and distances in the CoMo(373)/C and the Co(373)/C catalysts are equal within the experimental uncertainties. The result indicates a sixfold coordination of the Co atoms by sulfur atoms in the nearest neighboring shell. This high coordination number is accompanied by a Co-S(1) distance (2.26 Å) which is significantly larger than the shortest Co-S distance in the most stable cobalt sulfide under reaction conditions, Co_9S_8 (2.19 Å). Also the coordination number and the atomic distance for the Co-Co(1) next nearest neighbors are quite similar for the two catalysts and the coordination distance ($\approx$2.9 Å) is much larger than the first Co-Co distance in Co_9S_8 (2.50 Å).

The FT spectrum of the Co(673)/C catalyst was inverse Fourier transformed over the range 0.68-2.85 Å. In a first attempt the isolated FT^{-1} spectrum was fitted with two contributions: a Co-S(1) contribution at 2.20 Å and a Co-Co(1) contribution at 2.5 Å. Although this fit is already quite good, it could be improved

by adding a third shell. A Co-Co(2) contribution at 2.9 Å, as well as a Co-S(2) contribution at 2.8 Å, was investigated. The fit with a Co-S(2) contribution at 2.8 Å turned out to be the best one. The k^3 fits and the corresponding parameters are presented in Figures 3 and 4 and Table II, respectively. Compared to the Co(373)/C catalyst the coordination number as well as the coordination distance of the Co-S(1) contribution have decreased markedly. The values are in the range of the parameters reported for Co_9S_8.[27]

The FT spectrum of the CoMo(673)/C catalyst was inverse Fourier transformed over the range 0.76-3.21 Å. Clearly a multiple shell fit had to be performed. In a first attempt a fit with a Co-Mo(1) contribution at about 2.8 Å and a Co-S(1) contribution at about 2.20 Å was tried. This fit was not completely satisfactory. After addition of a Co-Co(1) contribution at 2.6 Å, a very good fit in k and R space could be obtained as is clear from Figures 3 and 4. This is the case for k^1 weighting (not shown) and k^3 weighting. The parameters are presented in Table II.

The Co-S(1) coordination number for both 673 K sulfided samples is significantly smaller than that for the samples sulfided at 373 K. As was already suggested from a qualitative inspection of the data, the coordination number of the Co atoms in the CoMo(673)/C catalyst is in between those of the Co(673)/C catalyst and the 373 K sulfided samples. Because EXAFS parameters are always mean values, this might indicate that Co in the CoMo(673)/C catalyst is partly sixfold and partly fourfold surrounded. In this respect, additional information can be obtained from the intensity of the 1s → 3d transition present in the XANES (X-ray absorption near edge structure) region. According to Bouwens et al.,[23] a high intensity of this transition indicates a high fraction of cobalt sites lacking a center of symmetry. They argued that a decrease of the pre-edge peak implies an increase of the fraction of octahedral or trigonal prismatic cobalt. The trend in the size of the pre-edge peak can be regarded as a unique "fingerprint" technique to obtain additional structural information. From Figure 5 it is clear that the step size in k space which is used in the present measurements is small enough to justify interpretation of the XANES region. Apparently all catalysts show a pre-edge peak. Only in the case where Co is perfectly octahedral or trigonal prismatic surrounded will no pre-edge peak be observed. In these highly dispersed catalysts this is almost never the case. Comparison of the pre-edge peaks in the absorption spectra of the four samples indicates that the peak height decreases in the sequence Co(673)/C > CoMo(673)/C > Co(373)/C = CoMo(373)/C, indicating that the fraction octahedral or trigonal prismatic Co increases in the same order.

MES Results. In Figure 6 the MES spectra of four catalysts, having the same composition as the catalysts in the present study, and made according to an identical preparation procedure, are presented.[15] It is clear that the spectra of the Co(373)/C and the CoMo(373)/C catalysts are similar and consist of a quadrupole doublet. The CoMo(673)/C catalyst is also characterized by a quadrupole doublet, but with a smaller splitting than observed for the Co(373)/C and CoMo(373)/C catalyst. The Co(673)/C catalyst is characterized by a doublet which appears to be a broad single line. In a previous paper[15] the MES spectra of the Co-(373)/C, the CoMo(373)/C, and the CoMo(673)/C catalysts were fitted with one quadrupole doublet. The spectrum of the Co(673)/C catalyst was fitted with two quadrupole doublets of which one had the parameters of Co_9S_8. In a more recent paper[24] it was concluded that a fit with two or even three doublets has no physical meaning. The proper way to fit the spectra is with a distribution in QS values. However, when this method is used, the interpretation of the spectra is the same as when they were fitted with one Lorentzian doublet with adjusted line width. Therefore, it was decided to present here the fits with one quadrupole doublet only.

Discussion

Discussion of the EXAFS Results. The EXAFS results of the catalysts sulfided at 373 K will be discussed first. From the EXAFS results presented in Table II it appears that the Co-S(1)
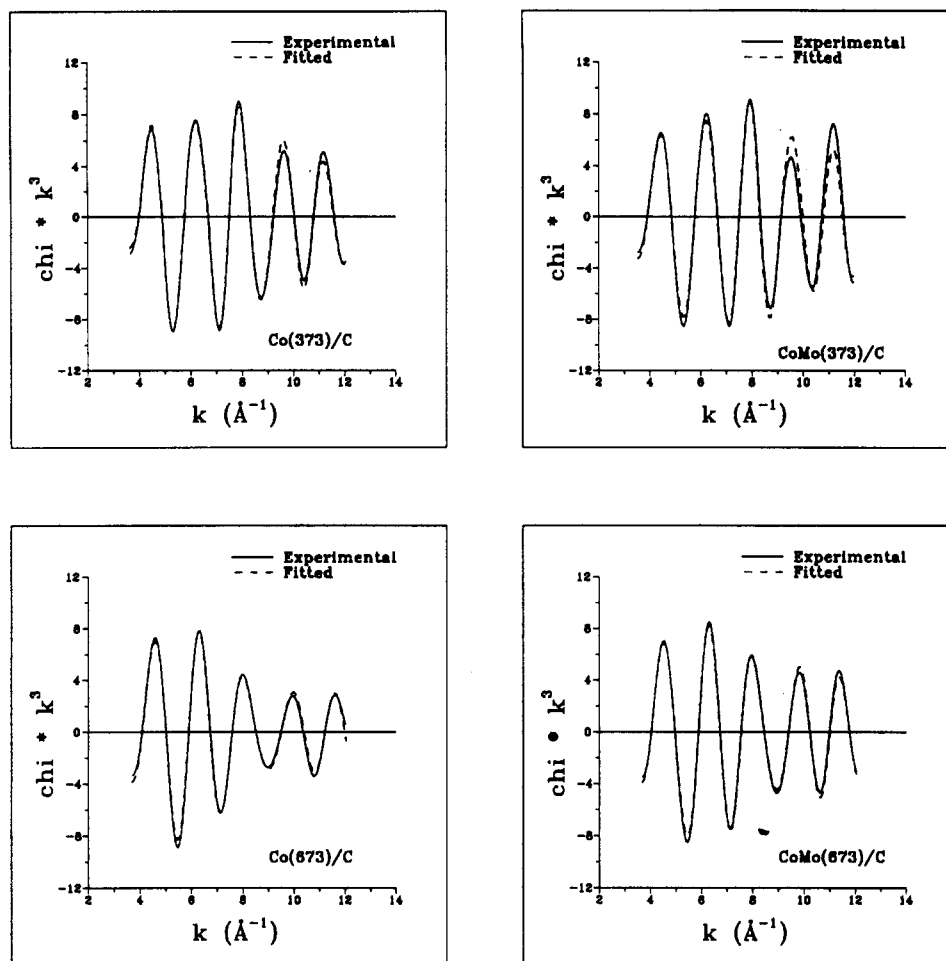
Figure 3. k^3-weighted spectra of the four samples and the final fits with the parameters as presented in Table II.

coordination number is almost six in both catalysts. This high coordination number is consistent with the presence of a small pre-edge peak in the XANES region and with the coordination number reported by Bouwens et al.[23] for their Co-Mo-S catalyst. For Ni-Mo-S on carbon Niemann et al.[25] have reported considerably lower coordination numbers, namely 4.6 or 4.7, whereas Bouwens et al.[18] and Louwers et al.[26] reported coordination numbers of 4.9 to 5.6 for Ni-Mo-S on carbon as well as Al$_2$O$_3$. Also the coordination distances of Co-S(1) are similar for Co-(373)/C and CoMo(373)/C, namely 2.25 and 2.26 Å, respectively. This is substantially higher than the value (2.19-2.21 Å) reported by Niemann et al.[25] and Bouwens et al.[23] It is remarkable that Bouwens et al. found a much higher Co-S coordination number than Niemann et al., but the same coordination distance. One would expect as also discussed by Niemann et al.[25] that a coordination number of 6 is more probable for a Co-S distance of 2.26 Å than for one as short as 2.21 Å, which distance corresponds with that of the nearest-neighbor value of the tetrahedrally surrounded Co in Co$_9$S$_8$. Even 2.26 Å is short compared with the Co-S distance of 2.36 Å of the six-coordinated Co in Co$_9$S$_8$.[27] In both the Co(373)/C and the CoMo(373)/C catalysts the next-nearest neighbors are Co atoms. The coordination numbers and distances are remarkably similar. Thus, in the Co(373)/C and CoMo(373)/C catalysts the Co atoms are nearly equally surrounded in the first and second shell. The third coordination is completely different, however. In the Co(373)/C catalyst a Co-S(2) contribution is found at 3.4 Å, whereas in the CoMo-(373)/C catalyst a Co-Co(2) contribution at 3.2 Å is found.

The Co-S(1) coordination number of about 6 for the Co-(373)/C and CoMo(373)/C catalysts is a first indication that in these catalysts no large amounts of Co$_9$S$_8$, in which Co has only four sulfur neighbors in the first shell,[27] are present. In addition to this, the Co-S(1) atomic distance of 2.25-2.26 Å is somewhat large compared to that in Co$_9$S$_8$, 2.19 Å. Furthermore, the atomic

distance belonging to the Co-Co(1) coordination is too large to be indicative for the presence of Co$_9$S$_8$. This atomic distance of 2.9 Å also rules out the presence of CoS$_2$, Co$_3$S$_4$, and Co$_2$S$_3$. In these sulfides, the Co-Co coordinations have considerably larger atomic distances of 3.33 Å and more.[28-30] Finally, also the presence of β-CoS or γ-CoS, cobalt sulfide with the millerite structure,[31] can be ruled out due to the absence of a Co-Co coordination around 2.54 Å.

Summarizing, one can conclude that in both catalysts, sulfided at 373 K, no familiar bulk cobalt sulfide is present. Still, all of the atomic distances reported in this work have been observed in cobalt-sulfur and nickel-sulfur systems. Tremel and Henkel, for example, have observed Ni-Ni distances of 2.87 and 3.33 Å in organometallic Ni-S clusters.[32] These values are close to the Co-Co distances in the CoMo(373)/C catalyst (2.9 and 3.2 Å). However, they also observed Ni-S atomic distances around 2.18 Å, somewhat shorter than those found in our catalysts. Others as well have reported Ni-Ni atomic distances which are close to 2.9 and 3.2 Å.[33-35] Also these authors saw those distances only in combination with relatively short Ni-S distances of 2.14-2.22 Å. Finally, Fleet[36] reported the structure of Ni$_{22.5}$S$_{19.3}$, a disorderly nickel sulfide. In this nickel sulfide Ni-S distances between 2.19-2.56 and 3.35-4.09 Å and Ni-Ni distances between 2.00-2.90 and 3.00-4.09 are present.

Concluding, although at present it is not possible to say what the structure of the cobalt sulfide or cobalt sulfides in the Co-(373)/C and CoMo(373)/C catalysts is, none of the observed coordination distances is impossible. It might be that, due to the small particle size in our catalysts and the interaction with the support, the Co-S structures are very disordered, and therefore have coordinations, not present in crystalline Co-S systems.

After sulfidation at 673 K, the EXAFS spectrum of the Co/C catalyst had changed substantially. The Co-S(1) coordination number had decreased from 6.0 to 3.6 and the coordination
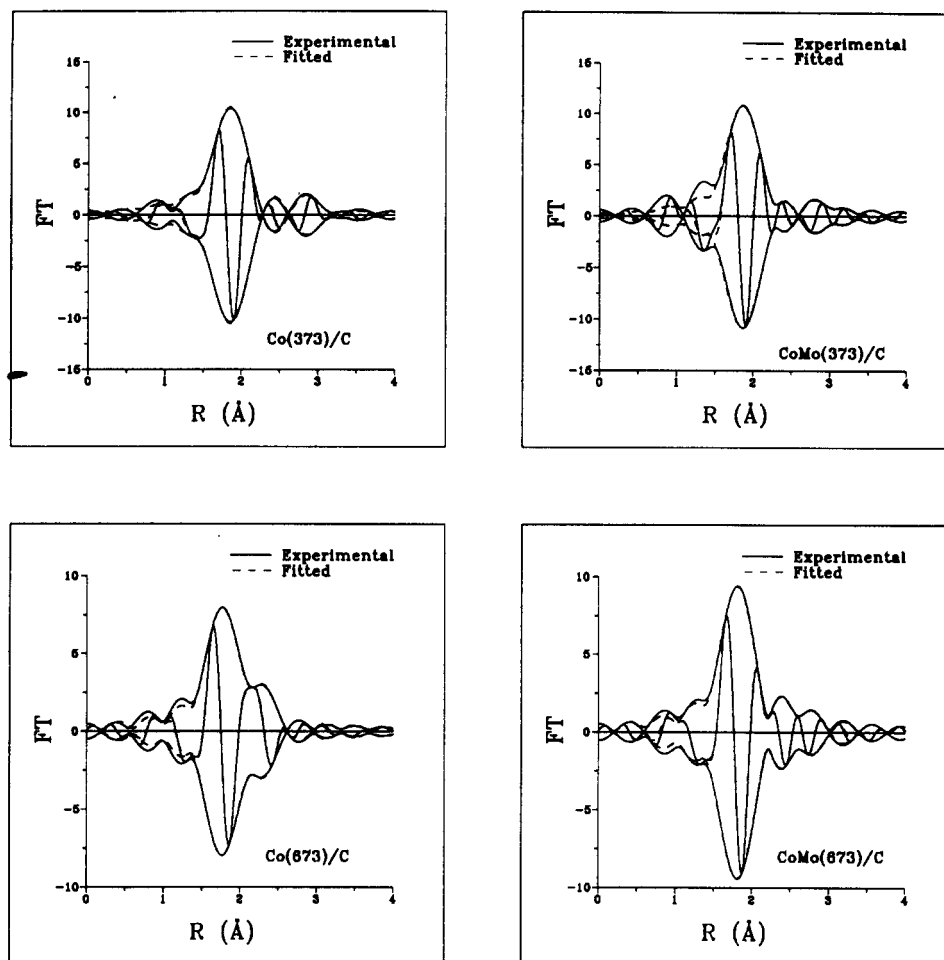
Figure 4. Absolute value and imaginary part of the FT spectra of the k^3-weighted EXAFS spectra and the fits with the parameters presented in Table II.
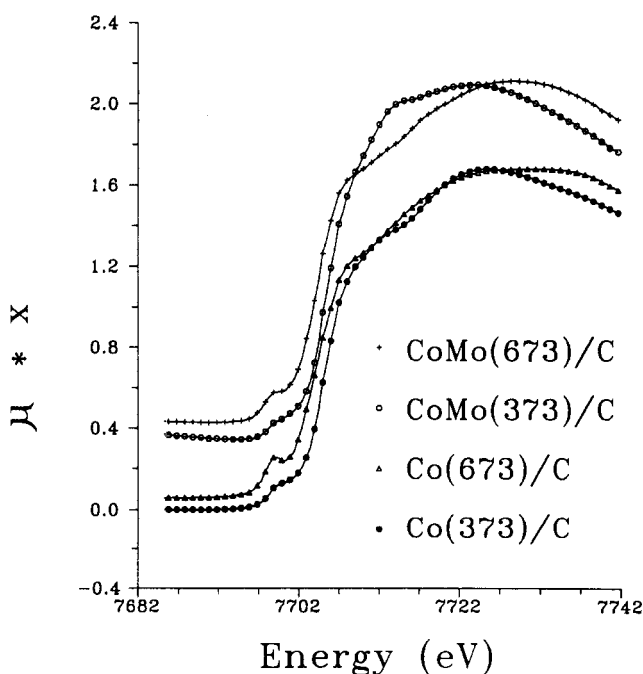

Figure 5. XANES region of the four examined samples. Each second data point is plotted.

Figure 6. MES spectra obtained on the four samples at 300 K.

distance from 2.25 to 2.20 Å. The Co–S(1) distance of 2.20 Å is in good agreement with that of the Co–S distance in tetrahedrally coordinated Co atoms in Co_9S_8. Also the observed Co–Co(1) distance of 2.50 Å is in good agreement with the value reported for Co_9S_8.[27] It is remarkable that the Co–Co(1) coor-
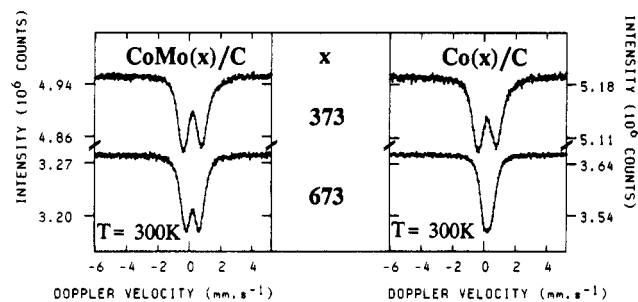
dination number has increased from 0.8 for Co(373)/C to 2.7 for Co(673)/C. Although the uncertainty in the Co–Co(1) coordination number is quite large, the observed increase is significant. It indicates that a strong sintering of the Co atoms has occurred. This might also explain the observed decrease of the coordination distances, as due to sintering the formation of small crystallites of cobalt sulfide has become possible. Because Co_9S_8 is the most stable cobalt sulfide under the present reaction conditions, it is likely that it will be formed. The Co–S(2) coordination at 2.8 Å agrees less well with the structure of Co_9S_8 where no Co–S atomic distance between 2.36 and 3.47 Å is found. However, as is seen from the small Co–Co(1) coordination number in the Co(673)/C catalyst and from the absence of a second Co–Co coordination, in our case the Co_9S_8 crystallites are very small. Also the relatively broad lines in the MES spectrum[15] indicate this. It might be possible that, because of this small particle size and because of a possible interaction with the support, a much smaller atomic distance than 3.47 Å can be found.

The first coordination of the CoMo(673)/C catalyst consists of sulfur with a coordination number of 5.1. This Co–S(1) co-

ordination number seems to be in disagreement with the observation of Bouwens et al.,[23] who found a coordination number of 6.2 for similar CoMo/C catalysts. It must be remembered, however, that EXAFS gives mean values for coordination numbers. Since the Co–Co(1) coordination at 2.6 Å is indicative for Co_9S_8, part of the Co atoms are fourfold surrounded by sulfur atoms. Thus, another part of the Co atoms must have six sulfur neighbors to arrive at an average coordination number of 5.1. This can also explain the size of the pre-edge peak in the absorption spectrum of the CoMo(673)/C catalyst. Although the size of the pre-edge peak for all catalysts is small, Figure 5 shows that the CoMo-(673)/C catalyst has a pre-edge which is in between those of Co(673)/C and of the catalysts sulfided at 373 K. In the Co-(673)/C catalyst the Co atoms are fourfold surrounded by sulfur, and consequently this catalyst shows a relative large pre-edge peak. Co(373)/C and CoMo(373)/C contain sixfold surrounded Co atoms, which give only a small pre-edge peak. The observation that the CoMo(673)/C catalyst has a pre-edge peak in between can be explained if part of the Co is fourfold surrounded by sulfur and part is sixfold surrounded. The Co–S(1) coordination of 5.1 for the CoMo(673)/C catalyst could also be explained by the model of Niemann et al.,[25] a fivefold sulfur-coordinated Co site in a tetragonal pyramid of sulfurs at the (1010) edge of MoS_2. However, the EXAFS results for the Co(373)/C, Co(673)/C, CoMo(373)/C, and CoMo(673)/C catalysts can only be explained in a consistent way as outlined in the foregoing. This is especially so if one considers that the Co–Co coordination at 2.6 Å in the CoMo(673)/C catalyst is indicative of Co_9S_8 type structures where the Co is fourfold coordinated with S.

Also in the second and the third coordination shell of the CoMo(673)/C catalyst substantial changes occurred due to the higher sulfiding temperature, which can be compared with the changes observed for the Co/C catalyst. It appears that the Co–Co(1) coordination distance and number decrease dramatically by sulfidation at 673 K. The second Co–Co(2) coordination in CoMo(373)/C disappears and is replaced by a Co–Mo(1) coordination. The Co–Co(1) distance (2.6 Å) is somewhat larger than that observed by Bouwens et al.[23] In addition, these authors found evidence for a second Co–Co coordination at 3.52 Å. The Co–Co distances of 2.53 and 3.52 Å which they obtained are indicative of Co_9S_8 (2.51 and 3.54 Å). The observed Co–Mo(1) distance of 2.8 Å in the CoMo(673)/C catalyst is in perfect agreement with the value obtained by Bouwens et al.[18] for Ni–Mo (Ni edge) and Mo–Ni (Mo edge) in Ni–Mo–S. Thus, in accordance with the findings of Bouwens et al.,[23] the EXAFS data suggest that a small part of the Co atoms are present as (slightly distorted) Co_9S_8, whereas the rest is located in a site in contact with the Mo. Bouwens et al.[23] have proposed a structural model for this site. In this model the Co atoms are situated on the MoS_2 edge, in a distorted sixfold sulfur coordination.

Discussion of the MES Results in Relation to the EXAFS Results. The MES spectra of the Co(373)/C and the CoMo(373)/C catalysts are indistinguishable. Moreover, their EXAFS spectra with respect to the first two coordination shells of Co–S(1) and Co–Co(1) are also equal. However, the EXAFS spectra differ with respect to the more distant neighbors. So, the similarity as indicated above means that MES is mainly sensitive to the first two coordination shells. This can be understood as follows. The QS measured in MES reflects the interaction of the electrical quadrupole moment of the nucleus (a constant) with the electrical field gradient (EFG) at the nucleus. The EFG originates from the charge distribution of the electrons of the atom itself and from charges on distant ions. These latter charges induce an EFG which depends on the distance (r) between the nucleus studied and the neighboring ions as $1/r^2$. Hence, the main contribution to the EFG, and therefore to the QS, will come from the nearest neighbors. Therefore, in the discussion these first two coordination shells will be emphasized. When this is applied to the 673 K sulfided samples, it follows that the QS is determined by the Co–S(1) coordination and the Co–Co(1) coordination.

The Co–S(1) and Co–Co(1) distances and the coordination numbers found for the Co(673)/C catalyst are in very good

agreement with the values reported for Co_9S_8. So, from the EXAFS data it may be concluded that small Co_9S_8-type structures are formed during sulfidation of the Co/C catalyst at 673 K. This appears to be conflicting with the MES results which indicate that no bulk Co_9S_8 is present in the Co(673)/C catalyst. However, it was reported by van der Kraan[37] that the MES parameters, viz., the QS value, of surface atoms can differ markedly from those of bulk atoms. In this way it can be understood why in the MES measurements of Co(673)/C the parameters of crystalline Co_9S_8 (QS = 0.26 mm/s[5]) are not found. From the FT spectra in Figure 2 it is clear that the Co_9S_8-type structures must be extremely small, because the ordering around the Co is restricted to 4 Å. Only the Co atoms in the center of the ultrasmall "crystallites" are in an almost crystalline Co_9S_8 environment and will give rise to a spectral contribution with QS = 0.26 mm/s. The other Co atoms, however, are present in a distorted Co_9S_8-type environment and this is reflected in the MES spectra by a much larger QS than 0.26 mm/s.

In comparing the results obtained for CoMo/C with those obtained for Co/C (Table II) we conclude that also in the former case the Co species tend to grow. Hence, the Co–S(1) coordination number and distance decrease. However, the deduced Co–S(1) coordination number (5.1) remains larger than the value for Co_9S_8. According to the interpretation of the pre-edge peaks in the XANES region Co is present in two different local environments. Some Co atoms are sixfold and some fourfold coordinated by sulfur. Following the model proposed by Bouwens et al.[23] the sixfold coordinated Co is present on edge positions of the MoS_2 crystallites. The fourfold coordinated Co is supposed to be present in a Co_9S_8-type structure. However, in the MES spectrum of the CoMo(673)/C catalyst no contribution of the characteristic MES spectrum of crystalline Co_9S_8 (QS = 0.26 mm/s) is observed, and the very low Co–Co(1) coordination number (0.6) observed for the CoMo(673)/C catalyst reveals at least that the eventually formed Co_9S_8-type structures must be very small. It was mentioned above that for such small particles the QS is expected to be much larger than 0.26 mm/s. The absence of the doublet characteristic for crystalline Co_9S_8, therefore, does not rule out the presence of very small Co_9S_8-type particles. These particles in the CoMo(673)/C catalyst must be much smaller than in the Co(673)/C catalyst. Although part of the Co is present in Co_9S_8-type structures, the sintering of these structures is strongly hindered by the presence of the MoS_2.

Concluding Remarks

Detailed structural information about sulfided Co(–Mo)/C catalysts has been obtained by performing EXAFS measurements on four catalysts with the same composition as their [57]Co containing counterparts which were previously characterized by MES. The S/N ratio of the EXAFS measurements is very good.

It turns out that the observed QS value in the MES spectrum is a measure for the dispersion of the cobalt sulfide present in the catalyst. Apparently the dispersion of the Co species in the catalysts is originally very high, both with and without Mo. In the 373 K sulfided CoMo/C catalyst the highly dispersed cobalt sulfide species has no interaction with the Mo which can be concluded from the absence of a Co–Mo coordination. Sulfidation at higher temperatures induces sintering of the cobalt sulfide phase. In the Co/C catalyst sintering is very easy because of the weak interaction of the cobalt sulfide particles with the inert carbon carrier. In the CoMo/C catalyst the MoS_2 strongly hinders the sintering of the cobalt sulfide phase. Part of the Co is present on edge positions of the MoS_2 and this Co turns out to be surrounded by six sulfur atoms. The rest of the Co is present in Co_9S_8-type structures but the MoS_2 strongly hinders sintering. The MES spectrum of these highly dispersed Co_9S_8-type structures turns out to have parameters which deviate markedly from the values for crystalline Co_9S_8, and which resemble the Co–Mo–S parameters if the structure is optimally dispersed.

References and Notes

(1) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979; p 411.

(2) Voorhoeve, R. J. H.; Stuiver, J. C. M. *J. Catal.* **1971,** *23,* 243.

(3) Farragher, A. L.; Cossee, P. In *Proceedings of the 5th International Congress on Catalysis, Palm Beach, 1972*; Hightower, J. W., Ed.; North-Holland: Amsterdam, 1973; p 301.

(4) Delmon, B. In *Proceedings of the 3rd International Conference on the Chemistry and Uses of Molybdenum, Ann Arbor, 1979*; Berry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Company: Ann Arbor, MI, p 73.

(5) Topsøe, H.; Clausen, B. S.; Candia, R.; Wivel, C.; Mørup, S. *J. Catal.* **1981,** *68,* 433.

(6) Wivel, C.; Candia, R.; Clausen, B. S.; Mørup, S.; Topsøe, H. *J. Catal.* **1981,** *68,* 453.

(7) Topsøe, H.; Candia, R.; Topsøe, N.-Y.; Clausen, B. S. *Bull. Soc. Chim. Belg.* **1984,** *93,* 783.

(8) Topsøe, H.; Clausen, B. S. *Appl. Catal.* **1986,** *25,* 273.

(9) Topsøe, H.; Topsøe, N.-Y.; Clausen, B. S. *12th Iberoam. Symp. Catal., Rio de Janeiro* **1990,** *2,* 762.

(10) Crajé, M. W. J.; de Beer, V. H. J.; van der Kraan, A. M. *Appl. Catal.* **1991,** *70,* L7.

(11) Vissers, J. P. R.; de Beer, V. H. J.; Prins, R. *J. Chem. Soc., Faraday Trans. 1* **1987,** *83,* 2145.

(12) De Beer, V. H. J.; Duchet, J. C.; Prins, R. *J. Catal.* **1981,** *72,* 369.

(13) Duchet, J. C.; van Oers, E. M.; de Beer, V. H. J.; Prins, R. *J. Catal.* **1983,** *80,* 386.

(14) Van der Kraan, A. M.; Crajé, M. W. J.; Gerkema, E.; Ramselaar, W. L. T. M.; de Beer, V. H. J. *Appl. Catal.* **1988,** *39,* L7.

(15) Van der Kraan, A. M.; Crajé, M. W. J.; Gerkema, E.; Ramselaar, W. L. T. M.; de Beer, V. H. J. *Hyp. Int.* **1989,** *46,* 567.

(16) Kampers, F. W. H.; Maas, T. M. J.; van Grondelle, J.; Brinkgreve, P.; Koningsberger, D. C. *Rev. Sci. Instrum.* **1989,** *60,* 2635.

(17) Cook, J. W.; Sayers, D. E. *J. Appl. Phys.* **1981,** *52,* 5024.

(18) Bouwens, S. M. A. M.; Koningsberger, D. C.; de Beer, V. H. J.; Louwers, S. P. A.; Prins, R. *Catal. Lett.* **1990,** *5,* 273.

(19) Teo, B. K.; Lee, P. A. *J. Am. Chem. Soc.* **1979,** *101,* 2815.

(20) Clausen, B. S.; Topsøe, H.; Candia, R.; Villadsen, J.; Lengeler, B.; Als-Nielsen, J.; Christensen, F. *J. Phys. Chem.* **1981,** *85,* 3868.

(21) Clausen, B. S.; Topsøe, H. *Hyp. Int.* **1989,** *47,* 203.

(22) Clausen, B. S.; Topsøe, H.; Candia, R.; Lengeler, B. *ACS Symp. Ser.* **1984,** *248,* 71.

(23) Bouwens, S. M. A. M.; van Veen, J. A. R.; Koningsberger, D. C.; de Beer, V. H. J.; Prins, R. *J. Phys. Chem.* **1991,** *95,* 123.

(24) Crajé, M. W. J.; de Beer, V. H. J.; van der Kraan, A. M. *Bull. Soc. Chim. Belg.* **1991,** *100,* 953.

(25) Niemann, W.; Clausen, B. S.; Topsøe, H. *Catal. Lett.* **1990,** *4,* 355.

(26) Louwers, S. P. A.; Prins, R. *J. Catal.* **1992,** *133,* 94.

(27) Rajamani, V.; Prewitt, C. T. *Can. Miner.* **1975,** *13,* 75.

(28) Elliot, N. *J. Chem. Phys.* **1960,** *33,* 903.

(29) Lundqvist, D.; Westgren, A. *Z. Anorg. Chem.* **1938,** *239,* 85.

(30) Buerger, M. J.; Robinson, D. W. *Proc. Natl. Acad. Sci. U.S.A.* **1955,** *41,* 199.

(31) Rajamani, V.; Prewitt, C. T. *Can. Miner.* **1974,** *12,* 253.

(32) Tremel, W.; Henkel, G. *Inorg. Chem.* **1988,** *27,* 3896.

(33) Baker, D. J.; Goodall, D. C.; Moss, D. S. *J. Chem. Soc., Chem. Commun.* **1969,** 325.

(34) Enemark, J. H.; Lipscomb, W. N. *Inorg. Chem.* **1965,** *4,* 1731.

(35) Tremel, W.; Kriege, M.; Krebs, B.; Henkel, G. *Inorg. Chem.* **1988,** *27,* 3886.

(36) Fleet, M. E. *Acta Crystallogr. B* **1972,** *28,* 1237.

(37) Van der Kraan, A. M. *Phys. Status Solidi (A)* **1973,** *18,* 215.

Uptake of Gas-Phase Aldehydes by Water Surfaces

J. T. Jayne,[†] **S. X. Duan, P. Davidovits,** *

Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02167

D. R. Worsnop, M. S. Zahniser, and C. E. Kolb

Aerodyne Research, Inc., Billerica, Massachusetts 01821 (Received: November 11, 1991; In Final Form: March 26, 1992)

The uptake of gas-phase formaldehyde and acetaldehyde by liquid water droplets was measured as a function of droplet pH and gas–droplet contact time and for formaldehyde also as a function of the sulfite ion density in the droplet. The mass accommodation coefficient for formaldehyde at 267 K is 0.020 ± 0.003. The mass accommodation coefficient for acetaldehyde at 267 K has a lower limit of 0.03, which is also our best estimate for its value. The uptake of formaldehyde is in accord with the liquid-phase solubility and reaction kinetics of the species. On the other hand, the uptake of acetaldehyde at short gas–droplet contact times is significantly greater than predicted by the calculations based on bulk-phase parameters. The time-dependent studies of the uptake suggest that the greater uptake is due to a chemisorbed surface complex at the gas–water interface. The implications of these results for atmospheric chemistry are examined. The small magnitudes of the uptake coefficients suggest that this parameter may be the limiting factor in the uptake rate of the aldehydes into cloud droplets. The chemisorbed surface species observed in the acetaldehyde experiments may explain the high measured concentrations of acetaldehyde in cloud water relative to the concentrations of formaldehyde.

1. Introduction

The study of the uptake of gas-phase aldehydes by aqueous surfaces is of interest from the point of view of basic chemistry as well as applied atmospheric chemistry. Aldehydes are released into the atmosphere as primary products of combustion and are also formed photochemically from various hydrocarbons.[1] The concentration of aldehydes in polluted atmospheres is high. For example, fog water collected in the urban areas of California coast contains formaldehyde concentrations[2] in the range 3–14 mg/L. The concentrations of other aldehydes such as acetaldehyde and benzaldehyde are comparable.[3] These species are toxic, and they

also play an active role in the chemistry of the atmosphere. As pointed out by Munger et al.[4] and Betterton and Hoffmann,[5] aldehyde–bisulfite adducts may tie up S(IV) in cloud and fog droplets and thereby retard the formation of sulfuric acid. Furthermore, photolysis of gas-phase CH_2O into HCO and H is a source of HO_2 which is an important, chemically active species in the atmosphere.[6]

Much of the atmospheric aldehyde chemistry occurs via heterogeneous processes inside the droplets of clouds and fogs. Therefore, a key to understanding the fate of aldehydes in the atmosphere involves the understanding of their interactions with atmospheric aqueous droplets. One fundamental parameter which determines the transfer rate of trace gases into atmospheric droplets is the mass accommodation (or sticking) coefficient, α,

[†] Present address: Department of Earth Atmosphere and Planetary Science, M.I.T., Cambridge, MA 02139.