X-RAY ABSORPTION STUDIES OF THE Ni ENVIRONMENT IN Ni-Mo-S

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The local environment of the Ni atoms in the Ni-Mo-S phase has been elucidated by Ni K-edge EXAFS and XANES measurements of carbon-supported sulfided Ni-Mo catalysts. The results show that the Ni atoms have a low sulfur coordination number (less than six). This is contrary to recent reports in which an octahedral-like sulfur coordination have been suggested. It is proposed that the Ni atoms in Ni-Mo-S are located at the $(10\bar{1}0)$ edges of the MoS_2 structure in square and tetragonal pyramidal type sites. These two types of sites can easily interconvert during sulfur addition/extraction and may as such be involved in the catalytic cycle.

1. Introduction

The catalytic activity of promoted Ni-Mo or Co-Mo hydrotreating catalysts is dominated by one type of structures, the so-called Ni-Mo-S or Co-Mo-S structures (see, e.g. ref. [1]). The Mo atoms in these structures were revealed by EXAFS to be present as small MoS_2-like domains [2] with the promoter atoms located along the edges of these structures [3,4]. The fact that the MoS_2 units–which have a layer structure–may be present as single S-Mo-S layers in the catalysts [5,6] rules out the early proposal by Farrager and Cossee [7] of edge intercalation between successive sulfur layers. In fact, the IR studies of NO adsorption on Co-Mo-S carried out by Topsøe and Topsøe [3] showed that the promoter atoms are located at the edges of the MoS_2 in the plane of the Mo atoms.

In spite of the progress made in identifying the active structure there still exists much debate in the literature on the precise location and detailed coordination geometry of the Ni (Co) atoms in these Ni-Mo-S (Co-Mo-S) structures. Based on EXAFS experiments at the Co K-edge of sulfided $Co-Mo/Al_2O_3$ catalysts, Clausen et al. [8] showed that the ligands nearest to the Co atoms in the Co-Mo-S structure are sulfur atoms with a Co-S distance of about 2.19 Å. In a subsequent study, Topsøe et al. [9] found the sulfur coordination number to be significantly

lower than six. This study confirmed the presence of a quite short Co-S distance (2.23 Å).

EXAFS studies of unsupported Co-Mo-S structures [10] also showed a low sulfur coordination number and a quite short Co-S distance. Recently, Bouwens et al. [11–13] have carried out extensive EXAFS and XANES studies on carbon and alumina supported Co-Mo and Ni-Mo catalysts. In many respects, the results agree with our earlier work (e.g. the presence of short Co-S (Ni-S) distances) but there are also a number of important differences. Notably, they report large coordination numbers for the carbon supported catalysts (e.g. 6.7 for Co-Mo/C). Based on these results and an analysis of the $1s \rightarrow 3d$ pre-edge peak they suggested octahedral (or recently trigonal prismatic [13]) sulfur coordination. Bouwens et al. attributed the high activity of carbon supported catalysts to the high sulfur coordination. Ledoux et al. [14,15] have recently given results which support in part the findings of Bouwens et al. since evidence for the presence of octahedrally coordinated Co atoms were obtained using solid state [59]Co NMR. Furthermore, these studies provided evidence for the presence of Co atoms in tetrahedral sulfur geometry which were proposed to be linked to the MoS_2 phase via the octahedral species.

In the present study we present both EXAFS and XANES studies of Ni-Mo/C catalysts and several Ni-S structural reference compounds with the aim of resolving the debate on the local coordination environment of the promoter atoms. Some of the preliminary EXAFS data were given in [16]. Carbon was chosen as a support in view of the previously observed differences between carbon and alumina supported catalysts. Furthermore, by using this support the interference from promoter atoms located in the support is avoided. To emphasize the quite narrow XANES region, which normally has a lot of fine structure, the absorption spectra have been obtained with a high energy resolution and a narrow step width between the data points.

2. Experimental

XANES and EXAFS spectra of several Ni-Mo/C catalysts and Ni-S structural reference compounds have been collected at DESY in Hamburg using the synchrotron radiation from the DORIS storage ring. The spectra were measured at the RÖMO-1 and RÖMO-2 EXAFS stations at HASYLAB using Si(311) monochromator crystals. The X-ray absorption measurements were carried out at room temperature in transmission mode using three N_2-filled ionization chambers in a row. In order to achieve accurate energy calibration, data of a catalyst sample and an energy reference sample were measured simultaneously. The sulfided catalysts were studied in situ by placing self-supporting wafers of pressed catalyst powder in specially designed cells equipped with X-ray transparent windows [8]. The catalyst samples were prepared as described in ref. [17] using

aqueous pore volume impregnation of the metals. The typical sample composition was 1 wt% Ni and 5 wt% Mo on a SC II coconut-type carbon with a specific surface area of about 900 m²/g. The catalysts were sulfided in a mixture of 2% H_2S/H_2 at 400°C for 2 hours and subsequently slowly cooled to room temperature in the same gas. The cells were then sealed off to keep the samples in the H_2S/H_2 gas mixture. Treatments like purging in an inert gas after sulfiding, which have been employed in other studies [11–13], have been avoided in this study in order to reduce the chance that traces of oxygen react with the sample surface. The absence of any oxidation was verified in each case by analyzing the edge features, which are highly sensitive to the presence of oxygen in the local environment of the promoter atoms [8,10]. Air-sensitive references like NiS_2, NiS, and Ni_3S_2 were also synthesized and measured in the in situ cells. Organometallic references were prepared according to procedures given in ref. [18] and enclosed in a polymer matrix [19]. Prior to the EXAFS measurements, the structures of the references were verified by X-ray diffraction. The EXAFS signal was extracted from the experimental data and subsequently analyzed on the basis of the plane-wave theory following the method described in ref. [20]. The data analysis in refs. [11–13] is based on the same formalism, and both analyses use experimental amplitudes and phases from structural references. In a recent work [21], it has been shown that the use of the curved-wave theory with theoretical amplitudes and phases gives very similar results for the major shell contributions.

3. Results and discussion

In fig. 1 the Ni K-edge XANES structures for the sulfided Ni-Mo/C catalyst, tetrahedral Ni_3S_2 and [Ph_4P][Ni(SPh)$_4$], square planar [Ni(EtXant)$_2$)], tetragonal pyramidal NiS (millerite structure), and octahedral [Me_3PhN][Ni(EtXant)$_3$], Ni(TTCN)$_2$, and NiS_2 are displayed. It has been shown (see, e.g. refs. [22,23]) that 3d metals with sulfur ligands in a non-centrosymmetric geometry exhibit a pronounced $1s \rightarrow 3d$ pre-edge peak. Normally, a small prepeak is found in octahedral structures, whereas e.g. tetrahedral or pentagonal structures show a large prepeak. From a comparison of the Ni-MO/C catalyst with the data for the reference compounds, it can be seen (fig. 2) that the catalyst has a prepeak which is significantly larger than the small prepeak of any of the octahedral references but comparable in height to the low symmetry tetrahedral and tetragonal pyramidal reference compounds. The present results and those given in ref. [9], are in contrast to the results reported by Bouwens et al. [12], who found that the $1s \rightarrow 3d$ pre-edge peak is similar for a sulfided Co-Mo/C catalyst and octahedral CoS_2 but much less intense than that of Co_9S_8 which is mainly tetrahedral. The reason for the different results is not clear, however, the data in ref. [12] were apparently recorded using a large step width between data points which could make a detailed evaluation difficult. In the present study, we find no support for
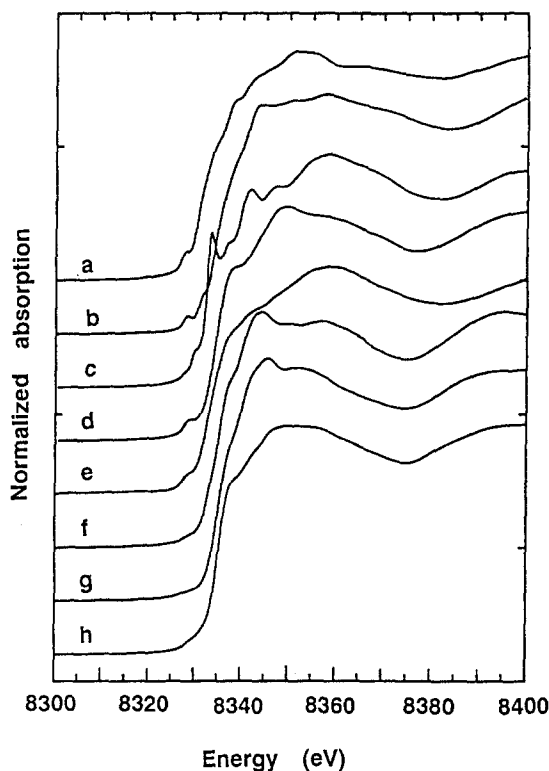
Fig. 1. Comparison of normalized Ni K-edge XANES spectra. a) tetrahedral Ni_3S_2, b) tetrahedral [Ph$_4$P][Ni(SPh)$_4$], c) square planar [Ni(EtXant)$_2$], d) tetragonal pyramidal NiS (millerite), e) sulfided Ni-Mo/C catalyst, and f) octahedral [Me$_3$PhN][Ni(EtXant)$_3$], g) octahedral Ni(TTCN)$_2$, and h) octahedral NiS_2.

a predominant octahedral coordination, rather the data are more in accordance with a lower sulfur coordination like that found in tetragonal pyramidal coordination geometry.

One should in general be cautious in drawing too firm conclusions from the XANES data since the intensity and shape of the 1s → 3d pre-edge peak, which is a forbidden transition for the isolated atom, is not only determined by the coordination symmetry but also by the interatomic distances and electronic configuration (degree of covalency, high spin/low spin, etc.). Furthermore, by comparing the XANES features of bulk structures with that of surface structures, like in the catalyst, one should keep in mind that possible surface relaxation effects may be present and this may also have an effect on the 1s → 3d pre-edge peak.

In view of the difficulties in reaching unambiguous conclusions solely from the XANES data, it is of importance to additionally analyze in detail the EXAFS structures thus taking advantage of the complementary information obtained from EXAFS and XANES. The Fourier transform of the *k*-weighted EXAFS
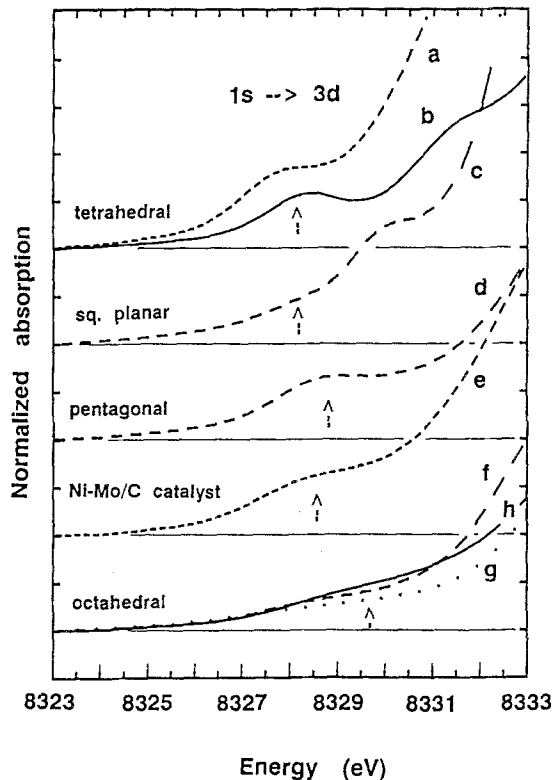
Fig. 2. Expanded view of the Ni K-edge region emphasizing the 1s → 3d pre-edge peak of the structures in fig. 1.

shows a single predominant peak due to the nearest-neighbor sulfur coordination shell around the Ni atoms [16]. The Fourier-filtered EXAFS of this peak has been fitted using experimental amplitudes and phases of the Ni-S pair in NiS_2. Amplitudes and phases were checked by successfully fitting the EXAFS of e.g. Ni_3S_2. With a simple single-atom (S), single distance model (i.e. one-shell model), we obtain a mean Ni-S distance of 2.21 Å ± 0.01 Å and an average sulfur coordination number of about 4.7 ± 0.5. In view of the uncertainties in the coordination number, these results are consistent with the presence of either a four coordinate (e.g. square planar-like) or a five coordinate (e.g. tetragonal pyramidal-like) structure. A distribution of configurations is of course also very probable.

The low sulfur coordination number agrees with our previous data as well as with the above assignments of our XANES results, but it is much lower than that found in the work by Bouwens et al. In agreement with the present assignment, it should be pointed out that the short mean Ni-S distance of 2.21 Å in the catalysts is much shorter than in typical octahedral Ni-S compounds (e.g. 2.40 Å for NiS_2 [24] and 2.43 Å for $[Me_3PhN][Ni(EtXant)_3]$ [18]). However, the distance in the

Table 1

Parameters from the fit of the k-weighted EXAFS of the sulfided Ni-Mo-S/C catalyst. Fitting range: 3.0 to 8.6 Å^{-1}. Typical errors: $\delta N = \pm 0.5$; $\delta R = \pm 0.01$ Å; errors in $\Delta\sigma^2$ are $\pm 30\%$ and errors in ΔE_0 are ± 1.0 eV.

	N	R(Å)	$\Delta\sigma^2$(Å^2)	ΔE_0(eV)[1]	χ^2
one shell Ni-S	4.7	2.21	$-0.6 \cdot 10^{-3}$	$+0.25$	0.0039
two shells Ni-S	3.7	2.23	$-0.37 \cdot 10^{-2}$	(0.25)	0.0027
	0.8	2.12	$-0.56 \cdot 10^{-2}$	(0.25)	

[1] Values in parenthesis have been kept fixed.

catalyst is very similar to the Ni-S distance of 2.24 Å in regular square planar [Ni(EtXant)$_2$] [25]. From the geometry of the MoS$_2$ units one would in fact expect a value of 2.24 Å for the Ni-S distance in a non-relaxed planar configuration at the (10$\bar{1}$0) edge of MoS$_2$. The Ni-S distance is somewhat shorter than the
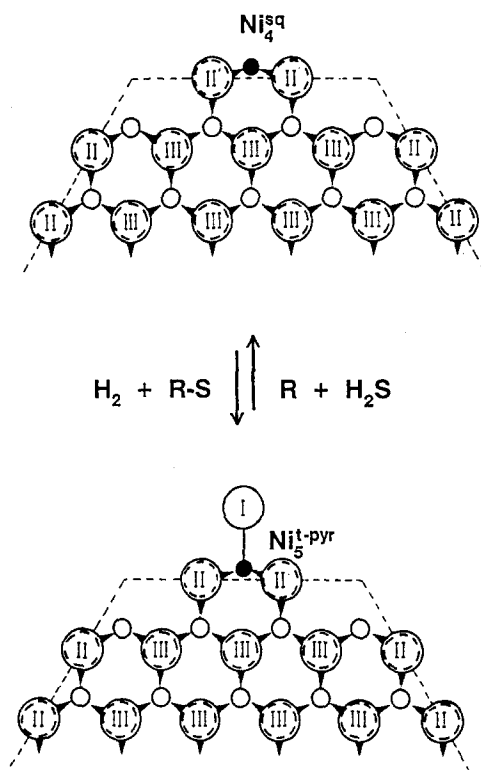

Fig. 3. Schematic drawing illustrating a possible change in local environments of the promoter atoms at the (10$\bar{1}$0) edge plane of MoS$_2$ from a four fold coordinated (Ni$_4^{sq}$) to a five fold coordinated site (Ni$_5^{t-pyr}$) during a HDS reaction cycle. The singly-bonded sulfur atom, I, is located in the plane of Mo. II and III denote doubly and triply bonded sulfur atoms which may be present both in the top and bottom sulfur layer.

typical Ni-S distance in tetrahedral compounds (e.g. 2.28 Å for Ni_3S_2). The presence of a regular MoS_2-type trigonal prismatic coordination can be ruled out from both the coordination number and Ni-S distance.

We found that a significant improvement in the fit of the EXAFS data could be obtained if we instead of a one-shell fit allowed two sulfur coordination spheres. The results showed (see table 1) that about four sulfur atoms are located at around 2.24 Å and about one sulfur atom at a significantly shorter distance (2.11 Å) as expected for a singly bonded sulfur atom (see, e.g. ref. [26]). These distances were found to agree nicely with the proposal [27] that the promoter atoms are most likely to occupy five coordinated sites at the ($10\bar{1}0$) edge planes of MoS_2 (Ni_5^{t-pyr}, see fig. 3). The five fold coordinated site (Ni_5^{t-pyr}) can be viewed as being formed from the four fold site (Ni_4^{sq}) by addition of sulfur. From a catalytic point of view such an easy interconversion is of course attractive and these sites may therefore be involved in the catalytic cycle as schematically indicated in the figure. This proposal needs to be investigated further and we do not rule out the possibility that during catalysis, sites with higher degree of coordinative unsaturation exist and are important. Also in the figure the addition of hydrogen is not shown but in this case it is envisaged to occur via the neighboring Mo sites.

4. Conclusion

In the present study we have presented several evidences that the promoter atoms in Ni-Mo-S (Co-Mo-S) have a sulfur coordination different from octahedral or trigonal prismatic. A consistent picture of the local structure of the Ni (Co) atoms in Ni-Mo-S (Co-Mo-S) is gained from EXAFS and XANES. The results (both distances and coordination numbers) are also consistent with the known Ni-S and Co-S coordination chemistry [27]. The short Ni-S distance, the relatively high intensity of the 1s → 3d pre-edge peak in the XANES spectra as well as the low sulfur coordination number all strongly suggest that the promoter atoms are not present in an octahedral coordination as suggested by Bouwens et al. [11–13].

The present results for carbon supported catalysts are quite similar to our earlier EXAFS results on alumina-supported Co-Mo-S structures [8,9]. This shows that the local environment of Ni (Co) in Ni-Mo-S (Co-Mo-S), contrary to the findings of Bouwens et al., does not depend much on the type of support. However, the present results are in agreement with earlier Mössbauer studies which showed that alumina and carbon supported Co-Mo-S structures have similar local environments [17,28,29].

It is therefore concluded that the activity differences between alumina and carbon supported catalysts is not related to very different types of coordination of the promoter atoms but is caused by the special interactions of the molybdenum with the alumina support giving rise to Type I Co-Mo-S structures [27–29]. For

carbon supported catalysts such interactions are absent and the more active Type II Co-Mo-S structures result [27–29]. From the present work, the most probable configuration of the promoter atoms is found to be five fold coordinated (tetragonal pyramidal) sites which can interconvert to a four fold square arrangement by removal of the sulfur atom with the short bond. Such coordinative unsaturated promoter sites (CUS) are attractive for adsorption of molecules and may, as indicated in fig. 3, be involved in the catalysis.

Acknowledgments

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