

## EXAFS STUDY OF THE LOCAL STRUCTURE OF Ni IN Ni-MoS<sub>2</sub>/C HYDRODESULFURIZATION CATALYSTS

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To study the local structure of the Ni promoter atom, the Ni and Mo K edge EXAFS spectra of Ni-MoS<sub>2</sub>/C hydrodesulfurization catalyst were measured in an in-situ EXAFS cell at 77 K. The Ni atom is situated in a square pyramid of five S atoms at a distance of 2.21 Å from the S atoms. In addition an EXAFS contribution due to a Mo atom at 2.82 Å from the Ni atom could be identified. This local structure indicates that the Ni atoms are situated on top of the S<sub>4</sub> squares at the MoS<sub>2</sub> edges in millerite-type Ni sites. The Ni atoms are situated in the planes of the Mo atoms and not in the intercalation plane midway between successive MoS<sub>2</sub> sandwich layers.

### 1. Introduction

Intensive research on the structure and role of the Co or Ni promoter atoms in hydrotreating catalysts has resulted in different views on the functions of the so-called promoter (Co, Ni) and catalyst (Mo, W) atoms [1]. Several structures and models have been published, such as the pseudo-intercalation or decoration model of Farragher and Cossee [2], the contact synergy model of Delmon c.s. [3], and the "Co-Mo-S" model of Topsøe et al. [4,5]. At present the Co-Mo-S model seems to be favored mainly because of the observation of a relationship between hydrodesulfurization activity and the amount of promoter in this Co-Mo-S phase [4].

The exact position of the Co or Ni atoms at the edges of the MoS<sub>2</sub> crystallites in the Co-Mo-S structure has still to be established, although informative EXAFS and XANES results have been published by Topsøe et al. [6] and by Bouwens et al. [7–10]. Since the beryllium windows of the in-situ EXAFS cell used in our investigations [7–10] contained a small amount of Ni, the Co EXAFS *k*-range which could be measured for Co-MoS<sub>2</sub> catalysts was somewhat limited. Therefore



we decided to study the Ni K edge EXAFS spectra of Ni-MoS<sub>2</sub>/C catalysts. With these catalysts the data analysis could be performed over an extended  $k$  range, which gave accurate information on the local Ni structure.

## 2. Experimental

EXAFS measurements were carried out at liquid nitrogen temperature on a freshly in-situ sulfided Ni-MoS<sub>2</sub>/C (1.5 wt% Ni, 7.6 wt% Mo) catalyst on EXAFS station 9.2 at the SRS in Daresbury, England. The catalyst was prepared according to the recipe described by Van Veen et al. [11] by aqueous pore volume impregnation of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> and NTA on Norit RX3-extra carbon (1190 m<sup>2</sup> · g<sup>-1</sup>, 1.0 cm<sup>3</sup> · g<sup>-1</sup>). Van Veen et al. proved [11] that the equivalent Co-Mo/C catalyst, prepared according to the same recipe, contains Co exclusively in the so-called 'Co-Mo-S' structure, with all Co atoms around the MoS<sub>2</sub> edges and no separate Co<sub>9</sub>S<sub>8</sub> or Co in the support [12]. The catalyst precursor was dried and pressed into a self-supporting disk with a thickness  $x$  such that  $\mu x \sim 2.5$  at the Ni or Mo K edge ( $\mu$  is the X-ray absorption coefficient). The catalyst disk was sulfided in an in-situ cell with 10% H<sub>2</sub>S in H<sub>2</sub> at a flow rate of 60 ml · min<sup>-1</sup> under atmospheric pressure. The temperature was linearly increased from room temperature to 673 K with 2 K · min<sup>-1</sup> and kept at 673 K for 1 h. Thereafter the catalyst was purged with He for 0.5 h at 673 K and cooled to room temperature under flowing He. The H<sub>2</sub> and He gases were purified by oxygen and water traps. To obtain references for the Ni-S, Ni-Ni and Ni-Mo absorber-scatterer pairs the Co and Ni EXAFS spectra of CoS<sub>2</sub>, NiO and [P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>Ni(MoS<sub>4</sub>)<sub>2</sub> (obtained from Dr. F. Bauman, University of Bielefeld, W.-Germany) were measured, respectively.

## 3. Results

The EXAFS functions of the catalyst and reference compounds were obtained from the X-ray absorption spectra by background subtraction and normalization by division by the Ni absorption edge height. To obtain phase shifts and backscattering amplitudes for the Ni-S, Ni-Ni and Ni-Mo pairs the EXAFS spectra of the reference compounds were Fourier transformed over as large a  $k$  range as possible. To avoid cut-off effects  $k_{\min}$  and  $k_{\max}$  were chosen in nodes of the EXAFS functions ( $k = 2.71\text{--}11.82 \text{ \AA}^{-1}$  for CoS<sub>2</sub>, 2.43–14.50 for NiO and 2.94–12.36 for [P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]<sub>2</sub>Ni(MoS<sub>4</sub>)<sub>2</sub>). An inverse transformation over a limited  $r$  range gave the EXAFS function of the desired single shell absorber-scatterer pair. Phase shifts and backscattering amplitudes for the Mo-S and Mo-Mo pairs were taken from the Mo K EXAFS spectrum of MoS<sub>2</sub> [9].



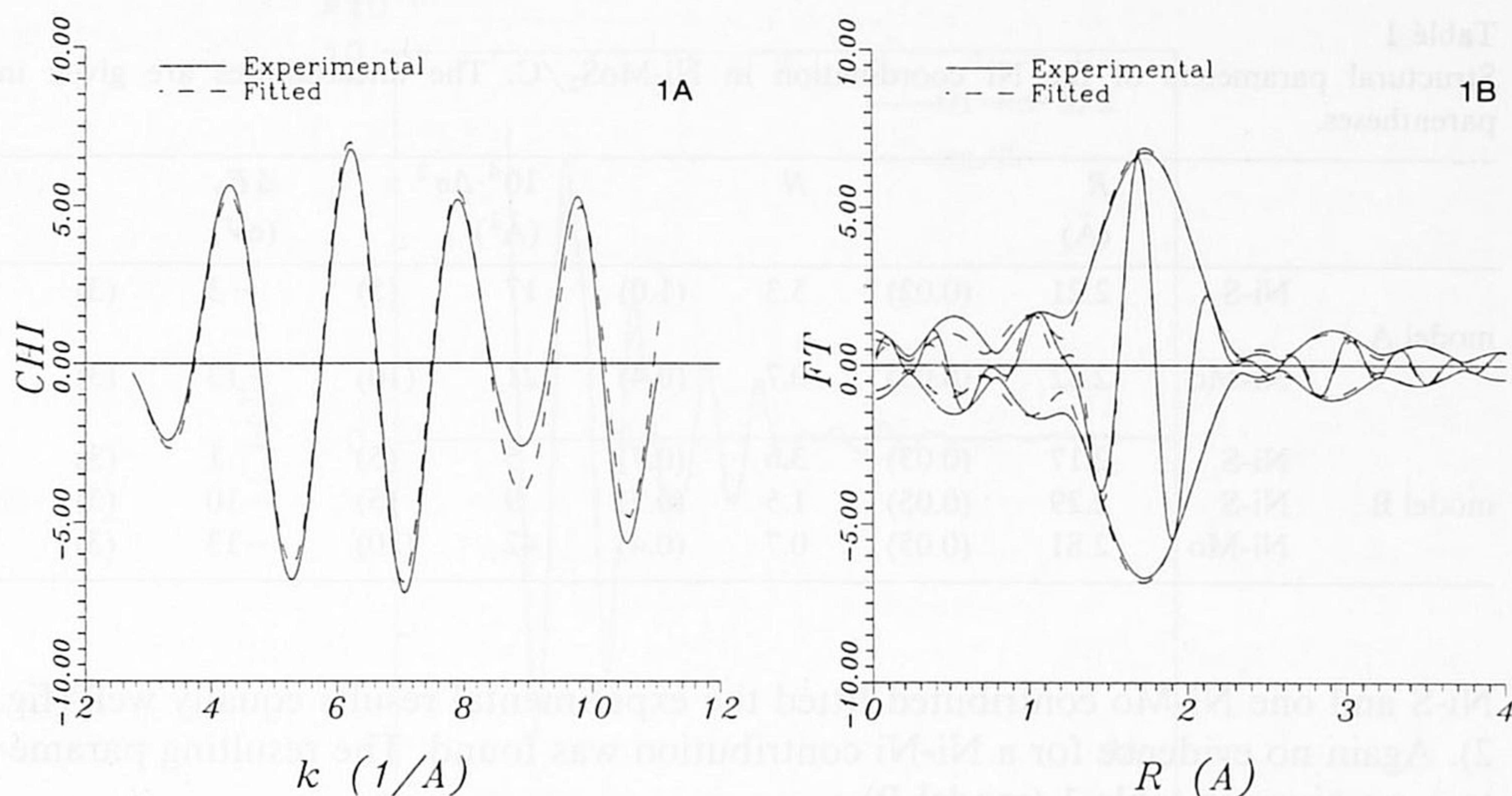


Fig. 1. Comparison of the experimental Ni K EXAFS spectrum (solid line) of Ni-MoS<sub>2</sub> (1.5 wt% Ni, 7.6 wt% Mo) on Norit RX3-extra activated carbon with the theoretical spectrum (dashed line) based on one Ni-S and one Ni-Mo contribution. A. EXAFS function (solid line) obtained after  $k^3$ -weighted Fourier transformation ( $k = 3.19\text{--}11.18 \text{ \AA}^{-1}$ ) and inverse Fourier transformation ( $r = 0.52\text{--}3.35 \text{ \AA}$ ) of the experimental spectrum, and the sum of the calculated Ni-S and Ni-Mo contributions (dotted line). B. Imaginary and absolute  $k^3$ -weighted Fourier transforms of the experimental EXAFS function (solid line) and the sum of the calculated Ni-S and Ni-Mo contributions (dotted line).

In order to remove higher shell contributions and contributions due to low and high frequency noise the Ni EXAFS spectrum of the Ni-MoS<sub>2</sub>/C catalyst was Fourier transformed over the interval  $k = 3.1\text{--}11.18 \text{ \AA}^{-1}$  ( $k^3$  weighing) and inverse Fourier transformed over the range  $R = 0.52\text{--}3.35 \text{ \AA}$ . A  $k^1$  and  $k^3$  weighted fit was performed on the spectrum thus obtained. In the analysis it was first assumed that there were three Ni-X contributions, namely Ni-S, Ni-Ni and Ni-Mo coordinations. The EXAFS spectrum of the Ni-MoS<sub>2</sub>/C catalyst could be fitted very well with Ni-S and Ni-Mo contributions only, without any Ni-Ni contribution. Figure 1A shows the comparison between the EXAFS function (solid line) and the sum of the Ni-S and Ni-Mo contributions (dotted line), while fig. 1B shows the comparison between the imaginary and absolute  $k^3$ -weighted Fourier transform of the experimental EXAFS function (solid line) and the sum of the Ni-S and Ni-Mo contributions. The resulting parameters are given in table 1 (model A). Since the analysis showed that the Ni atoms are surrounded by 5 sulfur atoms it seemed more logic to assume that there are actually two separate Ni-S distances, because the majority of 5-fold coordinated complexes have a trigonal bipyramidal or square pyramidal structure. Therefore the condition of only one Ni-S distance was relaxed to two Ni-S distances. The model with two



Table 1

Structural parameters of the Ni coordination in Ni-MoS<sub>2</sub>/C. The uncertainties are given in parentheses.

		$R$ (Å)		$N$		$10^4 \cdot \Delta\sigma^2$ (Å <sup>2</sup> )		$\Delta E_0$ (eV)	
model A	Ni-S	2.21	(0.02)	5.3	(1.0)	17	(5)	-3	(3)
	Ni-Mo	2.82	(0.05)	0.7	(0.4)	21	(10)	-13	(3)
model B	Ni-S	2.17	(0.03)	3.6	(0.7)	5	(5)	1	(3)
	Ni-S	2.29	(0.05)	1.5	(0.7)	9	(5)	-10	(3)
	Ni-Mo	2.81	(0.05)	0.7	(0.4)	42	(20)	-13	(3)

Ni-S and one Ni-Mo contributed fitted the experimental results equally well (fig. 2). Again no evidence for a Ni-Ni contribution was found. The resulting parameters are given in table 1 (model B).

The Mo EXAFS spectrum of the Ni-MoS<sub>2</sub>/C catalyst was  $k^3$ -Fourier transformed over the range  $k = 3.2-16.0 \text{ \AA}^{-1}$ , and inverse Fourier transformed from 1.0 to 3.2 Å. The resulting EXAFS function was fitted with Mo-S, Mo-Mo and Mo-Ni reference functions. The Mo-Ni functions were obtained from the Mo K EXAFS spectrum of  $[\text{P}(\text{C}_6\text{H}_5)_4]_2\text{Ni}(\text{MoS}_4)_2$  and the fitting was done in  $k$  space and  $R$  space ( $k^1$  as well as  $k^3$  weighted). In fig. 3 the Mo EXAFS spectrum of the Ni-MoS<sub>2</sub>/C catalyst and its Fourier transform magnitude are compared with

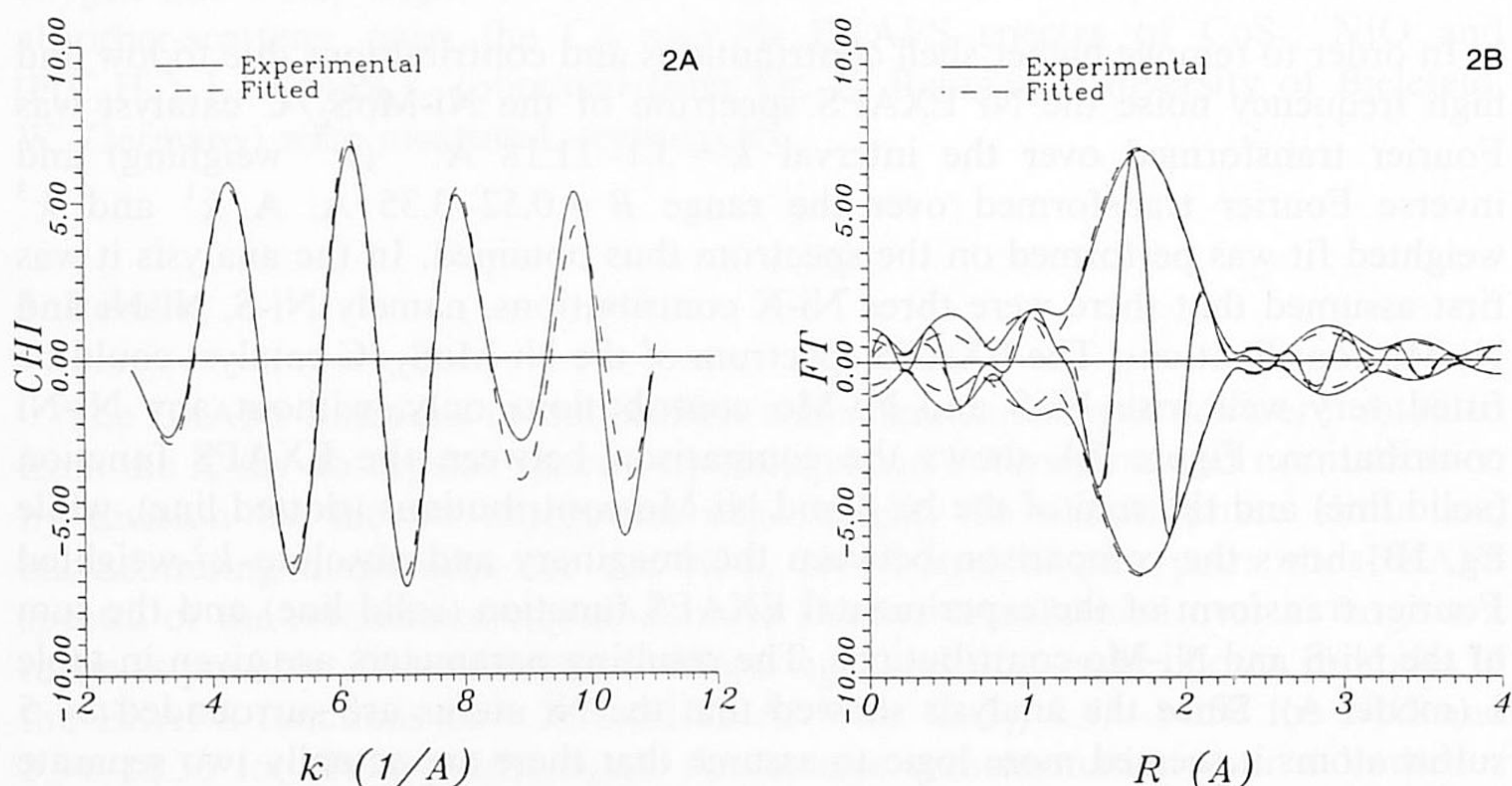


Fig. 2. Comparison of the experimental Ni K EXAFS spectrum (solid line) of Ni-MoS<sub>2</sub>/C (Norit RX3-extra) with the theoretical spectrum (dashed line) based on two Ni-S contributions and one Ni-Mo contribution. A. In  $k$  space (see caption to fig. 1). B. In  $r$  space (see caption to fig. 1).



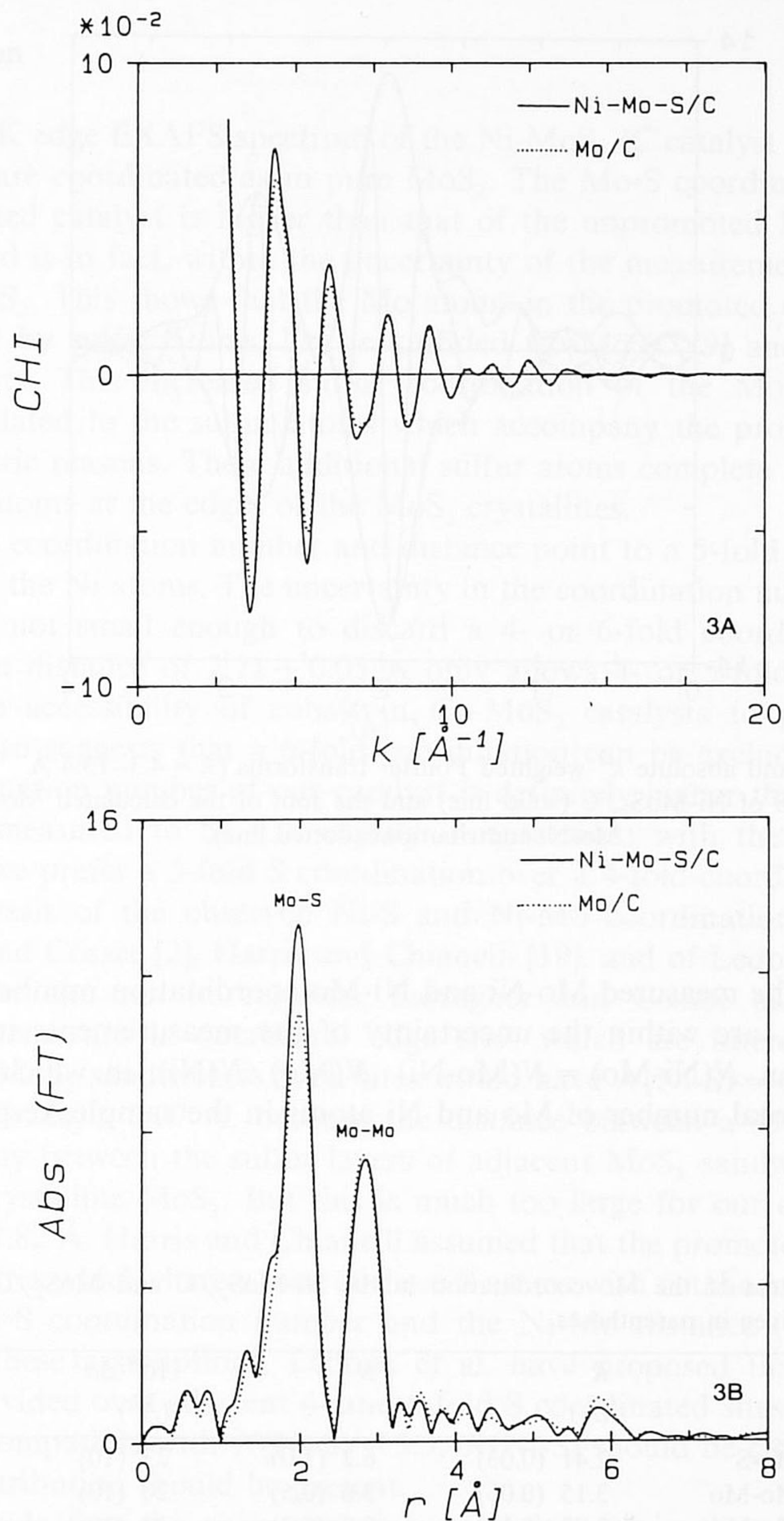


Fig. 3. Comparison of the Mo K EXAFS of Ni-MoS<sub>2</sub>/C with that of MoS<sub>2</sub>/C. A. Experimental EXAFS. B. Fourier transform magnitudes ( $k^3$ ,  $k = 3.2$ – $16$   $\text{\AA}^{-1}$ ).

those of an unpromoted MoS<sub>2</sub>/C catalyst. The results of the data analysis are presented in fig. 4 and in table 2. The good signal to noise ratio and the extended  $k$  range of the Mo EXAFS data allowed us to unequivocally detect the Mo-Ni



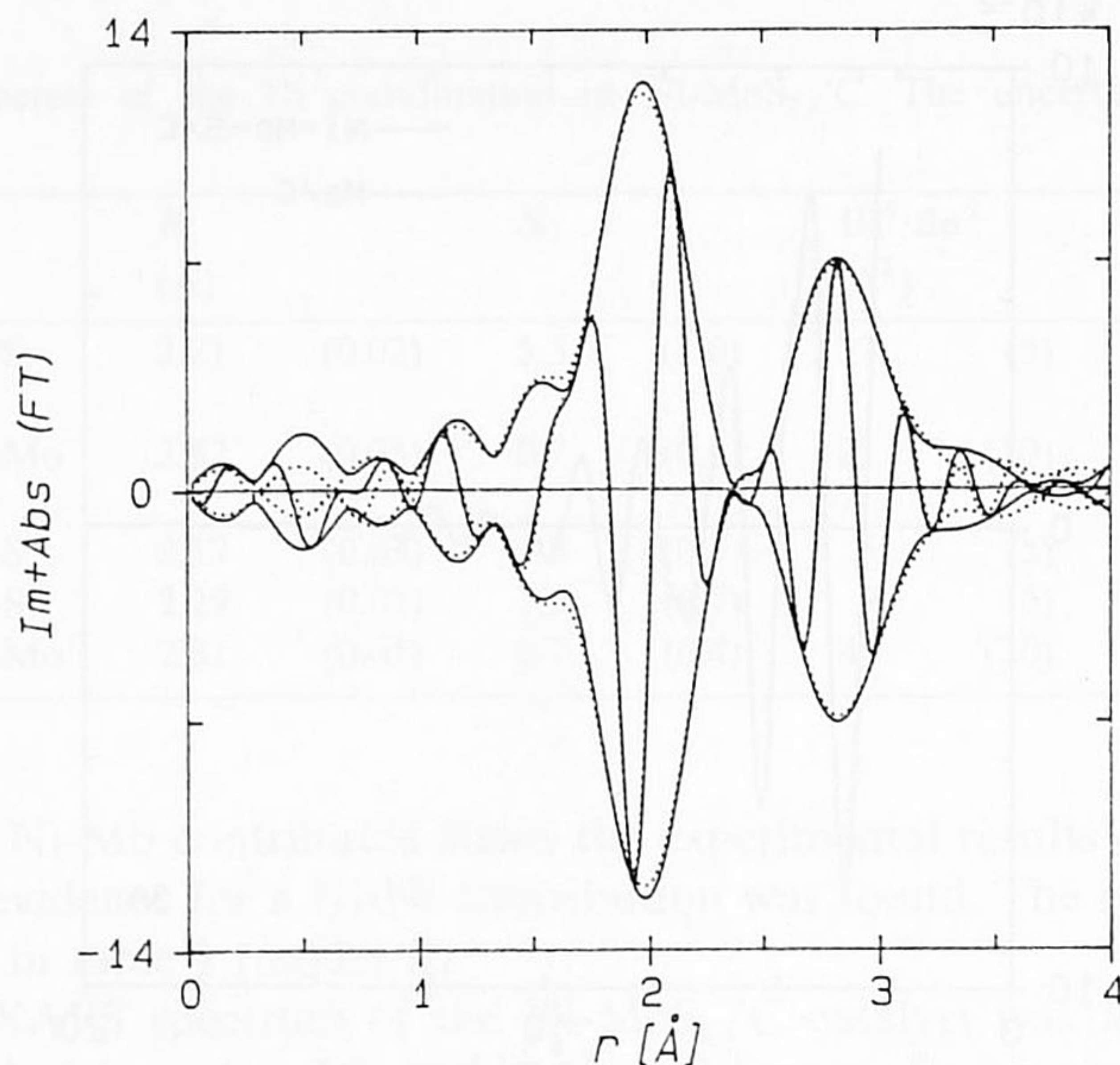


Fig. 4. Imaginary and absolute  $k^3$ -weighted Fourier transforms ( $k = 4.3\text{--}13.4 \text{ \AA}^{-1}$ ) of the experimental Mo EXAFS of Ni-MoS<sub>2</sub>/C (solid line) and the sum of the calculated Mo-S, Mo-Mo and Mo-Ni contributions (dotted line).

coordination. The measured Mo-Ni and Ni-Mo coordination numbers of 0.3 and 0.7 respectively, are within the uncertainty of the measurements in accordance with the relation  $N(\text{Ni-Mo}) = N(\text{Mo-Ni}) \cdot N(\text{Mo})/N(\text{Ni})$ , in which  $N(\text{Mo})$  and  $N(\text{Ni})$  are the total number of Mo and Ni atoms in the sample, respectively.

Table 2

Structural parameters of the Mo coordination in the Ni-MoS<sub>2</sub>/C and MoS<sub>2</sub>/C catalysts. The uncertainties are given in parentheses.

Ni-MoS <sub>2</sub> /C	$R$ (Å)	$N$	$10^4 \cdot \Delta\sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)
Mo-S	2.41 (0.03)	6.2 (1.0)	23 (10)	3 (3)
Mo-Mo	3.15 (0.05)	3.0 (0.5)	20 (10)	2 (3)
Mo-Ni	2.83 (0.10)	0.3 (0.3)	19 (10)	0 (3)
MoS <sub>2</sub> /C				
Mo-S	2.41 (0.03)	5.2 (1.0)	19 (10)	2 (3)
Mo-Mo	3.15 (0.05)	2.7 (0.5)	17 (10)	1 (3)



#### 4. Discussion

The Mo K edge EXAFS spectrum of the Ni-MoS<sub>2</sub>/C catalyst revealed that the Mo atoms are coordinated as in pure MoS<sub>2</sub>. The Mo-S coordination number of this promoted catalyst is higher than that of the unpromoted MoS<sub>2</sub>/C catalyst (table 2) and is in fact, within the uncertainty of the measurement, equal to that in bulk MoS<sub>2</sub>. This shows that the Mo atoms in the promoted catalyst are fully coordinated by sulfur atoms, like in sulfided Co-Mo/C [9] and Co-Mo/Al<sub>2</sub>O<sub>3</sub> [13] catalysts. This increased sulfur coordination of the Mo atoms is most probably related to the sulfur atoms which accompany the promoter atoms for stoichiometric reasons. These additional sulfur atoms complete the coordination of the Mo atoms at the edges of the MoS<sub>2</sub> crystallites.

The Ni-S coordination number and distance point to a 5-fold sulfur coordination around the Ni atoms. The uncertainty in the coordination number ( $5.3 \pm 1.0$ ) is certainly not small enough to discard a 4- or 6-fold coordination, but the coordination distance of  $2.21 \pm 0.05$  Å only allows 4- or 5-fold S coordination [14,15]. The accessibility of cobalt in Co-MoS<sub>2</sub> catalysts to probe molecules [5,16–18] also suggests that a 6-fold coordination can be excluded. Because the Ni-S coordination number of our catalyst is definitely higher than that of Ni<sub>3</sub>S<sub>2</sub> (which we measured to be 4.0, exactly in agreement with the tetrahedral site symmetry) we prefer a 5-fold S coordination over a 4-fold coordination.

On the basis of the observed Ni-S and Ni-Mo coordination the models of Farragher and Cossee [2], Harris and Chianelli [19], and of Ledoux et al. [20] for the promoter site can be rejected. Farragher and Cossee assumed that the promoter atoms are in octahedral edge sites which are intercalated between subsequent MoS<sub>2</sub> sandwiches. Such sites would have  $N(\text{Ni-S}) = 6$ ,  $R(\text{Ni-S}) \geq 2.3$  Å and  $R(\text{Ni-Mo}) \geq 3.07$  Å, because the distance between a Mo layer and the plane midway between the sulfur layers of adjacent MoS<sub>2</sub> sandwiches is already 3.07 Å in crystalline MoS<sub>2</sub>. But this is much too large for our observed Ni-Mo distance of 2.82 Å. Harris and Chianelli assumed that the promoter atoms occupy octahedral sites which share a face of three S atoms with octahedral Mo sites. The observed Ni-S coordination number and the Ni-Mo distance (2.82 Å) do not agree with these assumptions. Ledoux et al. have proposed that the promoter atoms are divided over adjacent 4- and 6-fold S coordinated sites. Although such a model is compatible with  $N(\text{Ni-S}) = 5.3$ ,  $R(\text{Ni-S})$  should be close to 2.3 Å and a Ni-Ni contribution should be present.

We conclude that the promoter atoms are situated in the plane of the Mo atoms, as originally suggested by Ratnasamy and Sivasanker [21] and Topsøe et al. [4,5]. Our EXAFS results (table 1) can be fitted with a model as presented in fig. 5. In this model the Ni atom is attached to the square face of a trigonal sulfur prism and has an additional fifth S ligand in the apical position. The Mo atoms in the nearby trigonal sulfur prisms account for the observed Ni-Mo EXAFS contribution. Along the (10 $\bar{1}$ 0) and ( $\bar{1}$ 010) MoS<sub>2</sub> edges, which one obtains by



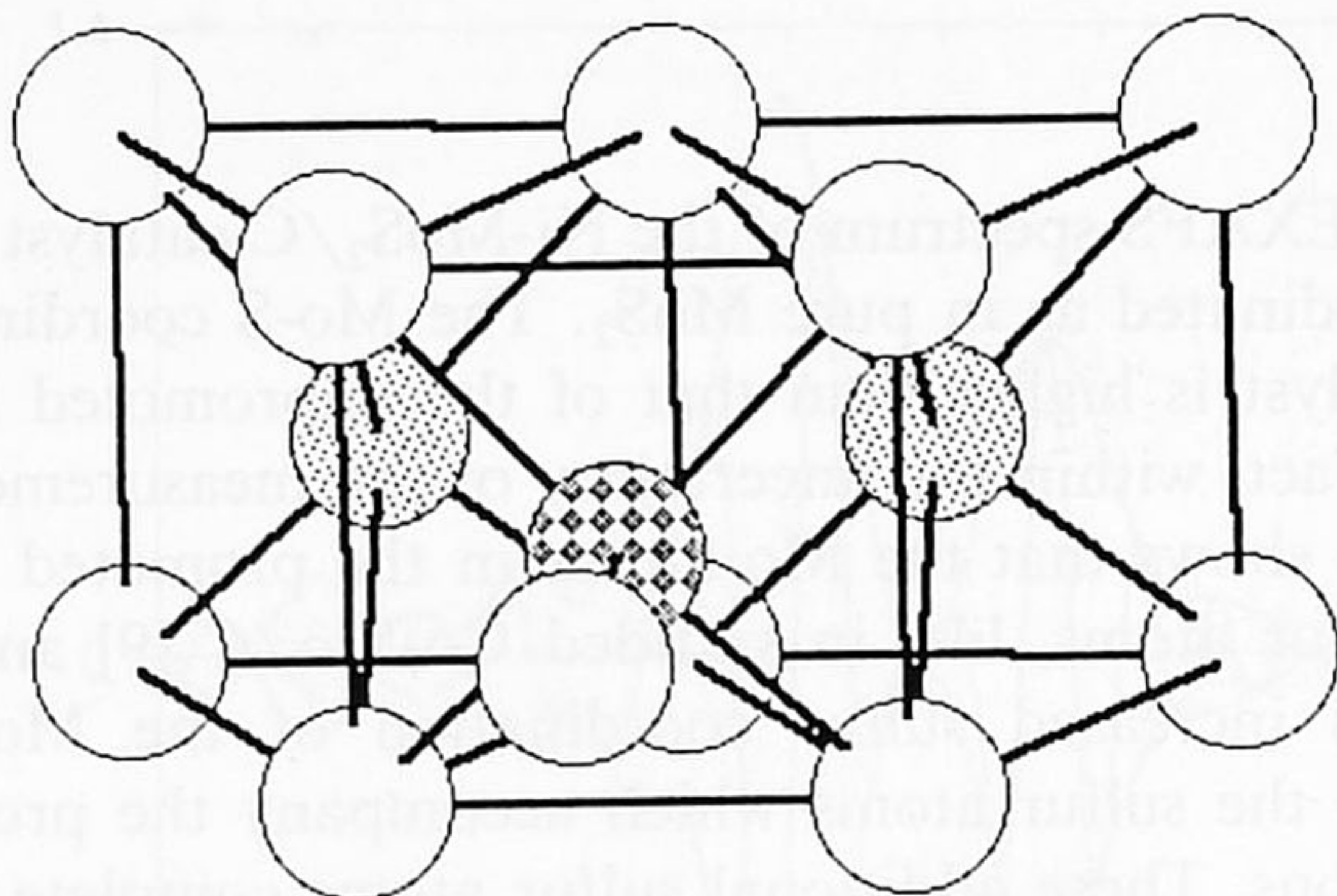


Fig. 5. Model of the local Ni structure in Ni-MoS<sub>2</sub>/C.

cleaving a MoS<sub>2</sub> crystal along the *c* axis and by applying the criterion of minimum charge separation [22], there are sites which have the required local structure for such a Ni atom (fig. 6A). But there are also Mo sites (the Ni atom is supposed to assume a Mo position along the edge) with a different structure. If the Ni atoms were to occupy the various types of edge sites as represented in fig. 6A, our EXAFS results would be difficult to understand. Namely, if the Ni atoms were distributed over several sites with different geometry and coordination one would expect much larger Debye Waller factors and/or small (apparent) coordination numbers, because of the interference between slightly different coordination distances [23]. But as fig. 6B demonstrates, a slight reconstruction of the 'original' MoS<sub>2</sub> edges [2] gives an edge surface in which all Mo (and thus Ni) surface atoms have the same local structure. They are all attached to a square of S atoms and have one or two neighbouring Mo atoms. This structure explains our results very well if it is further assumed that a fifth sulfur atom is attached to the Ni atom in the apical position. To obtain electrical neutrality two of the five ligands should be SH<sup>-</sup> groups. Only, the Ni-Mo coordination number would have been expected to be equal to 1 to 2. We have indeed observed values of 1.4, 1.5 and 2.3 for N(Co-Mo) in the equivalent Co-MoS<sub>2</sub> structures supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and C, respectively [10,13]. Why the M-Mo coordination number approaches 2 for the Co promoted catalysts, while it is about 1 for the Ni promoted catalyst, is not clear. It might be that there is a spread in the Ni-Mo distance, leading to some loss in intensity [23]. It should also be noted that the absolute uncertainties in the coordination numbers of higher shells can be substantial [24].

Goniometric calculations based on the observed Ni-S and Ni-Mo distances as presented in model A in table 1 and depicted in fig. 5, indicate that the Ni atom and the four edge S atoms are shifted from their 'bulk-like' positions. Actually, the Ni-S and Ni-Mo distances do not suffice to ascertain the position of the S atoms. Since the Mo-S distance in Ni-MoS<sub>2</sub>/C is equal to that in bulk MoS<sub>2</sub>, and



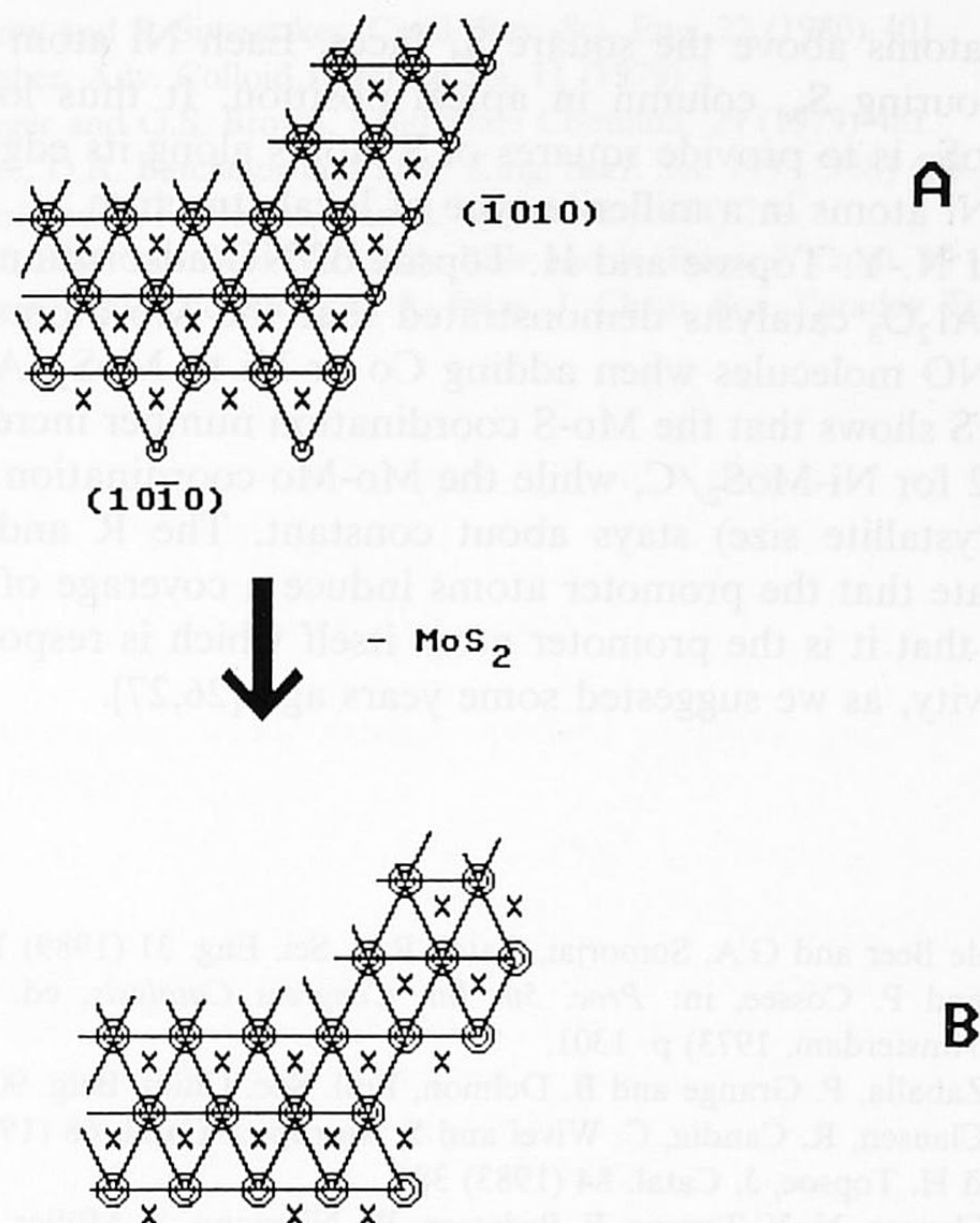


Fig. 6. A. Top-view of the unreconstructed (1010) and (1010) edges of a single slab of MoS<sub>2</sub>. B. Top-view of a reconstruction of the (1010) and (1010) edges of a single slab of MoS<sub>2</sub>. × Mo (or Ni at the edges). ○ single S atom. ⊙ two S atoms on top of each other.

the Debye Waller factor is not very large, we have assumed that the Mo-S distances at the edge are equal to the Mo-S bulk value. With the additional assumption that the four edges of the S<sub>4</sub> are equally contracted (and thus induce the least amount of stress on the S-S distances), it is calculated that the S<sub>4</sub> square has contracted by 0.10 Å (3%) along its edges and has moved outwardly by 0.04 Å compared to the unreconstructed bulk-like position. The Ni atom is located 0.47 Å above this S<sub>4</sub> square. This position differs considerably from the position which a Mo atom would occupy if it would be attached to the S<sub>4</sub> square and if two additional S atoms were added to complete the S<sub>6</sub> trigonal prism. The fact that the Ni atom is only 0.47 Å above the S<sub>4</sub> square (0.51 Å above the position of an unreconstructed S<sub>4</sub> plane) and the Mo atom 0.91 Å, is in agreement with the fact that the Ni atom has only one additional S ligand, while the Mo atom has two additional S ligands.

The observed 5-fold sulfur coordinated Ni structure is reminiscent of the NiS millerite structure [25], which can be considered to consist of triangular S<sub>3n</sub>



columns with Ni atoms above the square S<sub>4</sub> faces. Each Ni atom has a fifth S atom of a neighbouring S<sub>3n</sub> column in apical position. It thus looks as if the function of the MoS<sub>2</sub> is to provide squares of S atoms along its edges and in this way stabilize the Ni atoms in a millerite type of local structure.

The IR study of N.-Y. Topsøe and H. Topsøe of NO adsorption on Co-MoS<sub>2</sub> and Ni-MoS<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub> catalysts demonstrated that the Mo atoms become less accessible to the NO molecules when adding Co or Ni to MoS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [5]. Our Mo K edge EXAFS shows that the Mo-S coordination number increases from 5.2 for MoS<sub>2</sub>/C to 6.2 for Ni-MoS<sub>2</sub>/C, while the Mo-Mo coordination number (and thus the MoS<sub>2</sub> crystallite size) stays about constant. The R and the EXAFS studies thus indicate that the promoter atoms induce a coverage of the Mo edge atoms, suggesting that it is the promoter atom itself which is responsible for the high catalytic activity, as we suggested some years ago [26,27].

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Supported palladium-silver oxide catalyst, methane oxidation, diffusion control, ceramic wall reactor, reactor configuration

Supported palladium-silver oxides were used as catalysts for the partial oxidation of methane by molecular oxygen in a tubular reactor with ceramic wall separation. The ceramic wall controls the supply of the catalyst bed. The results indicate that the reactor will provide the first experimental step in methane oxidation: C, H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, CO, and H<sub>2</sub>O were obtained at intermediate pressures 300°C. At this temperature any contribution from homogeneous gas phase reaction can be ruled out.

## 1. Introduction

Coupling methane catalytically to form ethane and ethene is currently the subject of considerable research interest. Several research groups have concentrated their efforts in this area after the first report of Keller and Bhasin [1]. Lunsford et al. [2-4] have demonstrated that MgO and CaO, when promoted with nickel oxide, catalytically couple methane to ethane in the presence of oxygen. The Union Carbide work [1] describes a broad screening program involving single metal oxides. The Lyon work [5] investigated a multimetal oxide catalyst system containing a noble metal. The more promising catalysts include some members of the lanthanide oxide series [6,7] as well as a number of metal oxides promoted with group IA elements [8-10]. A major feature of these oxides is that they only became active for carbon-carbon bond forming reaction at high temperatures (> 700°C) and at such temperatures contribution from homogeneous gas phase reaction becomes significant [11,12]. Therefore fundamentally it is important to find a catalytic system capable of achieving considerable conversion and selectivity to C<sub>2</sub> hydrocarbons under moderate conditions. Recently Thampi et al. [13] have used a supported Pd catalyst and showed that it was able to catalyze this reaction at moderate temperatures (i.e. 315-400°C).