EXAFS INVESTIGATIONS OF Fe-, Ni-, Co- AND Cu- $MoS_2/\gamma\text{-}Al_2O_3$ HYDRODESULPHURIZATION CATALYST SYSTEMS **

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In-situ EXAFS studies have been carried out on several transition metal (T)-MoS_2 (T = Fe, Co, Ni or Cu) catalysts supported on γ-Al_2O_3. While Mo is present in small crystallites of MoS_2 in all the systems studied, the local sulphidic environment around the transition metal atom varies significantly with the catalytic activity. Short T-S distances (compared to the bulk sulphides) are found in the case of the Ni and Co catalysts due to the formation of the active 'Ni(Co)-Mo-S' state. In the case of Fe, which is not a good promotor, the Fe-S distance in the catalyst is only slightly shorter than in the bulk sulphides. No such short distance is found in the Cu-MoS_2/Al_2O_3 system since Cu acts as a poison; instead only bulk sulphides are formed. Effects of the method of preparation, order of impregnation, metal loading and other factors have been examined to arrive at the conditions favourable for the formation of the active Ni(Co)-Mo-S state.

Keywords: EXAFS, Sulphided Ni- and Co-Mo catalysts, Fe-MoS_2 catalyst, Cu-MoS_2 HDS catalysts supported on Al_2O_3.

1. Introduction

Molybdenum sulphide catalysts promoted by transition metals such as cobalt and nickel are of great technological importance, being used extensively in the hydrotreating of petroleum feedstocks. There is considerable discussion in the literature [1–3] as to why Ni and Co alone act as promotors in hydrodesulphurization (HDS) catalysis. Activity measurements of T-Mo (T = 3d metal) HDS catalysts have yielded the so-called 'volcano plots', showing that Fe does not improve the activity of the Mo catalyst. The catalytic activity increases with Co as the promotor and reaches a maximum in the case of Ni; the activity of the Cu-Mo system is lower than that of the unpromoted Mo catalyst. This behaviour is found irrespective of the support used and the type of hydrotreating reaction studied [2]. The Ni and Co HDS catalysts have been subjected to extensive investigations in the last few years with a view to identify the surface species

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responsible for the catalytic activity [4–8]. Extended X-ray Absorption Fine Structure (EXAFS) studies of the promotor transition metals on supported molybdenum sulphide catalysts have been most useful in this regard. It seems to be fairly established that the HDS activity of the Ni-Mo and the Co-Mo catalysts originates from the so-called 'Ni(Co)-Mo-S' state residing on the catalyst surface [4–8]. One of the current interests is to model the structure of the Ni(Co)-Mo-S state.

Pursuing our interest in the study of HDS catalysts [8,9], we have recently carried out detailed EXAFS investigations of several transition metal-MoS_2/γ-Al_2O_3 catalysts. In this communication we report the important results from our work in the light of two recent publications in this Journal [10,11]. Some of the important features of our investigations are the following:

(i) We have carried out a comparative study of Fe, Co, Ni and Cu-MoS_2/γ-Al_2O_3 catalysts in order to explain the differences in the catalytic activity.

(ii) We have employed transition metal/γ-Al_2O_3 system (without Mo) as the reference for comparison of the EXAFS data of the HDS catalysts since only the transition metal sulphide phases would be formed in the absence of Mo.

(iii) We have compared results from two methods of preparation, one involving sulphidation of the two-stage impregnated oxidic precursor (Type I) and another involving the sulphidation of the nitrilotriacetic acid (NTA) complex of Ni-Mo/γ-Al_2O_3 (Type II). We have also compared the results obtained with the usual HDS catalyst obtained by the impregnation of Ni after that of Mo with that obtained from coimpregnation and Ni (first) and Mo (second impregnation).

(iv) We have also examined the effect of the magnitude of transition metal loading, the calcination temperature, sulphidation temperature and the order of impregnation. These studies show interesting results which establish that the promoting action of Ni and Co to be due to their strong association with Mo as in the 'Ni(Co)-Mo-S' state involving short Ni(Co)-S distance compared to bulk sulphides. Such a state does not occur in the case of Cu which forms only bulk sulphides. The formation of the Ni(Co)-Mo-S state itself critically depends on various factors such as catalyst composition, method of preparation and the treatment of the catalysts.

2. Experimental

The Type I catalyst samples were prepared by the pore-volume impregnation of γ-Al_2O_3 (200 m^2/g) with aqueous solutions of ammonium helptamolybdate and the transition metal nitrate taken in appropriate proportions. The various catalysts prepared by this method are: (i) Fe, Co, Ni and Cu (each 2 wt%) on γ-Al_2O_3; (ii) Fe, Co, Ni and Cu (each 2 wt%) on Mo (12 wt%)/γ-Al_2O_3 by second stage impregnation of the transition metal and also several other Co-Mo and Ni-Mo catalyst samples with different loadings of the transition metal with

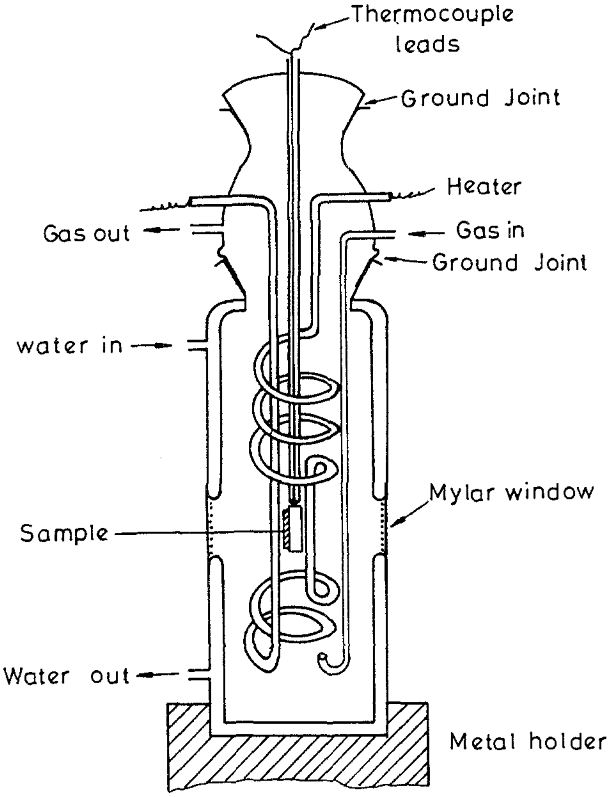

Fig. 1. Schematic diagram of the *in-situ* EXAFS cell made of quartz.

respect to Mo by the same method, (iii) Ni (2 wt%)-Mo (12 wt%)/γ-Al_2O_3 by coimpregnation of Ni and Mo and also by second stage impregnation of Mo (12 wt%) on Ni (2 wt%)/γ-Al_2O_3. Type II catalysts were prepared by coimpregnating Ni (4 wt%) and Mo (12 wt%) with required amount of nitrilotriacetic acid, NTA, (NTA/Mo = 1.2 mol/mol), on γ-Al_2O_3 [12]. After each impregnation the samples were dried in air at 370 K for 12 h. The dried samples of the Type I catalysts were calcined in air at 770 K for 6 h before sulphidation. The Type II catalysts were subjected to sulphidation after drying without any calcination. In the text that follows we have shown only the numbers for wt% for purpose of brevity.

The oxide catalysts were pressed into self-supporting wafers after mixing with a carbon binder. The thickness of the samples was adjusted so that the edge jump ($\mu.d$) was ~ 1.5 in every case. The wafers were mounted in a locally fabricated all-quartz *in-situ* EXAFS cell shown in fig. 1. Sulphidation was carried out in a gas mixture of (10% H_2S + 90% H_2) at a flow rate of 60 cm^3 min^{-1} under atmospheric pressure. The temperature was increased from 293 to 673 K at a rate of 6 deg min^{-1} and was kept constant at 673 K for 2 h. After sulphidation, the samples were cooled to room temperature under the same gas mixture. Systems such as Ni/Al_2O_3 which showed incomplete sulphidation were subjected to

Table 1
Structural parameters of some bulk reference sulphides

System	Atom-pair [a]	N	R (Å)
FeS_2	Fe(o)-S	6	2.259
CoS_2	Co(o)-S	6	2.315
Co_9S_8	Co(t)-S	1	2.13
[Co(t):Co(o) = 8 : 1]		3	2.23
	Co(o)-S	6	2.36
NiS_2	Ni(o)-S	6	2.396
Ni_3S_2	Ni(t)-S	2	2.27
		2	2.29
MoS_2	Mo(o)-S	6	2.41
	Mo-Mo	6	3.16

[a] o and t stand for octahedral and tetrahedral coordinations respectively.

prolonged reaction till the characteristic 'white line' of the oxide was not seen in EXAFS measurement.

EXAFS spectra were recorded at room temperature using a Rigaku spectrometer with a rotating anode X-ray generator (Ru-200B, Rigaku, Japan). A Ge(220) crystal was used as the monochromator with 0.1 mm slit. The K-EXAFS of the transition metals were recorded using X-rays from a Mo-target while the Mo K-EXAFS data was collected using a Cu-target. The spectral resolution was about 5 eV at 9 keV incident energy. Pre-edge data was collected in steps of 5 eV for 100 eV and data upto 700 eV after the edge was collected in steps of 1 eV. The EXAFS data was treated using the multiphasic model involving the additive relationship of EXAFS function [13,14]. The EXAFS of the reference compounds, NiS_2 and MoS_2, were recorded under the same conditions after mixing them with appropriate quantities of γ-Al_2O_3 to achieve the same signal to noise ratio. Fourier Transforms (FT) of the EXAFS data were obtained with $k_{min} \sim 3.5$ and $k_{max} \sim 11.5$ Å^{-1} after weighting the data by k^3. The structural parameters of some of the bulk reference sulphides are listed in table 1.

3. Results and discussion

EXAFS of the Transition metals (Ni, Co, Fe and Cu

We shall first discuss transition metal K-EXAFS data in the various catalysts. The Fourier transforms (FTs) of the Ni K-EXAFS of the sulphided Ni(2)/γ-Al_2O_3, Ni(2)-Mo(12)/γ-Al_2O_3 catalysts as well as the Co K-EXAFS of the sulphided Co(2)/γ-Al_2O_3 and Co(2)-Mo(12)/γ-Al_2O_3 catalysts are shown in fig. 2. The Ni-Mo and Co-Mo HDS catalysts show the first peak around 1.7 Å. This distance is much shorter (by ~ 0.3 Å) than that shown by the bulk NiS_2 (2.0 Å). The first major peak in the FT of Ni(2)/γ-Al_2O_3 occurs around 1.82 Å whereas

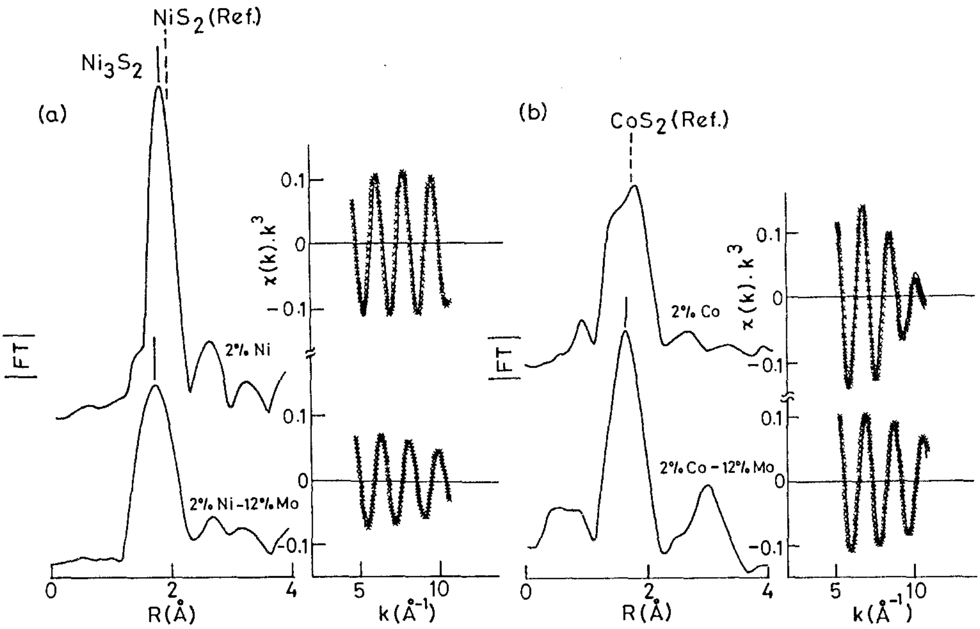

Fig. 2. Fourier transforms of the Ni(Co) K-EXAFS of sulphided (a) nickel and (b) cobalt catalysts supported on γ-Al_2O_3. The best fits obtained in the curve fitting of the inverse transformed data ($\Delta R \approx 0.4$ Å) are also shown.

that of Co(2)/γ-Al_2O_3 shows two features at 1.55 and 1.82 Å. These observations indicated that the transition metal atoms in some of the catalyst samples may be in a multiphasic environment. We therefore carried out a multiphasic curve fitting analysis [13,14] on the inverse-transformed data (r-window: 1.4–2.0 Å) using phase and amplitude parameters of Ni-S in NiS_2. The use of Ni-S parameters for analysis of Co-systems is justified since Co and Ni are neighbouring atoms in the periodic table and the parameters would not differ significantly. The compositions of the different phases in these systems were calculated using the additive EXAFS relation [13],

$$\chi_{\text{total}}(k) = \sum_{i,m} x_i C_{i,m} \chi_{i,m}(k),$$

where x_i is the fraction of the absorbing element in the ith phase ($\Sigma_i x_i = 1$) and $C_{i,m}$ is the fraction of the absorbing element in the mth coordination of the ith phase ($\Sigma_m C_{i,m} = 1$).

The inverse-transformed data of Ni(2)/γ-Al_2O_3 fits well with one Ni-S distance (2.28 Å) with a coordination number 4.8 (table 2). In fig. 2 we also show the curve-fitting of the inverse-transformed data (k = 4–12 Å). In fig. 3 we show the Fourier-deconvolution of the fitted data. This distance is typical of Ni_3S_2 (table 1) . We did not see any significant improvement in the fit when two Ni-S distances (2.27, 2.29 Å) were employed. Multiphasic analysis of the Co(2)/γ-Al_2O_3 system yields three Co-S distances characteristic of Co_9S_8 (2.11, 2.22 and 2.34 Å)

Table 2
Structural parameters from the Ni(Co) K-EXAFS of sulphided catalysts (Ni(Co)-S coordination)

Catalyst	N	R	$\Delta\sigma^2$
2%Ni/γ-Al_2O_3	4.8	2.28	0.0004
2%Ni-12%Mo/γ-Al_2O_3	3.3	2.23	0.001
	1.0	2.15	0.001
2%Co/γ-Al_2O_3	1.2	2.34	0.001
	1.0	2.29	0.0007
	3.2	2.22	0.001
	2.4	2.11	0.0008
2%Co-12%Mo/γ-Al_2O_3	4.8	2.14	0.0005

and of CoS_2 (2.29 Å) (see fig. 3). The excellence of the curve-fitting of this data is also shown in fig. 2. The phase composition is estimated to be 20% CoS_2 and 80% Co_9S_8.

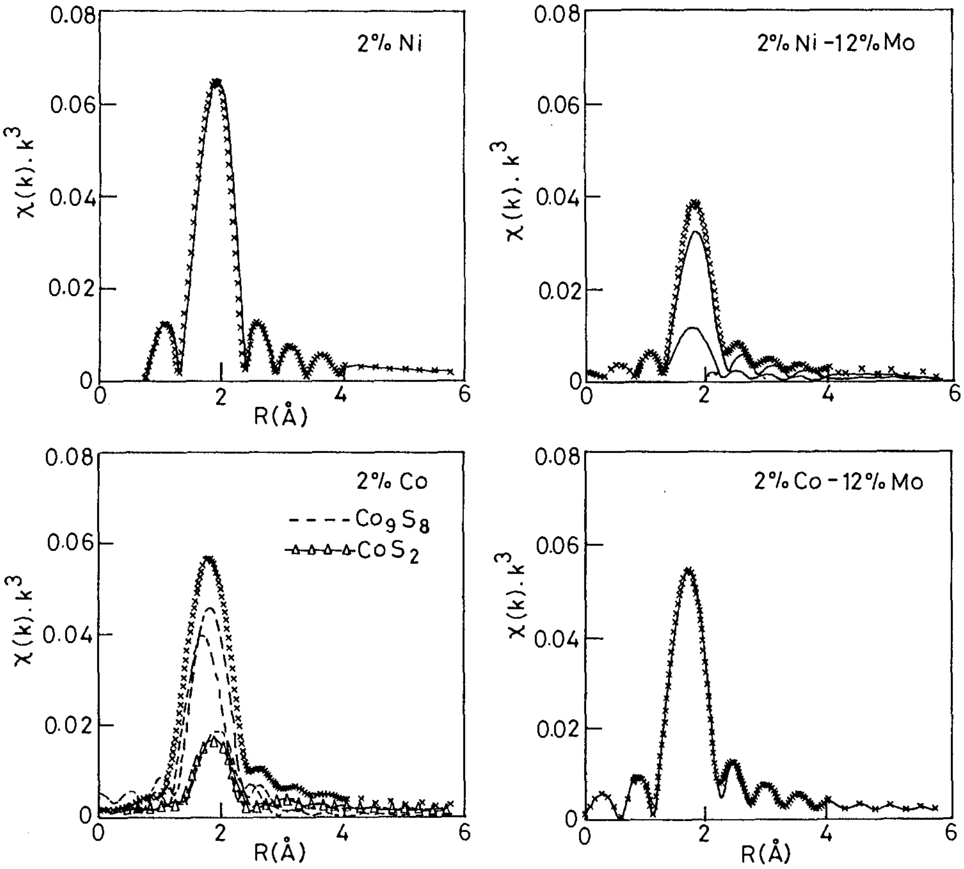

Fig. 3. Fourier deconvolution of the fitted Ni(Co) K-EXAFS of sulphided nickel and cobalt catalysts supported as γ-Al_2O_3 employing upto four Ni(Co)-S distances.

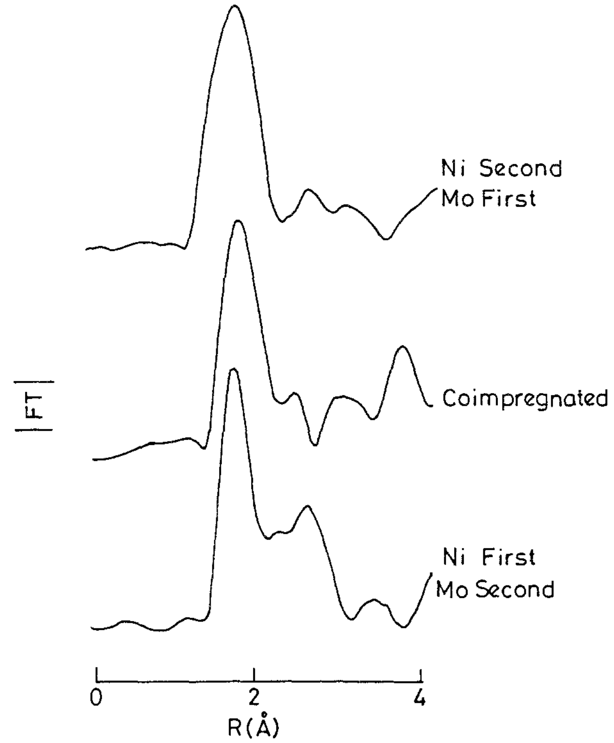

Fig. 4. Fourier-transforms of the Ni K-EXAFS of two-stage impregnated and coimpregnated sulphided 2%Ni-12%Mo/γ-Al_2O_3 catalyst.

Unlike the Ni or Co/Al_2O_3 systems, the Ni-Mo and Co-Mo catalysts exhibit very short Ni(Co)-S distances and show no evidence for the respective bulk sulphides. The inverse-transformed data of the Ni-Mo catalyst could be fitted as shown in fig. 2, with a five-coordinated Ni involving two Ni-S distances, with one S around 2.15 Å and four S atoms at 2.23 Å. In the Co-Mo catalyst, on the other hand, Co has a five-fold coordination with the S atoms at 2.14 Å. These findings are similar to those of Niemann et al. [10] and Bouwens et al. [11,15] who examined carbon supported Ni and Co-Mo catalysts. The short Ni(Co)-S distances found in the Ni (Co)-Mo HDS catalysts are likely to be associated with the catalytically active Ni(Co)-Mo-S state, in which Ni(Co) is present on the edges of the MoS_2 crystallites replacing the Mo atoms and having a nearly five-fold coordination of sulphur. The absence of bulk sulphides in these catalysts indicates that all the Ni(Co) atoms occur in association with Mo leading to the Ni(Co)-Mo-S state.

We could confirm the formation of the Ni(Co)-Mo-S type state in HDS catalysts by a study of coimpregnated Ni(2)-Mo(12)/γ-Al_2O_3 and Ni (2%, first impregnation)-Mo (12%, second impregnation)/γ-Al_2O_3. FTs of these sulphided catalysts are shown in fig. 4 along with the FT of the Ni-Mo HDS catalyst (Ni second-Mo first). The results of our analysis are summarized in table 3. The

Table 3
Structural parameters from the Ni-K-EXAFS (Ni-S coordination)

Catalyst	N	R	$\Delta\sigma^2$
2%Ni-12%Mo/γ-Al_2O_3			
Ni Second-Mo First	3.3	2.23	0.001
	1.0	2.15	0.001
Coimpregnated	0.5	2.28	0.0001
	3.2	2.23	0.0003
	0.5	2.14	0.0004
Ni First-Mo Second	1.0	2.43	0.0003
	3.2	2.22	0.0
	0.7	2.14	0.0001
4%Ni-12%Mo Type I	3.6	2.22	0.0002
	1.0	2.15	0.0
Type II	4.1	2.23	0.0003
2%Ni-12%Mo/γ-Al_2O_3	2.8	2.43	0.0004
(Oven-dried after coimpregnation)	3.6	2.17	0.0007
2%Ni-12%Mo/γ-Al_2O_3	0.7	2.42	0.0003
sulphided at 870 K	3.1	2.2	0.0008
	0.5	2.15	0.0002

catalyst where Ni and Mo are coimpregnated and that where Mo is second-impregnated on Ni/γ-Al_2O_3 show coordinations characteristic of the bulk as well as the Ni-Mo-S state. It appears that if, during the catalyst preparation, Ni(Co) is allowed to interact with the Al_2O_3 support, bulk sulphides are formed on sulphidation and only a fraction of the Ni(Co) forms the catalytically active state with Mo. This result indicates that there is a delicate association of Ni with Mo in the oxidic precursor state so as to yield the active Ni-Mo-S state.

It is known that when nitrilotriacetic acid (NTA) is used as a complexing agent, direct fraction of Ni(Co) and Mo with the support is inhibited but still maintaining good dispersion. The FT of a sulphided Type II Ni catalyst prepared through the NTA route is shown in fig. 5 along with that of the Type I catalyst prepared by the sulphidation of the oxidic precursor. Curve fitting analysis (table 3) shows that Ni in the Type II catalyst occurs in an environment similar to that of the Type I catalyst with short Ni-S distances (~ 2.23 Å). The best fit of this data is also shown in fig. 5. It is noteworthy that in the absence of the complexing agent, there would be a good proportion of bulk sulphides on sulphidation of the dried precursor. In the inset of fig. 5 we show the FTs of two Type I catalysts prepared by the sulphidation of an oven-dried precursor and a calcined precursor. The former shows a shoulder on the first peak at a higher r-value, characteristic of bulk Ni-sulphide (sulphidation of the calcined precursor does not show the

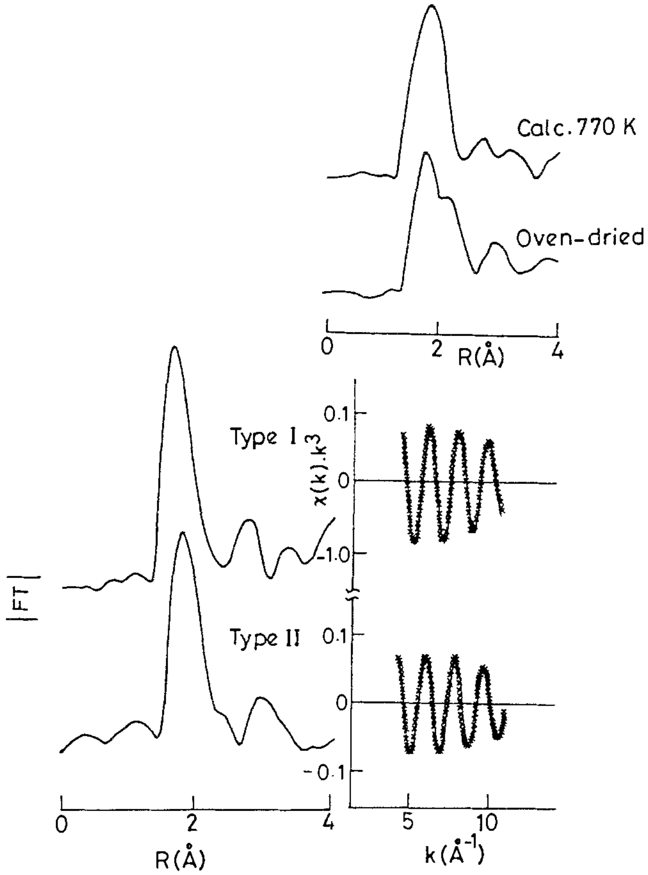

Fig. 5. Fourier-transforms of the Ni K-EXAFS of sulphided Type I and Type II 4%Ni-12%Mo/γ-Al_2O_3 catalysts. The best fits obtained in the curve-fitting of the inverse-transformed data are also shown. Inset shows Fourier-transforms of the Ni K-EXAFS of sulphided 2%Ni-12%Mo/γ-Al_2O_3 catalysts with and without calcination before sulphidation.

bulk sulphide). Similar observations have been made by Bouwens et al. [15] in the case of carbon supported Co catalysts and Rob Van Veen et al. [12] in the case of Al_2O_3, SiO_2 and carbon supported Co catalysts.

The heating rate, the final sulphidation temperature as well as the time of reaction are all critical in deciding the fate of the Ni(Co)-Mo-S state. The rate of heating has to be gradual and the time for the reaction should be relatively short (~ 2 h). It is interesting to note that a Type I Ni(2)-Mo(12)/γ-Al_2O_3 catalyst sulphided at 873 K showed small amounts of bulk sulphides compared to that sulphided at 670 K.

We have also carried out a systematic study of the effect of composition of Ni(Co) and Mo. In fig. 6 we show the FTs of sulphided Co-Mo catalysts with 12 wt% Mo with varying Co loading. Catalysts with 2% and 4% Co loading contain all the Co in the Co-Mo-S state while higher loadings give some proportion of

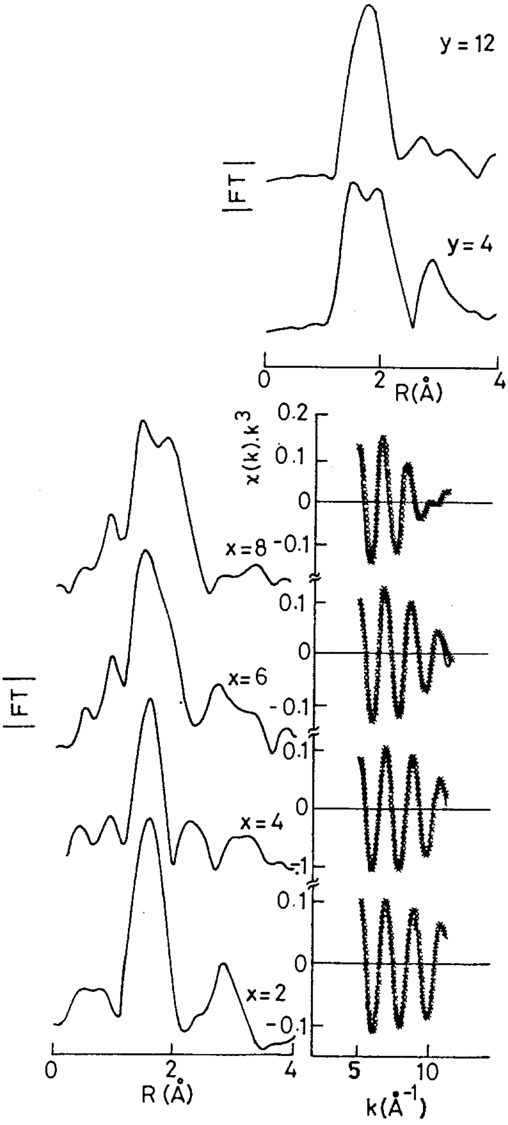

Fig. 6. Fourier-transforms of the Co K-EXAFS of sulphided x%Co-12%Mo/γ-Al_2O_3 ($x = 2$, 4, 6 and 8) catalysts. The best fits obtained in the curve-fitting of the inverse-transformed data are also shown. The inset shows the Fourier-transforms of the Ni K-EXAFS of sulphided 2%Ni-y%Mo/γ-Al_2O_3 ($y = 4$ and 12).

bulk Co_9S_8. The curve-fitting of the data are also shown in fig. 6. The percentage of Co_9S_8 in 6% and 8% Co catalysts are estimated to be 30% and 60% respectively. The Ni-Mo catalyst also shows a similar behaviour. When the Ni loading is above 6%, bulk NiS_2 is found. In the inset of fig. 6 we compare the FT of Ni(2)-Mo(4)/γ-Al_2O_3 catalyst with that of Ni(2)-Mo(12)/γ-Al_2O_3. The catalyst with lower Mo loading exhibits two features in the main peak of the FT. Curve-fitting of the inverse-transformed data of this catalyst was achieved with

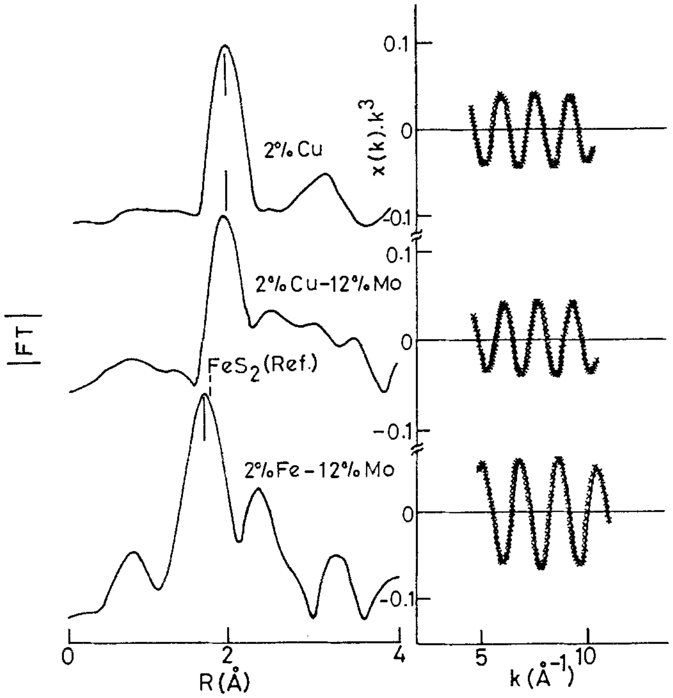

Fig. 7. Fourier-transforms of the Fe(Cu) K-EXAFS of sulphided Fe and Cu catalysts supported in γ-Al_2O_3. The best fits obtained in the curve-fitting of the inverse-transformed data are also shown.

one Ni-O (1.93 Å) and two Ni-S distances (2.2 and 2.28 Å). An estimation of the phase compositions showed that Ni occurs mainly in Ni_3S_2 (~ 50%) and only a small proportion in the Ni-Mo-S phase (~ 10%). The oxidic interaction seems to originate from a surface aluminate species [16]. It is to be noted that this aluminate would have converted to bulk sulphides as in the case of Ni(2)/γ-Al_2O_3, had the sulphidation continued for a longer time.

We have carried out EXAFS of sulphided Fe-Mo and Cu-Mo catalysts prepared under conditions similar to those employed in the case of Ni-Mo and Co-Mo HDS catalysts. In fig. 7 we show the FT of Fe K-EXAFS of the sulphided Fe(2)-Mo(12)/γ-Al_2O_3 catalyst along with curve-fitting of its inverse-transformed data. Compared to bulk FeS_2 (2.26 Å), the Fe-Mo catalyst shows a shorter Fe-S distance of 2.11 Å (table 4), but the difference is relatively small compared to Ni

Table 4
Structural parameters from the Cu and Fe K-EXAFS

Catalyst	N	R	$\Delta\sigma^2$
2%Cu/γ-Al_2O_3	2.8	2.31	0.0002
2%Cu-12%Mo/γ-Al_2O_3	2.7	2.31	0.0001
2%Fe-12%Mo/γ-Al_2O_3	3.6	2.11	0.0001

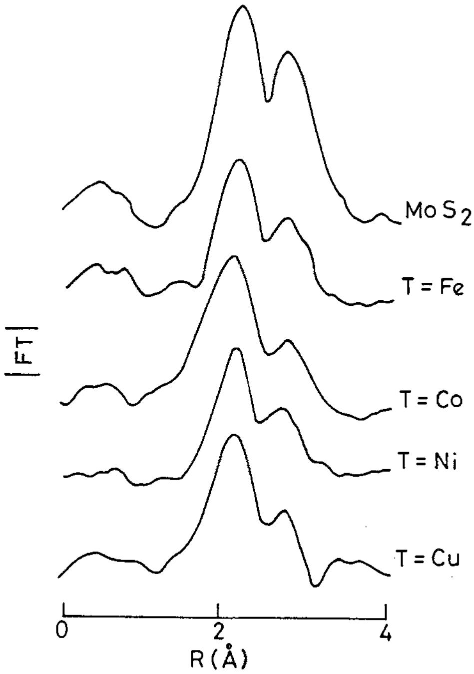

Fig. 8. Fourier-transforms of the Mo K-EXAFS of sulphided 2%T-12%Mo/γ-Al_2O_3 (T = Fe, Co, Ni and Cu) catalysts along with the FT of reference MoS_2.

or Co HDS catalyst. The absence of bulk sulphides, however, indicates that all Fe is in association with Mo in the Fe-Mo-S state.

In fig. 7 we also show the FTs of Cu K-EXAFS of sulphided Cu(2)/γ-Al_2O_3 and Cu(2)-Mo(12)/γ-Al_2O_3 catalysts along with the curve-fitting of the inverse-transformed data. No shift is seen in the position of the first peak of the Cu-Mo catalyst as compared with that of pure Cu catalyst. Interestingly, curve-fitting analysis (table 4) shows that Cu has 3S atoms in the first coordination at ~ 2.3 Å irrespective of the presence or absence of Mo. Compared with the results of Fe, Co and Ni HDS catalysts, this is uniquely different and provides an explanation of the poisoning effect of Cu on the MoS_2/γ-Al_2O_3 catalyst. The electronic factors responsible for the promotion effect of Ni and Co and the poisoning effect of Cu in MoS_2 HDS catalysts have been discussed by Harris and Chianelli [1].

Mo EXAFS

In fig. 8 we show the FTs of the Mo K-EXAFS of Fe-, Co-, Ni- and Cu-Mo/Al_2O_3 catalysts along with the reference compound, MoS_2. The position of the Mo-S and Mo-Mo peaks in the FTs of catalysts are close to those of MoS_2, although there is some reduction in the magnitude of the FT peaks. Curve-fitting analysis of the inverse-transformed data shows that the coordination has reduced from 6 in MoS_2 to about 4 in these catalysts. The reduction in coordination number is still more pronounced in the case of second shell (Mo-Mo). This coordination number is between 2 and 3 for catalysts compared to 6 in MoS_2. This result indicates that MoS_2 is present in the form of small crystallites in the catalysts wherein a large fraction of the atoms are located at the surface. This observation agrees with earlier studies [9,17]. The crystallite size of MoS_2 is estimated to be around 10 Å in the catalyst systems studied by us.

4. Conclusions

Our main conclusions are as follows: (i) A comparison of the EXAFS data of sulphided Ni-Mo/γ-Al_2O_3 and Co-Mo/γ-Al_2O_3 catalysts with the reference Ni/γ-Al_2O_3 and Co/γ-Al_2O_3 systems shows that the Ni(Co)-S distances are much shorter in the HDS catalysts, ascribable to the formation of the active Ni(Co)-Mo-S state in the catalysts. (In the absence of Mo, as in the reference systems, only bulk sulphides (Ni_3S_2, CoS_2 and Co_9S_8) are formed.) (ii) The results obtained for the Ni-Mo catalyst prepared through the NTA route (Type II) are similar to those from the oxide precursor route (Type I), the complexing agent only helping to minimize the interaction of Ni(Co) with the oxide support. In the case of a non-oxidic support such as carbon where calcination cannot be done, it becomes necessary to use a complexing agent such as NTA. (iii) The Ni(Co)-Mo-S state occurs along with the bulk sulphides if Ni(Co) and Mo are coimpregnated or Ni(Co) is impregnated prior to the impregnation of Mo on the Al_2O_3 support. It is important to adopt the right order of impregnation (Mo First-Ni(Co) Second); that calcination (~ 770 K) should be carried out after each stage of impregnation in order to avoid the formation of bulk sulphides and to maximise the formation of Ni(Co)-Mo-S state. (iv) In the case of the Ni(Co)-Mo(12)/γ-Al_2O_3 catalyst, bulk sulphides form when the Ni(Co) loading is above 4 wt%. (v) The Fe-Mo/γ-Al_2O_3 catalyst shows only a slightly shorter Fe-S distance than the bulk sulphide suggesting that we may not have an active 'Fe-Mo-S' type state similar to the 'Ni(Co)-Mo-S' state. The Cu-S distances in the Cu-Mo/γ-Al_2O_3 catalyst are identical to those of bulk sulphide. The absence of short Cu-S distances is related to the absence of catalytic activity.

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