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An EXAFS study of the Mo/TiO_2 hydrodesulphurization catalysis *

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In-situ EXAFS studies of sulphided Mo/TiO_2 catalysts have shown that at low Mo loadings (2–4 wt%), an active species with a short Mo-S distance of 2.25 Å is formed, while on Mo/TiO_2 with high Mo loadings as well as on $Mo/\gamma\text{-}Al_2O_3$, bulk MoS_2 (Mo-S, 2.42 Å) is formed. The species with the short Mo-S distance has Mo in an oxidation state close to 6+ and is likely to result from the sulphidation of the tetrahedral molybdate species present in the oxidic precursor at low Mo loadings. The calcination temperature of the oxidic precursor appears crucial, a high calcination temperature of 973 K favouring the formation of MoS_3 on sulphidation, and a low calcination temperature of 623 K favouring MoS_2.

Keywords: HDS catalysts; Mo/TiO_2 catalyst; $Mo/\gamma\text{-}Al_2O_3$ catalyst

1. Introduction

Hydrodesulphurization (HDS) catalysts generally involve Co- or Ni-promoted molybdenum sulphide supported on $\gamma\text{-}Al_2O_3$ ($T\text{-}MoS_2/\gamma\text{-}Al_2O_3$, T = Co, Ni). These catalysts have been investigated extensively in the literature [1,2]. EXAFS studies of the HDS catalysts have revealed vital information on the nature of the active surface species responsible for catalytic activity [3,4]. HDS activity has been reported by a few workers [5–8] with molybdenum catalysts supported on TiO_2. It has been shown that at low Mo loadings, titania-supported catalysts are more active in the HDS reaction than alumina supported catalysts [6]. The specific thiophene HDS rate becomes maximum for 2–3 wt% MoO_3 on TiO_2, decreasing progressively with higher Mo loadings. It has been suggested that the oxidic precursor in the most active composition for HDS may contain surface

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molybdate ions with a tetrahedrally coordinated Mo [8,9]. The nature of the active surface species in the sulphided Mo/TiO_2 catalyst is however not known. We considered it important to carry out an EXAFS investigation on sulphided Mo/TiO_2 catalysts to probe the nature of the sulphidic molybdenum species in the active catalyst. The present study suggests that active species with a short Mo-S distance results from the sulphidation of the tetrahedral molybdate species in the oxide precursor.

2. Experimental

The TiO_2 support was prepared by the hydrolysis of $TiCl_4$ at 273 K followed by treatment with dilute ammonia solution. The resulting gel was dried at 380 K and calcined at 673 K to yield TiO_2 of surface area ~ 50 m^2/g and pore volume ~ 0.25 ml/g. The TiO_2 so prepared was in the anatase form as found by X-ray diffraction. Mo/TiO_2 catalyst samples were prepared by wet impregnation of TiO_2 with aqueous solution of ammonium heptamolybdate. Catalysts with Mo loadings of 2, 4, 6 and 10 wt% were prepared. Throughout the text we have shown only the number of wt% for purpose on brevity. Mo catalysts supported on γ-Al_2O_3 (~ 200 m^2/g) were prepared with similar Mo loadings by a similar procedure. All the catalysts samples were dried at 380 K overnight and were calcined at 773 K for 6 h. In order to study the effect of calcination temperature, the Mo(4 wt%)/TiO_2 catalyst was calcined at 623 and 973 K.

The catalysts were pressed into self-supporting wafers after mixing with a carbon binder. The thickness of the wafer 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, details of which are given elsewhere [4]. 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 623 K at a rate of 6 deg min^{-1} and was kept constant at 623 K for 2 h. After sulphidation, the samples were cooled to room temperature under the same gas mixture.

Mo K-EXAFS was recorded at room temperature using a Rigaku spectrometer with a rotating anode X-ray generator (Ru-200B, Rigaku, Japan). A Ge(440) crystal was used as the monochromator with 0.1 mm slit for X-rays from a Cu-target. The spectral resolution was 7 eV at 20 keV incident energy. Pre-edge data was collected in steps of 5 eV for 100 eV and data up to 800 eV after the edge was collected in steps of 1 eV. EXAFs data was treated using the multiphasic model involving the additive relationship of EXAFS function [10,11]. EXAFS of the reference compound, MoS_2, was recorded under the same conditions after mixing with an appropriate quantity of TiO_2 to achieve the same signal to noise ratio. Fourier transforms (FT) of the EXAFS data were obtained with k_{min} ~ 3.5 and k_{max} ~ 13.0 $\AA^{-1}$ after weighting the data by k^3.

3. Results and discussion

Fourier transforms of the Mo K-EXAFS of sulphided Mo(x)/TiO_2 ($x = 2$, 4, 6 and 10 wt%) catalysts are shown in fig. 1 along with the FT of MoS_2, employed as a reference compound. Catalyst samples with $x = 2$ and 4 wt% show the first peak in the FT around 1.9 Å which is considerably shorter (by 0.15 Å) than that in MoS_2. Catalysts with higher Mo loadings however show the first peak around the same position as MoS_2. Curve-fitting of the inverse-transformed data by employing the phase and amplitude parameters of Mo-S in MoS_2, gave the results listed in table 1. The excellence of the fit can be seen from fig. 1. The actual Mo-S distance in Mo(2)/TiO_2 and Mo(4)/TiO_2 catalysts is 2.23 and 2.27 Å respectively whereas in catalysts with higher Mo loadings, the distance is 2.42 Å just as in MoS_2. The existence of a short Mo-S distance is indicative of the occurrence of Mo in the 5+ of the 6+ state. The Mo-S distance in $(NH_4)_2MoS_4$ containing Mo in 6+ oxidation state is around 2.2 Å [12]. X-ray photoelectron spectroscopic studies of sulphided Mo/TiO_2 catalysts with low Mo loadings have indeed shown the probable presence of Mo in oxidation states higher than 4+ [9]. All the catalyst compositions have a low sulphur coordination of around 2 except Mo(10)/TiO_2, in which the coordination is close to 4 (but still less than in MoS_2). The low coordination numbers in catalysts especially at low Mo loadings are likely to be due to the high dispersion of the sulphidic species on the TiO_2 support.

In fig. 2 we show the FTs of the Mo K-EXAFS of sulphided Mo(x)/γ-Al_2O_3 ($x = 2$, 4 and 6 wt%). We see that there is no shift in the position of the first peak of the catalyst samples compared to that of MoS_2. The inverse-transformed data of these catalysts fit well with a Mo-S distance of 2.41 Å with a coordination number of 2.0 (see fig. 2). The structural parameters are listed in table 2. The absence of the species with a short Mo-S distance (observed on the TiO_2 support) on the γ-Al_2O_3 support suggests that Mo exists in the form of small crystallites of MoS_2 on this support and the absence of strong interaction between Mo and the support.

The FT of MoS_2 is characterized by a peak around 2.86 Å due to the Mo-Mo distance. Mo/TiO_2 catalysts with 2 and 4 wt% Mo loadings showing the presence of an active species with a short Mo-S distance do not show a clear Mo-Mo peak in the FTs (fig. 1). Instead, they exhibit a shoulder at 2.42 Å possibly due to Mo-Ti bonding. A distinct Mo-Mo peak as in MoS_2 however appears when the Mo loading is above 6 wt% (with a coordination around 2) where indeed we see a Mo-S distance close to that in MoS_2.

A Raman study of oxidic Mo/TiO_2 precursors [8] had suggested that the extent to which the catalyst becomes active upon sulphidation for the HDS reaction depended on the surface species present in the oxidic precursor. We have examined the EXAFS of sulphided Mo/TiO_2 catalysts as a function of calcination temperature. The FTs of the sulphided MO(4)/TiO_2 catalyst cal-

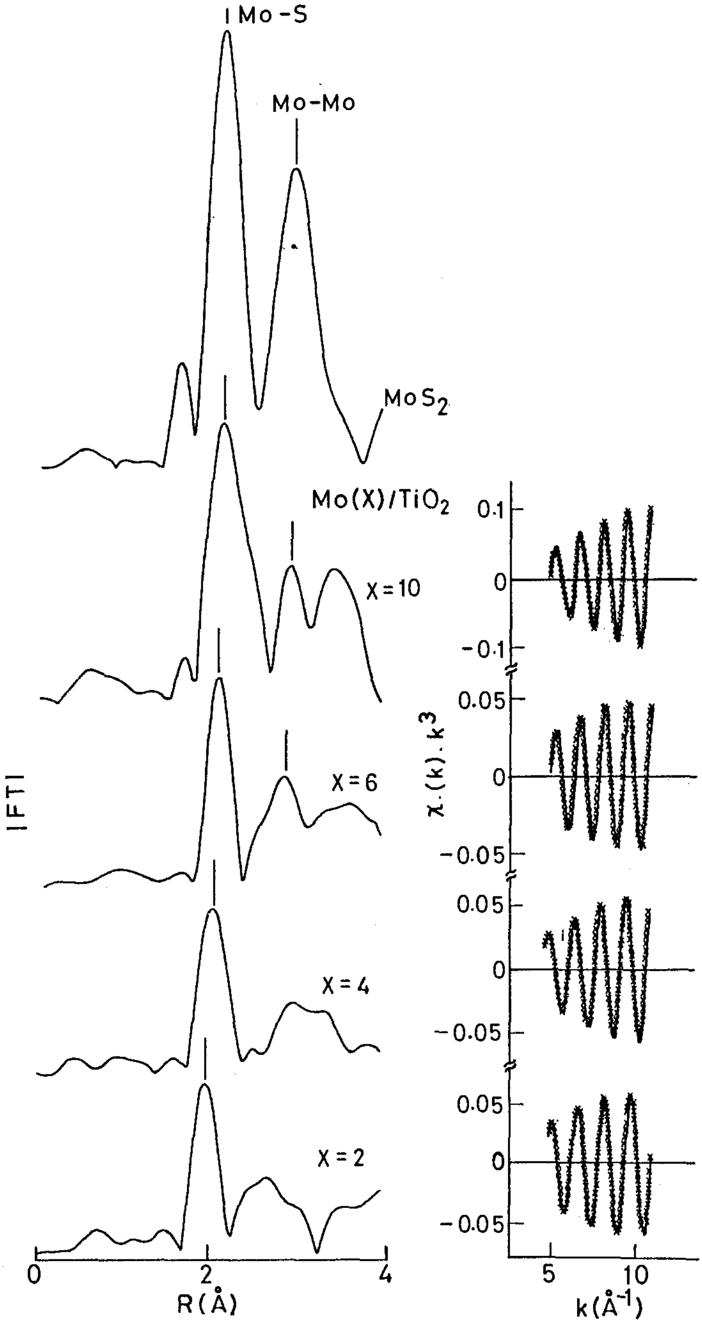

Fig. 1. Fourier transforms of the Mo K-EXAFS of sulphided Mo(x)/TiO_2 ($x = 2$, 4, 6 and 10 wt%) catalysts along with the FT of the reference compound, MoS_2. Curve-fitting of the inverse-transformed data (r-window: 1.7–2.1 Å), with one Mo-S distance employing phase and amplitude parameters of Mo-S in MoS_2 is also shown.

Table 1
Structural parameters from Mo K-EXAFS of sulphided Mo(x)/TiO_2 catalysts [a] for Mo-S coordination

x (wt%)	N	R (Å)	$\Delta\sigma^2$ (Å^2)
10	3.8	2.41	0.0001
6	2.6	2.40	0.0003
4	2.0	2.27	0.0005
2	2.2	2.23	0.0001

[a] Calcined at 773 K and sulphided at 623 K.

cined at 623, 773 and 973 K are shown in fig. 3 along with the curve fits of the inverse-transformed data. The FT of the catalyst calcined at 623 K prior to sulphidation, resembles that of MoS_2 with a Mo-S coordination of 3.3 and Mo-Mo coordination of 3.0. The catalyst calcined at 773 K and subjected to sulphidation shows the short Mo-S distance (2.27 Å) due to the active species and does not show the feature ascribable to the Mo-Mo distance. The catalyst calcined at 973 K exhibits a Mo-S distance of 2.42 Å just as MoS_2, but showing the second peak in the FT which is different from that of MoS_2. Curve-fitting of the inverse-transformed data of the second peak (r-window: 2.3–2.5 Å), employing phase and amplitude parameters of Mo-Mo in MoS_2, yielded a Mo-Mo coordination of 1.2 at 2.73 Å. This is to be contrasted with the Mo-Mo distance of 3.16 Å in MoS_2 and in the Mo/TiO_2 catalysts with high Mo loadings ($>$ 4 wt%) shown in fig. 1 and the Mo(4)/TiO_2 catalyst calcined at 623 K shown in fig. 3 (see table 3). The FT of the Mo/TiO_2 catalyst calcined at 973 K is identical to that of MoS_3 reported in the literature [12] with Mo-S and Mo-Mo distances of 2.44 and 2.75 Å respectively.

4. Conclusions

The main conclusions from the present study are as follows: (i) A comparative EXAFS study of sulphided Mo/TiO_2 and Mo/γ-Al_2O_3 catalysts reveals that active Mo/TiO_2 catalysts with 2–4 wt% Mo loading have a short Mo-S distance ($\sim$ 2.25 Å) with little or no Mo-Mo coordination, suggesting strong interaction

Table 2
Structural parameters from Mo K-EXAFS of sulphided Mo(x)/γ-Al_2O_3 catalysts for Mo-S coordination

x (wt%)	N	R (Å)	$\Delta\sigma^2$ (Å^2)
6	2.2	2.42	0.0002
4	2.0	2.42	0.0003
2	2.0	2.42	0.0005

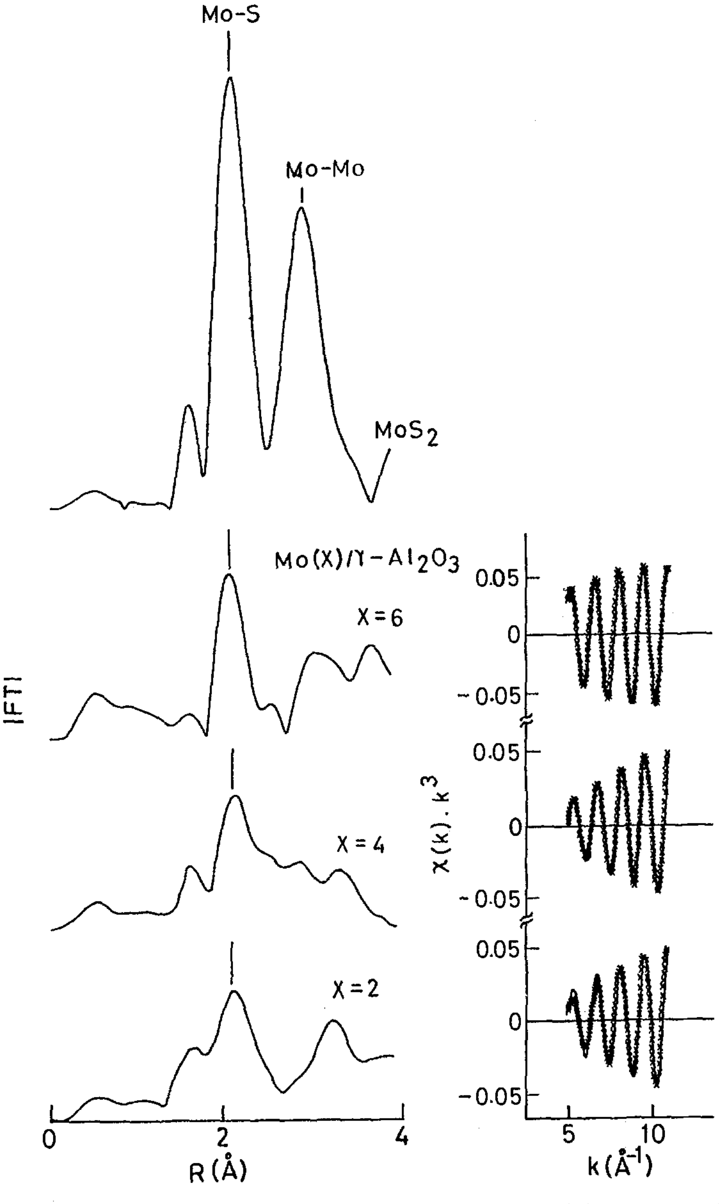

Fig. 2. Fourier transforms of the Mo K-EXAFS of sulphided Mo(x)/γ-Al_2O_3 ($x = 2$, 4 and 6 wt%) catalysts along with the FT of MoS_2. Curve-fitting of the inverse-transformed data is also shown.

of Mo with the TiO_2 support. In Mo/TiO_2 catalysts with high Mo loadings, Mo exists essentially as MoS_2 just as in sulphided Mo/γ-Al_2O_3. (ii) The active species with the short Mo-S distance has Mo in an oxidation state close to $6+$ and is probably the product of sulfidation of the tetrahedral molybdate species present in the oxidic precursor [9]. With increase in Mo loading, the oxidic

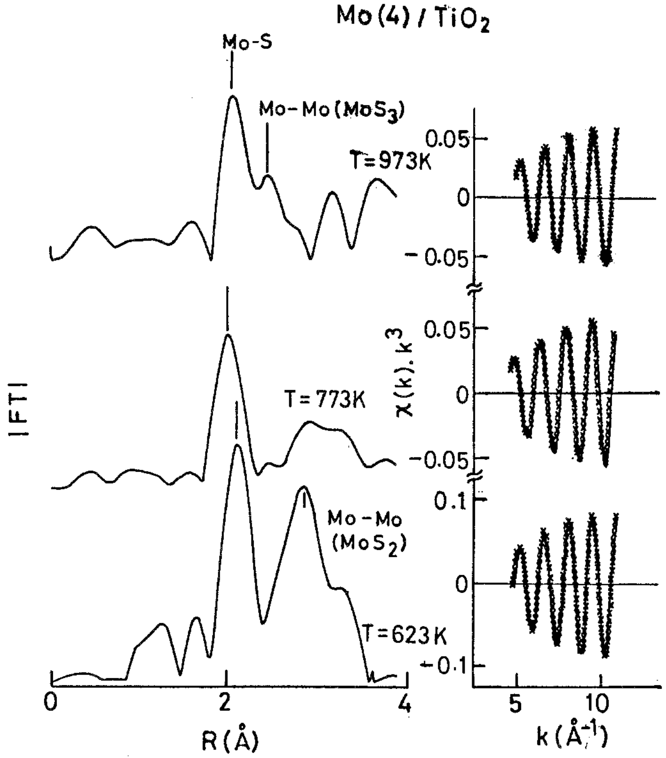

Fig. 3. Fourier transforms of the Mo K-EXAFS of sulphided Mo(4 wt%)/TiO_2 catalysts calcined at different temperatures. Curve-fitting of the inverse-transformed data is also shown.

Table 3

Mo-S and Mo-Mo distances in sulphided Mo/TiO_2 catalysts in comparison with those in reference Mo sulphides

System	Mo-S (Å)	Mo-Mo (Å)
Mo(2)/TiO_2 [a]	2.23	– [b]
Mo(4)/TiO_2 [a]	2.27	– [b]
Mo(6)/TiO_2 [a]	2.40	3.16
Mo(10)/TiO_2 [a]	2.41	3.16
Mo(4)/TiO_2 [c]	2.42	3.16
Mo(4)/TiO_2 [d]	2.42	2.73
MoS_2 (Mo^{4+})	2.42	3.16
$(NH_4)_2MoS_4$ (Mo^{6+})	2.19	– [b]
MoS_3 [e]	2.44	2.75

[a] Calcined at 773 K and sulphided at 623 K.

[b] Not evident.

[c] Calcined at 623 K and sulphided at 623 K.

[d] Calcined at 973 K and sulphided at 623 K.

[e] MoS_3 is an amorphous insulator.

precursor would contain polymeric molybdate and MoO_3 which in turn give MoS_2 on sulphidation. (iii) A high calcination temperature ($\sim$ 973 K) yields the MoS_3 phase on sulphidation while a low calcination temperature ($\sim$ 623 K) favours MoS_2. The active Mo/TiO_2 with the short Mo-S distance is found when the calcination temperature is moderate (773 K).

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