Solution interaction of O-donor ligand metal complexes with thiocarbonyl compounds—a new general route to metal sulfide materials

Gulaim A. Seisenbaeva,[a] Suresh Gohil,[a] Kjell Jansson,[b] Konrad Herbst,[c] Michael Brorson[c] and Vadim G. Kessler*[a]

[a] *Department of Chemistry, SLU, Box 7015, 75007, Uppsala, Sweden*
[b] *Inorganic Chemistry, Stockholm University, 10690, Stockholm, Sweden*
[c] *Haldor Topsøe A/S, Nymøllevej 55, DK-2800, Lyngby, Denmark*

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Molybdenum and tungsten oxoalkoxides {[MO(OMe)$_4$]; M = Mo, W} and rhenium heptaoxide (Re_2O_7) reacted at room temperature with thiocarbonyl compounds such as *N*,*N*-dimethylthioformamide (DMTF), producing the crystalline metal sulfides MoS_2, WS_3 and Re_2S_7, respectively. The reaction mechanism involves, as the first step, the coordination of DMTF to a metal *via* the sulfur donor atom, followed by the subsequent metathesis of the latter with the doubly bonded oxygen atom. The final product is, depending on reaction conditions, a colloidal metal sulfide or up to 0.1 mm large metal sulfide crystals. By carrying out the reaction within a mesoporous alumina matrix, supported metal sulfide catalysts were obtained in one step. These catalysts were tested for catalytic hydrodesulfurization and their activity compared with catalysts prepared by traditional methods. Reaction of nickel and zinc acetylacetonates and aminoalkoxides with DMTF in hydrocarbon media was found to provide colloids and, on aging, fine powder precipitates of NiS and ZnS.

Introduction

Transition metal sulfide systems are of considerable interest in both biological and industrial catalysis. Sulfur-coordinated transition metals are engaged in facile electron- and proton-transfer processes, which are important for active site turnover in biological systems.[1] Colloid solutions of rhenium sulfide are used in the treatment of breast cancer[2] and leaver carcinoma.[3] The alumina-supported metal sulfides MoS_2 and WS_2 are used as hydrodesulfurization catalysts in key oil refinery processes for the removal of sulfur and nitrogen from petroleum fractions.[4,5] The sulfides of divalent metals such as nickel, zinc and cadmium are widely used in industry as semiconductor materials and have recently attracted increasing attention in connection with the preparation of nano-level defined systems.[6]

The traditional solid state synthetic approaches to heavy transition metal sulfides comprise either thermal decomposition of thiosalts (NR_4)[MoS_4] (R = H, Me, Bu),[7–9] amorphous MoS_3,[10] and $(NH_4)_2[Mo^{IV}{}_3S_{13}]$[11,12] or the sulfidation of metal oxides[13] and naphthenates.[14] The thioperrhenate compounds have long been used as precursors in the preparation of rhenium-based sulfide catalysts.[15] Gas phase decomposition of $Mo(CO)_6$ in the presence of H_2S[16] also gives MoS_2. Solution routes to MoS_2 studied so far are based on reduction of ammonium thiomolybdate with agents such as hydroxylamine or hydrazine.[17] A typical way of preparing supported hydrodesulfurization catalysts involves impregnation of the shaped alumina support with a suitable metal salt, followed by calcination to oxide and treatment of the oxide with H_2S/H_2 to give the catalytically active metal sulfide.[4]

Recently reported new routes to low-valent metal sulfides include the sol-gel processing of metal alkoxides in hydrogen sulfide atmosphere whereby germanium sulfide[18] and sulfides of lanthanides[19], for example, have been prepared. Thermolysis in high-boiling-point organic media of single-source precursors like thiosemicarbazides constitutes another new route.[20]

Until now nothing has been reported on the possibility of obtaining sulfides directly *via* reactions of transition metal complexes with oxygen-donor ligands and neutral sulfur-donor molecules. We report here the study of reactions of heavy transition metal oxoalkoxides, rhenium(VII) oxide and late transition metal β-diketonates and aminoalkoxides with *N*,*N*-dimethylthioformamide (DMTF), leading to the formation of fine metal sulfides particles at room temperature.

Experimental

Materials and methods

All manipulations were carried out in dry nitrogen atmosphere using a Schlenk line or a dry box. Metal alkoxides, $MO(OMe)_4$ (M = Mo, W), $MoO(O^iPr)_4$ and $Nb(O^iPr)_5$, were obtained by anodic oxidation of metals and purified using conventional techniques.[21] Molybdenum–niobium oxoalkoxide, $Mo_4Nb_2O_8(O^iPr)_{14}$, was obtained by solution thermolysis of a mixture of homometallic alkoxides in toluene.[22] Rhenium heptoxide, Re_2O_7, was purchased from Aldrich and used without further purification. Zinc and nickel acetylacetonates were purchased from Aldrich and purified by repeated recrystallization from dry toluene. Nickel 1-dimethylamino-2-isopropoxide was obtained by metathesis of $[Ni(NH_3)_6]Cl_2$ with the corresponding sodium alkoxide according to ref. 23. Toluene was dried by distillation over $LiAlH_4$. *N*,*N*-Dimethyldithioformamide (DMTF) was purchased from Aldrich and used without further purification.

Volatiles were analyzed by GC-MS using a Hewlett Packard 5890 Series II gas chromatograph equipped with a capillary separative column with DB-Wax film phase (manufactured by J&W Scientific, USA) and coupled with a Jeol JMS-SX/

SX102A tandem mass spectrometer. NMR spectra were obtained on a Bruker 400 MHz spectrometer using $CDCl_3$ as the solvent. X-Ray powder patterns of the solid products were registered using the Guinier technique. The scanning electron micrographs of the samples were obtained in a JEOL-820 scanning electron microscope (SEM), equipped with a Link AN-10000 energy dispersive spectrometer (EDS). Transmission electron microscopy (TEM) images were obtained on a JEOL 2010 microscope.

Sample preparation

The standard procedure included dissolution of ≈0.25 g of metal oxoalkoxide, oxide or acetylacetonate in a solution prepared by mixing 5 ml toluene with 0.5 ml DMTF at room temperature. For the preparation of the heterogeneous catalysts, approximately 1 g of mesoporous γ-alumina (10 nm pore diameter) predried for 2 h at 300 °C and cooled in dry nitrogen atmosphere, was added to the solution immediately after the dissolution of a late transition metal derivative, that is before the solution turned turbid. Reference catalysts were prepared by impregnation of alumina with aquoes solutions of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ and NH_4ReO_4, respectively, followed by calcination for 2 h at 450 °C in order to form supported oxides. Conversion to sulfides took place in connection with the catalytic activity measurements (see below).

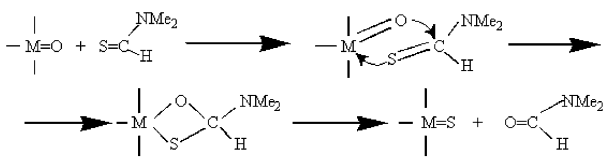
Catalytical measurements

Catalytic tests were made in a tubular 7.5 mm inner diameter, high-pressure reactor loaded with a mixture of 0.30 g catalyst in the form of 600–850 μm mesh granulates and glass microbeads. The feed was an *n*-heptane solution containing 3.0% dibenzothiophene, 0.5% indole, 1.0% naphthalene, 2.5% dimethyldisulfide and 0.5% *n*-nonane; the latter substance was added to serve as an internal GC standard. Upon entry into the hot reactor the liquid feed evaporated and was mixed with a stream of H_2. The total pressure (reactants + *n*-heptane + H_2) at the reactor temperature of 350 °C was 50 atm, corresponding to $p(H_2) = 38$ atm. The liquid feed-to-gaseous H_2 ratio was 0.5 $ml\cdot min^{-1}$:250 ml min^{-1}. Under these conditions all dimethyldisulfide in the feed quickly undergoes complete hydrodesulfurization to produce a background partial pressure of H_2S in the reactor. This partial pressure of H_2S ensures that catalysts remain fully sulfided during the catalytic tests. In order to ensure that catalysts are fully sulfided before catalytic tests, *in situ* sulfidation was made for 4 h at 350 °C by means of a 2.5% solution of dimethyldisulfide (DMDS) in *n*-heptane and with $p(H_2) = 42$ atm. For comparative reasons, this sulfidation procedure was carried out both for catalysts prepared by the traditional method and for catalysts prepared by the new method described in this paper.

During the ≈24 h catalytic test of a catalyst sample, the composition of the exit gas from the reactor was continuously monitored and quantified by GC-FID. The retention times of the various reactant and product species were known from previous GC-MS analyses using the same column (non-polar WCOT, Hewlett-Packard Ultra 2) as the GC-FID. Under the reaction conditions employed the catalysts in question gives rise to the following reactions. Dibenzothiophene (DBT) is desulfurized by two parallel routes, yielding either biphenyl (BP) or cyclohexylbenzene (CHB) as products. Indole is denitrogenated to yield ethylbenzene and ethylcyclohexane as products. Naphthalene is hydrogenated to tetralene. The conversions determined were expressed as pseudo-first-order rate constants for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD), respectively (Table 1).

Table 1 Catalytic activities of hydrodesulfurization catalysts prepared by a traditional method and by the new method described in this paper (rate constants in h^{-1})

	k(HDS)	*k*(BP)	*k*(CHB)	*k*(HDN)	*k*(HYD)
New method					
9 wt·% Mo/Al_2O_3	2.4	1.9	0.5	9.2	5.1
Traditional method					
8 wt·% Mo/Al_2O_3	2.7	2.4	0.3	4.6	3.3
New method					
6 wt·% Re/Al_2O_3	2.0	2.0	0.0	6.4	0.5
Traditional method					
6 wt·% Re/Al_2O_3	3.7	3.7	0.0	2.0	0.4



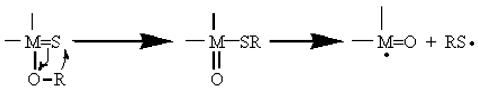
Scheme 1

Results and discussion

The reaction of $MO(OMe)_4$ (M = Mo, W) or Re_2O_7 with DMTF was associated with distinct color changes—from orange to dark brown for Mo and W and from green to orange-brown and then dark brown for Re. All solutions lost transparence in 2–3 h, indicating the formation of colloid systems. Essentially complete precipitation of sulfides occured in 3–4 days in the absence of alumina support and in a few minutes when alumina was present. This indicates that alumina plays a catalytic role. The light heating of solutions (to 40–50 °C) dramatically accelerated the precipitation, which could then be completed in 1–2 h in the absence of alumina. The X-ray powder and SEM-EDS studies revealed the solids to be MoS_2, WS_3 and Re_2S_7, respectively. The GC-MS studies of the vapor phase over solutions, obtained after precipitation of the sulfides, showed the formation of exclusively *N*,*N*-dimethylformamide (DMF) in the case of rhenium oxide [Fig. 1(a)], DMF and mainly dimethylsulfide, Me_2S, in the case of $WO(OMe)_4$, and DMF, traces of Me_2S and a mixture of sulfur-containing oxidation products like dimethyldisulfide, Me_2S_2, in the first hand, in case of $MoO(OMe)_4$ [Fig. 1(b)].

These data suggest that the mechanism of this reaction (see Scheme 1) includes as the first step the formation of an oxo-metal complex with S-ligating DMTF, which is then, *via* an electronic rearrangement, converted into a thio-metal complex with DMF. The latter is either released *via* dissociation or replaced directly by the next DMTF ligand. In the case of Re_2O_7, this process eventually leads to the formation of metal sulfide molecules. In the case of molybdenum or tungsten alkoxides further transformations include first alkyl cation transfer from athe lkoxo oxygen atom to the doubly bonded sulfur and then the elimination of dialkylsulfide or dissociative cleavage of M–(SR) bonds with formation of alkylpolysulfides (see Scheme 2).

The kinetic studies carried out with the help of ^1H NMR (Fig. 2) showed that all the steps of this process occur practically simultaneously: the signal of the methyl protons from



Scheme 2

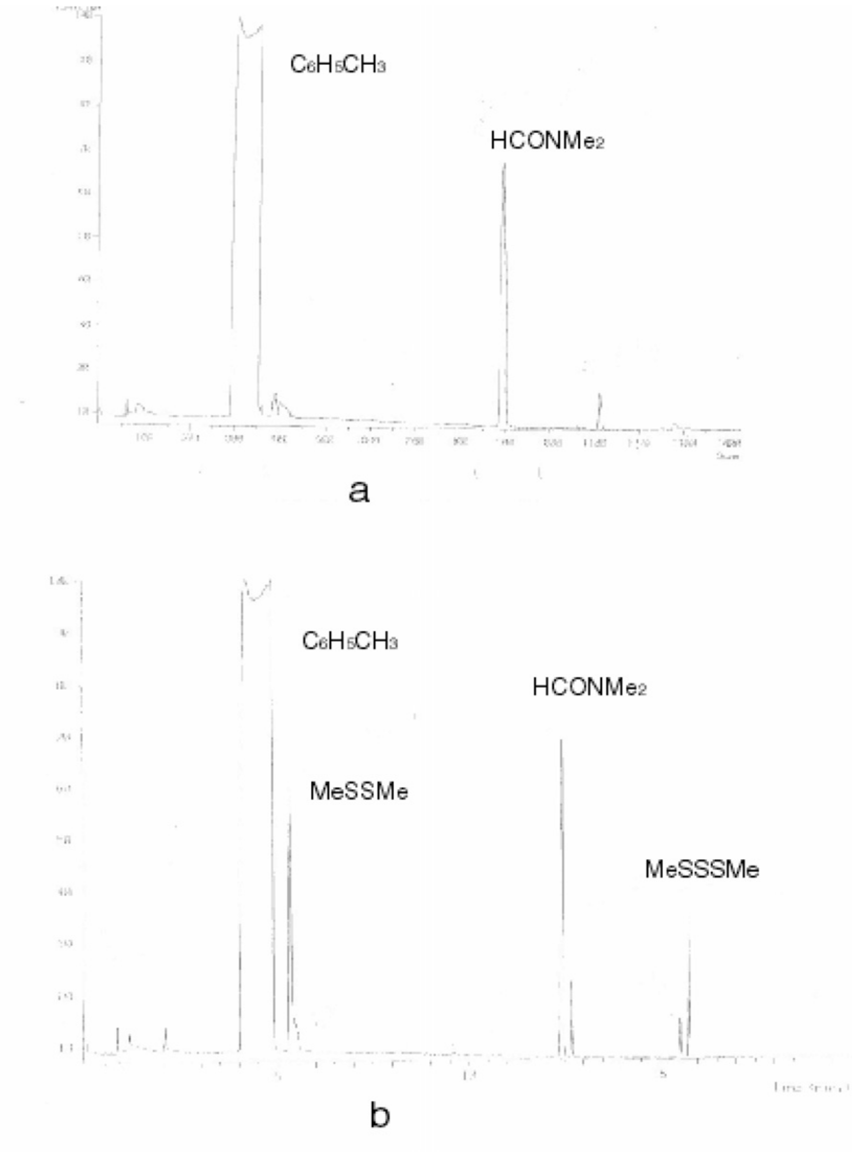


Fig. 1 Gas chromatograms of the products of the reactions of (a) Re_2O_7 and of (b) $MoO(OMe)_4$ with DMTF in toluene.

the methoxide groups (a singlet at 4.21 ppm at 300 K) decreases in intensity and disappears, being replaced with a number of signals (between 4.1 and 4.6 ppm) corresponding to methyl protons in methoxide and thiomethoxide groups in the various thioalkoxides formed (their intensity decreases gradually over time). The new signals that appear in the spectrum indicate the formation of dimethylformamide (7.80 ppm singlet, CH; 2.65 and 2.75 ppm singlets CH_3) and alkylsulfides (singlets at 2.06, 2.21 and 2.30 ppm). The studies using solutions with different concentrations have shown the reaction to be on average of first order with respect to both the molybdenum alkoxide and DMTF.

In principle, the mechanism described provides in all the cases studied discrete metal sulfide molecules. The subsequent formation of solid metal sulfides, that is materials with extended structures, is very sensitive to the thermal and chemical conditions employed. In this way control of the size of the crystallites obtained is possible. Carrying out of the process constantly at room temperature provides crystals that vary significantly in size—from single crystals distinguishable by a bare eye (about 0.1 mm) to aggregates consisting of crystallites of about 0.1 μm (100 nm) in size. Only the latter (and much more uniform in size) were obtained by heating of solutions to 40–50 °C. The introduction of alumina provides apparently much easier and more uniform crystal growth, facilitating the precipitation of the solid products. The initially smooth alumina surface [Fig. 3(a)] becomes covered by approximately 1 μm broad thin plates of Re_2S_7 [Fig. 3(b)] or MoS_2 [Fig. 3(c)]. EDS analysis showed a uniform distribution of metal sulfides throughout the alumina particles, indicating that not only the outer surface but also the pore system is covered with the sulfide formed. The TEM images of the MoS_2/Al_2O_3 samples obtained (Fig. 4) do not allow to distinguish the single particles of the sulfide, but the higher absorption of the electrons (darker coloration) of the spaces between the alumina crystallites indicates the presence of nanoparticles of the molybdenum sulfide inside the pores of the matrix. The EDS analysis of the small particles of crushed composite indicates clearly that the distribution of molybdenum sulfide is fairly uniform and corresponds to the reported average of approximately 9 wt·% Mo in Al_2O_3. The electron diffraction pattern of the composite contains only the lines interpretable as reflections from the applied γ-alumina support (Fig. 4).

We have investigated also the possibility of transforming heterometallic oxoalkoxide complexes into sulfides using the reaction with DMTF. The EDS analysis of the sediment formed from the solution of the $Mo_4Nb_2O_8(O^iPr)_{14}$ complex in toluene on addition of DMTF indicated the sulfide formed to have a $Mo_4Nb_2S_9$ composition, the metal ratio being thus

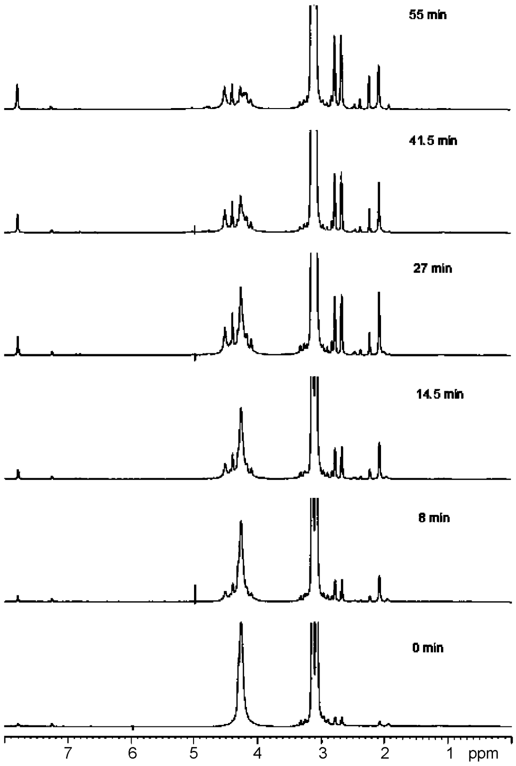


Fig. 2 The transformation of the ^{1}H NMR spectrum of the $MoO(OMe)_4$–Me_2NCHS system with time.

preserved upon transformation into sulfide. The sulfide was found to be amorphous in the X-ray powder study, but the SEM image (Fig. 5) indicates the presence of regularly shaped particles. The absence of a distinguishable X-ray pattern is thus supposedly due to low reflective ability or low long-range order in the crystals.

The reaction with DMTF of the nickel or zinc acetylacetonates or nickel dimethylaminoisopropoxide was found to lead to colloidal solutions and the subsequent precipitation of sulfides with NiS and ZnS compositions (according to SEM-EDS), also at room temperature. These reactions do not appear to be as fast as the reactions involving the heavy transition metals. It was completed in a week at room temperature, compared with 3–4 days for Mo and Re. The GC-MS analysis of the reaction products indicated the major organic reaction products to be 2,4-pentanedione (Hacac), dimethylformamide and also condensation products such as 4-(*N*,*N*-dimethylamino)-2-pentenone, 4-(*N*,*N*-dimethylamino)-2-butenone, 3-thio-2,3,4-pentanetrione, butadione, *N*,*N*-dimethylacetamide, *etc.* The reaction mechanism presumably involves condensation between the acetylacetonate ligand and *N*,*N*-dimethylthioformamide as the first step, resulting in simultaneous *in situ* formation of water and hydrogen sulfide. The latter finally transforms the acetylacetonate complex present into free acetylacetone and molecular metal sulfide. Further aggregation of the sulfide molecules leads to formation of extremely fine microcrystallites. The TEM investigation of the precipitate from the obtained colloidal solutions of ZnS (Fig. 6) showed that it consisted of very small (about 5 nm in diameter), very strongly aggregated particles of sphalerite. The surface of the precipitate is pronouncedly developed and clearly has a fractal character, indicating that the speed of particle growth is comparable with that of aggregation.[24] This allows to suppose that the discovered reaction may provide an attractive approach to nanoparticles of semiconductors with controllable morphology on introduction of appropriate surfactants.[25]

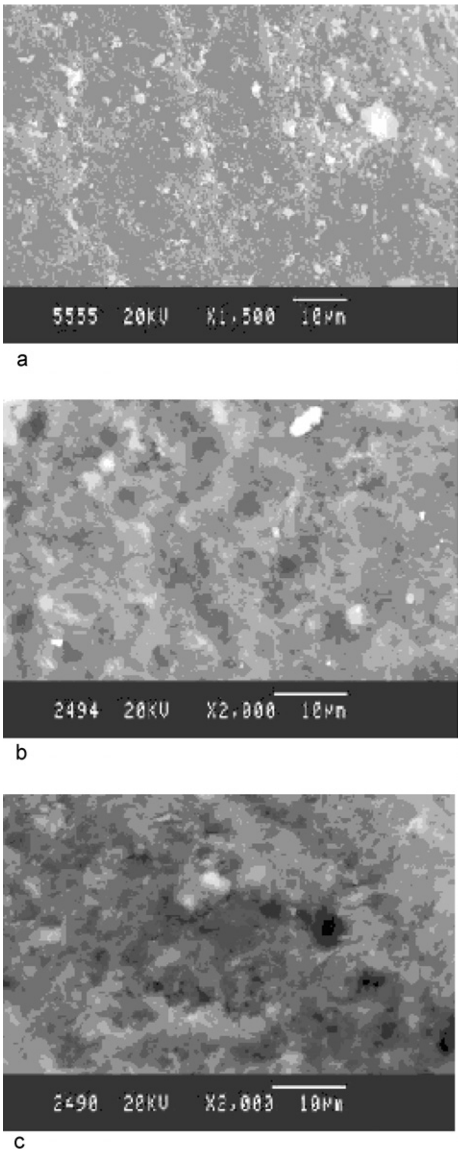


Fig. 3 SEM micrographs of (a) untreated alumina support, (b) alumina support with Re_2S_7 deposit and (c) alumina support with MoS_2 deposit.

The results of catalytic activity studies of alumina-supported molybdenum and rhenium sulfide are shown in Table 1. Each of the two catalysts prepared by the new method described in this paper is compared with a catalyst of similar metal loading prepared by a traditional aqueous impregnation route, in which metal sulfide is formed upon sulfidation of supported metal oxide *after* loading into the catalytic reactor. Activities are generally low as is expected for pure metal sulfides; the industrially used catalysts contain MoS_2 promoted by Co or Ni and thus have much higher activity.[4] The catalytic activity of MoS_2 appears to be quite similar whatever the preparation method. That indicates that both materials contain approximately the same amount of catalytic sites. The most pronounced difference between the new and traditionally prepared catalysts is found in their activity for hydrodenitrogenation (HDN); samples prepared by the new method are more than twice as active for HDN. Thus, this new preparation method produces metal sulfide structures with altered catalytic selectivties. The ability to vary selectivities in such a way is important both in connection with the understanding of the catalytic mechanism and in connection with the development of new improved catalysts for industrial application.

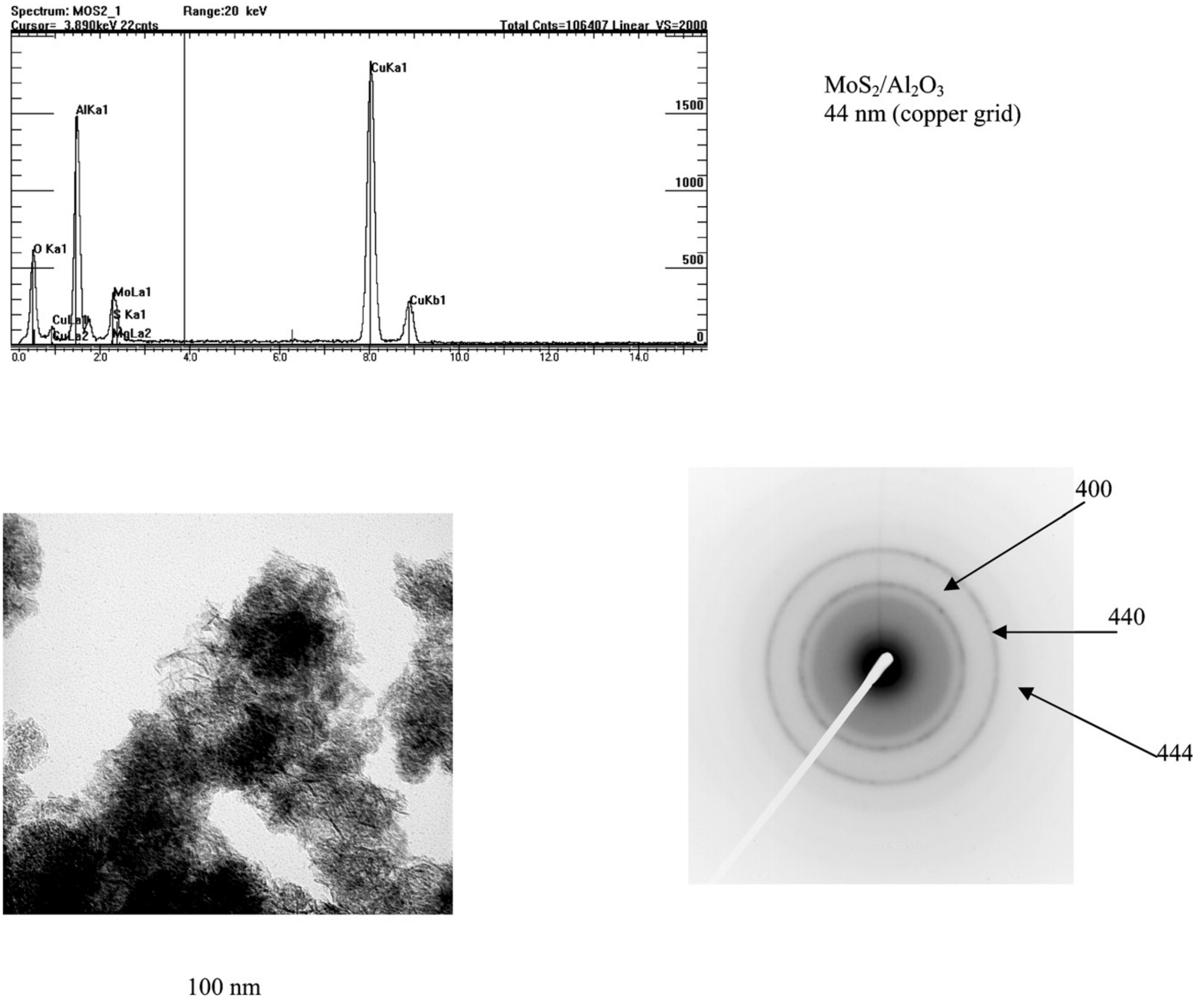


Fig. 4 EDS spectrum, TEM image and the electron diffraction pattern of the MoS$_2$/Al$_2$O$_3$ nanocomposite (the indexing is given for γ-Al$_2$O$_3$).

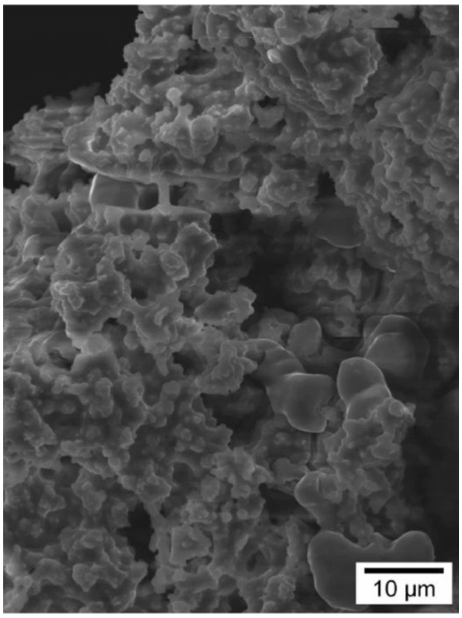


Fig. 5 SEM micrograph of the Mo$_4$Nb$_2$S$_9$ phase obtained by reaction of Mo$_4$Nb$_2$O$_8$(O^{i}Pr)$_{14}$ with DMTF.

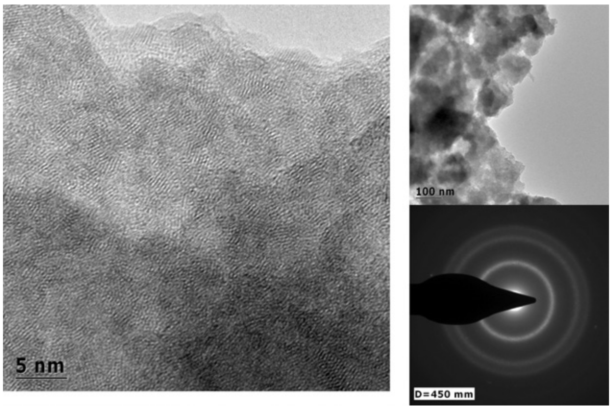


Fig. 6 TEM, HREM images and the electron diffraction pattern for the ZnS sample obtained by reaction of Zn(acac)$_2$ with DMTF.

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