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Complete List of Authors:	Ramos, Manuel; Instituto de Ingenieria y Tecnologia, Fisica y Matematicas Torres, Brenda; The University of Texas at El Paso, MRTI Bahena, Daniel; The University of Texas at San Antonio, Physics Yacaman, Miguel; University of Texas at San Antonio, Department of Physics and Astronomy Alvarez-Contreras, Lorena; CIMAV-Chihuahua, Catalysis Chianelli, Russell; UTEP, MRTI; none,
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Structural Aspects of Ternary Phase Ni/$MoWS_2$ Catalyst: An Aberration Corrected HRTEM Study

M. Ramos[1,2], B. Torres[1], Daniel Bahena[3], M. José-Yacamán[3], Lorena Alvares-Contreras[4] and R.R. Chianelli[1]

1) Materials Research and Technology Institute, University of Texas at El Paso, 500W University Ave, El Paso, TX. 79968, U.S.
2) Departmento de Física y Matemáticas, Universidad Autónoma de Ciudad Juárez, Avenida del Charro #450 N Ciudad Juarez, Chihuahua, MX. 32310
3) Department of Physics, University of Texas at San Antonio, One UTSA Circle, 78249 U.S.
4) Centro de Investigación en Materiales Avanzados S.C., Laboratorio Nacional de Catalysis-Chihuahua Miguel de Cervantes 120, Complejo Industrial Chihuahua, Chihuahua, Apdo. Postal 31109 México

Abstract

In the past 20 years, one of the best catalytic materials for hydrodesulphurization reactions of crude oil has been the transition sulfides, MoS_2, known also as the "workhorse" of the refinery industry. It has been proven by this and other research groups that the MoS_2 laminar structure can increase its catalytic activity when promoted with cobalt or nickel. The location of active sites seem to be at rim and edge sites on that particular laminar structure, as demonstrated using Mössbauer spectroscopy and x-ray techniques. However, due to maximum capability of this promoted systems, Co(Ni)/MoS_2 to remove heterogeneous atoms (S, N, O) - a search for new catalytic materials has currently been an ongoing activity in the HDS community. Here, we will present the new family of ternary phase catalyst with special emphasis on their structural aspects, as revealed by aberration corrected (Cs) high-resolution transmission electron microscopy techniques, in an attempt to describe the nature of active sites on this porous nano-rod like catalytic materials.

Key Words: MoS_2, HRTEM, Catalytic, HDS

Corresponding author: maramos1@utep.edu, manuel.ramos@uacj.mx

1. Introduction

The usage of characterization techniques, such as high-resolution transmission electron microscope (HRTEM), has been a method of high success [1]. By using HREM technique, it was possible to understand the honeycomb-like structure in MoS_2 laminar structure [2]. Found experimentally by doing a combination of HRTEM measurements and computer assisted simulations, the slabs were held together by weak Van der Waals bonding at a distance of 0.62nm [3] in agreement with crystallographic information [4]. Later, another study indicated that honeycomb structures are created due to a formation of Moiré pattern in the basal (001) plane of MoS_2, leading to a creation of metallic states on the edge of laminar structure [5, 6]. One of principal applications for this laminar MoS2 material is to be used as catalytic material.

Edges of laminar MoS_2 structure are able to attract heterogeneous atoms of Sulfur, Nitrogen, Oxygen as contained in crude oil [7], and that catalytic activity can be enhanced by introducing Cobalt or Nickel at the edge of laminar structures (1010)-plane. This effect is known as "promoting systems" [8]. HRTEM techniques have shown that laminar MoS_2 or WS_2 structure can form different final morphologies (i. e. Nanorods, nanotubes, spheres, bundles, etc.) depending only on the selection of precursors and synthesis routes [9, 10]. Those final morphologies, considered as "Nano technological materials", is what makes them unique to study using HRTEM techniques. A full survey and description of WS_2 nanotubes can be found in the literature [11]. In addition, *in-situ* HTREM studies, using heating stage holders to produce carbide reaction between MoS_2 and carbon content in TEM grid, proved that carbon provokes MoS_2 laminates to bend [12]. Measurement of mechanical strength for WS_2, obtaining a Young´s modulus of 217 GPa, was possible using HRTEM cantilever holders with an image resolution of 2 nm [13]. In here, a study using aberration corrected (Cs) ultra-high resolution transmission electron microscope is presented to depict structural aspects for new family of ternary catalyst ($Ni/MoWS_2$).

2. Cs-corrected ultra-HRTEM

Experimental imaging of ultra-high resolution TEM was performed in a JEOL ARM (200F) with an operational voltage of 200 kV equipped with a Cs corrector (CEOS GmbH) and FEG-STEM/TEM unit. HAADF probe size was set to 0.095 nm with a current of 23.2 pA for bright field imaging, Condenser Lens aperture size was set to 40μm. A camera length (CL) of 8 cm/6cm and collection angle of 68–280 mrad/90–270 mrad was set for STEM images, to eliminate contributions from un-scattered beams.

3. Experimental Synthesis of Ternary Catalyst

Two solutions, one of ammonium thiotungstate $(NH_4)_2WoS_4$ prepared using 10 mL of water and a second solution of ammonium thiomolybdate $(NH_4)_2MoS_4$ was mixed at room temperature. The resulting mixture solution was added to a third aqueous solution of $NiCl_2$ under vigorous stirring; it was possible to detect black precipitate forming rapidly.

The final product (tri-metallic) was vacuum filtered to extract a precursor paste. The solutions stoichiometric equations are as follows:

$$(NH_4)_2MoS_4 + (NH_4)_2WS_4 \longrightarrow 2(NH_4)_2WMoS_4 \quad (2.2.1)$$

$$2(NH_4)_2WMoS_4 + 0.5NiCl_2 \longrightarrow Ni_{0.5}/[(NH_4)_2WMoS_4]_2 + 2NH_4Cl \quad (2.2.2)$$

Later, a hydrothermal reaction occurred using about 5 grams of tri-metallic product that was added to 50 ml of water. The new solution was placed inside the reactor of 0.5 liter at room temperature. The reactor was purged with nitrogen gas and the temperature rose to 300ºC achieving a final pressure of 1200 psi. Maintained for two hours it was later allowed to let the reactor cool down to room temperature to collect sample, which was washed using isopropanol.

4. Results and Discussion

Ternary Ni/$MoWS_2$ catalyst synthesized using hydrothermal methods, present a nano-rod like morphology as presented in figure 1. Some aggregations are noticeable at edge and bottom part of the nanorod. In order to understand those segregate portions, enhancements of those areas were made (*at red dotted circle*) and are presented in figure 2, which corresponds to MoS_2 laminar structures as revealed by characteristic fringes [14].

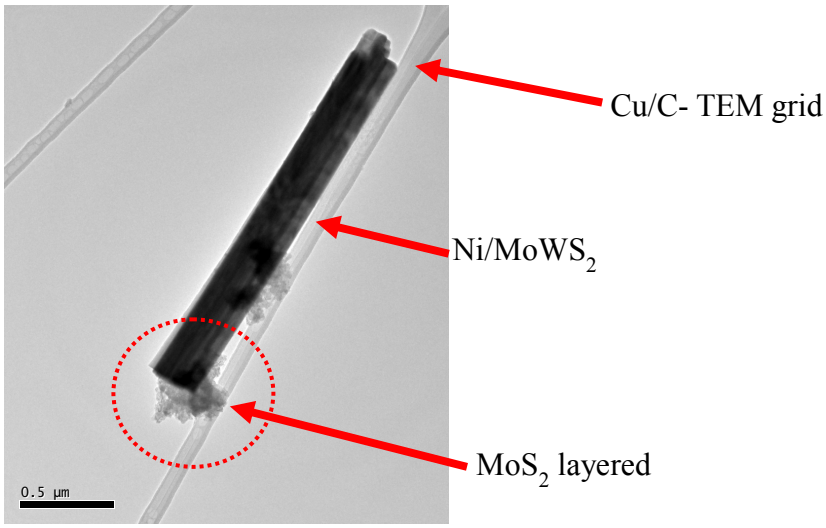

Figure 1: HRTEM image showing a nanorod-like structure in ternary Ni/$MoWS_2$ catalyst.

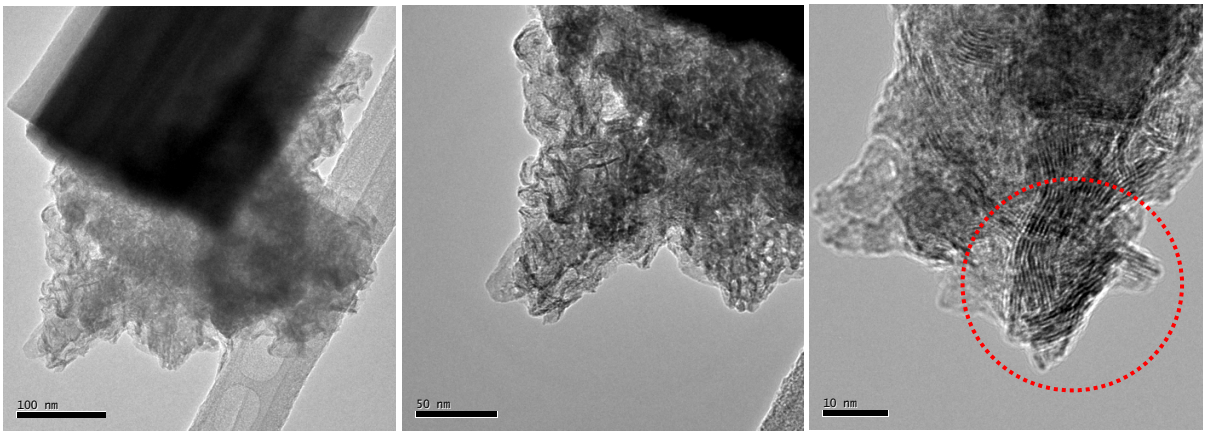

Figure 2: Sequence of HRTEM images of segregates that corresponds to 2H-MoS_2 slabs, as indicated by characteristic fringes in red dotted circle [14].

Further survey was completed in dark field ultra-high resolution STEM mode. Results indicate that rods are empty inside, concluding a nanotube like structure. It is clear that further analysis using Cs-corrected Ultramicroscopy tools can provide more details regarding the structural aspects on these catalytic materials. Figure 3 presents results for STEM mode at 20nm resolution scale. The profile on the right is indicating the width of nanotube and one can see clearly two crests and a trough. Width of nanotube is 108.4 nm as measured digitally using ®Digital Micrograph package.

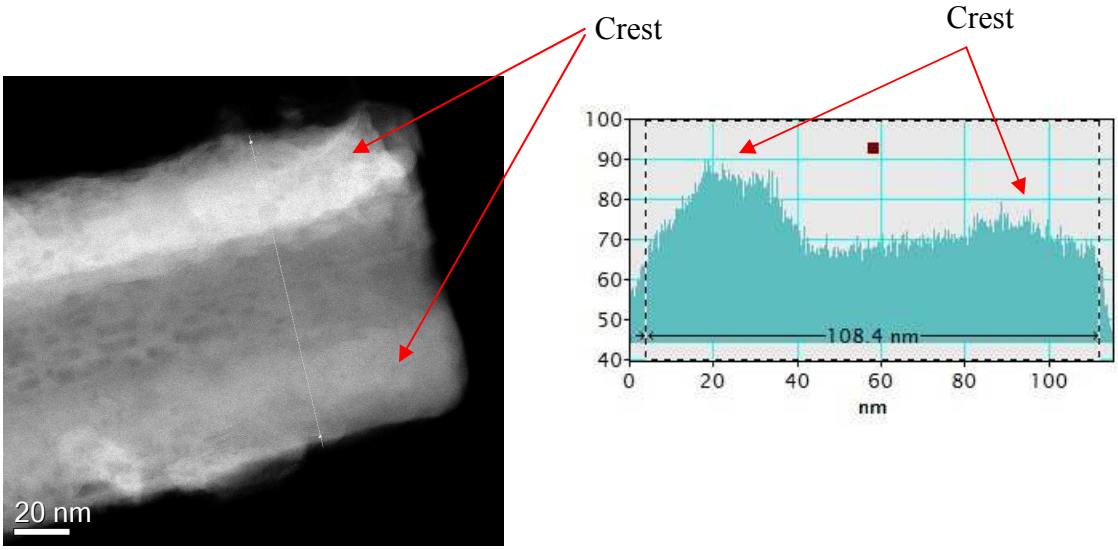

Figure 3: Dark field Scanning Transmission Electron image of ternary Ni/$MoWS_2$ catalyst.

In similar fashion further analysis as completed in bright field STEM mode. It was possible to detect the fringes at the edge of nanotubes. Figure 4, presents a detail of the structure, interlayer distance was found to be 0.65nm in agreement with experimental crystallographic results for either WS_2 or MoS_2 [4, 12, 14], which opens a question: *Are nanotubes walls made out of Molybdenum or Tungsten di-sulfide?*

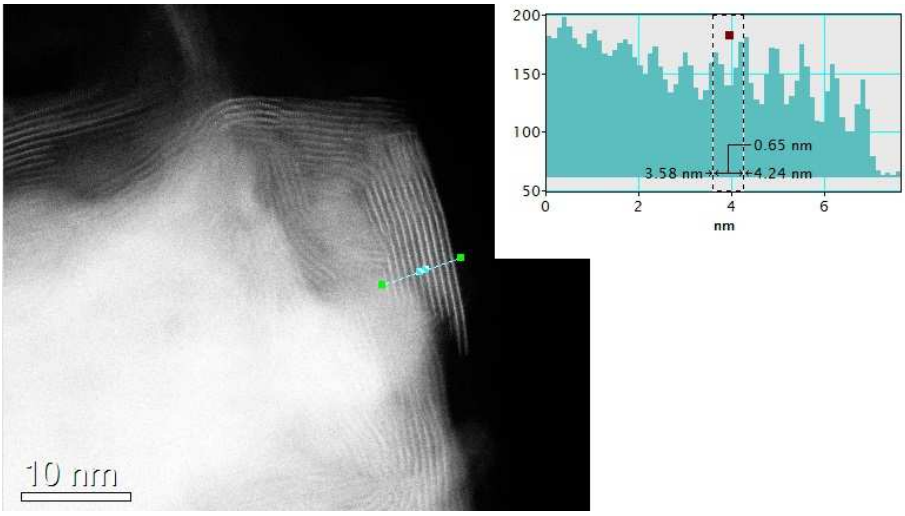

Figure 4: Bright field Scanning Transmission Electron image of ternary Ni/$MoWS_2$ catalyst.

To answer that question, further analysis needs to be completed using Electron Energy Loss Spectroscopy (EELS) in order also to collect information about the chemical bonding which will satisfy a localization of catalytic sites for HDS to occur.

CONCLUSIONS

A successful synthesis of ternary Ni/$MoWS_2$ catalyst is presented here. Samples were prepared using a mixture of two aqueous solutions thiotungstate $(NH_4)_2WoS_4$ and ammonium thiomolybdate $(NH_4)_2MoS_4$ under hydrothermal conditions. Complete detailed analysis to depict structural aspects, by meaning of Cs-corrected ultra-high resolution TEM, indicates a nanorod-like structure. Further analysis using STEM revealed a nanotube-like structure, with a width size of 108.4 nm. Aggregates of MoS_2 was detected at bottom part of nano-tube (nano-rod), measurements of interlayered distance was confirmed to be 0.65 nm, in agreement with 0.62nm theoretically [3]. Lastly, the usage of ultra-high resolution TEM seems to be a very suitable characterization when surveying structure/function aspects of catalytic materials.

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