



Double promotion effect on HDS CoNiMo/Al₂O₃ catalysts applied in the hydrodesulfurization of dibenzothiophene



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ABSTRACT

In this work, we present Co_xNi_yMo/Al₂O₃ catalysts. Those trimetallic catalysts exhibited well catalytic activity in the hydrodesulfurization of dibenzothiophene (DBT). We report here an optimal proportion between the Co and Ni promoters that allow us to obtain better textural, crystalline and catalytic properties in the MoS₂ based catalysts.

INTRODUCTION

There is a global demand for clean fuels and consequently of highly active catalysts to achieve the production of ultra-low sulfur fuels (<15 ppm S for diesel). Improvements in catalyst formulation as adding of a third metal or organic additives can prevent promoter migration or increase the MoS₂ crystallites dispersion [1]. The double promotion of cobalt and nickel also results in synergistic improvement in the CoNiMo/γ-Al₂O₃ catalytic performance [2].

The trimetallic site formation has been the key to high catalytic activities in deep HDS of fuels [2]. In this work we explore four different compositions in CoNiMo/γ-Al₂O₃ sulfides that have been prepared by the co-impregnation method.

EXPERIMENTAL

A series of Co_xNi_yMo/Al₂O₃ catalysts where x and y refers to the molar ratio of Co/(Co+Ni) and Ni/(Ni+Co) respectively (x=Co/(Co+Ni)= 0, 0.65, 0.75, 0.85, 0.95 and 1.0 and x+y=1) is presented. The impregnated materials were dried at 80 °C and then calcined at 500 °C in the air atmosphere during four h. In the final stage, CoNiMo catalysts were obtained by sulfurization at 400 °C per 1 h in a 15% H₂S / H₂ gas flow.

RESULTS

TEXTURAL PROPERTIES, UV-VIS, H₂-TPR AND TEM IMAGES

The diffuse reflectance UV-vis spectra of catalysts with different Co/Co+Ni molar ratio has a plateau (from 545 nm to 630 nm) related to β-CoMoO₄, where the Mo⁶⁺ presents tetrahedral coordination while Co²⁺ stills in octahedral coordination. This plateau has overlapped signals, with the contribution of tetrahedral Ni species (NiAl₂O₄ spinels), in which the primary signal is located at 635 nm. NiAl₂O₄ spinels usually are related to inactive nickel compounds. These profiles present peaks in two intervals (regions between 400-600 °C and above 600 °C). The reduction profile of Co_{0.65}Ni_{0.35}Mo catalysts exhibits three reduction temperature peaks at T ~495, 567, and 745.

For the Co_{0.65}Ni_{0.35}Mo catalyst, the peak at 490 °C represents the reduction of β-NiMoO₄. Additionally, the increase of Co cations at Co_{0.95}Ni_{0.05}Mo catalyst shifts the reduction of the octahedral Mo₆₊ to a higher T related to the interaction between Co and Mo species. The second stage of molybdenum oxide reduction and β-CoMoO₄ reduction occurs at higher temperatures (776 °C and 582 °C, respectively).

XRD patterns of the catalysts in oxide state exhibited the CoMoO₄ phase; that phase is a good precursor of highly disperse sulfides [3] as can be observed in the corresponding XRD pattern of the sulfide catalysts. All catalysts present a type-4 isotherm. Our micrographs from the TEM results indicated a better performance in the Co_xNi_yMo/Al₂O₃ catalyst with slab length of 1.5 nm.

Table 1. Theoretical metallic content of MoO₃, NiO and CoO.

Catalyst	%MoO ₃	%NiO	%CoO
0.65	17	1.35	2.55
0.75	17	1.00	2.90
0.85	17	0.60	3.30
0.95	17	0.20	3.7

Table 2. Textural properties of MoS₂ catalysts.

Cat.	S _{BET} (m ² g ⁻¹)	V _P (cc/g).
0.65	89	0.09
0.75	132	0.11
0.85	164	0.15
0.95	170	0.16

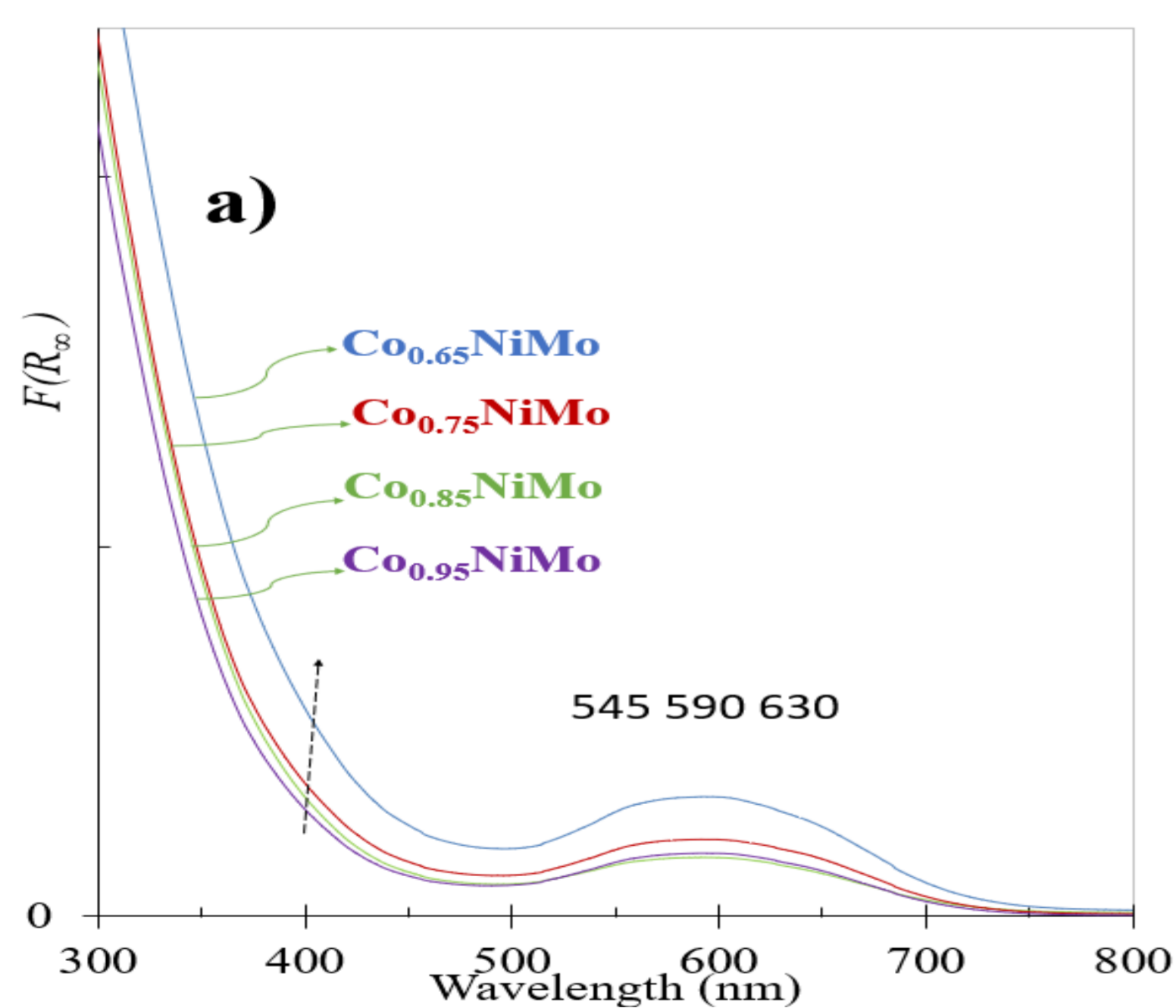


Figure 1. Diffuse reflectance UV-vis spectra of oxide catalysts.

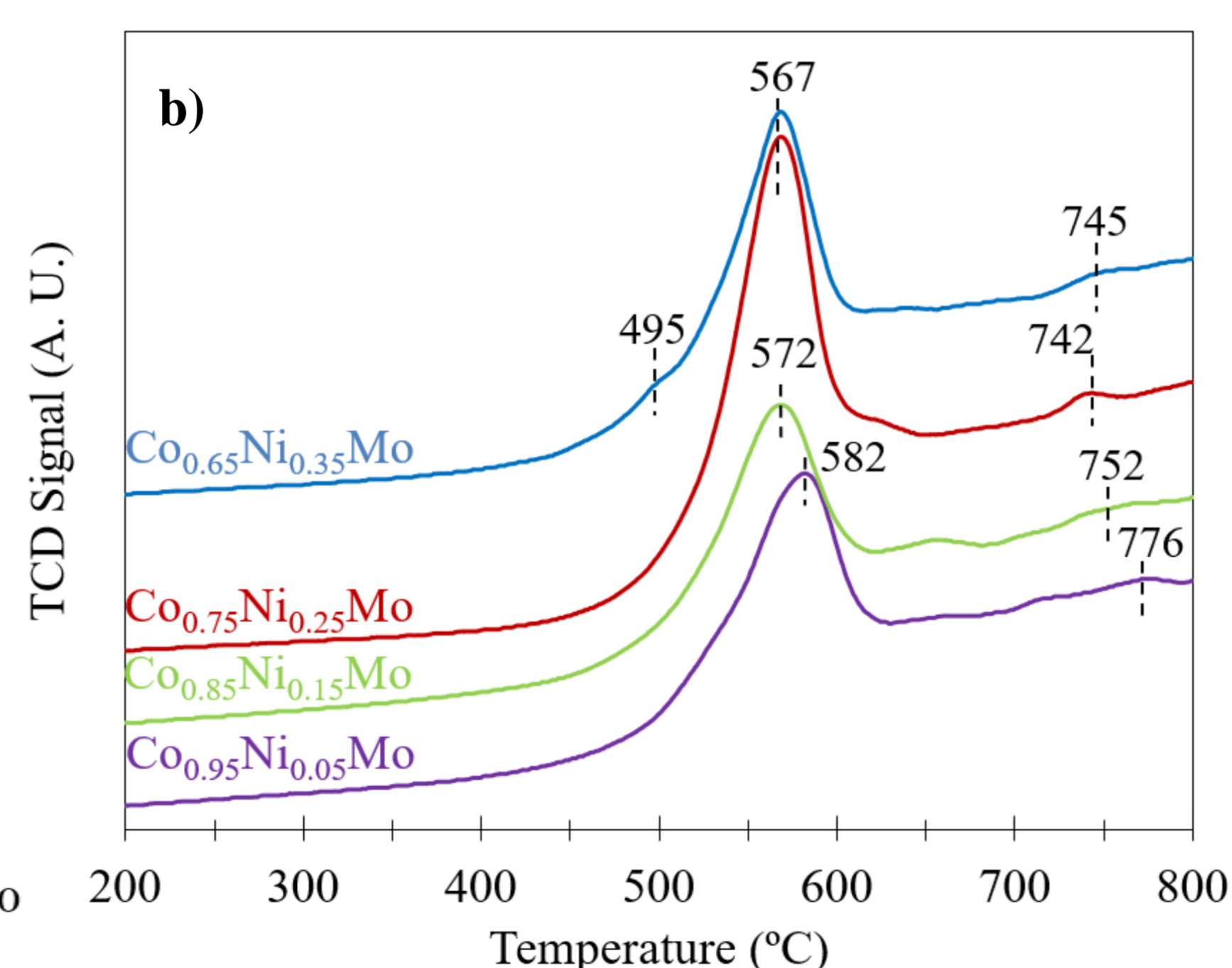


Figure 2. H₂-TPR profiles of the CoNiMo oxide samples.

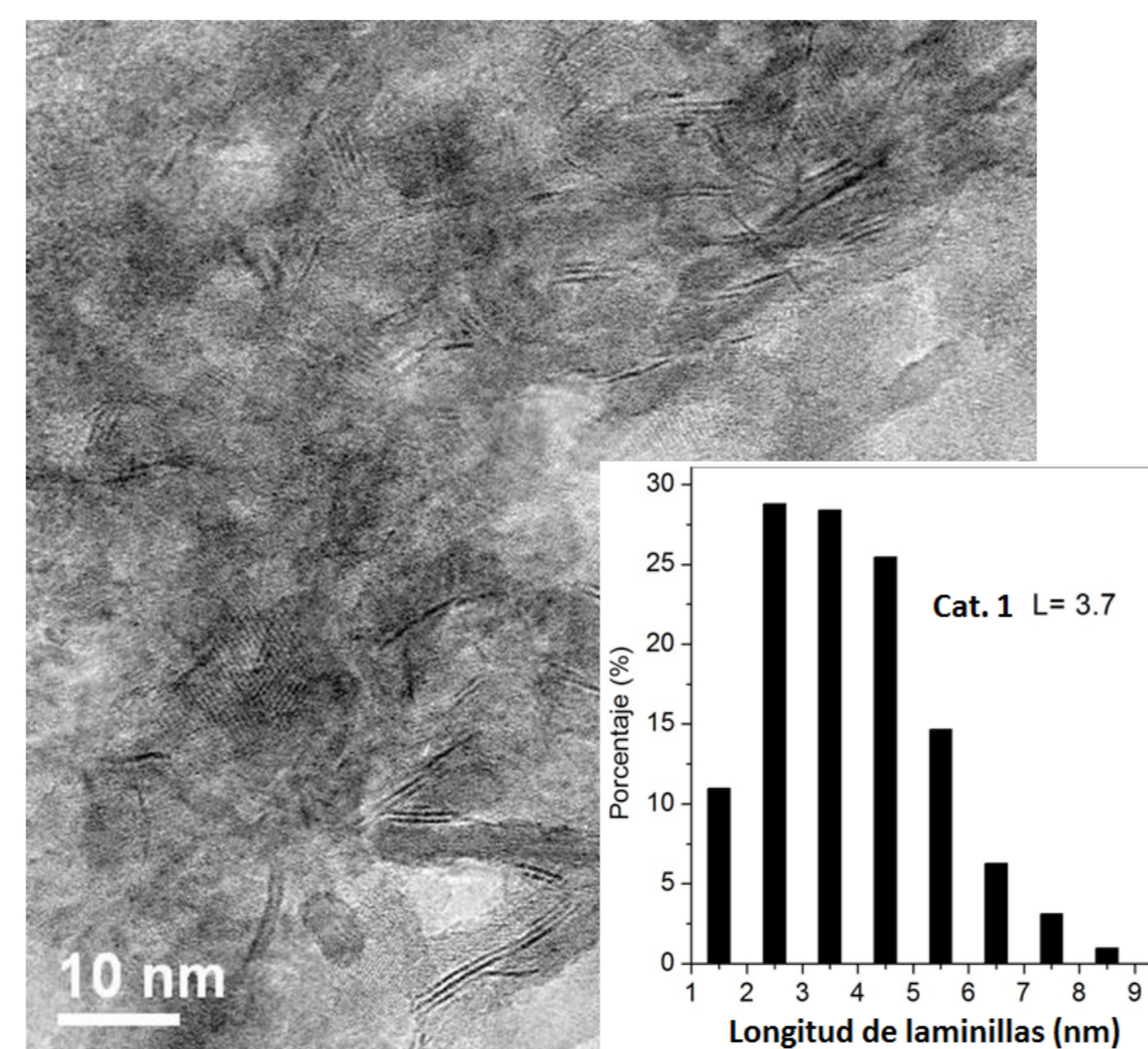
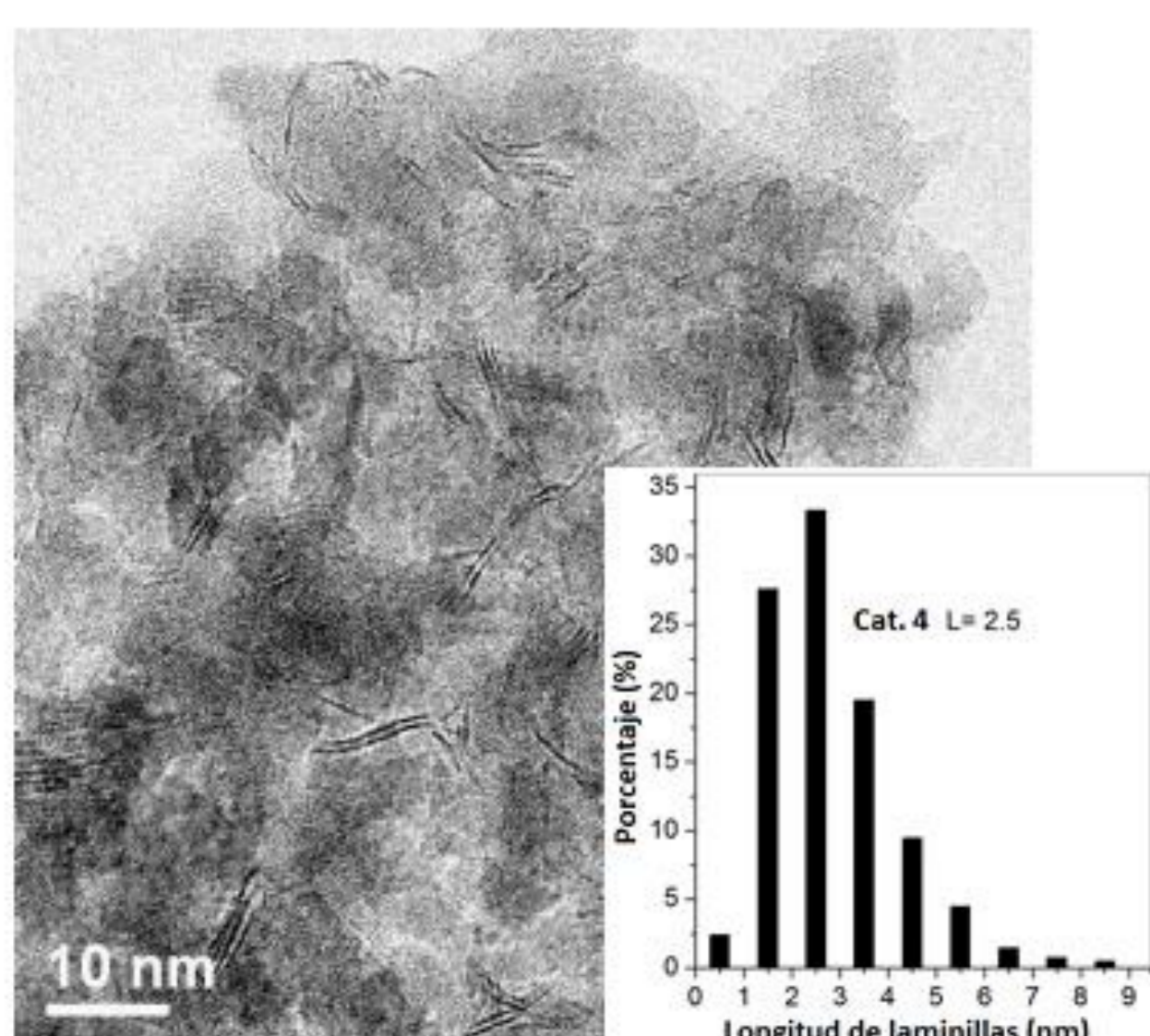


Figure 3. TEM micrographs of the (a) Co_{0.95}Ni_{0.05}MoS₂ and (b) Co_{0.65}Ni_{0.35}MoS₂ catalysts.

N₂-PHYSISORPTION ISOTHERMS, XRD PATTERNS AND HDS OF DBT REACTION

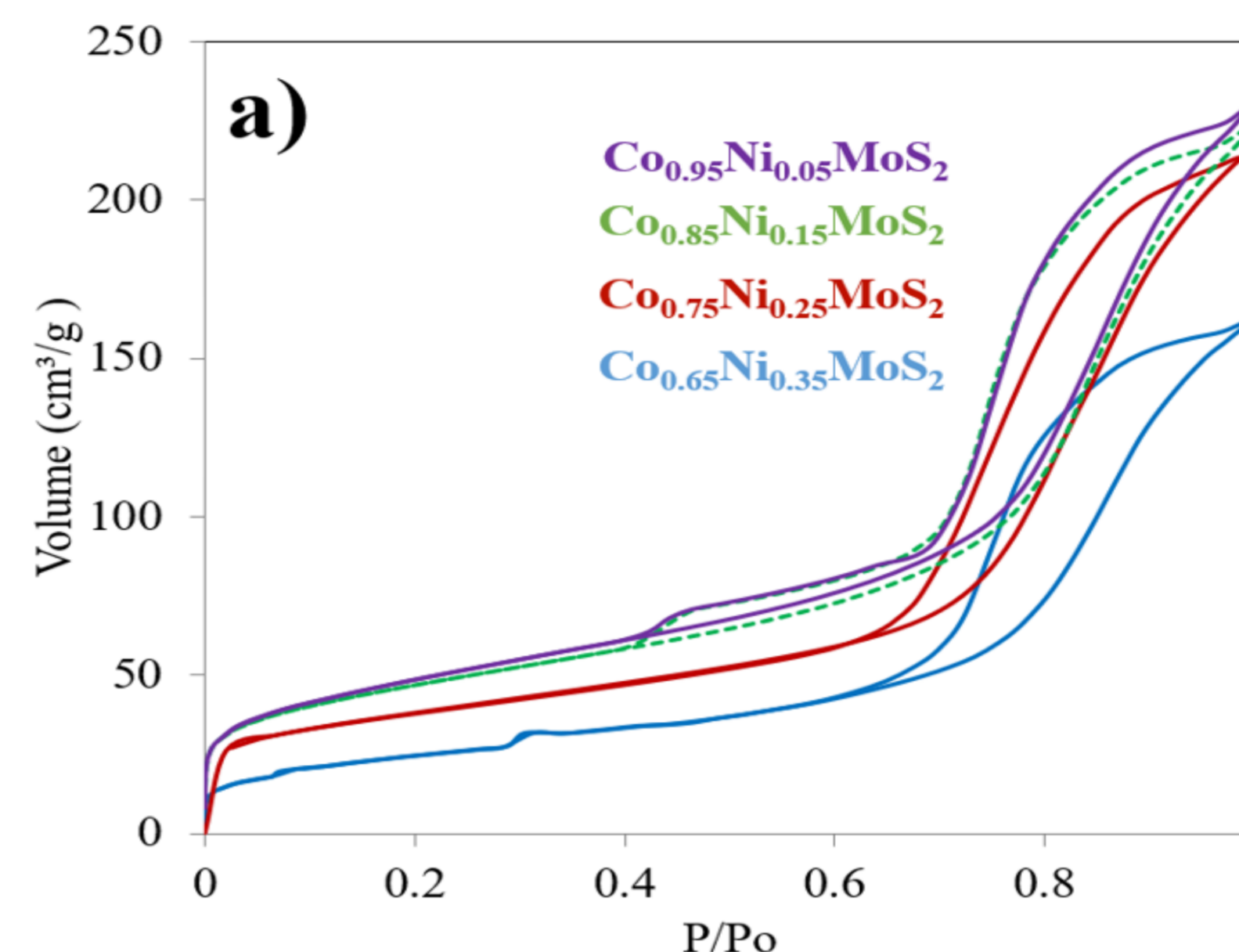


Figure 4. N₂ Adsorption-desorption isotherms of trimetallic catalysts in the sulfide state..

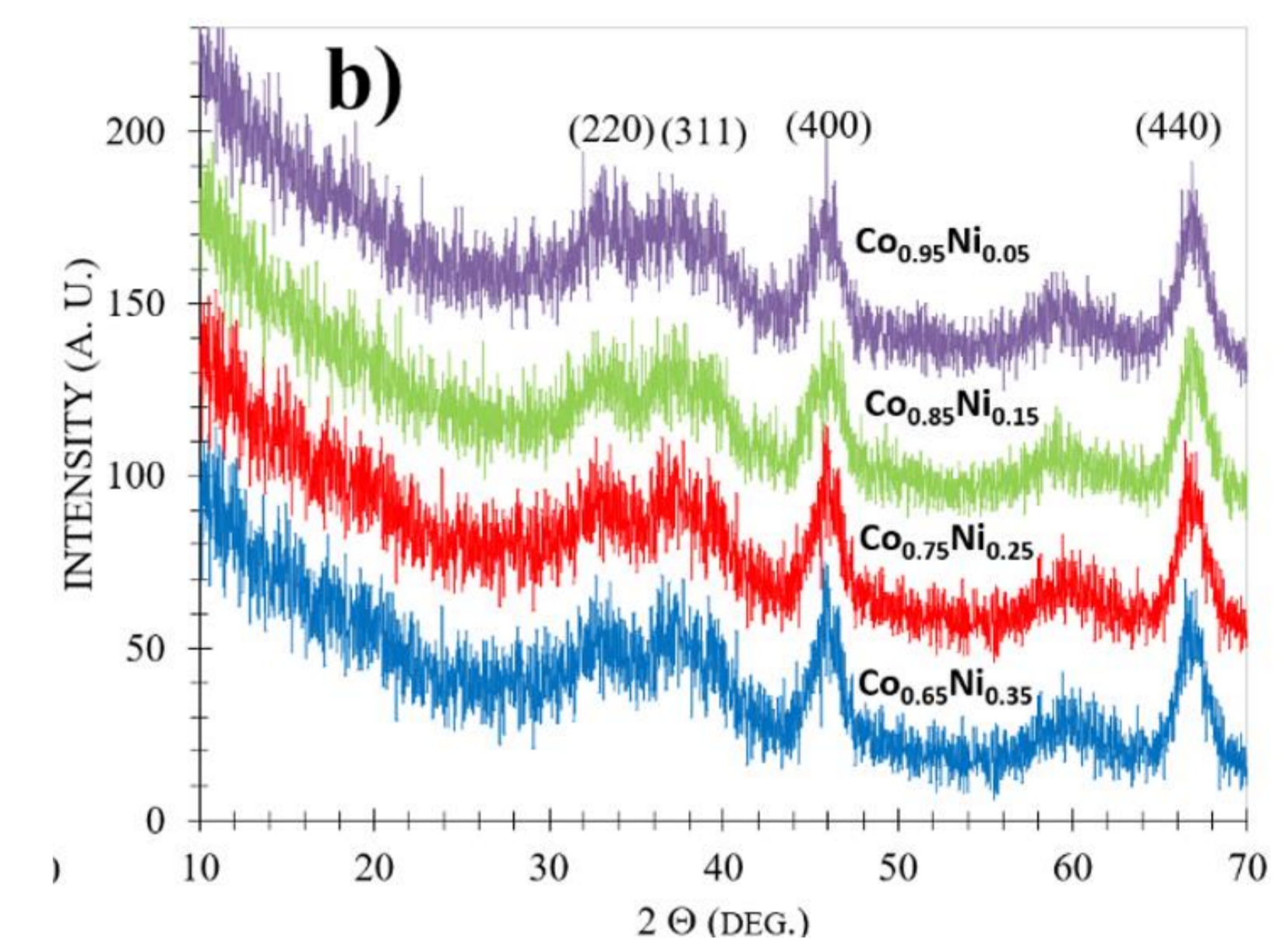


Figure 5. XRD patterns of trimetallic catalysts in the sulfide state.

Table 3. Initial reaction rate, surface area and slab length of MoS₂ based catalysts.

Cat.	V _r initial (X10 ⁻⁸ mol _{DBT} g ⁻¹ S ⁻¹)	L (nm)
0.65	71.3	3.7
0.75	107.4	3.0
0.85	145.4	2.9
0.95	155.4	2.5

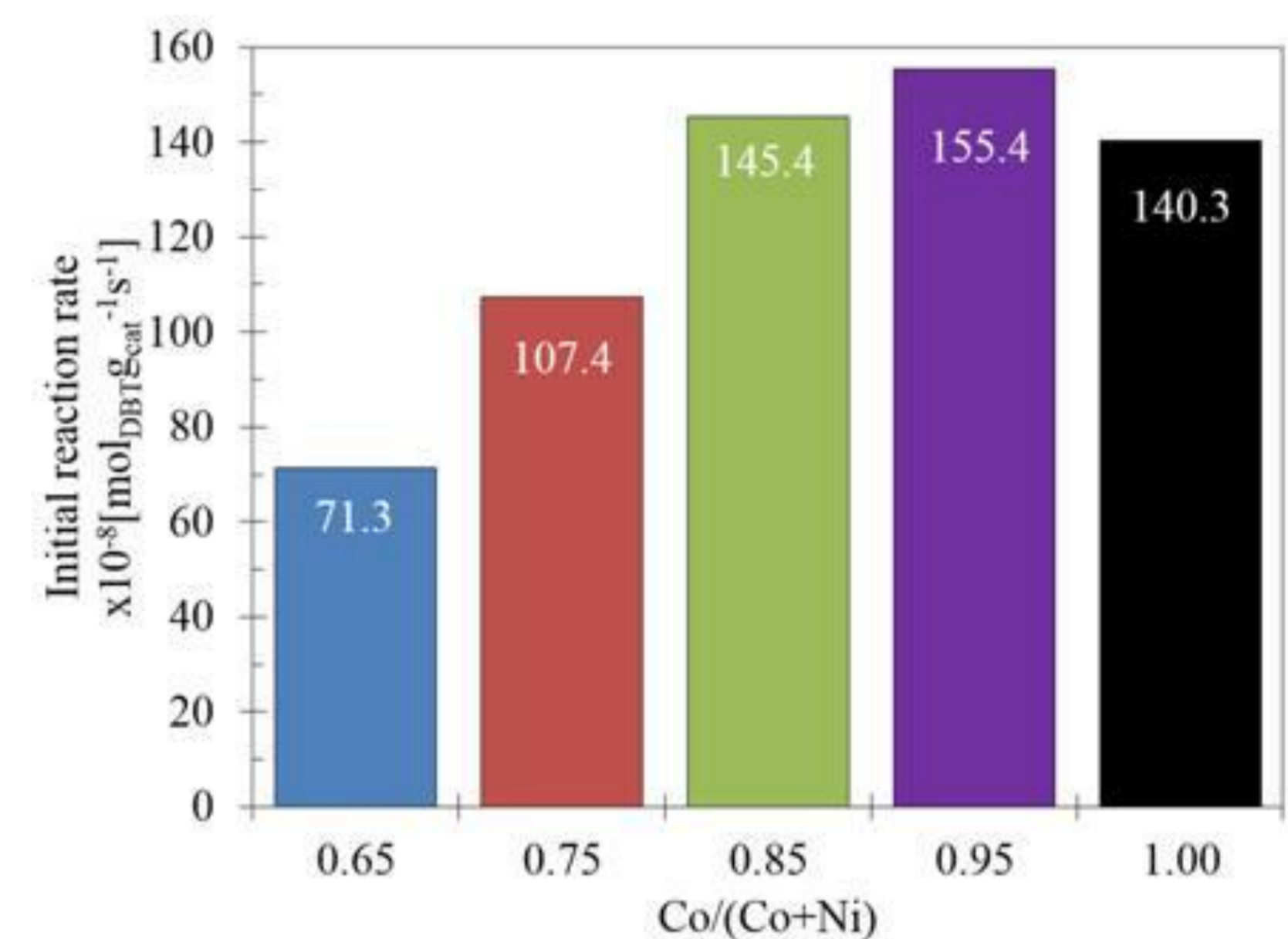


Figure 6. Catalytic activity of Co_xNi_yMo/Al₂O₃ catalysts in the HDS of DBT reaction.

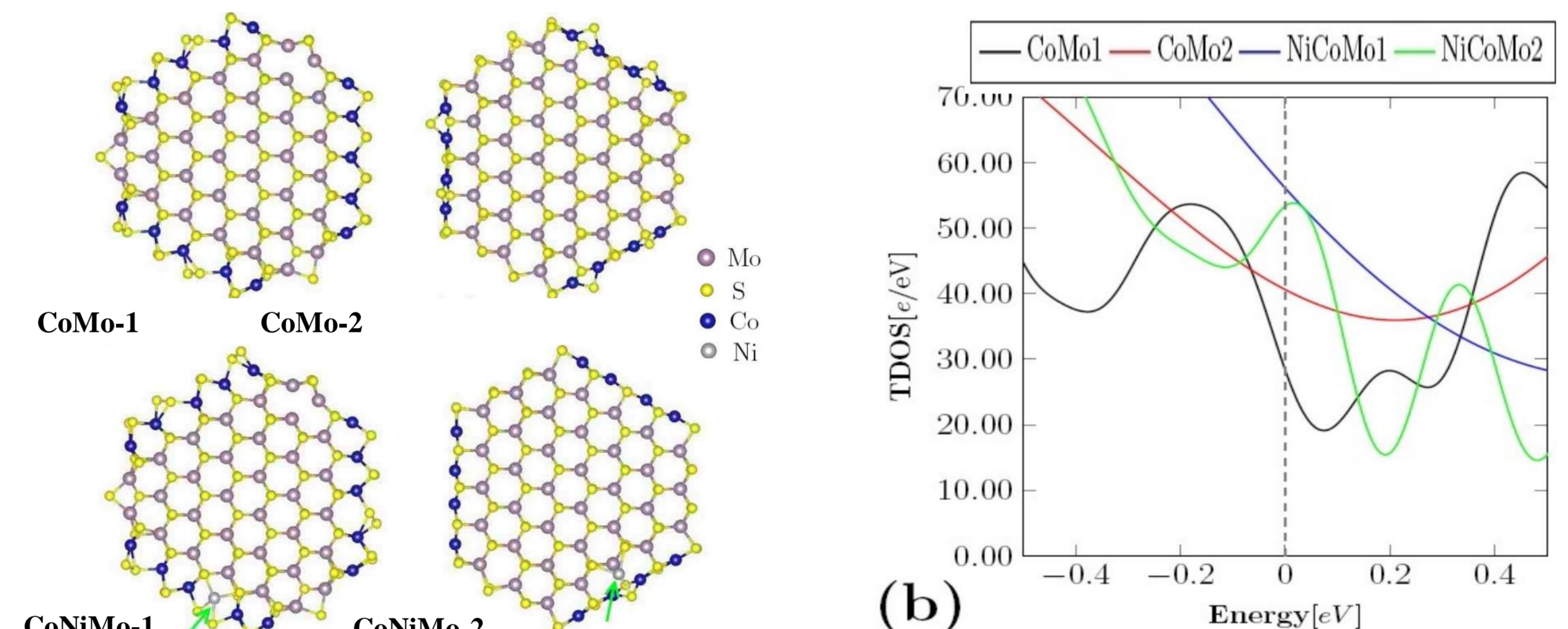


Figure 7. Theoretical DFT results. Figure 7a shows the four bimetallic (top) and trimetallic (down) structures analyzed for this work. Figure 7b showed that the ternary metal sulfide edge has a higher population of the d-type states over the Fermi level than the bimetallic ones. This population increase leads to enhanced reactivity of the sulfide surface towards electron-donating species [4].

CONCLUSIONS

UV-Vis spectra showed the simultaneous incorporation of Co and Ni promoters exhibited preference toward Co to form bimetallic CoMoO₄ oxides. The small nickel amount in Co_{0.95}Ni_{0.05}Mo might be enhanced the catalytic activity with further reducibility to the Co-Mo-S than Ni-Mo-S active sites. The TPR results indicated that low nickel content has a favorable effect in the Co_{0.85}NiMo and Co_{0.95}NiMo catalysts delaying the reduction temperature of the active component, Mo oxide species. Delay of reduction temperature has the effect of preventing the promoter, Co(Ni), segregation under the effect of the sulfidation H₂/H₂S conditions [1]. From TEM analysis the better promotion effect was associated with a slab length decrease of the MoS₂ particle size, resulting in an apparent synergy effect on MoS₂ active site promotion by increasing the catalytic activity. At higher nickel amounts, we observed low activity of Co_{0.75}Ni_{0.25}Mo and Co_{0.65}Ni_{0.35}Mo that can be explained either as a moderate dispersion of nickel in MoS₂ nanostructure or by the formation of segregated nickel species like NiAl₂O₄ structures decreasing textural properties. All five synthesized catalysts exhibited higher activity than an industrial CoMo/Al₂O₃ reference. The increased activity was explained in terms of a co-electronic promotion induced in Mo atoms by the presence of Co and Ni atoms in the edge of MoS₂ slabs. Our theoretical DFT results showed that Co and Ni atoms modify Mo local coordination to promote Mo atoms' electronic participation at the metallic edges of trimetallic sulfides, increasing their reactivity.

REFERENCES

- [1] N. Rinaldi, Usman, K. Al-Dalama, T. Kubota, Y. Okamoto, Appl. Catal. A 2009, 360, 130–136.
- [2] S. Badoga, A. Ganesan, A.K. Dalai, S. Chand, Catalysis Today, 291 (2017) 160–171.
- [3] V. La Parola, B. Dragoi, A. Ungureanu, E. Dumitriu, A. M. Venezia. Appl. Catal. A General 386(2010) 43–50.
- [4] Olivas, A.; Antúnez-García, J.; Fuentes, S.; Galván, D. H. Catalysis Today 2014, 220–222, 106–112.

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