



NiMoW catalysts supported on MgO-Al₂O₃ mixed oxides for the hydrodesulfurization of dibenzothiophene

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MgO-Al₂O₃x materials were synthesized as supports for NiMo catalysts used in the hydrodesulfurization of dibenzothiophene. The binary MgO Al₂O₃x mixed oxides were labeled as MgAl-x with x=Al/(Al+Mg)= 0, 0.20, 0.25, 0.33, and 1. An improved activity in the hydrodesulfurization (HDS) reaction of dibenzothiophene (DBT) was showed at x=0.20. The developed NiMoW/MgAl-0.20 catalyst exhibited a higher rate than the industrial catalyst. The increased activity was explained in terms of a co-electronic promotion induced in Mo atoms by the presence of W atoms in the MoS₂ slabs.

INTRODUCTION

Nowadays, it is necessary to develop a new generation of catalysts that will remove sulfur impurities of fuels at the ultra-low sulfur level required by environmental regulations ($S < 15$ ppm). The use of mixed MgO-Al₂O₃ as TMS supports resulted in enhancing the catalytic activity [1]. This variation in the catalytic properties was explained in terms of a modulator effect where the interaction between Mo species and mixed MgO-Al₂O₃ supports was drastically changed [2]. High hydrodesulfurization activities exhibited by trimetallic NiMoW catalysts in theoretical-experimental studies were attributed to the mixed Mo_{1-x}W_xS₂ sulfide phases [3]. Recently, NiMoW sulfides supported on Mg-Al binary oxides were reported as catalysts for carbon monoxide catalytic hydrogenation to produce high alcohol synthesis [2]. A synergistic effect from tungsten doping MoS₂ slabs was suggested as the active phase formation. Herein, we present a new approach to obtain NiMoW/MgO-Al₂O₃ catalysts. We analyzed the influence of tungsten in the catalytic properties for the HDS of DBT, comparing NiMoW/MgO-Al₂O₃ and NiMo/MgO-Al₂O₃ sulfide catalysts. We calculated Mo_{1-x}W_xS₂ phases by DFT analysis to explain W enhanced HDS reactivity.

EXPERIMENTAL.

A series of MgAl-x ($x = \text{Al}/(\text{Al}+\text{Mg}) = 0, 0.20, 0.25, 0.33, \text{ and } 1$) supports were synthesized from calcination of hydrotalcites [4]. The MgAl-x oxides were co-impregnated with Ni and Mo (the metal content was MoO₃ = 13%, NiO = 3% per gram of support). After calcination and sulfidation the NiMo/MgAl-x catalysts were obtained and evaluated in the hydrodesulfurization of dibenzothiophene (HDS of DBT). The catalysts were characterized by N₂ physisorption, UV-Vis spectroscopy, XRD and TEM.

RESULTS

Table 1. Textural properties and basicity for the NiMo(W)/MgAl-x materials.

MgAl-x	S _{BET} P _s (nm)	P _v (cm ³ ·g ⁻¹)	XPS X ^b	Basicity ^c (mmol·g ⁻¹)	S _{BET} (m ² ·g ⁻¹)	P _s (nm)	P _v (cm ³ ·g ⁻¹)	
X ^a nominal	Supports		NiMo(W) sulfides					
0.00	200	17.0	1.14	0.0	0.30	65(36)	4.5(5)	0.14(0.03)
0.20	133	22.3	0.84	0.28	0.17	130(n.d.)	7.8(n.d.)	0.33(n.d.)
0.25	127	12.8	0.51	0.30	0.23	39(12)	24(6)	0.25(0.02)
0.33	119	17.9	0.24	0.4	0.17	23(20)	35(6)	0.21(0.03)
1.00	262	5.4	0.46	1.0	0.12	23(110)	35(4)	0.21(0.19)

^ab: x = Al/(Al+Mg) nominal and surface compositions, ^c Titration with benzoic acid.

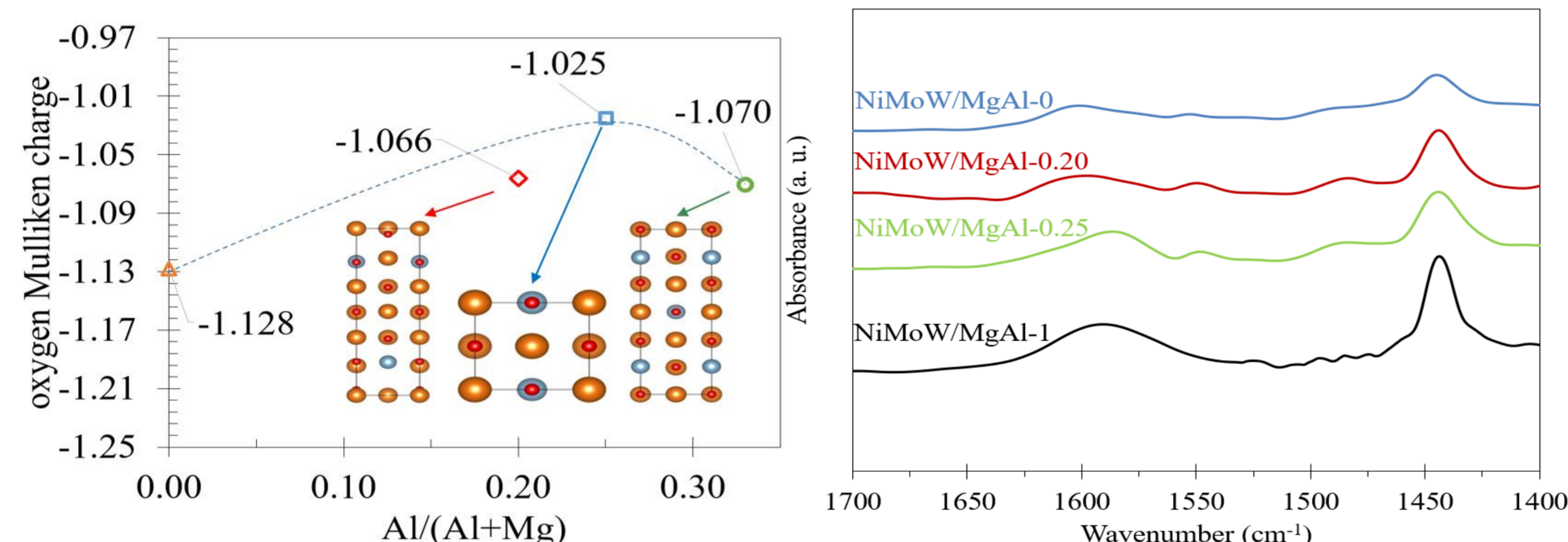


Figure 1. The unit cell of bulk MgO (space group, Fm-3m) modified by isomorphic substitution of Mg atoms by Al atoms to build distinct Al_xMg_{1-x}O ($x = \text{Al}/(\text{Al}+\text{Mg}) = 0, 0.20, 0.25, 0.33$) oxides is also shown (left). The Mulliken charges of oxygen atoms in these mixed oxides obtained by DFT calculations are included. Theoretical DFT studies showed that the maximum basicity decrease occurs at $x = 0.25$. At this value of Al/(Al+Mg) ratio the Al atoms participate at the Fermi level, and the Mg atoms decrease its participation, consequently we observed the maximum decrease on the MgO total basicity.

FTIR spectra of pyridine adsorbed in fresh sulfide catalysts (right). The differences in acidity observed as a function of the Al content are due to the support. The NiMoW/MgAl-0, NiMoW/MgAl-0.20, and NiMoW/MgAl-0.25 catalysts led to small bands centered in 1548 cm⁻¹ which were assigned to pyridinium ion related to Brønsted acid sites. Otherwise, the NiMoW/MgAl-0 and NiMoW/MgAl-0.20 catalysts exhibited a broad signal at 1600 cm⁻¹ that shows an increase of intensity and broadening for $x=0.25$ and $x=1$ attributed to an increase of the Lewis acid strength with the Al content. The composition $x=0.25$, corresponds to the maximum participation of the acidity provided by the Al atoms calculated by XPS and theoretical DFT approximation [4].

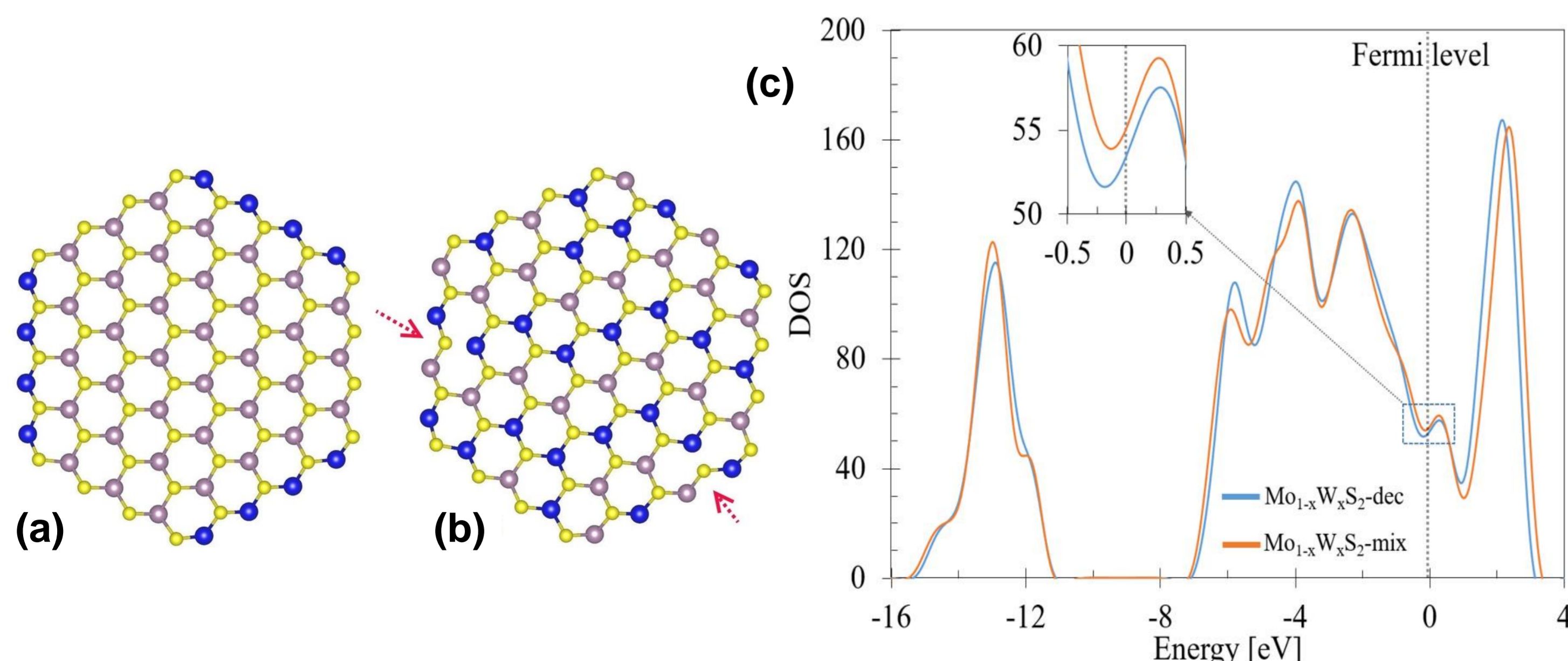


Figure 2. Theoretical modeling results: (a) Mo_{1-x}W_xS₂ decorated, (b) Mo_{1-x}W_xS₂ mixed, (c) total density of states (DOS). Two Mo_{1-x}W_xS₂ structures with a different W atom distribution on the hexagonal MoS₂ slab were optimized (W replace Mo atoms in the MoS₂ structure). The first structure exhibited W atoms decorating the hexagonal borders of the MoS₂ slab (Fig. 2a). In the second Mo_{1-x}W_xS₂ structure (Fig. 2b), W atoms optimized positions are presented in a mixed distribution in the entire MoS₂ slab. Fig. 2c compare the density of states of the two optimized structures; the Mo_{1-x}W_xS₂-dec cluster resulted in lower DOS than the corresponding DOS in the Mo_{1-x}W_xS₂-mix cluster. In general, high values over the Fermi level correspond to an improvement in the electronic properties and frequently are correlated to an enhancement in reactivity [5].

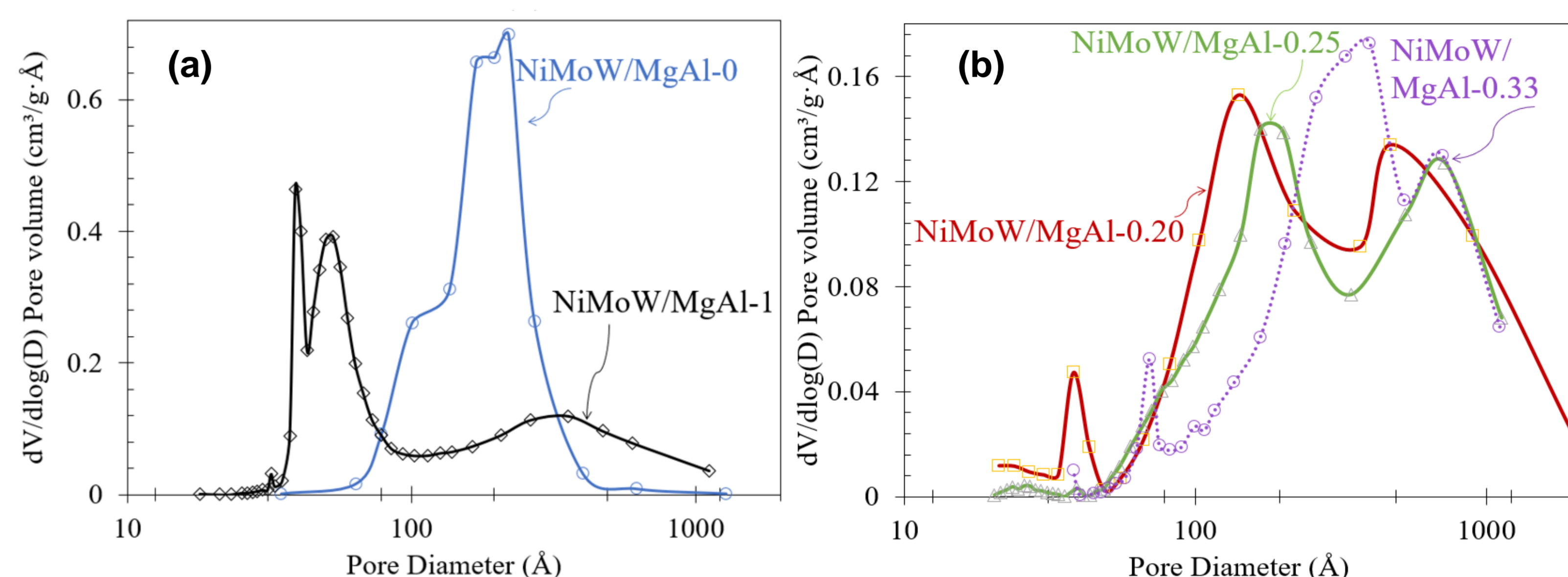


Figure 3. Average pore size distribution of (a) pure and (b) mixed NiMoW sulfides.

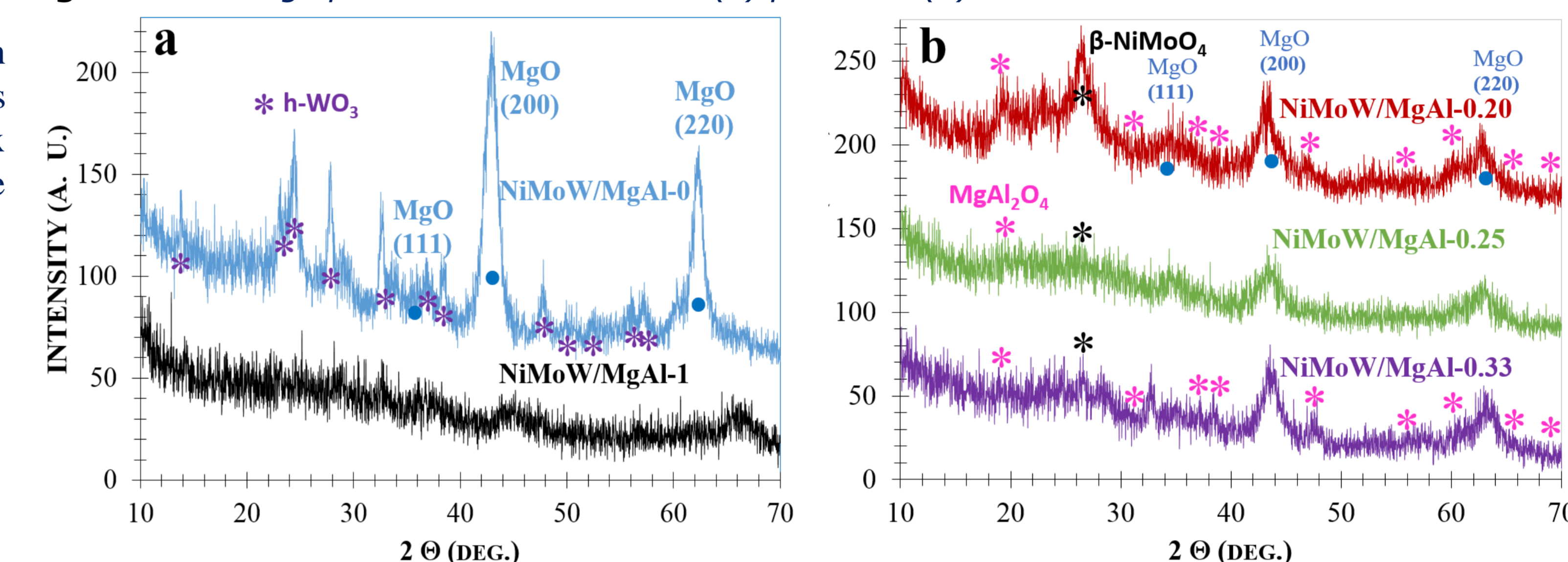


Figure 4. XRD patterns of (a) pure and (b) mixed NiMoW sulfides.

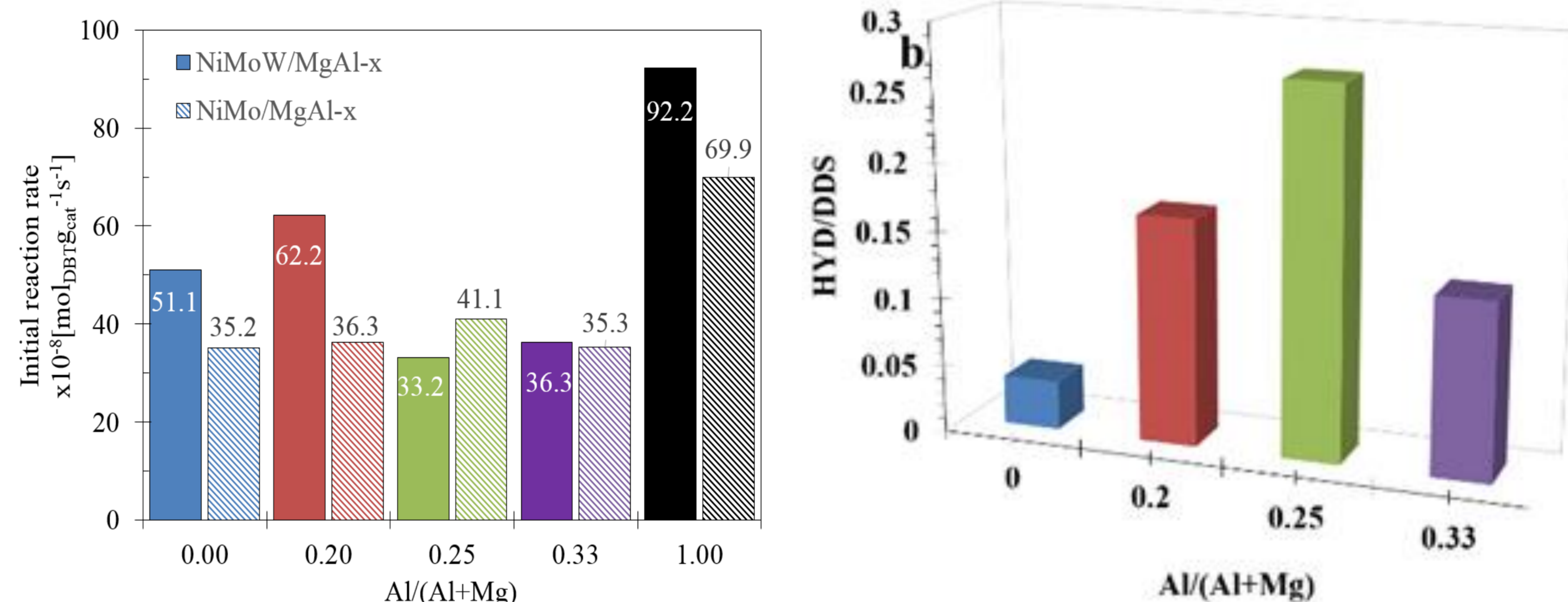


Figure 5. (a) Initial reaction rate of bimetallic and trimetallic systems and (b) selectivity of bimetallic NiMo/MgAl-x catalysts. Bimetallic and trimetallic sulfides showed higher hydrogenation at $x=0.25$. For trimetallic systems the selectivity towards HYD follows the order: NiMoW/MgAl-1 (7.14) < NiMoW/MgAl-0 (11.12) ~ < NiMoW/MgAl-0.20 (12.12) < NiMoW/MgAl-0.33 (13.79) < NiMoW/MgAl-0.25 (14.82).

CONCLUSION:

- The incorporation of Al to the MgO support induces a change in the **acidity properties**. The composition $x=0.25$ corresponds to the maximum participation of the acidity provided by the Al atoms calculated by theoretical DFT approximation, XPS, and FTIR spectra of pyridine.
- The **selectivity** results for the bimetallic NiMo/MgAl-x catalysts show a typical volcano curve centered at the NiMo/MgAl-0.25 catalysts. Therefore, the effect of Al on MgO was to strengthen the acidity (Brønsted acid sites), which in turns increased the HYD selectivity and catalytic activity [6]. For tungsten content systems (NiMoW/MgAl-x), **activity** was obtained the best performance in NiMoW/MgAl-0.20 sulfide. The last trimetallic catalyst displayed almost 50% more activity than that of the highest bimetallic sulfides.
- From **porosity** analysis, we observed that low Al/(Al+Mg) content in MgO ($x=0.20$) containing catalysts increased small mesopores formation and a higher reaction rate. To a higher Al content, mesopores were shifted to larger mesopores and macropores. It is proposed that the mesopore confinement in the supports between 4-7 nm disperse improved MoS₂ active sites and increase DBT accessibility to those sites. As the XRD results pointed out, the MgO phase could coexist with the MgAl₂O₄ surface spinels in our mixed oxides samples. Thus, MgAl₂O₄ could help MgO to influence active-metal coordination and impart better dispersion to the NiMo(W)S active sites. We observed h-WO₃ crystalline planes only in the XRD pattern of the NiMoW/MgAl-0 system. TEM micrographs confirmed these planes. Additionally, the h-WO₃ phase is sensitive to sulfidation conditions, which affects the structure and morphology of the WS₂ material [1]. The presence of this h-WO₃ structure could be related to the higher basicity of the MgO support, i.e., without aluminum. The higher **density of states** for the Mo_{1-x}W_xS₂-mixed than decorated Mo_{1-x}W_xS₂ cluster corresponds with increased HDS of DBT activity previously informed [1], thus higher acid character(promotional effect) due to W intercalation is expected.

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