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# Structure and quantification of edge sites of $WS_2/Al_2O_3$ catalysts coupling IR/CO spectroscopy and DFT calculations

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**KEYWORDS:** Hydrotreating catalyst, Tungsten disulfide ( $WS_2$ ), CO adsorption, IR spectroscopy, density functional theory, morphology.

## ABSTRACT

IR spectroscopy of CO adsorption (IR/CO) and Density Functional Theory (DFT) calculations on sulfide W/Al<sub>2</sub>O<sub>3</sub> catalyst were investigated for an insight into the sulfide edge sites. Parallel between experimental and theoretical results allow to assign the  $\nu(\text{CO})$  bands at 2121 and 2066 cm<sup>-1</sup> to CO adsorption on M- and S-edge sites of WS<sub>2</sub> phase, respectively.

Through a careful analysis of CO spectra on well-selected W catalysts, the molar attenuation coefficients for CO adsorbed on the two exposed edges could be determined. This allowed the morphology of WS<sub>2</sub> slabs to be calculated. This work shows that increasing the W loading (6-20 wt% W) changes the slab morphology from an almost pure triangle exhibiting mostly M-edge to a truncated triangle.

On W as well as on Mo sulfide catalysts, IR spectroscopy and DFT calculation show that CO adsorption allows to account for M- and S-edge sites, and thus of the morphology of sulfide slabs. It was shown that increasing the W loading shifts the slab morphology from a triangle exposing predominantly M-edge towards a more hexagonal shape. For close to monolayer coverage of alumina, Mo and W sulfide slabs present similar shape i.e. truncated triangle. However, edge sites of WS<sub>2</sub> slabs clearly exhibit greater stability under H<sub>2</sub> atmosphere than Mo sulfided ones.

## 1. INTRODUCTION

Hydrotreating (HDT) of petroleum fractions is one of the central refining processes to produce clean fuels that meet stringent current ecological requirements. The present challenge is to meet the current requirements for ultra-low sulfur content in fuels by

extracting from heavier oil deposits. Hydrodesulfurization (HDS) is a key process in refineries where transition metal disulfides (TMS) supported on gamma alumina ( $\gamma$ - $\text{Al}_2\text{O}_3$ ) are used for HDT processes. Among the different metals, Mo or W disulfides with Co or Ni metals as promoters have shown the most promising results in this field. The CoMo and NiMo/ $\text{Al}_2\text{O}_3$  catalysts have been extensively studied, meanwhile NiW catalysts have remained less investigated.<sup>[1]</sup> The importance of NiW/ $\text{Al}_2\text{O}_3$  sulfide catalysts is given by their excellent performance in hydrogenation reactions for deep HDS, providing a high potential for the conversion of alkyl-dibenzothiophenes (alkyl-DBTs).<sup>[2,3]</sup> HDS catalysts have been the subject of numerous characterization studies,<sup>[4]</sup> and presently there is a general agreement that the sulfide phase  $\text{MoS}_2$  ( $\text{WS}_2$ ) presents a lamellar structure, formed by layers of  $\text{MS}_2$  ( $\text{M}=\text{W}, \text{Mo}$ ). The 2D morphology of these layers, their average stacking ( $\sim 2$  to 4) and their average size ( $\sim 3$  to 6 nm) depends on the sulfidation conditions, the metal loading among other parameters. Many correlations between the structure and the activity of these systems link the catalytic reaction to the sites along the edges of the individual layers  $\text{MS}_2$ . At this location, the promoter atoms are also found in the so-called CoMoS type structures (NiMoS, CoWS and NiWS).<sup>[5]</sup> The  $\text{MS}_2$  slabs expose principally two types of edges: the metal terminated edge (M-edge) and the sulfur terminated edge (S-edge). Studies also indicates that M-edge and S-edge sites have different intrinsic activities in HDS reactions, S-edge being more active and more favorable for the promotion and the formation of the promoted phase.<sup>[6]</sup>

An informative way to characterize sulfide sites on these catalysts is the low temperature CO adsorption followed by IR spectroscopy (IR/CO). In addition to the detection of the sulfide sites, this characterization offers the advantage of quantifying

their concentration by means of the molar attenuation coefficient, and thus gives access to sulfide phase dispersion and intrinsic activity of the sulfide sites (ref).<sup>[7]</sup> It should be mentioned that several  $\nu(\text{CO})$  bands characterized the sulfide sites, even on unpromoted catalysts. Unequivocal attribution of the CO adsorption bands to sites of specific sulfide structures cannot be achieved by IR spectroscopy alone. The continuous development of modeling techniques as the Density Functional Theory (DFT) allows defining realistic surfaces models. The modeling of the stable sulfide surfaces according to the sulfide atmosphere is a powerful approach to obtain a description of the various CO adsorption sites.<sup>[8,9]</sup> Hence for  $\text{MoS}_2$ , Travert et al. demonstrated that the coupling of techniques as IR/CO and DFT permitted to attribute the main  $\nu(\text{CO})$  bands to M-edge sites and to S-edge sites as well as to show that these sulfide sites can be modified by post-treatments with hydrogen.<sup>[10,11]</sup> Further, determination of the molar attenuation coefficients of  $\nu(\text{CO})$  band characteristics of the M-edge and S-edge sites allowed quantification of these two edges and thus assessment of the morphology of  $\text{MoS}_2$  slabs.<sup>[12]</sup> It was thus possible to demonstrate that the  $\text{MoS}_2$  morphology (expressed by  $S_{\text{edge}}/M_{\text{edge}}$  ratio) varies with the preparation parameters (metal loading, chelating agent addition, support nature)<sup>[7,13–15]</sup> and the sulfidation conditions.<sup>[13,16]</sup> Recent observations of the sulfide catalysts by STEM HAADF confirmed the morphology of the  $\text{MoS}_2$  slabs deduced from the spectroscopic analysis<sup>[17]</sup>. These knowledge allows a controlled design of the  $\text{MoS}_2$ -based slabs from a slightly truncated to heavily truncated triangle sulfided slab morphology.

In comparison with Mo catalysts, W based ones are less documented in literature.<sup>[18]</sup> Although a considerable amount of research has been made on their

activity, selectivity and in general catalytic properties of the W catalysts, an accurate description of the active sites is still lacking.<sup>[13,19,20]</sup> So far the available CO spectra representing W-based catalyst are rather limited, and no reports were established on the assignment of their specific IR/CO bands, neither on the quantification of these edge sites. Hence, this paper presents an insight into the sulfided W/Al<sub>2</sub>O<sub>3</sub> system characterized through IR spectroscopy and DFT calculation. We first perform the IR/CO adsorption experiments over W/Al<sub>2</sub>O<sub>3</sub> catalyst, later the modeling of the WS<sub>2</sub> (1 0 0) stable surfaces and the calculation of the stretching frequencies of CO adsorbed on these surfaces. The parallel between experimental and theoretical results allows assigning the bands at 2121 and ~2066 cm<sup>-1</sup> to CO adsorbed on M- and S-edge sites, respectively. In a further step, the molar attenuation coefficient of these bands was determined that allows accounting for the effect of W loading on the WS<sub>2</sub> slab morphology.

## **2. EXPERIMENTAL SECTION**

### **2.1. Catalyst preparation.**

The studied materials consisted in a series of non-promoted W/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by a one-step pore volume impregnation method with variable W loading (6, 9, 12, 16 and 20 W wt. %), 20 W wt. % corresponding to 3.3 atoms·nm<sup>-2</sup>, e.g. a submonolayer of W atoms (oxidic form). The catalysts were impregnated with an aqueous solution of appropriate amounts of hydrated ammonium metatungstate ((NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>·H<sub>2</sub>O SIGMA-ALDRICH) on commercial γ-Al<sub>2</sub>O<sub>3</sub> support (SASOL extrudates, specific surface area of 252 m<sup>2</sup>·g<sup>-1</sup> and pore volume of 0.82 ml·g<sup>-1</sup>, precalcined in air flow at 723 K for 4

h. After impregnation, the materials were left for maturation at room temperature for 2 h and subsequently the complete catalyst series was thermally treated at 383 K for 16 h inside a rotatory furnace under air  $100 \text{ ml}\cdot\text{min}^{-1}$  flow and a heating rate of  $3 \text{ K}\cdot\text{min}^{-1}$ . Hereinafter, the  $W/\text{Al}_2\text{O}_3$  catalysts are denoted as  $X\_W/\text{Al}_2\text{O}_3$  where X refers to the W wt. % loading in the catalysts.

## **2.2. Low temperature CO adsorption followed by IR spectroscopy characterization (IR/CO).**

The  $\text{WS}_2$  edge sites of these catalysts were characterized by low-temperature ( $\sim 100 \text{ K}$ ) CO adsorption followed by IR spectroscopy (IR/CO). CO adsorption was performed at low temperature to avoid any reaction with the catalysts surface and to strengthen the interaction with the weakest adsorption sites of the catalyst surface. The oxide catalyst was grounded and pressed into self-supported wafer (ca. 10 mg, precisely weighted, for a  $2.01 \text{ cm}^2$  disc) and placed into a quartz IR cell with  $\text{CaF}_2$  windows. After *in situ* sulfidation under 10%  $\text{H}_2\text{S}/\text{H}_2$  with a flow rate of  $30 \text{ ml}\cdot\text{min}^{-1}$  for 2 h at 673 K (sulfidation starting from room temperature with a heating rate of  $3 \text{ K}\cdot\text{min}^{-1}$ ), the cell was flushed with Ar for 10 min and evacuated down to  $P < 1 \cdot 10^{-4} \text{ Pa}$  maintaining the 673 K temperature during 1 h. Finally, the sample was cooled down to room temperature and further down to 100 K under vacuum. CO adsorption experiments were performed introducing small calibrated CO doses and then an equilibrium pressure of 133 Pa. Note that it was ensured that this protocol of sulfidation yields to catalysts with a  $\text{WS}_2$  amount that is comprised between 92 and 100% whatever the W loading.

After the sulfidation following the previous procedure, pure hydrogen post-treatment was performed on the  $20\_W/\text{Al}_2\text{O}_3$  catalyst. In such a case, the sulfide catalyst was *in*

*situ* reduced under pure H<sub>2</sub> with a flow rate of 50 ml·min<sup>-1</sup> at 673 K for 2 h. After the aforementioned treatment, the sample was flushed under Ar flow for 10 minutes and the temperature was cooled down under high vacuum (P = 9.7 × 10<sup>-5</sup> Pa residual pressure) to room temperature and then to 100 K to perform CO adsorption.

FTIR spectra were recorded with 256 scans and a resolution of 4 cm<sup>-1</sup> using Nicolet Nexus FTIR spectrometer equipped with a MCT detector (FTIR= Fourier Transform Infrared; MCT=Mercury-Cadmium-Tellurium). All spectra were normalized to a disc of 5 mg·cm<sup>-2</sup>. The bands of the adsorbed CO species were obtained by subtracting the spectra recorded after CO adsorption minus before. All experiments were duplicated, with a maximum error of 5%. The band areas of the different  $\nu(\text{CO})$  components that characterize the WS<sub>2</sub> can be obtained by careful spectrum decomposition. In this work, the decomposition was done with Peakfit V4.12 software using the “Autofit peak III decomposition Method”. Before the decomposition, second derivative of the spectra was performed to determine the number of bands. For the decomposition, the center and full width at half height (FWHH) of each band are allowed to vary in a small range ( $\pm 3 \text{ cm}^{-1}$ ).

## **2.3. Computational techniques.**

### **2.3.1. Method description: computational parameters.**

The density functional theory (DFT) calculations were carried out with the Vienna Ab initio Simulation Package (VASP) software.<sup>[21,22]</sup> The energy is calculated using the non-local functional generalized gradient corrections (GGA) approximation as parameterized by Perdew et al.<sup>[23,24]</sup> The wave function is expanded in a plane wave basis set, and the

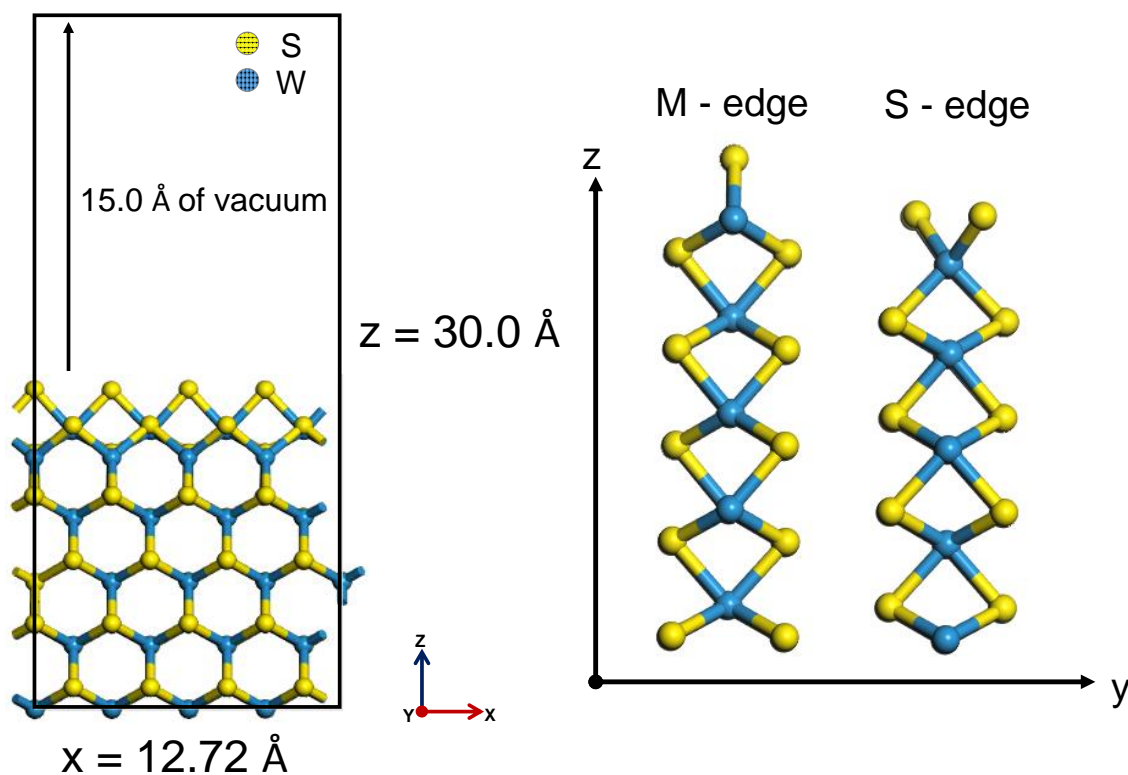


electron–ion interactions are defined using the Projector Augmented Plane Wave (PAW) method.<sup>[25]</sup> In order to compute reliable adsorption energies, Van der Waals forces were considered in the calculations. The Perdew-Burke-Ernzerhof (PBE) functional was employed with 0.1 eV Gaussian smearing.<sup>[26]</sup> It has been shown that PBE gives good results in ionic systems if the Van der Waals interactions are considered.<sup>[27]</sup> The solution of the Kohn–Sham equation was improved self-consistently until a difference lower than  $10^{-5}$  eV was obtained between successive iterations. The atomic positions were optimized until the forces become less than  $0.03 \text{ eV}\cdot\text{\AA}^{-1}$ . Test calculations were made by varying cut-off energy from 300 to 600 eV and using the K-points mesh from  $3 \times 1 \times 1$  to  $5 \times 3 \times 1$  following Monkhorst–Pack<sup>[28]</sup> schemes to define calculation parameters. From these evaluations, all the bulk and surface calculations were performed with a 550 eV cut-off energy, using a  $3 \times 3 \times 1$  K-point mesh for all surface calculations. Using these parameters, the accuracy of the DFT calculation is expected to be better than 0.1 eV for the calculated adsorption energy.

### **2.3.2. Surface model description.**

In the present work we have used a large supercell ( $12.72 \times 12.50 \times 30 \text{ \AA}^3$ ) that allows a good description of the  $\text{WS}_2$  surface dimensions (see **Figure 1**). This supercell model containing four rows in the x-direction, two layers along the y-direction, and five in the z-direction is appropriate for describing the structural and adsorption properties of the (1 0 0)  $\text{WS}_2$  surface. A vacuum layer of  $15 \text{ \AA}$  is located above the  $\text{WS}_2$  slab in the z direction in order to avoid interactions between slabs. The three upper W rows and the adsorbed molecules were allowed to relax during the geometry optimization, while the two lower ones were kept fixed at the bulk geometry. The CO vibration frequencies were

calculated by numerical differentiation of the force matrix. The CO stretching vibrational mode being very weakly coupled with the vibration of the surface, only the part of the matrix corresponding to the atoms closest to CO was considered in the diagonalization process of the Hessian matrix.



**Figure 1.** Representation of the supercell used for the calculations, showing the axes. On the left, cell showing the cut  $WS_2$  (1 0 0) surface. Dark circles: W; light circles: S

In order to determine the sulfur coverage of the stable edges, we performed a systematic study varying the sulfur coverage of both edge between 0 and 8, ie starting for the pure W termination to a fully sulfur saturated surfaces. We have taken into account the effect of the temperature and pressure by calculation the thermodynamic correction using the classical statistical thermodynamic formalism.<sup>[29]</sup> At 673 K, the main

contribution to these correction (c.a. 95%) is due to gas phase molecules ( $H_2$  and  $H_2S$ ) entropy differences. The surfaces are labeled according to the number of sulfur atoms on the two edges: this is  $[S \text{ atoms}_{M\text{-edge}} - S \text{ atoms}_{S\text{-edge}}]$ . The stability of the surface have been computed using the [4-4] one as reference.

#### **2.4. Determination of molar attenuation coefficients for CO adsorbed on M-edge and S-edge of site $WS_2$ catalysts.**

According to the adapted Beer-Lambert law (Eq. 1) to solid materials, the concentration of sites ( $n$ ,  $\mu\text{mol}\cdot\text{g}^{-1}$ ) on which CO is adsorbed can be calculated using the associated CO molar attenuation coefficient ( $\epsilon$ ,  $\text{cm}\cdot\mu\text{mol}^{-1}$ ) and the area of  $\nu(\text{CO})$  band ( $A$ ,  $\text{cm}^{-1}$ ) normalized to the surface ( $S$ ,  $\text{cm}^2$ ) and to the mass ( $m$ , g) of the catalyst wafer measured after sulfidation:

$$n = \frac{A \times S}{\epsilon \times m} \quad (1)$$

The typical CO adsorption experiments on  $WS_2/Al_2O_3$  are performed by adding small CO doses, starting from  $9.0 \times 10^{-3} \mu\text{mol}$  up to  $8.64 \mu\text{mol}$  (cumulative doses). The  $\epsilon$  values can be deduced from the slope of the linear relationship between the area of  $\nu(\text{CO})$  band ( $A_{\text{CO}}$ ) and the amount of CO introduced onto the sample ( $n_{\text{CO}}$ ) considering that all the introduced doses are adsorbed on the pellet (no residual pressure could be detected in the IR cell). However, the determination of the amount of CO adsorbed on a given site can be very delicate when the CO introduced interacts with several adsorbing sites.

In the present case, we had to determine the molar attenuation coefficient of two  $\nu(\text{CO})$  bands corresponding to two adsorption sites. It has firstly required the selection

of samples for which analysis of the spectra from the very first doses of CO shows adsorption on only one type of site (Type 1). Thus, the molar attenuation coefficient ( $\epsilon_1$ ) could be determined using eq. (1).

Then for Type 2 site, the methodology had to be different since none of the spectra whatever the samples show only CO adsorption on this site. Thus, for spectra that present two contributions, the Beer Lambert law can be written as:

$$n_{CO} = \frac{A_{CO_1}S}{m\epsilon_1} + \frac{A_{CO_2}S}{m\epsilon_2} \quad (2)$$

The molar attenuation coefficient of CO adsorbed on the second contribution ( $\epsilon_2$ ) can be determined as follows: after the determination of the area of the two contributions ( $A_{CO_1}$ ,  $A_{CO_2}$ ), the number of CO adsorbed on the site 1 ( $n_{CO_1}$ ) can be calculated from the previously determined  $\epsilon_1$  value. Then, the number of CO adsorbed on the site 2 ( $n_{CO_2}$ ) is determined by subtracting from the total amount of CO introduced  $n_{CO}$ , the amount of CO adsorbed on site 1,  $n_{CO_1}$ . Further, the  $\epsilon_{CO_2}$  value can be calculated from eq. (2).

The  $\nu(\text{CO})$  band area of the components of CO adsorbed on  $\text{WS}_2$  massif was obtained by careful spectrum decomposition using parameters described previously in Section 2.2.

### 3. RESULTS AND DISCUSSION

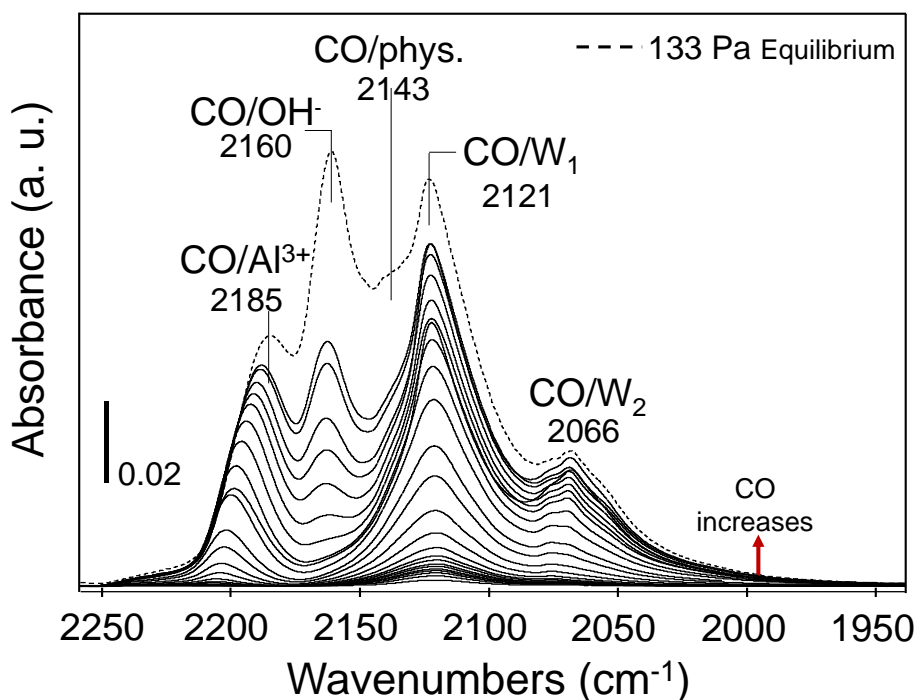
#### 3.1. Characterization by low-temperature IR spectroscopy of CO.

##### 3.1.1. IR/CO of sulfided $WS_2/Al_2O_3$ catalyst.

The IR spectra of CO adsorbed on sulfided 20\_W/ $Al_2O_3$  catalyst are presented in **Figure 2**. Four main bands at 2185, 2160, 2121, and 2066  $cm^{-1}$  were detected. The intensity of these bands increases with the amount of CO introduced. The higher wavenumber bands, namely 2185 and 2160  $cm^{-1}$ , are attributed to coordination of CO on Lewis acid sites ( $Al^{3+}$ ) of the alumina support and CO on hydrogen bonding with the support hydroxyl groups (OH), respectively.<sup>[12,30,31]</sup> Whereas the bands located at 2121  $cm^{-1}$  and 2066  $cm^{-1}$  are attributed to CO adsorbed on edge sites of the  $WS_2$  slabs. At higher CO uptake appears a shoulder at 2141  $cm^{-1}$ , corresponding to physisorbed CO. The two bands at 2121  $cm^{-1}$  and 2066  $cm^{-1}$  were observed since the very first introduced CO doses and were attributed to CO in interaction with coordinatively unsaturated W sites (CUS) of low oxidation state.<sup>[32]</sup> Early work of *Duchet*<sup>[30]</sup> on W/ $Al_2O_3$  catalysts already reported the presence of two bands at 2110  $cm^{-1}$  and 2060  $cm^{-1}$  on sulfided phase, called  $W_1$  and  $W_2$ , respectively. On the other hand, *Crepeau* in his work on  $WS_2/ASA$ ,<sup>[33]</sup> reported the presence of  $W_1$  and  $W_2$  bands at 2127  $cm^{-1}$  and 2072  $cm^{-1}$ . The difference in the wavenumber between that reported by *Duchet* on  $WS_2/Al_2O_3$  and by *Crepeau* on  $WS_2/ASA$  shows that the bands characteristic of the  $WS_2$  phase are also sensitive to the nature of the support.

The inset **Figure 3-A** that reports the spectra normalized to the most intense band, reveals that the band width located at 2121  $cm^{-1}$  ( $W_1$ ) remains without alteration whatever the amount of CO introduced meanwhile the band at  $\sim 2066$   $cm^{-1}$  shifts and

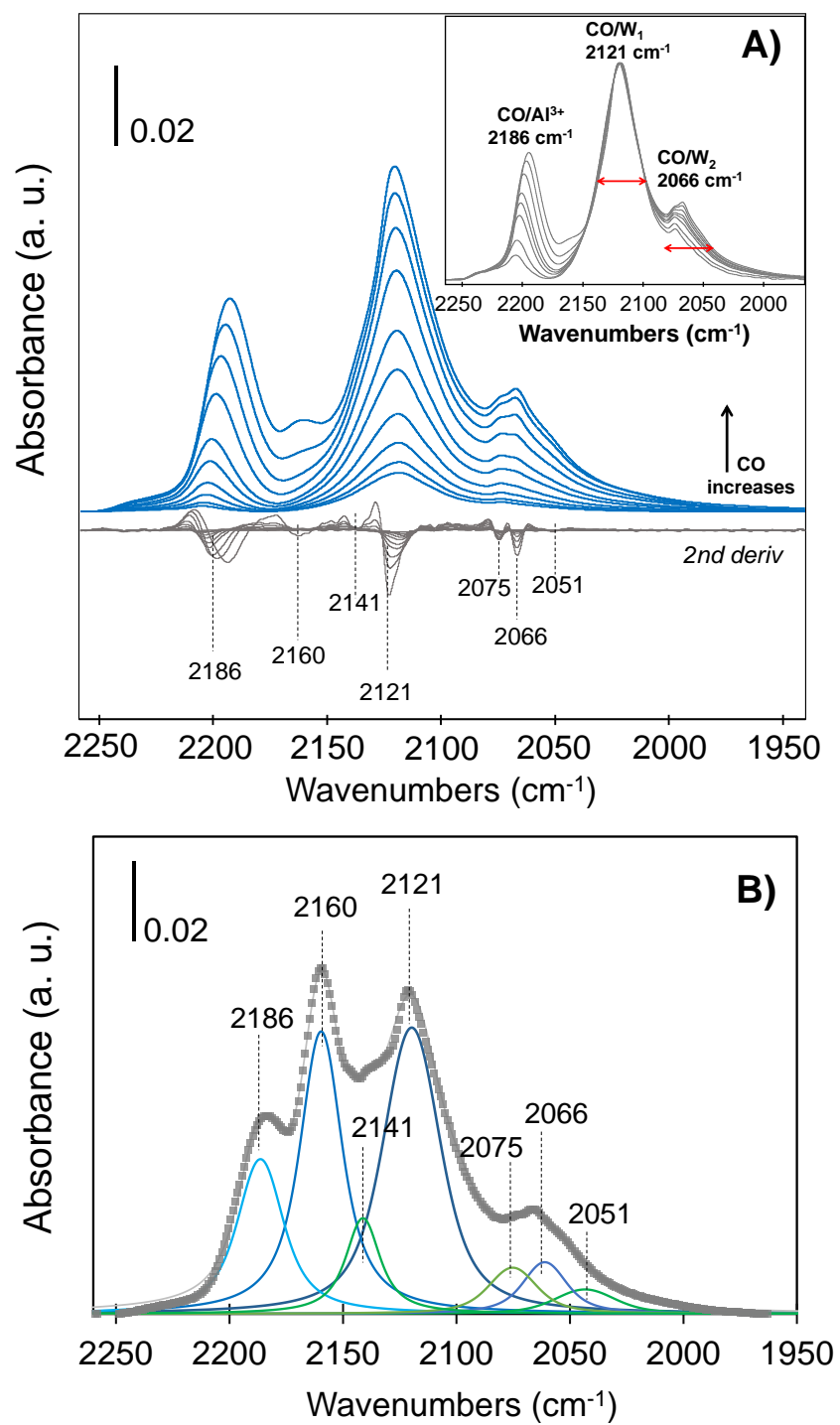
widens. A closer inspection to the spectra at intermediate CO doses was carried out with the help of the second derivative function (**Figure 3-A**). This analysis points out that at least three components (2075, 2066 and 2051  $\text{cm}^{-1}$ ) can be distinguished in the  $W_2$  band whereas the  $W_1$  band only comprised one component at 2121  $\text{cm}^{-1}$ . This analysis that specifies the maximum of the  $\nu(\text{CO})$  bands allows to carry out a proper decomposition of the CO spectra.



**Figure 2.** IR spectra of increasing CO doses (up to 133 Pa at equilibrium) adsorbed at 100 K on 20\_W/ $\text{Al}_2\text{O}_3$  catalyst sulfided with 10%  $\text{H}_2\text{S}/\text{H}_2$  at 673 K and 0.1 MPa.

As shown in **Figure 3-B**, on sulfided W/ $\text{Al}_2\text{O}_3$  catalyst, the obtained IR spectrum was fitted with seven Voigt peaks. The three highest wavenumber peaks used to fit the  $\nu(\text{CO})$  bands were ascribed to: CO coordinated to Lewis acid sites of the alumina support ( $\text{Al}^{3+}$ ): 2186  $\text{cm}^{-1}$ , CO in hydrogen bonding with the support hydroxyl groups: 2160  $\text{cm}^{-1}$ , and physisorbed CO molecules: 2140  $\text{cm}^{-1}$ . Four peaks were generated in

order to fit properly the  $\nu(\text{CO})$  bands on  $\text{WS}_2$  phase. One peak was used to fit the  $\nu(\text{CO})$  band on  $W_1$ -edge, which is located at  $2121 \text{ cm}^{-1}$ . Three peaks were employed to fit the  $\nu(\text{CO})$  band on  $W_2$ -edge, which are located at  $2075$ ,  $2066$  and  $2051 \text{ cm}^{-1}$ . This confirms that  $W_1$  band only comprised one single component whereas  $W_2$  band comprised several components whose ratios change with CO doses.

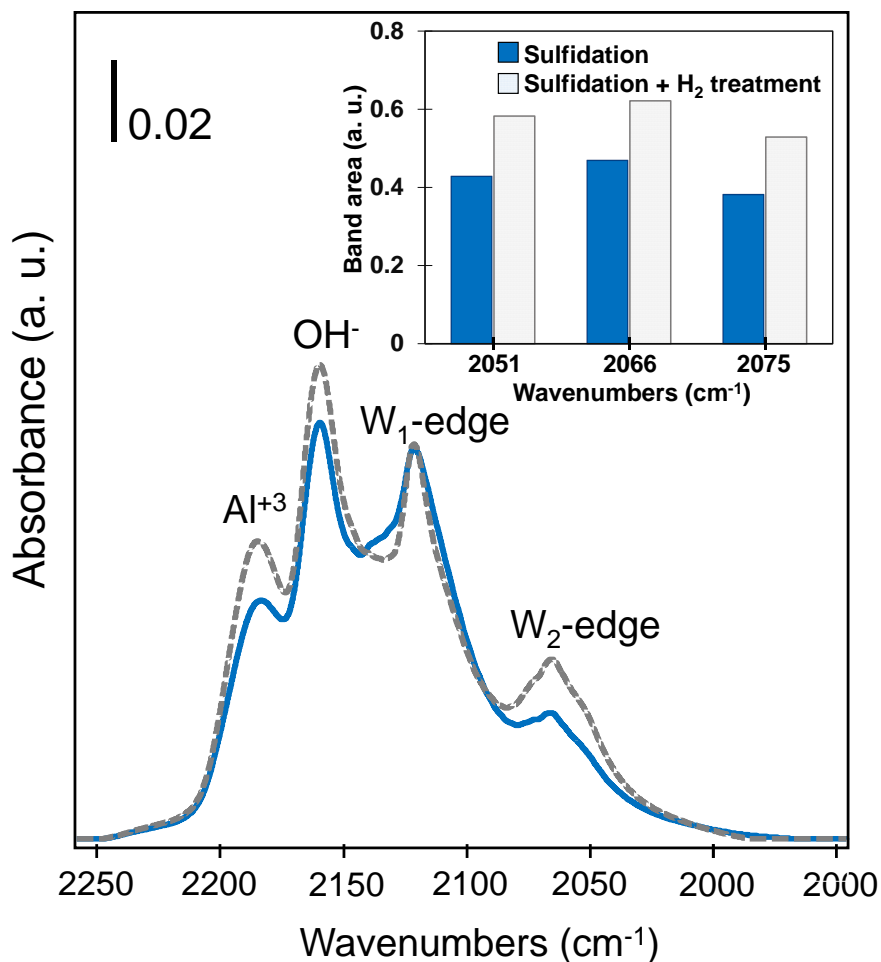


**Figure 3.** (A) IR spectra of intermediate CO doses adsorbed at 100 K on 20\_W/Al<sub>2</sub>O<sub>3</sub> catalyst sulfided at 673 K, with their second derivative ; (B) decomposition of the IR spectrum of CO adsorption (P<sub>CO</sub>=133 Pa at equilibrium).



### 3.1.2. IR/CO of H<sub>2</sub>-treated WS<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

As hydrogen is one of the reactants during the HDS process, its reactivity with HDS catalysts is of great importance.<sup>[7,34]</sup> Molecular hydrogen can be adsorbed dissociatively on WS<sub>2</sub> edges, leading to the creation of sulfur vacancies by removing sulfur in the form of H<sub>2</sub>S and resulting in the WS<sub>2</sub> edges with lower sulfur coverage. The sulfur coverage at the edges of TMS nanoparticles depends on the H<sub>2</sub>S/H<sub>2</sub> ratio. Thus, the ease for the creation of sulfur vacancies on the edge sites of the TMS catalyst can be evaluated by comparing the CO uptake before and after the H<sub>2</sub> treatment.<sup>[35]</sup> In order to investigate the effect of reductive treatment, the sulfided 20\_W/Al<sub>2</sub>O<sub>3</sub> catalyst was treated under pure H<sub>2</sub> flow for 2 h at 673 K at 1 atm pressure before being characterized by IR/CO. **Figure 4** shows that H<sub>2</sub> post-treatment leads to the increase of intensity of the 2160 and 2186 cm<sup>-1</sup> bands ascribed to Al<sup>3+</sup> vacancies and hydroxyl groups of the support: this increase could be explained by evacuation of some adsorbed H<sub>2</sub>S during the heating process. As observed in **Figure 4**, the H<sub>2</sub> post-treatment also leads to some increase of the  $\nu(\text{CO})$  intensity in the region corresponding to W<sub>2</sub>-edge (2000-2100 cm<sup>-1</sup>), while the  $\nu(\text{CO}/\text{W}_1\text{-edge})$  remained practically unchanged. These results indicate that vacancies creation occurs more easily on the W<sub>2</sub>-edge and only limited amount of S atoms can be removed from the W<sub>1</sub> edge by H<sub>2</sub> treatment. An inspection in more detail of the three components associated with the W<sub>2</sub>-edge reveal that they all increase with a same proportion (Inset **Figure 4**). Nevertheless, it should be underlined that intensity increases of the W<sub>2</sub> bands are small, suggesting that the edges of the sulfided WS<sub>2</sub> slabs are rather stable upon H<sub>2</sub>-treatment.



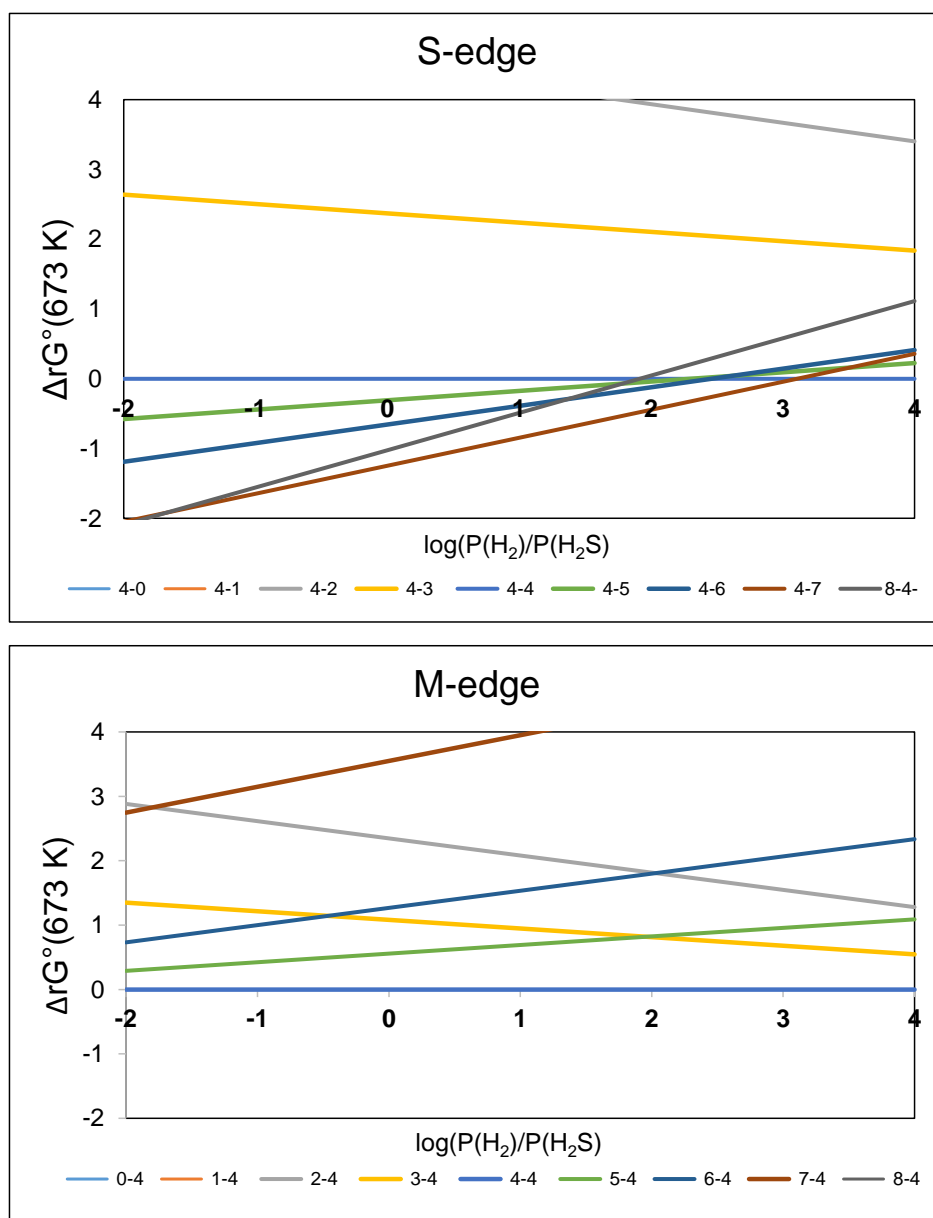
**Figure 4.** Effect of H<sub>2</sub> treatment at 673 K on CO adsorption (100 K, 133 Pa at equilibrium) on sulfided 20\_W/Al<sub>2</sub>O<sub>3</sub> catalyst. IR/CO spectrum obtained after sulfidation (continuous line) and after 2 h of H<sub>2</sub> treatment at 673 K (dashed line); Inset: Effect of the H<sub>2</sub> treatment on the area of the IR/CO bands of the three components of W<sub>2</sub> sites.

## 3.2. DFT calculations

### 3.2.1. Sulfur coverage and surfaces to study.

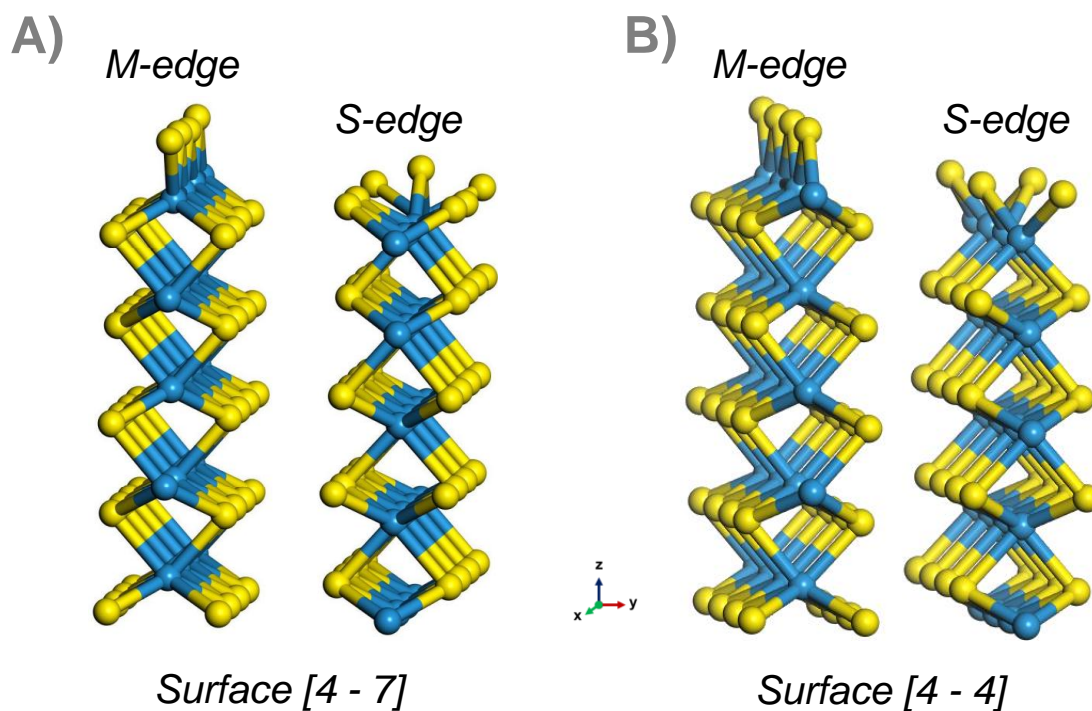
By observing the crystallographic structure of the WS<sub>2</sub> slabs, two types of edges are considered, namely, the metallic edge (M-edge) and the sulfur edge (S-edge). It has been shown that the number of sulfur atoms present at the edges of the slabs depends

on the  $H_2/H_2S$  molar ratio. Each surface is designated by the number of sulfur atoms exposed on each of the two edges: this is  $[S \text{ atoms}_{M\text{-edge}} - S \text{ atoms}_{S\text{-edge}}]$ . The stability of the surface, compared to the [4-4] one, at 673K, as a function the partial pressure  $P(H_2)/P(H_2S)$  logarithm have been computed (**Figure 5**).



**Figure 5.** Free formation enthalpy (in eV) of the edges starting from the [4-4] surface at 673 K, as a function of  $\log \left( \frac{P_{H_2}}{P_{H_2S}} \right)$ .

In sulfidation conditions, the most stable surface corresponds to [4 - 7] (**Figure 6-A**). The coordination of both the W atoms of the M-edge is six (VI) while on the sulfur edge, the coordination is five (V) for two W atoms and six (VI) for two W ones. Under this configuration, each W atom in the M-edge is bridged to 2 S atoms in the plane above the surface of the W atoms, while two W atoms in the S-edge are bridged to 4 S atoms in the plane above the surface of the W atoms and the two other ones bridges to only 3 S atoms. The second stable surface under reductive conditions is the [4 - 4] (**Figure 6-B**). The coordination numbers of W atoms are 6 on the M-edge ( $W_{6c}$ ) and 4 ( $W_{4c}$ ) on the S-edge. The terminal S atoms are in bridging position between two W atoms on both edges, the W-S distances are similar to the distances in the crystal (2.40 Å). Considering only coordination numbers, we can suppose that CO adsorption on the S-edge will be favored in a reductive environment. Here, the coordination of the W atoms of the S-edge decreases from V-VI to IV and the number of CUS increases when increasing the  $H_2/H_2S$  ratio, while no change was observed in the geometry of the M-edge.



**Figure 6.** Depiction of the thermodynamic WS<sub>2</sub> stable surfaces according to the H<sub>2</sub>S/H<sub>2</sub> partial pressures: (A) surface [4-7], stable surface when H<sub>2</sub>/H<sub>2</sub>S < 500; (B) surface [4 - 4], stable surface when H<sub>2</sub>/H<sub>2</sub>S > 500.

### 3.2.2. Calculation of CO adsorption

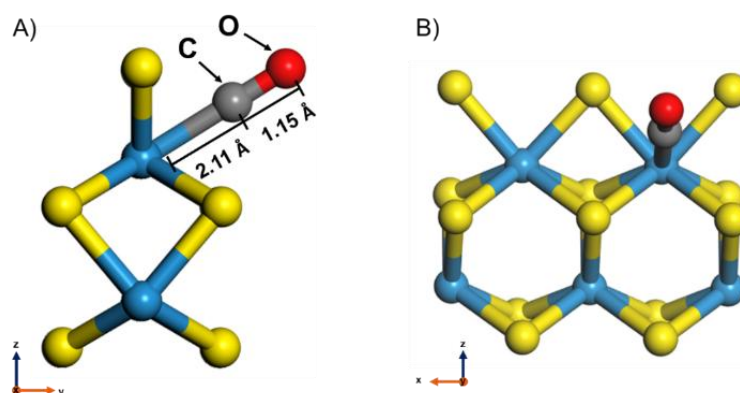
The treatments to which the catalysts were subjected before the adsorption of CO were carried out to correspond to two of the three stable surfaces of the WS<sub>2</sub> edges. The stable zone corresponding to the sulfidation procedure under pure H<sub>2</sub>S was not considered in our case since it is less frequently used at industrial level. All computed adsorption energies and vibrational frequencies of CO on [4 - 7] and [4 - 4] surfaces for both edges are reported in **Table I**.

**Table I.** Calculated parameters of CO adsorbed on M-edge (W) and S-edge (S) of WS<sub>2</sub>.

Edge	Conditions	Surface	W coordination	E ads (eV)	$\nu(\text{CO})$ (cm <sup>-1</sup> )	D <sub>W-C</sub> (Å)	D <sub>C-O</sub> (Å)
M-	sulfidation	[4-x]	6	-0.63 to -0.70	2025	2.11	1.15
M-	reductive	[4-x]	6	-0.63 to -0.70	2025	2.11	1.15
S-	sulfidation	[x-7]	5	-0.40	1957	2.09	1.16
S-	reductive	[x-4]	4	-0.83 ; 1.04	1949 ; 1959	2.09	1.16

On the M-edge either in sulfiding or in reducing conditions [4 – x], CO adsorption can take place with an adsorption energy ranging between -0.63 to -0.70 eV, depending on the exact geometry of the M-edge. The geometry of the W surface is subject to Peierls distortion, but this does not lead to any effect on the  $\nu(\text{CO})$  frequency that is 2025 cm<sup>-1</sup>.

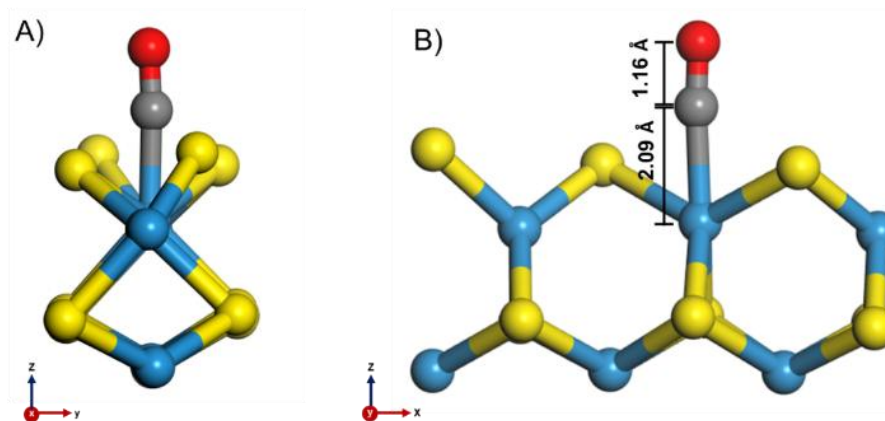
**Figure 7** represents the optimized geometry of the structure of the M-edge where the CO interacts with a single W atom. In **Figure 7-A** the optimized distances are depicted while in **Figure 7-B** the coordination of the tungsten on the M-edge is shown.



**Figure 7.** Optimized configuration for one CO molecule adsorbed on the M-edge [4-x] of WS<sub>2</sub> surface. A) Front view of the optimized distances between the W atom and the CO molecule. B) Side view of the M-edge showing the W coordination.

In sulfiding condition, the stable surface of the S-edge is  $[x - 7]$ , a top CO adsorption on  $W_{5c}$  is also possible with adsorption energy of -0.40 eV. In this configuration, the CO molecule is almost perpendicular to the surface and the  $\nu(\text{CO})$  wavenumber is now calculated at  $1957 \text{ cm}^{-1}$ . In conditions corresponding to high hydrogen amount, the stable surface is the  $[x - 4]$ . The 3 S atoms are removed, creating 4 CUS sites ( $W_{4c}$  atoms) on the S-edge. The S atoms on the S-edge form a zigzag chain that is flexible. The sulfur atom can move from one side of the plan defined by the W atoms to the other side easily. On the most stable geometry, the adsorption energy is -1.04 eV and the associated wavenumber is  $1959 \text{ cm}^{-1}$ . The displacement of a sulfur atom from one side of the W plane to the other one reduced the stability of the S-edge, the adsorption energy is then -0.83 eV. In this configuration, the CO stretching wavenumber is computed at  $1949 \text{ cm}^{-1}$ . Thus there is a difference around  $70 \text{ cm}^{-1}$  between CO adsorbed on the S-edge and on the M-edge. Due to the multiple configurations of the S atoms on the S-edge, a broadening of the  $\nu(\text{CO})$  band on S-edge is expected.

A representation of the most stable structure is given in **Figure 8**. The CO molecule is adsorbed on the S-edge perpendicular to the surface (**Figure 8-A**).



**Figure 8.** Optimized configuration for one CO molecule adsorbed on the S-edge [x-4] of  $WS_2$  surface. A) Front view of the optimized distances between the W atom and the CO molecule. B) Side view of the S-edge showing the W coordination.

### 3.2.3. CO adsorption: Experiment vs Calculation

Experimental spectra present two main  $\nu(\text{CO})$  bands ( $W_1$ ,  $W_2$ ) separated by  $\sim 55 \text{ cm}^{-1}$ . Their intensity ratio varies significantly with the conditions of treatment and preparation (**Figure 4** and **Figure 9**) indicating that they are characteristics of two distinct sites of the sulfided slabs. In parallel, DFT calculations show that CO adsorption on M-edge and on S-edge of  $WS_2$  surface gives rise to  $\nu(\text{CO})$  bands separated by  $\sim 70 \text{ cm}^{-1}$ . This allows us to propose assigning the high wavenumber band ( $W_1$ ,  $2121 \text{ cm}^{-1}$ ) to CO adsorbed on M-edge and the low wavenumber band ( $W_2$ ,  $2066 \text{ cm}^{-1}$ ) to CO adsorbed on S-edge. It should be mentioned that, as for DFT calculation, the differences of wavenumber are more reliable than the value of wavenumbers since no scaling factor nor anharmonic correction have been taken into account.

Other interesting parallels between experiment and calculation on W system appears. First, the experimental spectra (**Figure 3 A and B**) point out that the  $W_1$  band



at  $2121\text{ cm}^{-1}$  correspond to one single species and DFT calculation reports that there is one single geometry for CO adsorption on M-edge. Second, experiments show that the  $W_2$  component comprised several bands ( $2075, 2066, 2051\text{ cm}^{-1}$ ) and calculation shows for the CO adsorption on the S-edge that numerous geometries and orientations of the S atoms are stable, giving rise to more than one type of possible adsorption of CO at this edge. Moreover, despite the existence of different types of geometry, the variation of the calculated wavenumber from one band to another is relatively small ( $10\text{ cm}^{-1}$ ).

Another feature to mention is that reductive treatment leads to almost no change of intensity of  $W_1$  bands, while  $W_2$  band increases slightly (**Figure 4**). This is in good agreement with trends reported by calculation that indicates no change in W coordination on M-edge and some changes in the W coordination on S-edge between sulfiding and reductive conditions (**Table I**) and also that the number of CUS site on the S-edge will increase in reducing conditions, while this number is constant on the M-edge.

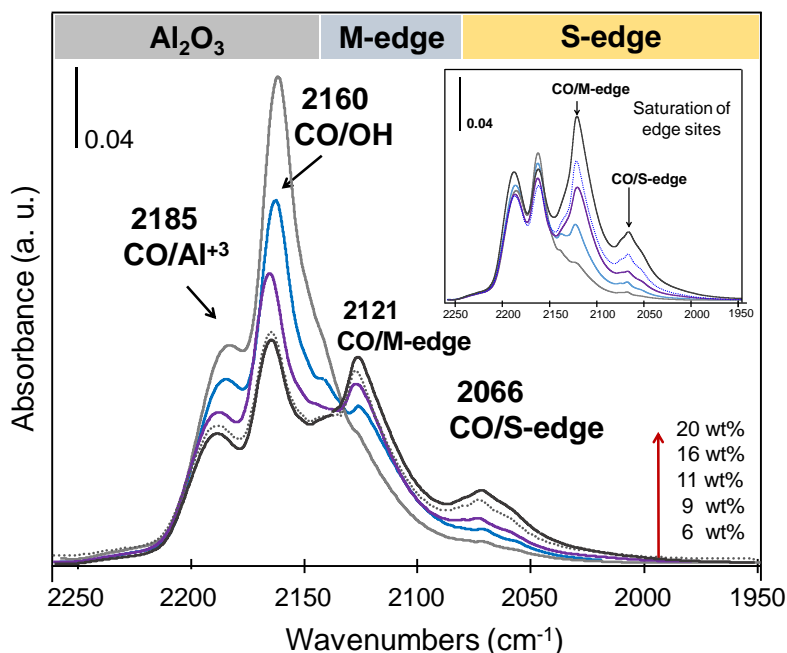
The agreement between experimental and calculated features supports the assignment of the band at  $2121\text{ cm}^{-1}$  to CO adsorption on M-edge ( $\text{CO}_{\text{M-edge}}$ ) and that at  $\sim 2066\text{ cm}^{-1}$  to CO adsorption on S-edge ( $\text{CO}_{\text{S-edge}}$ ).

### **3.3. Influence of W loading on W- and S-edge bands.**

A series of  $\text{W}/\text{Al}_2\text{O}_3$  catalysts, in which the W coverage was increased from 0.85 to 3.3 atoms $\cdot\text{nm}^{-2}$  (i.e. from 6 to 20 wt% W), has been analyzed by IR/CO from small CO doses up to 133 Pa at equilibrium. **Figure 9** compares the spectra obtained at 113 Pa

CO at equilibrium of the different W-catalysts, the inset shows the IR spectra obtained at sulfide site saturation.

As a general manner, bands similar as those reported on W<sub>20</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst (**Figure 2**) are observed although with intensity and ratio that depends on the W amount and on the alumina coverage **Figure 9**. At the lowest metal loading (6 wt. %) and under 133 Pa of CO,  $\nu(\text{CO})$  bands in the 2130-2000 cm<sup>-1</sup> region are almost undetectable (**Figure 9**). This is partly due to the high intensity of the  $\nu(\text{CO})$  bands associated with the support, which overshadow the signal corresponding to the sulfided sites. As the W concentration increases, the  $\nu(\text{CO})$  bands associated to WS<sub>2</sub> sites gain intensity and are better defined (**Figure 9** – see insert). In addition to the well-visible band CO<sub>M-edge</sub> band, centered at 2121 cm<sup>-1</sup>, the CO<sub>S-edge</sub> band begins to appear at 2066 cm<sup>-1</sup>. The intensity of CO<sub>S-edge</sub> band increases with the W loading in the catalyst. On the other hand, the intensity of the  $\nu(\text{CO})$  bands associated to the support (Al<sup>3+</sup> Lewis acid sites and OH groups of Al<sub>2</sub>O<sub>3</sub>) decrease as a result of a more covered surface of the alumina support by WS<sub>2</sub>, which agrees with the increase of the W loading.



**Figure 9.** IR spectra of CO adsorption on  $WS_2/Al_2O_3$  prepared with different W loading (Main: 133 Pa CO at equilibrium, Insert: at sulfide site saturation, both at 100 K). The  $WS_2/Al_2O_3$  catalysts were obtained by sulfidation at 673 K and 0.1 MPa with 10%  $H_2S/H_2$ .

### 3.4. Determination of molar attenuation coefficients for W- and S-edge bands

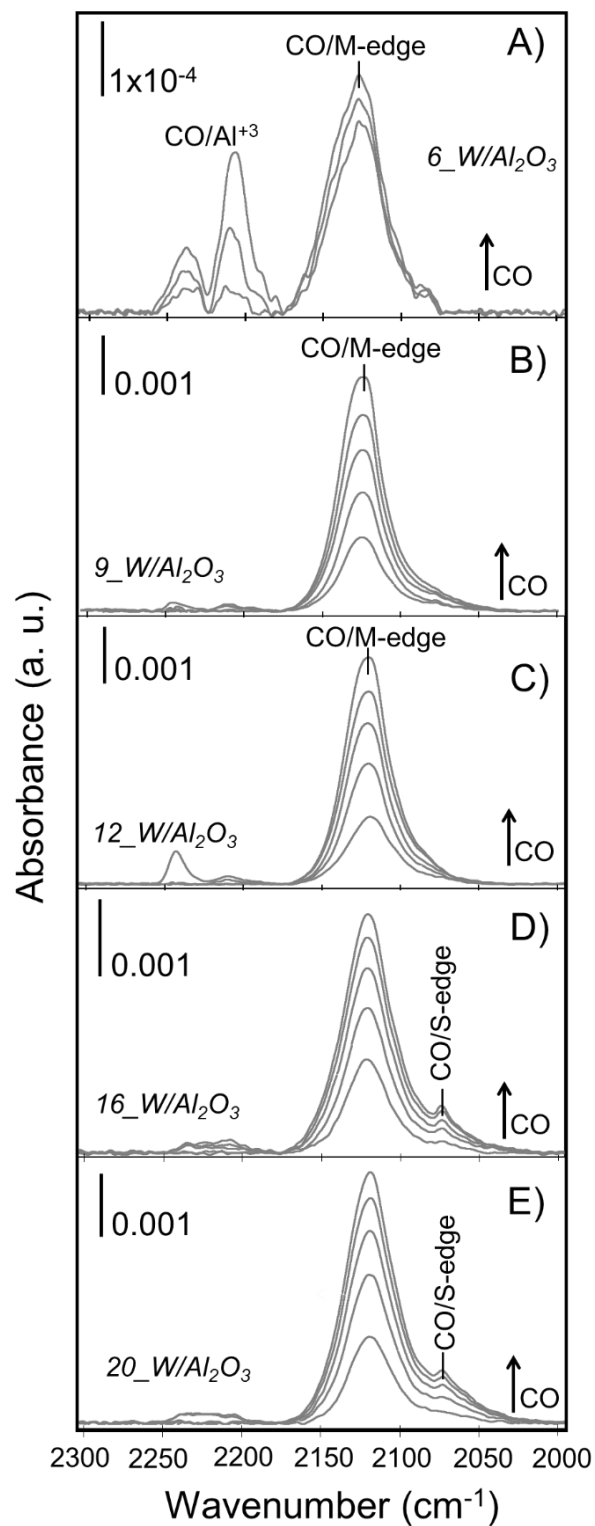
In previous works of our group on  $MoS_2$ -based catalysts,<sup>[36]</sup> distinct molar attenuation coefficient values were obtained for CO adsorbed on either M-edge ( $\epsilon_{CO/M-edge}$ ) or S-edge ( $\epsilon_{CO/S-edge}$ ) (Table II). These values allowed the quantification of  $MoS_2$  sites of each edges and thus calculation of the S-/M-edge ratio that defines the morphology of the  $MoS_2$  slabs.<sup>[14]</sup> Recent work on sulfided  $Mo/Al_2O_3$  catalysts prepared with and without citric acid showed a good agreement between sulfided slab shape determined from IR/CO, and that observed on transmission electron microscope by STEM-HAADF.<sup>[17]</sup> This gave a proof by image of the morphological changes of the catalyst according to the preparation modes, and also underlined that IR/CO method allows to reach a representative average picture of the sulfided slab shapes. Thus, the

determination of the morphology of the  $WS_2$  particles requires the measurement of the molar attenuation coefficients of the  $\nu(\text{CO})$  bands characteristics of M-edge and S-edge. In the literature, no  $\epsilon_{\text{CO}}$  values for M-edge and S-edge are reported for any of the species formed in the  $WS_2$  or NiWS catalysts. A close inspection of the spectra obtained for the first doses of CO introduced shows that, at low W loading, only one  $\nu(\text{CO})$  band characteristic of M-edge sites appears (**Figure 10 A-C**). However, spectra obtained on  $6\_W/\text{Al}_2\text{O}_3$  present signals associated to CO adsorbed on alumina Lewis acid sites from the first CO doses. This is in agreement with the very limited support coverage by W phase ( $0.85 \text{ atoms}\cdot\text{nm}^{-2}$ ), but this prevents using the spectra obtained on the catalyst with the lowest W amount to calculate  $\epsilon_{\text{CO/M-edge}}$  sites. However, when the W amount is somehow greater as for  $9\_W/\text{Al}_2\text{O}_3$  and  $12\_W/\text{Al}_2\text{O}_3$ , the relationship between the variation of the band area of CO adsorbed on M-edge and the number of CO introduced can be used to calculate the  $\epsilon_{\text{CO/M-edge}}$ . As shown on **Figure 11**, close  $\epsilon_{\text{CO/M-edge}}$  values were obtained for these two catalysts i.e.  $11.4 \pm 2 \text{ cm}\cdot\mu\text{mol}^{-1}$  for  $9\_W/\text{Al}_2\text{O}_3$  and  $12.2 \pm 2 \text{ cm}\cdot\mu\text{mol}^{-1}$  for  $12\_W/\text{Al}_2\text{O}_3$ . At higher W loading (**Figure 10 D-E**) i.e. for  $16\_W/\text{Al}_2\text{O}_3$  and  $20\_W/\text{Al}_2\text{O}_3$ , two  $\nu(\text{CO})$  bands are detected even for low CO doses. They correspond to CO interaction with the M-edge site ( $2121 \text{ cm}^{-1}$ ) and the S-edge site ( $2072 \text{ cm}^{-1}$ ). With the molar attenuation coefficient of CO adsorbed on M-edge ( $\epsilon_{\text{CO/M-edge}}$ ) already determined, the amount of CO adsorbed specifically on M-edge sites can be calculated from the band area of these sites and using the methodology described in section 3.5. Hence, a relationship between the variation of the band area of CO adsorbed on S-edge and the number of CO adsorbed on S-edge sites (calculated from the total number of CO introduced in the cell minus the number of CO adsorbed on M-edge sites) was used

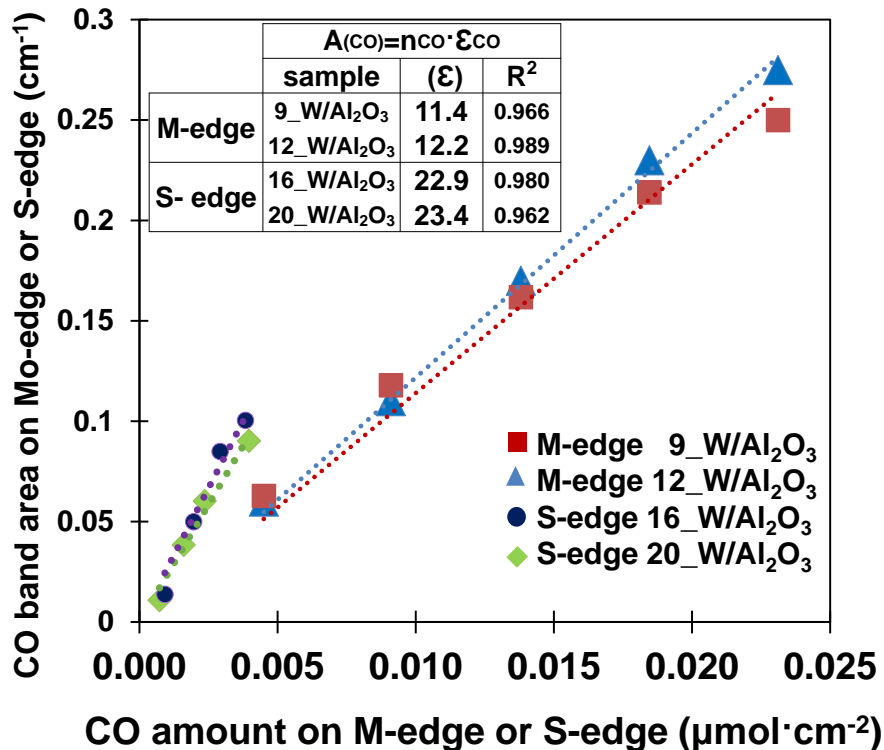
to calculate the attenuation coefficient of CO adsorbed on S-edge ( $\epsilon_{\text{CO/S-edge}}$ ). The slope of this relationship is the  $\epsilon_{\text{CO/S-edge}}$ .

$$\left[ \frac{n_T}{S} - \frac{A_{M-edge}}{\epsilon_{M-edge}} \right] \epsilon_{M-edge} = A_{S-edge} \quad (3)$$

Note that a CO band specific of Lewis acid sites appears from the third CO doses, but the signal being low, it has been neglected in the  $\epsilon_{\text{CO/M-edge}}$  calculations. **Figure 11** shows that close  $\epsilon_{\text{CO/S-edge}}$  values are obtained for these two catalysts i.e.  $22.9 \pm 6 \text{ cm} \cdot \mu\text{mol}^{-1}$  for 16\_W/Al<sub>2</sub>O<sub>3</sub> and  $23.4 \pm 6 \text{ cm} \cdot \mu\text{mol}^{-1}$  for 20\_W/Al<sub>2</sub>O<sub>3</sub>. Thus, the average molar attenuation coefficients  $\epsilon_{\text{CO/M-edge}}$  and  $\epsilon_{\text{CO/S-edge}}$  for sulfided W/Al<sub>2</sub>O<sub>3</sub> catalysts are  $11.9 \pm 2 \text{ cm} \cdot \mu\text{mol}^{-1}$  and  $23.1 \pm 6 \text{ cm} \cdot \mu\text{mol}^{-1}$  respectively. Note that in all the calculations (**Figure 11**) an adequate fit and line tendency were obtained.



**Figure 10.** IR spectra of the first CO doses adsorbed ( $T = 100$  K) on sulfided  $W/Al_2O_3$  at different metal loadings. Intermediate W concentrations results on CO adsorption only on the metallic edge. (first doses:  $0.001, 0.002, 0.003,$  and  $0.004 \mu\text{mol CO}\cdot\text{mg}^{-1}$  sulfided catalyst).

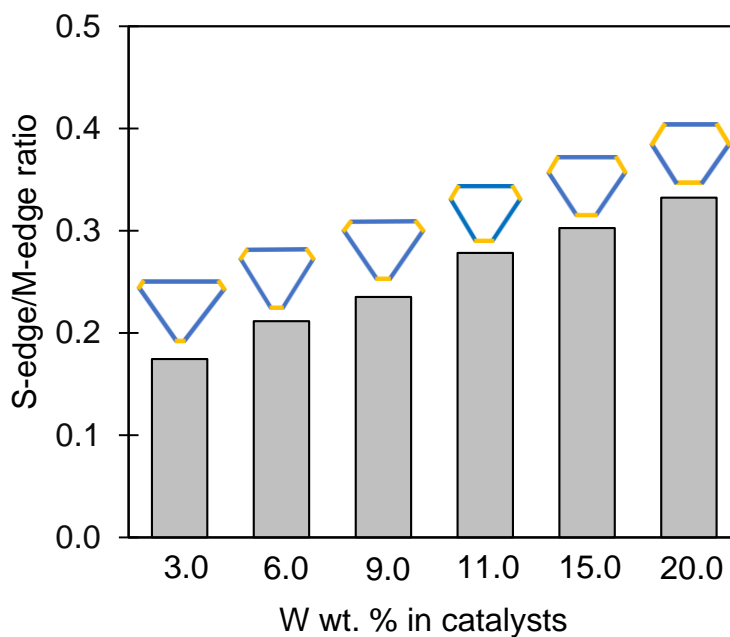


**Figure 11.** Determination of the molar attenuation coefficients ( $\epsilon$ ) of CO adsorbed on  $\text{WS}_2$ . The spectra for  $\epsilon$  determination are reported in **Figure 9**. The  $\epsilon$  values are the slope of the linear relationship between the area of  $\nu(\text{CO})$  band and the amount of CO introduced onto a  $\text{cm}^2$  of the sample.

### 3.5. The influence of W loading on $\text{WS}_2$ slab morphology.

As observed in **Figure 9**, the increase of metal loading has an effect not only on the intensity of the bands associated to the M- and S- edges, but also on their ratio. From the molar attenuation coefficients for both edge sites, the S-edge/M-edge ratio can be calculated for the various W catalysts (**Figure 12**). The value of the ratio undergoes a steady increase along with the W loading and shows that the morphology of the  $\text{WS}_2$  slabs changes from slightly truncated triangles exposing mainly the M-edge (S-edge/M-edge = 0.17) to a more heavily truncated triangle exposing more S-edge (S-edge/M-

edge = 0.32). Similar effect of metal loading has been earlier reported for  $\text{MoS}_2/\text{Al}_2\text{O}_3$  catalysts.<sup>[13]</sup> In Mo system, this phenomenon was associated to a change in the sulfide phase - support interactions with metal loading. This, since the  $\text{MS}_2$  phase interacts with  $\text{Al}_2\text{O}_3$  support by the M–O–Al linkages that are located at the edges of the slabs instead of at the core slab sites.<sup>[13,37]</sup> Similarly, the concentration of the W–O–Al linkages will decrease with increasing  $\text{WS}_2$  size. It is observed that the  $\text{WS}_2$  slabs on  $\text{WS}_2/\text{Al}_2\text{O}_3$  catalysts exposed more S-edge with increasing the W loading. All these results suggest that the  $\text{WS}_2\text{--Al}_2\text{O}_3$  interactions decrease with increasing W loading.



**Figure 12.** The ratios of S-edge/M-edge and corresponding morphologies of  $\text{WS}_2$  slabs as function of W loading of  $\text{WS}_2/\text{Al}_2\text{O}_3$  catalysts.

### 3.6. Comparison between W and Mo sulfide catalysts.

As summarized in **Table II**, many similarities appear for CO adsorption on W and Mo sulfide catalysts.



For sulfide W as well as for sulfide Mo catalysts, CO adsorbed on sulfide slabs gives rise to 2 IR bands separated by about  $50\text{ cm}^{-1}$  that allows distinguishing M-edge ( $\text{CO}_{\text{M-edge}}$ ) and S-edge ( $\text{CO}_{\text{S-edge}}$ ). On both systems, the frequencies of  $\text{CO}_{\text{M-edge}}$  appear at greater frequency than the  $\text{CO}_{\text{S-edge}}$ . This is in agreement with the calculated Mo and W coordination that is greater on M-edge ( $\text{M}_{6\text{C}}$ ) than on S-edge ( $\text{M}_{4\text{C}}$ ) (Table 1, Ref. [10]). In agreement with their higher frequencies, molar attenuation coefficient ( $\epsilon$ ) for  $\text{CO}_{\text{M-edge}}$  is greater than for  $\text{CO}_{\text{S-edge}}$ . From these values, the morphology of the TMS slabs could be calculated. For alumina supported catalysts with metal amount corresponding to monolayer coverage, sulfided slabs with very close morphology i.e. highly truncated triangle (S-/M- ratio = 0.30-0.32) are formed on alumina supported Mo and W catalysts.

In both systems, an accurate analysis shows that CO adsorbed on S-edge is characterized by a broad band consisting of several  $\nu(\text{CO})$  components. The three bands ( $2065$ ,  $2045$  and  $2020\text{ cm}^{-1}$ ) characterizing CO adsorption on S-edge of  $\text{Mo}/\text{Al}_2\text{O}_3$  have been associated to different CO coverages. [10,11,36,38] Whereas the three components ( $2075$ ,  $2066$  and  $2051\text{ cm}^{-1}$ ) detected on S-edge of  $\text{W}/\text{Al}_2\text{O}_3$  have been associated to various orientations of the edge sulfur atoms giving rise to more than one  $\nu(\text{CO})$  band. It must be noted that the relatively small model used to describe the  $\text{MoS}_2$  S edge, does not allow various geometries. By contrast, M-edge sites present a more homogeneous geometry. For W catalyst, only one component is detected whatever the  $\text{H}_2\text{S}/\text{H}_2$  ratio whereas for  $\text{Mo}/\text{Al}_2\text{O}_3$  system, a band is detected at  $2110\text{ cm}^{-1}$  after sulfidation while a second one develops under reductive atmosphere ( $2098\text{ cm}^{-1}$ ). [10,36]

A noticeable difference between the Mo and W systems is their difference of stability toward reductive treatment. When submitted to  $\text{H}_2$ -post-treatment, the stability

of the edge sites of sulfide W catalyst is remarkable (only S-edge site amount increases by 16%). By contrast, on Mo system, the CO uptake increases of about 55% both on M- and S-edges. This great sulfur depletion of MoS<sub>2</sub> edge is in agreement with the appearance of a new band (2098 cm<sup>-1</sup>) after reductive treatment whereas no frequency shift are observed on W catalysts.

Hence, sulfided slabs of Mo and W alumina supported catalysts present similar morphologies but different stability regarding H<sub>2</sub> treatment.

**Table II.** Comparison of experimental  $\nu(\text{CO})$  frequencies and molar attenuation coefficients of CO on M- and S-edge, as well as MS<sub>2</sub> slab morphology for (9 %) Mo/Al<sub>2</sub>O<sub>3</sub> and (20 %) W/Al<sub>2</sub>O<sub>3</sub> catalysts sulfided under H<sub>2</sub>S/H<sub>2</sub>\* or post –treated under H<sub>2</sub> at 473K atmosphere.

Catalyst	Edge type	Sulfidation		H <sub>2</sub> post-treatment vs sulfidation
		$\nu(\text{CO})$ frequency (cm <sup>-1</sup> )	Epsilon, $\epsilon_{\text{CO}}$ (cm· $\mu\text{mol}^{-1}$ )	CO band area enhancement
<b>Mo</b>	M-edge	2110	20.0 ± 3	+60%
	S-edge	2065	35.0 ± 9	+54%
	Slab morphology	Truncated triangle Ratio S/M = 0.30		
<b>W</b>	M-edge	2121	11.9 ± 2	~0%
	S-edge	2066	23.1 ± 6	+16%
	Slab morphology	Truncated triangle Ratio S/M = 0.32		

\* Values corresponding to a metal close to monolayer (at the oxidic state) on the alumina surface. Sulfidation conditions: Mo/Al<sub>2</sub>O<sub>3</sub> Ts = 423 K, 2h : W/Al<sub>2</sub>O<sub>3</sub> Ts = 473 K, 2h.

## 4. CONCLUSIONS

In the present work, carbon monoxide adsorption on alumina-supported sulfided W catalysts was studied by means of IR spectroscopy pairing with DFT calculations. The parallel between experimental and calculated data allowed us to attribute, for the first time, the two  $\nu(\text{CO})$  bands observed at  $2121\text{ cm}^{-1}$  and about  $2066\text{ cm}^{-1}$  to CO adsorbed on the M-edge and S-edge sites of the  $\text{WS}_2$  slabs, respectively.

The integrated molar attenuation coefficients of CO associated with the M- and S-edge sites were determined, allowing determination of the  $\text{WS}_2$  morphology. Increasing the W loading (3-20 wt% W) allows going from an almost pure triangle exhibiting mostly M-edge to a truncated triangle.

Parallel between experiments and DFT calculation of CO adsorption on W and Mo sulfide catalysts provides evidence for many similarities between the two systems. On both TMS, CO adsorption give rise to two main  $\nu(\text{CO})$  bands separated by about  $50\text{ cm}^{-1}$  that allowed to discriminate M-edge and S-edge sites. For M loading close to monolayer coverage of alumina (in oxidic form), Mo and W sulfide slab present a similar shape i.e. truncated triangle. However, edge sites of  $\text{WS}_2$  slabs clearly exhibit greater stability under  $\text{H}_2$  atmosphere than Mo sulfided ones.

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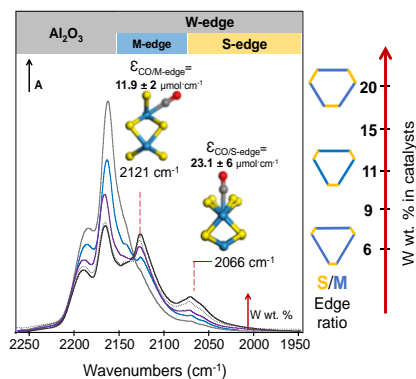
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## Entry for the Table of Contents



Text for Table of Contents:

CO adsorption on sulfided  $\text{W}/\text{Al}_2\text{O}_3$  catalysts was studied by IR spectroscopy pairing with DFT calculations. Parallel between experimental and calculated data allowed to attribute, for the first time, the two  $\nu(\text{CO})$  bands observed at  $2121 \text{ cm}^{-1}$  and  $\sim 2066 \text{ cm}^{-1}$  to CO adsorbed on the M-edge and S-edge sites respectively. The molar attenuation coefficients for CO adsorbed at the M-edge and the S-edge were determined. This allowed the morphology of the  $\text{WS}_2$  slabs to be calculated.