

## Tungsten disulfide catalysts from tetraalkylammonium thiotungstates by ex situ activation, their properties and HDS activity

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### ABSTRACT

The role of carbon coming from tetraalkylammonium thiotungstate precursors during the ex situ activation of WS<sub>2</sub> catalysts was herein studied through the comparison of two different thiosalts, ammonium tetrathiotungstate (ATT, without carbon) and cetyltrimethylammonium tetrathiotungstate (CTATT, with carbon). The influence on the resulting WS<sub>2</sub> catalysts, of a N<sub>2</sub> vs a H<sub>2</sub>S/H<sub>2</sub> (20% H<sub>2</sub>S) atmosphere during ex situ activation was also evaluated. Freshly obtained catalysts were characterized by N<sub>2</sub> adsorption–desorption isotherms, X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX), while their catalytic properties were evaluated in the hydrosulfurization of dibenzothiophene at 3.1 MPa and 623 K. No significant difference was found in the textural and morphological properties of the final WS<sub>2</sub> catalysts derived from thermal decomposition of ATT under N<sub>2</sub> flow, compared to 20% H<sub>2</sub>S/H<sub>2</sub> flow. In contrast, the textural, morphological and catalytic properties of WS<sub>2</sub> catalysts derived from CTATT were strongly influenced by the nature of the atmosphere. Samples of WS<sub>2</sub> derived from ATT showed an absence of porosity, while WS<sub>2</sub> catalysts formed from CTATT presented a mesoporous organization characterized by type IV N<sub>2</sub> isotherms. XRD and TEM showed that the use of CTATT induces a strong destacking of the WS<sub>2</sub> particles and the excessive formation of amorphous carbon, thus yielding less active WS<sub>2</sub> catalysts which confirm the negative role of carbon-containing tetraalkylammonium precursors in the activation of WS<sub>2</sub> catalysts, as opposed to their positive influence in the activation of MoS<sub>2</sub> catalysts. The very high activity of the WS<sub>2</sub> catalyst obtained from ATT is attributed to an optimized incorporation of structural carbon inside the WS<sub>2</sub> structure. Finally, selectivity results show the depleted hydrogenating character of the WS<sub>2</sub> catalysts formed from CTATT.

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### 1. Introduction

Hydrotreating catalysts based on transition metal sulfides were developed in the 1930s in order to reduce the presence of oil fractions containing heteroatoms, which hindered the refining process and yielded pollutants upon combustion. Depending on the heteroatom, hydrotreating reactions include hydrosulfurization (HDS), hydrodenitrogenation, hydrodeoxygenation, and hydrogenation [1–4].

Preparation of molybdenum or tungsten sulfide catalysts, with surface areas in the order of 5–50 m<sup>2</sup>/g have been achieved by several methods in the past 40 years, most noticeably by sulfidation

of co-precipitated oxides [5,6], comaceration [7,8], homogeneous sulfide precipitation [9,10], ceramic method [11], and impregnated thiosalt decomposition [12–15].

An alternative to improving catalytic activity by increasing the surface area of molybdenum or tungsten sulfide, is to use precursors containing both sulfur and carbon. In this respect, tetraalkylammonium thiometalates have been initially synthesized by the metathesis reaction between ammonium tetrathiomolybdate, (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> (ATM) with tetraalkylammonium chlorides [16] or tetraalkylammonium hydroxides using acetonitrile as solvent [17]. More recently, Alonso et al. [18,19] have improved this synthesis technique by preparing, in high yield and in aqueous solution, the same kind of transition metal sulfide precursors (NR<sub>4</sub>)<sub>2</sub>MS<sub>4</sub>, where R = H, CH<sub>3</sub>, or C<sub>4</sub>H<sub>9</sub> (butyl) and M = Mo or W through the reaction between ammonium tetrathiomolybdate and the corresponding tetraalkylammonium bromide. The as-obtained precursors are

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then decomposed in situ during the course of the HDS reaction, into the final MoS<sub>2</sub> or WS<sub>2</sub> catalysts. The in situ decomposition of tetraalkylammonium thiomolybdates yields MoS<sub>2</sub> catalysts with high surface area and improved catalytic properties in the HDS of dibenzothiophene (DBT). This behavior has been associated with the presence of structural carbon in substitution of edge sulfur atoms, generating systems like MoS<sub>2-x</sub>C<sub>x</sub> [20–22]. Carbon content has also been observed in ruthenium sulfides yielding the general formula RuS<sub>2-x</sub>C<sub>x</sub> [23], again showing a substitution of sulfur edge atoms by structural carbon. Moreover, after HDS an initial excess of sulfur in Ru and Mo sulfide catalysts has lead to a greater amount of carbon being included into the stable steady state of molybdenum sulfide [24].

Afanasiev et al. [25] found that highly dispersed molybdenum sulfides were produced by ex situ decomposition of ATM in the presence of reducing agents like hydroxylamine sulfate or hydrazine hydrate, and of a non-stoichiometric amount of cetyltrimethylammonium chloride (CTAC), with surface areas reaching values up to 211 m<sup>2</sup>/g. Recently, Soto-Puente et al. [26] and Romero-Rivera et al. [27] have found that the treatment of ATM using different ATM/CTAC ratios, including the stoichiometric 1:2 ratio, produces carbon-containing precursors that yield MoS<sub>2</sub> catalysts with surface areas comparable to those obtained by Afanasiev et al. [25].

While intense research has been performed on MoS<sub>2</sub>-based catalysts obtained by activation of tetraalkylammonium thiosalts, studies on WS<sub>2</sub>-based catalysts are scarce, with activation performed mainly by in situ decomposition of the thiosalts during the HDS test [19,28–32]. The present study will therefore address the role of carbon derived from tetraalkylammonium precursors during the ex situ activation of WS<sub>2</sub> catalysts. For this purpose, two different precursors, ATT (without carbon) and cetyltrimethylammonium thiotungstate (CTATT, with carbon) will be compared during their ex situ decomposition into WS<sub>2</sub> catalysts. Moreover, the effect of the atmosphere used to ex situ decompose the thiotungstate precursors will be evaluated using both N<sub>2</sub> or 20% H<sub>2</sub>S/H<sub>2</sub> atmospheres.

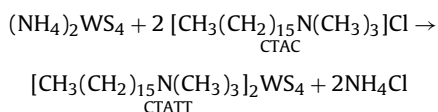
## 2. Experimental

### 2.1. Preparation of ammonium tetrathiotungstate

(NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> was prepared according to the method described in [33] based on the heating at 60 °C for 4 h of a mixture comprising ammonium metatungstate, NH<sub>4</sub>OH, H<sub>2</sub>S and water to produce a dark yellow crystalline precipitate. The resulting thiosalt was isolated by vacuum filtration, washed with isopropyl alcohol and dried at room temperature, then readily used for the activation of WS<sub>2</sub> catalysts.

### 2.2. Preparation of WS<sub>2</sub> precursor from cetyltrimethylammonium tetrathiotungstate (CTATT)

For this purpose, a modified version of the procedure used by Afanasiev et al. [25] to treat ammonium thiomolybdates was employed. In this modified version, a 1:2 stoichiometric ratio for ATT:cetyltrimethylammonium chloride was used yielding cetyltrimethylammonium tetrathiotungstate (CTATT) according to the following metathesis reaction:



First, 4.0 g (11.5 mmol) of freshly prepared (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> was dissolved in 100 mL of water while stirring. An aqueous solution (23.0 mmol in 100 mL water) of R(CH<sub>3</sub>)<sub>3</sub>NCl, (where R = cetyl) was then added and the mixture was stirred at room temperature, yielding a yellow precipitate which acquired a greenish color after being refluxed for 24 h. The mixture was then cooled, vacuum filtered and the recovered solid precursor (CTATT) was washed first with cold water and then with isopropyl alcohol. The solid was dried at room temperature and readily used for the activation of WS<sub>2</sub> catalysts.

### 2.3. Synthesis of WS<sub>2</sub> catalysts

The WS<sub>2</sub> catalysts WS-1 and WS-2 were obtained by ex situ decomposition in N<sub>2</sub> from ATT and CTATT respectively. The WS<sub>2</sub> catalysts WS-3 and WS-4 were obtained by ex situ decomposition from ATT and CTATT respectively in a H<sub>2</sub>S/H<sub>2</sub> (20% H<sub>2</sub>S) atmosphere. After grinding, 1.0 g of the different precursors was placed in a porcelain boat which was then introduced into the alumina tube of a tubular furnace. The temperature was set to 723 K (heating rate: 10 K/min) and kept constant for 2 h. Upon cooling the furnace to 473 K, the gas flow was stopped and the system allowed to cool down to room temperature. The resulting samples were kept under N<sub>2</sub> atmosphere.

### 2.4. Characterization of samples

Specific surface areas were measured with a Quantachrome AUTOSORB-1 by N<sub>2</sub> absorption at 77 K using the BET isotherm and a sample mass of 0.2–0.3 g. Samples were degassed under flowing argon at 473 K for 2 h before N<sub>2</sub> adsorption. The pore size distribution and total pore volume were obtained from the desorption data following the BJH method. The mean standard deviation for the surface area measurements was about 2%.

The X-ray diffraction patterns of the prepared samples were obtained with a Philips X'Pert analytical diffractometer for powder samples using Cu Kα radiation. Their phases were identified with reference to the database of the International Centre for Diffraction Data.

A Jeol JSM5800 IV scanning electron microscope was used to perform EDX elemental analysis of all the prepared catalysts. EDX analysis were performed with an eBX-ZAF system using a WS<sub>2</sub> reference sample to deconvolute the L lines of S and W. Transmission electron microscopy was done on a Philips FEG TECNAI F20 transmission electron microscope operated at 200 kV.

### 2.5. Catalytic activity and selectivity

The HDS of DBT was tested in a 300 mL high pressure Parr reactor containing 4.4 g DBT, 100 mL of decalin, and 300 mg of catalyst. The reactor was purged of residual air, pressurized with H<sub>2</sub> to 3.1 MPa (450 psi) and then heated to the reaction temperature of 623 K. A stirring rate of 600 rpm was used. The course of the reaction was monitored by gas chromatography with a HP 6890 gas chromatograph using a J&B DB640 capillary column (30 m × 0.32 mm × 0.5 μm). Samples were taken every 20 min during the first hour, then every 30 min for the next 4 h. Reduction of sample volume due to sampling was ≤5% of total volume. The identity of the reaction products was confirmed by mass spectrometry with a HP 6890 GC-MS using a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). Catalytic activity was expressed in terms of % conversion of DBT vs reaction time, and from this data, the reaction rate was calculated for each catalyst. The mean standard deviation for catalytic measurements was about 2.5%.

The HDS of DBT yields mainly biphenyl (BP) through the direct desulfurization (DDS) pathway, and cyclohexylbenzene (CHB) and tetrahydrodibenzothiophene (THDBT) through the hydrogenation

**Table 1**

Specific surface areas, total pore volumes and atomic ratios determined by EDX elemental analysis for the ex situ prepared WS catalysts obtained from the ATT and CTATT precursors after activation under N<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>S: WS-1 (ATT-N<sub>2</sub>), WS-2 (CTATT-N<sub>2</sub>), WS-3 (ATT-H<sub>2</sub>/H<sub>2</sub>S), and WS-4 (CTATT-H<sub>2</sub>/H<sub>2</sub>S). The EDX values are for HDS-tested samples.

Catalyst	Surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	S/W	C/W
WS-1	54	0.047	1.43	0.40
WS-2	43	0.230	1.33	3.33
WS-3	49	0.041	1.52	0.34
WS-4	73	0.148	1.68	5.80

(HYD) pathway. Cyclohexylcyclopentylmethane (CHCPM) and dicyclohexyl (DCH) can also be detected along the HYD pathway.

### 3. Results and discussion

#### 3.1. Elemental analysis

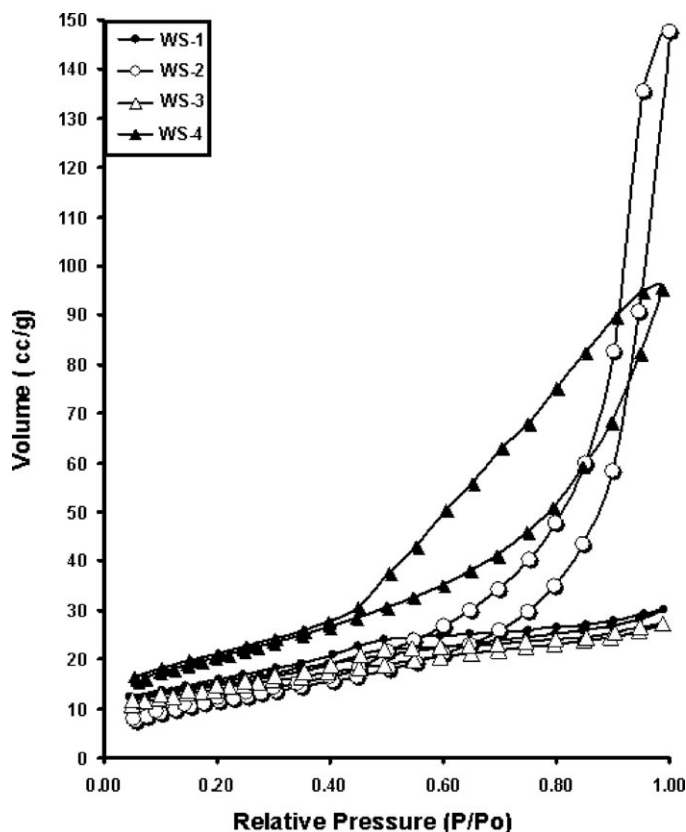
The S/W and C/W metal ratios were first determined by EDX on HDS tested samples and results are reported in Table 1. All the different solids have S/W ratios lower than the stoichiometric value of 2. However, compared to the N<sub>2</sub> activation, using a H<sub>2</sub>/H<sub>2</sub>S atmosphere during the ex situ activation can limit the loss of sulfur, particularly for the WS<sub>2</sub> catalyst obtained from CTATT (S/W = 1.68 with H<sub>2</sub>/H<sub>2</sub>S vs 1.33 with N<sub>2</sub>). The C/W ratios of the WS-2 and WS-4 catalysts obtained from the CTATT precursor exhibit very high values, particularly when activate under H<sub>2</sub>/H<sub>2</sub>S (WS-4) with a C/W value of 5.80. In contrast, the C/W ratios of the WS-1 and WS-3 catalysts remain low (0.40 with N<sub>2</sub> and 0.34 with H<sub>2</sub>/H<sub>2</sub>S). While the carbon of the WS-1 and WS-3 catalysts is due from to solvent (decaline) decomposition, most of the carbon extra carbon in the WS-2 and WS-4 catalysts is attributed to the decomposition of the precursor's alkyl groups during activation.

#### 3.2. Textural properties

The specific surface areas and total pore volumes of the different WS<sub>2</sub> catalysts are reported in Table 1. The solids obtained by ex situ decomposition of the ATT precursor exhibit surface areas around 50–55 m<sup>2</sup>/g, in agreement with values reported by An et al. [29] (51 m<sup>2</sup>/g). The nature of the atmosphere used during their activation does not significantly influence the surface area values.

For the WS<sub>2</sub> catalysts obtained from CTATT, the ex situ activation under N<sub>2</sub> (WS-2) leads to a slightly lower surface area than that of the WS<sub>2</sub> catalysts obtained under the same conditions from the ATT precursor (WS-1), while the WS-4 catalyst obtained from CTATT and activated under H<sub>2</sub>/H<sub>2</sub>S presents a surface area of 73 m<sup>2</sup>/g, which is considerably higher than the 49 m<sup>2</sup>/g of the WS<sub>2</sub> catalyst obtained under H<sub>2</sub>/H<sub>2</sub>S from the ATT precursor (WS-3). Thus, the nature of the atmosphere used during activation does significantly influence the textural properties of the catalysts obtained from the C-containing CTATT precursor, where the increase of surface area is accompanied by a decrease of the total pore volume from 0.230 cm<sup>3</sup>/g when activated under N<sub>2</sub> to 0.148 cm<sup>3</sup>/g when activated by H<sub>2</sub>/H<sub>2</sub>S. This fact, combined with a higher C/W ratio when treated under H<sub>2</sub>/H<sub>2</sub>S, suggests the formation of larger pores compensated by an increase of the surface area induced by carbon.

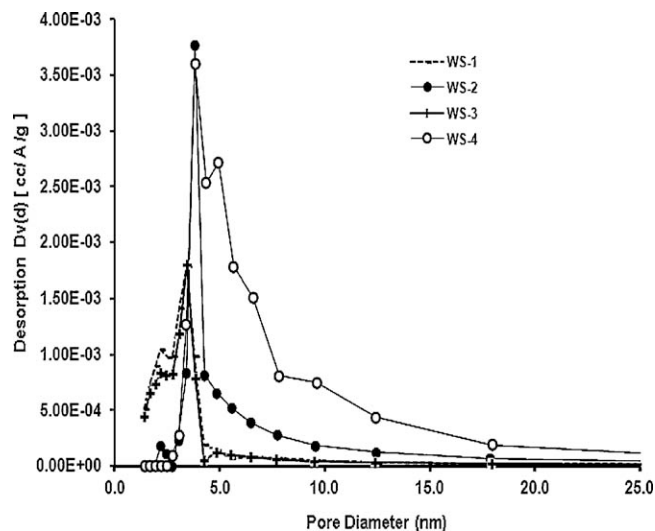
For the WS<sub>2</sub> catalysts formed from ATT, in both cases the total pore volume values are very low, implying a scarce development of porosity. This fact was confirmed by the N<sub>2</sub> adsorption–desorption isotherms shown in Fig. 1. The WS-1 and WS-3 catalysts obtained from the ATT precursor and activated, respectively, under N<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>S do not present any real porosity, with a very poorly developed hysteresis loop. This situation is similar to those previously observed by An et al. [29]. The BJH pore size distribution confirms



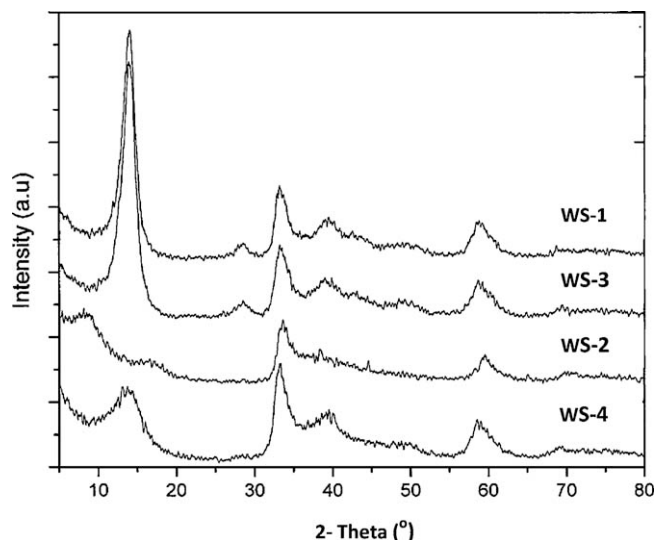
**Fig. 1.** N<sub>2</sub> adsorption–desorption isotherms of the different WS<sub>2</sub> catalysts prepared by ex situ decomposition of the ATT and CTATT precursors under N<sub>2</sub> or 20% H<sub>2</sub>S/H<sub>2</sub>: WS-1 (ATT-N<sub>2</sub>), WS-2 (CTATT-N<sub>2</sub>), WS-3 (ATT-H<sub>2</sub>/H<sub>2</sub>S), WS-4 (CTATT-H<sub>2</sub>/H<sub>2</sub>S).

this fact with a peak of low intensity centered around 35 Å (Fig. 2). However, the presence of some pores in the microporous region is noted.

In contrast, the N<sub>2</sub> adsorption–desorption isotherms of the WS<sub>2</sub> catalysts obtained from CTATT exhibit substantial porosity. Both WS-2 and WS-4 catalysts exhibit type IV isotherms characteristic of a mesoporous organization. This result is in agreement with previous studies showing that the use of tetraalkylammonium thiomolybdates or thiotungstates leads to a well-developed



**Fig. 2.** BJH pore size distributions of the different WS<sub>2</sub> catalysts prepared by ex situ decomposition of the ATT and CTATT precursors under N<sub>2</sub> or 20% H<sub>2</sub>S/H<sub>2</sub>: WS-1 (ATT-N<sub>2</sub>), WS-2 (CTATT-N<sub>2</sub>), WS-3 (ATT-H<sub>2</sub>/H<sub>2</sub>S), WS-4 (CTATT-H<sub>2</sub>/H<sub>2</sub>S).



**Fig. 3.** XRD patterns of the different WS<sub>2</sub> catalysts prepared by ex situ decomposition of the ATT and CTATT precursors under N<sub>2</sub> or 20% H<sub>2</sub>S/H<sub>2</sub>: WS-1 (ATT-N<sub>2</sub>), WS-2 (CTATT-N<sub>2</sub>), WS-3 (ATT-H<sub>2</sub>/H<sub>2</sub>S), WS-4 (CTATT-H<sub>2</sub>/H<sub>2</sub>S).

mesoporosity, even if better mesoporosity and higher surface areas are generally obtained using in situ methods of activation [31,32,34–38]. However, while the WS-4 catalyst obtained by N<sub>2</sub> activation shows a broad H2 hysteresis loop characteristic of interconnected mesopores, the WS-2 catalyst obtained by H<sub>2</sub>/H<sub>2</sub>S activation exhibits an H1 hysteresis loop with a profile characteristic of a narrower pore size distribution of mesopores. These facts are confirmed by their respective BJH pore size distributions as shown in Fig. 2. While the WS-2 catalyst presents a narrow size distribution centered around 4.0 nm, the WS-4 catalyst (activated under H<sub>2</sub>/H<sub>2</sub>S) shows a similar maximum around 4.0 nm, but with significant contributions of larger pore diameters, confirming the formation of bigger pores if the CTATT precursor is activated under H<sub>2</sub>/H<sub>2</sub>S. This result was previously observed by Alonso et al. [31] during the in situ activation of cetyltrimethylammonium thiontungstate, showing that the presence of a long alkyl chain like cetyl (C<sub>16</sub>) led to the formation of a more open porosity with larger pores, whatever the method of decomposition.

### 3.3. X-ray diffraction

The XRD patterns of the different WS<sub>2</sub> solids obtained by ex situ activation of ATT or CTATT precursors under N<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>S are reported in Fig. 3. All the XRD profiles correspond to the 2H-WS<sub>2</sub> phase with main contributions at  $2\theta = 13.5^\circ$  (002),  $28.1^\circ$  (004),  $33.0^\circ$  (100),  $39.5^\circ$  (103),  $49.2^\circ$  (105) and  $58.4^\circ$  (111) (JCPDS: 00-008-0237). However, differences can be noticed between the XRD patterns of the WS<sub>2</sub> catalysts obtained from the ATT precursor and those acquired for WS<sub>2</sub> solids formed from CTATT.

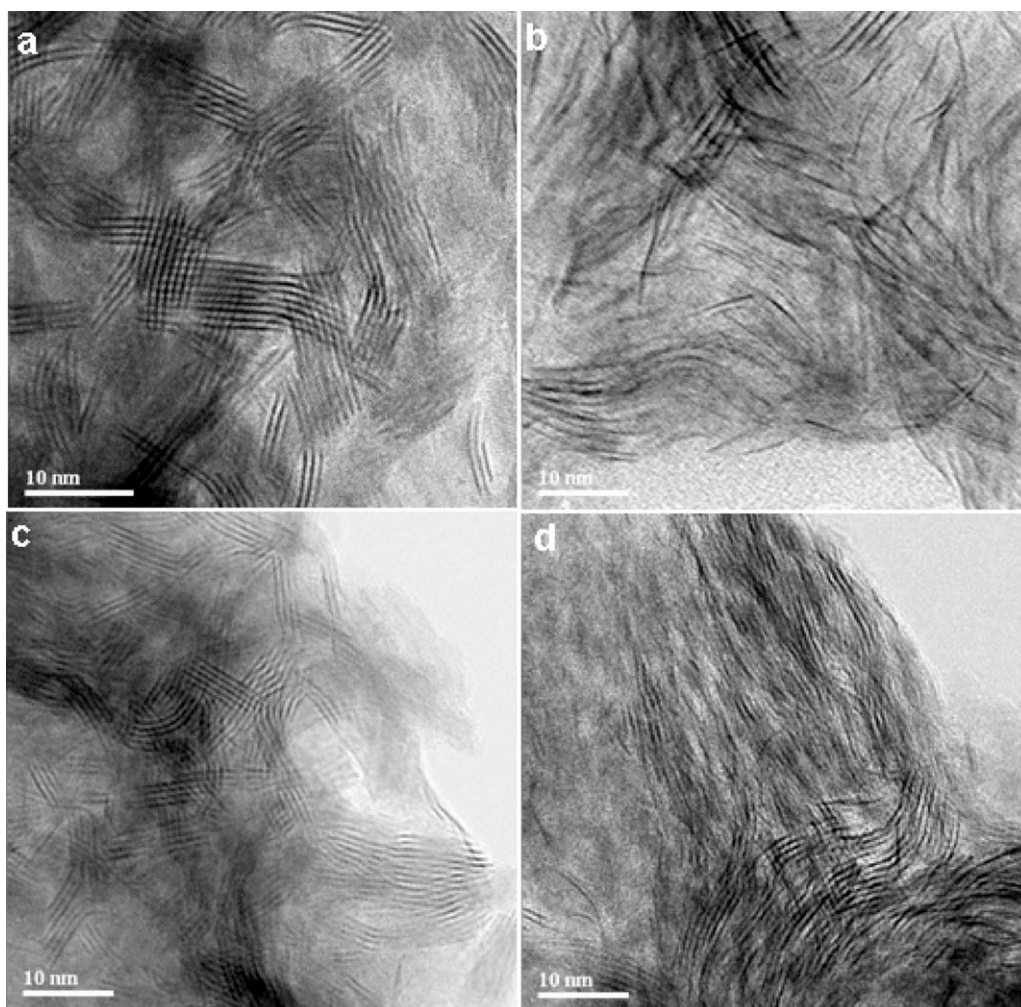
The XRD profiles of WS-1 and WS-3 (obtained by ex situ activation of ATT) are very similar, with a high intensity (002) diffraction peak characteristic of a significant stacking along the *c* direction. Once again, the nature of the atmosphere (N<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>S) used during the ex situ activation does not influence the final morphology. The situation appears strikingly different for the WS<sub>2</sub> catalysts obtained by ex situ activation of CTATT. In that case, the intensity of the (002) peak is strongly diminished. This is particularly the case for the WS-2 catalyst obtained by ex situ activation of CTATT under N<sub>2</sub> with a complete disappearance of the (002) diffraction peak. This destacking phenomenon was already observed previously when using carbon-containing thiomolybdate precursors confirming the role of carbon in suppressing the stacking of MoS<sub>2</sub>

or WS<sub>2</sub> particles [34–36]. This effect was ascribed to an initial bending of the slabs induced by the replacement of sulfur edge atoms by structural carbon [39]. This bending effect would weaken the van der Waals interaction maintaining slabs stacked together and then would induce the formation of stabilized single layers. Preceding studies [31,32] have shown that in the presence of a source of carbon, the crystallization rate of the WS<sub>2</sub> slabs is often accelerated using tetraalkylammonium thiontungstate precursors with alkyl chains as long as heptyl. On the other hand, the use of longer alkyl chains such as cetyl (C<sub>16</sub>) was also found to lead to a strong decrease of the (002) diffraction peak due to a very high amount of excess carbon [31]. This point observed for the in situ activation of CTATT [31] is confirmed here for ex situ activation. In the case of the WS-2 catalyst, the formation of excess carbon is confirmed by the appearance of new XRD peaks at around  $2\theta$  values of  $9.0^\circ$  and  $16.5^\circ$ . Once again, for WS<sub>2</sub> solids obtained from CTATT, the nature of the atmosphere used during the ex situ activation has some influence on the final morphology. Indeed, contrary to the activation under N<sub>2</sub> leading to a complete suppression of the (002) diffraction peak intensity, under H<sub>2</sub>/H<sub>2</sub>S, a low broad (002) peak is still observed. A similar situation was previously found for the WS<sub>2</sub> catalyst obtained by in situ activation of CTATT [31]. Since the H<sub>2</sub>/H<sub>2</sub>S atmosphere used for the preparation of the WS-4 catalyst presents conditions close to those prevailing during the in situ decomposition under HDS conditions, these results show that the H<sub>2</sub>/H<sub>2</sub>S atmosphere can help in restoring a partial stacking of the WS<sub>2</sub> slabs. Finally, all the diffraction patterns present an asymmetry of the (100) diffraction peak at  $2\theta = 33^\circ$  characteristic of a misalignment of the slabs along the *c* direction, with layers displaced randomly with respect to one another, i.e. turbostraticity [40–42].

### 3.4. Transmission electron microscopy

TEM micrographs reported in Fig. 4 confirm the results obtained previously by XRD diffraction. All the images present fringes characteristic of WS<sub>2</sub> layers with an interlayer spacing of 0.62 nm. Substantial differences can however be observed for the different samples. The TEM micrographs of the WS-1 (activated under N<sub>2</sub>) and of the WS-3 catalysts (activated under H<sub>2</sub>/H<sub>2</sub>S) obtained from ATT are essentially similar, showing that WS<sub>2</sub> particles are formed of highly stacked slabs which confirm the absence of effect of the atmosphere used during the ex situ activation on the final morphology. Moreover, as shown in Fig. 5, their average slab sizes are essentially similar, with values of 85 Å and 93 Å for WS-1 and WS-3, respectively. These results are in agreement with those found previously by Chianelli et al. [43]. This situation differs strikingly from the one prevailing for the WS<sub>2</sub> particles formed from CTATT. The WS-2 catalyst obtained from CTATT after activation under N<sub>2</sub> presents mainly single layers and only a few stacked layers, confirming the XRD results about the suppression of the stacking along the *c* direction. Moreover, the WS<sub>2</sub> particles seem to be spread on fluffy zones characteristic of the presence of amorphous carbon in excess [21]. The morphology of the WS<sub>2</sub> particles of the WS-4 catalyst (activated under H<sub>2</sub>/H<sub>2</sub>S) appears intermediate between that observed for WS-1 and WS-3 on one side and for WS-2 on the other side. Indeed, in this case, the WS<sub>2</sub> particles present a low stacking degree (2–3 layers) in agreement with the presence of a broad low intensity (002) diffraction peak on the XRD pattern of this catalyst (Fig. 3). Moreover, on WS-4, the WS<sub>2</sub> slabs exhibit a higher tendency to bend as expected from a WS<sub>2</sub> solid prepared in the presence of a carbon source [39]. This effect seems less obvious for the WS-2 catalyst. Indeed, the formation of single layers is not expected to favor slab bending due to a relaxation effect relieving the strain effects induced by the curvature of the layers [44,45].





**Fig. 4.** TEM micrographs of the different WS<sub>2</sub> catalysts prepared from the ATT and CTATT precursors: (a) WS-1 (ATT-N<sub>2</sub>), (b) WS-2 (CTATT-N<sub>2</sub>), (c) WS-3 (ATT-H<sub>2</sub>/H<sub>2</sub>S), and (d) WS-4 (CTATT-H<sub>2</sub>/H<sub>2</sub>S).

### 3.5. Catalytic activity and selectivity

The DBT HDS activity and selectivity results of the different WS<sub>2</sub> catalysts obtained from ATT or CTATT under N<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>S are reported in Table 2. Activity results show a strong difference in catalytic behavior between the WS<sub>2</sub> catalysts obtained from the ATT or the CTATT precursor. The use of the alkyltrimethylammonium thiotungstate precursor CTATT results in a much lower activity than using the ATT precursor, whatever the atmosphere used during the ex situ activation. These results confirm the previous findings about the negative impact of using carbon-containing tetraalkylammonium thiotungstate precursors for the activation of tungsten sulfide catalysts [31,32]. Indeed, previous results have shown that the use

of tetraheptylammonium thiotungstate (THepATT) or CTATT for the in situ activation of WS<sub>2</sub> catalysts yields slightly less active catalysts, with rate constants of  $6.1$  and  $5.6 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1}$ , respectively, compared to using ATT ( $6.5 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1}$ ). A similar situation is therefore observed here for ex situ activated tetraalkylammonium thiotungstate precursors. The rate constants of the catalysts prepared from ATT reported in this work are higher than those of other supported catalysts recently published in the literature, where similar equipment was used for the catalytic activity measurements [46]. The presence of a very high amount of amorphous carbon is probably the reason for such a negative effect through the blocking of active sites. These results are in agreement with elemental analysis, XRD and TEM studies which have

**Table 2**

Activity and selectivity results in the HDS of DBT of the different WS<sub>2</sub> catalysts prepared by ex situ activation of the ATT and CTATT precursors under N<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>S: WS-1 (ATT-N<sub>2</sub>), WS-2 (CTATT-N<sub>2</sub>), WS-3 (ATT-H<sub>2</sub>/H<sub>2</sub>S), and WS-4 (CTATT-H<sub>2</sub>/H<sub>2</sub>S). The HYD/DDS ratios take into account all the products obtained along the HYD pathway: THDBT (tetrahydrodibenzothiophene), CHB (cyclohexylbenzene), DCH (dicyclohexyl) and CHCPM (cyclohexylcyclopentylmethane) while BP (biphenyl) was considered for the DDS pathway. DBT conversions are given after 5 h of reaction. Reaction rate constants are given considering, respectively, all the reaction products for  $k$  and only the desulfurized products for  $k_{\text{HDS}}$ .

Catalyst	Selectivity (%)					DBT conversion (%)	HYD/DDS	$k$ ( $\times 10^7 \text{ mol s}^{-1} \text{ g}^{-1}$ )	$k_{\text{HDS}}$ ( $\times 10^7 \text{ mol s}^{-1} \text{ g}^{-1}$ )
	CHCPM	DCH	CHB	BP	THDBT				
WS-1	13	16	37	25	9	73	3.1	34.0	30.8
WS-2	3	4	29	49	15	31	1.0	13.2	11.2
WS-3	14	14	36	21	15	65	3.8	26.6	22.6
WS-4	–	5	19	55	21	17	0.8	6.3	4.9

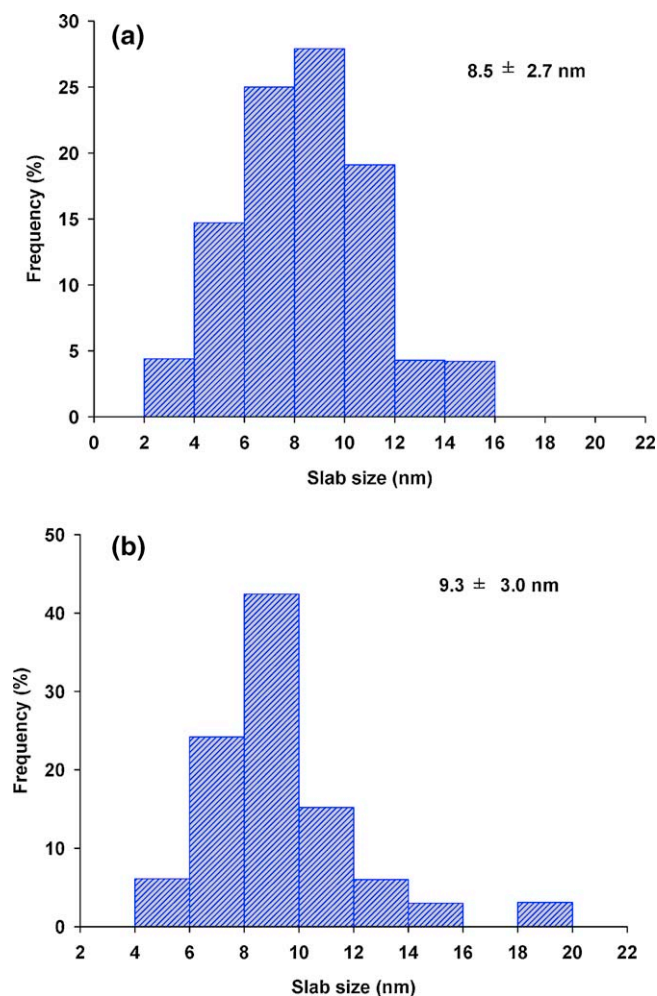


Fig. 5. Frequency distribution of the slab size of WS<sub>2</sub> particles for: (a) the WS-1 catalyst obtained from ATT and activated under N<sub>2</sub> and (b) the WS-3 catalyst obtained from ATT and activated under H<sub>2</sub>/H<sub>2</sub>S.

shown the formation of a large amount of carbon during the ex situ activation of the CTATT precursor both under N<sub>2</sub> and under H<sub>2</sub>/H<sub>2</sub>S. However, one should note that the activation of the CTATT precursor under N<sub>2</sub> led to 110% more catalytic activity than under H<sub>2</sub>/H<sub>2</sub>S. The lower amount of carbon produced in the former case (cf. Table 1) could partly explain the higher activity observed for the N<sub>2</sub>-activated CTATT sample. It should also be kept in mind that the activity of WS-2 (CTATT-N<sub>2</sub>) is much higher than those reported previously for an ex situ H<sub>2</sub>/H<sub>2</sub>S activated ATT precursor ( $4.7 \times 10^{-7} \text{ mol s}^{-1} \text{ g}^{-1}$ ) [30] contrary to the WS-4 catalyst (CTATT-H<sub>2</sub>/H<sub>2</sub>S) which presents similar HDS activity.

Strikingly, the activity results of the WS<sub>2</sub> catalysts obtained from ATT are much higher than those reported using the CTATT precursor in this study or by comparison to the results obtained previously for the H<sub>2</sub>/H<sub>2</sub>S ex situ activation of ATT [30]. Once again, the use of a N<sub>2</sub> atmosphere instead of the classical H<sub>2</sub>/H<sub>2</sub>S activation leads to a higher final activity (+35%) showing the advantage of using a N<sub>2</sub> ex situ activation of thiotungstate precursors. As stated before, the activity results measured herein for the WS<sub>2</sub> catalysts obtained from the ATT precursor are much higher than those previously obtained using an ex situ activation of ATT. In this respect, the WS-3 catalyst obtained after H<sub>2</sub>/H<sub>2</sub>S ex situ activation of ATT presents an activity 4.8 times higher than in our previous study [30–32]. The exact reason for such a high activity observed herein is not completely understood. However, contrary to preceding studies, the ATT thiosalt precursor was directly ex situ activated after its

synthesis instead of being stored under inert gas before use. The use of a freshly sulfided ATT precursor therefore seems to strongly increase the final HDS activity. One possible reason would be related to a better incorporation of structural carbon inside the WS<sub>2</sub> structure during the HDS catalytic test leading to improved catalytic properties. Indeed, if one takes into account that the steady-state active phase under DBT HDS conditions incorporates structural carbon at the edges of WS<sub>2</sub> slabs [21,22,39], the absence of formation of amorphous carbon in excess during the initial ex situ activation, combined with the formation of a freshly sulfided reactive WS<sub>2</sub> catalyst, might favor the incorporation of structural carbon leading to enhanced activities. In this respect, the C/W ratios determined by EDX after the catalytic test (Table 1) combined with the slab size as calculated from TEM images (Fig. 5) can provide an estimation of the proportion of edge sulfur atoms that can be replaced by carbon. Recent DFT results have also showed that incorporation of C<sub>2</sub> groups are favored in replacement of edge sulfur atoms of Mo(W)S<sub>2</sub> slabs [47] in accord with Kelty et al. [22]. For WS-1, the replacement of sulfur edge atoms by carbon would lead to a final stoichiometry WS<sub>1.86</sub>C<sub>0.30</sub>. The experimental C/W ratio is 0.40 showing a good agreement and therefore supporting the hypothesis of formation of almost only structural carbon in this case. Similarly, for the WS-3 catalyst, the replacement of sulfur edge atoms by carbon would lead to a final stoichiometry WS<sub>1.87</sub>C<sub>0.28</sub> while the experimental C/W ratio is 0.34. However, these assumptions must be confirmed through further studies by using different thiosalt precursors aged for varied times before being used in the HDS of DBT tests.

Selectivity results also showed striking differences between the WS<sub>2</sub> catalysts obtained from ATT or CTATT precursors. The WS-1 and WS-3 catalysts obtained from ATT respectively after ex situ activation under N<sub>2</sub> or H<sub>2</sub>/H<sub>2</sub>S exhibit higher hydrogenating character than their CTATT ex situ activated counterparts making them ideal candidates for desulfurizing more refractory compounds like dialkyldibenzothiophenes known to be converted mainly along the hydrogenation pathway [48–50]. Indeed, HYD/DDS ratios of 3.1 and 3.8 were obtained respectively for WS-1 and WS-3 catalysts vs 1.0 and 0.8 for WS-2 and WS-4. The selectivity into the different products (Table 2) clearly emphasized this point by showing a DDS selectivity (biphenyl (BP) formation only) of 49% and 55% respectively for WS-2 and WS-4, vs only 25% and 21% for WS-1 and WS-3. BP selectivity results combined with the distribution of HYD products also clearly evidence a marginal effect of the atmosphere used during the ex situ activation on the final selectivity properties, showing mainly an effect related to the nature of the precursor. It should also be noted that HYD products are not only composed of tetrahydrodibenzothiophene (THDBT) and cyclohexylbenzene (CHB) but also of further hydrogenated products like dicyclohexyl (DCH) obtained from hydrogenation of CHB but also of cyclohexylcyclopentylmethane (CHCPM) confirming its formation as already observed in mass spectra analysis by Romero-Rivera et al. [51]. Both CHCPM and DCH are expected to be formed from a cyclohexylcyclohexene (CHCHE) intermediate. However, while DCH is found by direct hydrogenation of CHCHE, CHCPM is obtained first by a ring contraction reaction of CHCHE into a methylcyclohexylcyclopentene intermediate followed by hydrogenation. Such a ring contraction step suggests the presence of a higher acidic character on the WS-1 and WS-3 catalysts, leading to a significant selectivity of 13–14% of CHCPM. On the contrary, very low selectivity (if any) for CHCPM is obtained on the WS<sub>2</sub> catalysts formed from CTATT, probably due to a neutralization of this acidic character by the formation of excess carbon. Similarly, the DCH selectivity reaches values of 14–16% on WS-1 and WS-3 vs only 3–4% on WS-2 and WS-4 formed from ATT.

Depletion of the hydrogenating character of the WS<sub>2</sub> catalysts obtained from the CTATT precursor is a phenomenon generally

observed for the activation of tetraalkylammonium thiometalate precursors [31,32,34–36]. This effect is directly related to the formation of a mesoporous organization when using carbon-containing thiosalt precursors, as also observed in the present case (Fig. 1). WS<sub>2</sub> slabs located inside these mesoporous cavities present a depleted hydrogenating character. This effect was ascribed previously, in agreement with the Rim-Edge model [52], to a sterically demanding  $\eta^6$  adsorption of the DBT molecule hindered inside the mesoporous cavities of these WS<sub>2</sub> slabs. Indeed, according to the Rim-Edge model, in the HDS of DBT, two modes of adsorption are expected to occur: (1) a  $\eta^1$ (S) mode of adsorption prerequisite of the C–S bond rupture or (2) a  $\eta^6$  flat adsorption by the phenyl ring leading to hydrogenation of the aromatic cycles. While the  $\eta^1$ (S) mode of adsorption would be able to occur on all edge active sites, the  $\eta^6$  mode would occur only on rim sites located on external layers of stacked MoS<sub>2</sub> or WS<sub>2</sub> particles. For internal layers, this sterically hindered mode of adsorption will be disfavored due to the presence of neighboring slabs. Similarly, mesoporous cavities of the WS<sub>2</sub> catalysts formed from CTATT would also create unfavorable conditions for the  $\eta^6$  mode of adsorption, limiting the hydrogenating character of the WS-2 and WS-4 samples.

#### 4. Conclusions

WS<sub>2</sub> catalysts were prepared by ex situ activation of ammonium tetrathiotungstate (ATT) or cetyltrimethylammonium tetrathiotungstate (CTATT) precursors. Two different atmospheres were used for the activation procedure: N<sub>2</sub> or 20% H<sub>2</sub>S/H<sub>2</sub>. Results show that the key for the optimized activation of WS<sub>2</sub> catalysts is the nature of the precursor used, while the atmosphere plays a minor role. The presence of a carbon source in the CTATT precursor strongly impacts textural and morphological properties. Formation of amorphous carbon in excess is observed by EDX, XRD and TEM studies. The use of the CTATT precursor also led to the formation of mesopores and to a strong destacking of the WS<sub>2</sub> particles. In contrast, highly stacked non-porous solids without excessive formation of amorphous carbon are formed using ATT.

The formation of excess amorphous carbon in the case of CTATT led to lower final activity of the WS<sub>2</sub> catalysts through blocking of active sites. Using ATT, very high HDS activity can be obtained, probably through optimized incorporation of structural carbon during the test, as suggested both by C/W ratios determined by EDX and particle size measured by TEM on DBT-tested samples. Finally, a confinement effect due to the localization of WS<sub>2</sub> slabs inside mesopores led to a depleted hydrogenating character for the samples formed from CTATT.

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