Comparative study of MoS$_2$ and Co/MoS$_2$ catalysts prepared by ex situ/in situ activation of ammonium and tetraalkylammonium thiomolybdates

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Abstract

Ex situ and in situ decompositions of ammonium and tetraalkylammonium thiomolybdates were used to synthesize unsupported MoS$_2$ and CoMo catalysts. The ex situ activation was performed under a H$_2$S/H$_2$ flow whereas the in situ activation consists in decomposing the thiosalt precursors in the presence of a hydrocarbon solvent during the hydrodesulfurization (HDS) of dibenzothiophene (DBT). Particular attention was devoted to the use of carbon-containing precursors and to the synergetic effect of cobalt. Ammonium thiomolybdate (ATM), tetramethylammonium thiomolybdate (TMATM), and tetrapropylammonium thiomolybdate (TPATM) and their cobalt-promoted counterparts were studied. Catalysts were characterized by XRD, scanning electron microscopy (SEM) and specific surface area measurements (BET, BJH). Catalysts were evaluated for the HDS of DBT. The in situ method of preparation allows to obtain catalysts with larger superficial areas than those obtained with the ex situ method. The cobalt synergetic effect depends both on the method of activation and the presence of carbon in the precursor. For in situ activated catalysts, the promotional effect of cobalt is well-observed if carbon is present in the precursor while an opposite effect is shown for ex situ activated catalysts.
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1. Introduction

New environmental legislation reduces drastically the amount of sulfur, nitrogen and other polluting agents authorized in vehicle transportation fuels. For instance, EU regulations about the sulfur content in gasoline will be lower than 10 ppm in 2011 [1]. Catalytic desulfurization is the most commonly technique used to remove organic sulfur compounds from crude oil [2,3]. Due to their exceptional resistance to poisons, transition metal sulfides, mainly molybdenum and tungsten disulfide, promoted with cobalt or nickel, are widely used in this process [4]. Generally, molybdenum and tungsten sulfide catalysts are prepared from oxide precursors by sulfidation using either H$_2$/H$_2$S or an organic sulfur compound like dimethyldisulfide (DMDS). However, particularly for tungsten-based catalysts, sulfidation could be difficult to perform and complete sulfidation of the active phase could not be achieved [5–7]. An alternative to the oxide-sulfide transformation is to use precursor compounds already sulfided like ammonium thiometalates precursors $(NR_4)_2MeS_4$ (R: H or alkyl; Me: Mo or W). However, for unsupported hydrodesulfurization (HDS) catalysts, surface areas and catalytic properties depend strongly upon the atmosphere as well as the experimental conditions used during the activation process. For instance, large variations of surface areas have been reported for MoS$_2$ and WS$_2$ catalysts, ranging from few to several hundred square meters per gram depending on the decomposition conditions [8,9]. In this respect, ex situ activation, i.e. activation under a H$_2$S/H$_2$ gas mixture leads to catalytic systems with a very

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low surface area [10]. Recently, unsupported molybdenum and tungsten sulfide catalysts with high superficial areas have been synthesized using thiosalts as precursors by an in situ method of activation [11–13]. In this in situ method of preparation, the thiosalt precursor is decomposed directly in an autoclave in the presence of a hydrocarbon solvent. Moreover, the use of a carbon-containing thiosalt precursor like tetraalkylammonium thiomolybdates or thiotungstates leads to an increase in the HDS activity [14–16]. The in situ activation of tetraalkylammonium thiometalates (M: Mo or W) led to a structural replacement of sulfur by carbon on the edges of MoS_2 and WS_2 layers and to a final surface $MeS_{2-x}C_x$ stoichiometry [12,13]. This mode of decomposition could also promote interesting changes in selectivity thanks to the formation of a mesoporous catalytic system [11]. Cobalt-promoted unsupported catalysts prepared from the decomposition of thiosalts have also shown higher catalytic activities than promoted catalysts obtained by others methods of preparation [17,18]. Consequently, the in situ decomposition of tetraalkylammonium thiomolybdate precursors can improve the activity of CoMo catalysts and the cobalt synergetic effect was enhanced by the use of carbon-containing precursors. In order to better ascertain the role of carbon coming from the precursor toward the promoting effect of Co, ex situ activation of tetraalkylammonium precursors was compared to the in situ activation for preparing MoS_2 and CoMo catalysts. Therefore, a series of cobalt promoted unsupported catalysts was prepared using ammonium thiomolybdate precursors with or without alkyl groups. The effect of an in situ or ex situ method of activation on the morphological and catalytic properties of these catalysts was evaluated.

2. Experimental

2.1. Preparation of samples

Ammonium tetrathiomolybdate (ATM) was first obtained by bubbling H_2S/H_2 in an aqueous solution of ammonium heptamolybdate according to the method reported previously [19]. The tetraalkylammonium tetrathiomolybdate precursors [tetrametylammonium thiomolybdate (TMATM) and tetrapropylammonium thiomolybdate (TPATM)] were synthesized following a slightly modified version of the one reported by Alonso et al. [20,21]. Indeed, the tetraalkylammonium thiomolybdate salts were obtained by mixing their corresponding tetraalkylammonium bromide salts with ATM at 333 K instead of room temperature. This increase in temperature makes the reaction faster and cleaner and limits the amount of impurities. If promoted, in a second step, the required amount of $Co(NO_3)_2 \cdot 6H_2O$ to give an atomic ratio $R = Co/(Co + Mo) = 0.3$ was added to the minimum amount of water and was dripped to an aqueous solution of ATM, TMATM, or TPATM. The resulting mixture was a soft paste which was then dried at 393 K

for 2 h. The MoS_2 and co-promoted MoS_2 catalysts were obtained using either an ex situ or an in situ activation. In the ex situ method of activation, the precursors were decomposed under H_2S/H_2 (15% (v/v) H_2S) at 673 K for 4 h. $MoS_{2\,ex\,situ}$, C_1-$MoS_{2\,ex\,situ}$, C_3-$MoS_{2\,ex\,situ}$ catalysts were prepared from ATM, TMATM and TPATM, respectively and cobalt-promoted $Co/MoS_{2\,ex\,situ}$, Co/C_1-$MoS_{2\,ex\,situ}$, Co/C_3-$MoS_{2\,ex\,situ}$ catalysts from Co/ATM, Co/TMATM, and Co/TPATM, respectively. On the other hand, in the in situ activation, precursors were decomposed in the reaction media during the HDS of DBT. However, it should be noted that complete decomposition of the precursors occurs before the temperature of 623 K for the DBT HDS test [20,21]. Moreover, the 50 K difference in the temperature of activation between the two methods of preparation (623 K for in situ, 673 K for ex situ) led to minor differences in crystallinity as observed by Wildervanck and Jellinek [22]. $MoS_{2\,in\,situ}$, C_1-$MoS_{2\,in\,situ}$, C_3-$MoS_{2\,in\,situ}$ catalysts were prepared from ATM, TMATM, and TPATM, respectively, and cobalt-promoted $Co/MoS_{2\,in\,situ}$, Co/C_1-$MoS_{2\,in\,situ}$, and Co/C_3-$MoS_{2\,in\,situ}$ catalysts from Co/ATM, Co/TMATM, and Co/TPATM, respectively.

2.2. Catalyst characterization

The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the different thiosalt precursors were obtained simultaneously on a TA instruments SDT 2960 DTA–TGA equipment, heating the sample from 298 to 823 K at 4 K/min under dry nitrogen flow.

Ex situ activated catalysts were characterized before and after the HDS reaction while the characterization of the in situ activated catalysts was performed after the HDS catalytic test only. Specific surface areas were measured with a Quantachrome Nova 1000 series by nitrogen adsorption at 77 K using the BET method. The pore distribution was obtained from the desorption isotherm following the BJH method. Samples were degassed under vacuum at 523 K before nitrogen adsorption. Catalyst morphology and EDS elemental analyses were studied using a JEOL JSM-58000LV scanning electron microscope analyzing several fields at different magnifications. EDX analysis was performed using an eBX-ZAF system. MoS_2 reference compounds were used to deconvolute K lines of S and L lines of Mo.

2.3. Catalytic activity and selectivity

The HDS of DBT was carried out in a Parr Model 4520 high-pressure batch reactor (volume: 1 l) (Fig. 1) equipped with a magnetically driven turbine which prevents vortex formation and allows a good dispersion of the gas into the liquid phase. The ex situ activated catalyst (1.0 g) or, for the in situ mode of activation, the appropriate amount of precursor to yield 1 g of MoS_2 or Co/MoS_2 catalyst was placed in the reactor. Particles were selected in a 35–50 mesh size range to avoid any intraparticle mass transfer resistance. The
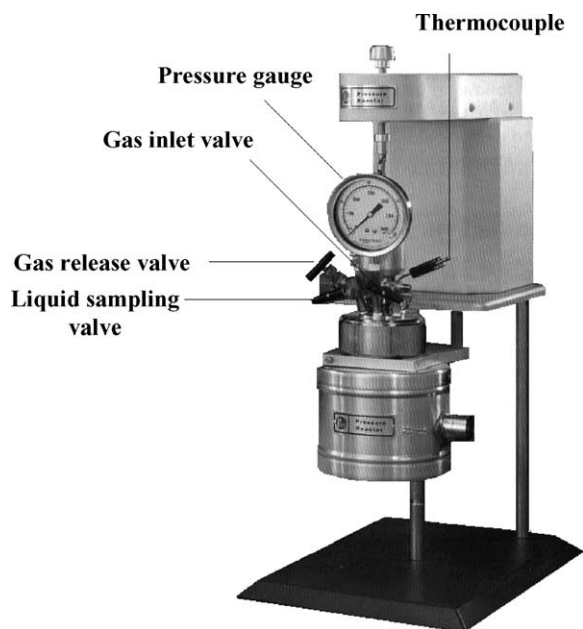
Fig. 1. High-pressure batch reactor used for the in situ decompostion of the thiomolybdate precursors and for the HDS of DBT.

reactant mixture (5% volume of DBT in decalin, total volume: 150 ml) was then added and the autoclave was pressurized with hydrogen to 3.1 MPa and heated up to 623 K at 10 K/min. The stirring speed was kept equal to 600 rpm. At this stirring rate, under our conditions, reaction rates were free of external mass transfer limitations. Once at 623 K, the reaction was followed for 5 h by analyzing samples using a Perkin-Elmer AutoSystem XL gas chromatography equipped with a OV-17 packed column. Results were reproduced for both in situ and ex situ activated catalysts to check the accuracy of activity data.

DBT conversion increases linearly with time as expected for a pseudo-zero order reaction [23]. The main reaction products for the HDS of DBT are biphenyl (BiPh) formed by direct C–S bond cleavage of DBT (the so-called direct desulfurization pathway, DDS), and phenylcyclohexane (PhCH) formed by an initial hydrogenation of one of the aromatic rings of DBT followed by C–S bond rupture (the hydrogenating pathway, HYD). The selectivity for the main reaction products was determined for MoS$_2$ and Co promoted-MoS$_2$ catalysts. The HYD/DDS selectivity ratio is based on the product concentration ratio (PhCH/BiPh). It should be noted that an intermediate primary hydrogenated product, tetrahydrodibenzothiophene (THDBT) is also formed along the HYD pathway. Its concentration remains low and could be neglected when calculating the HYD/DDS ratio. Moreover, this compound is not an HDS product since still containing sulfur. The mean standard deviation for catalytic measurements was about 2.5%. After the DBT reaction, the catalysts were separated from the reaction mixture by filtration, washed with isopropanol to remove residual hydrocarbons and dried at room temperature.

3. Results

3.1. Thermal analysis

TGA–DTA curves for the thermal decomposition of Co/ATM, Co/TMATM, and Co/TPATM precursors are reported in Fig. 2a–c. Corresponding DTA–TGA studies for the non-promoted ATM, TMATM and TPATM precursors were reported previously [20,21]. Small weight losses attributed to the elimination of water (3% for Co/ATM and Co/TMATM and about 2% for Co/TPATM) were observed at low temperatures, around 400–450 K.

The Co/ATM, Co/TMATM, and Co/TPATM bimetallic precursors decompose according to the model proposed by Pedraza and Fuentes [24]. The decomposition of the Co/ATM precursor is complicated. Indeed, during the preparation, cobalt nitrate reacts first with ammonium tetrathiomolybdate according to the following reaction
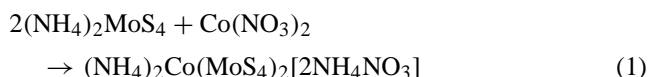
$$2(NH_4)_2MoS_4 + Co(NO_3)_2$$
$$\rightarrow (NH_4)_2Co(MoS_4)_2[2NH_4NO_3] \qquad (1)$$

when dried at 393 K during the preparation, ammonium nitrate leaves the system forming nitric acid and ammonia

$$(NH_4)_2Co(MoS_4)_2 [2NH_4NO_3]$$
$$\rightarrow (NH_4)_2Co(MoS_4)_2 + 2HNO_3 + 2NH_3 \qquad (2)$$
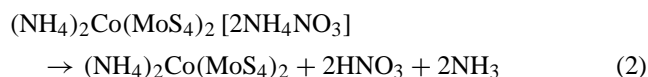
The as-formed precursor $(NH_4)_2Co(MoS_4)_2$ shows three steps of decomposition. The first step occurs in the 370–460 K temperature range. The weight loss is 12% (theoretical 11.8%) and corresponds to the elimination of $2S^0$

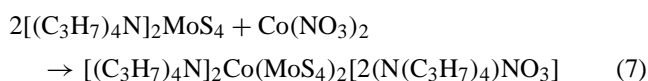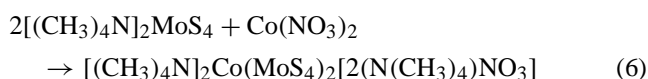$$(NH_4)_2Co(MoS_4)_2 \rightarrow (NH_4)_2Co(MoS_3)_2 + 2S^0 \qquad (3)$$
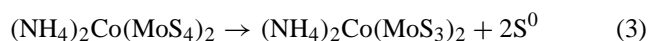
The second step is clearly endothermic and occurs at 475–525 K. The weight loss is 12% (theoretical 11.8%) and corresponds to the elimination of ammonium sulfide

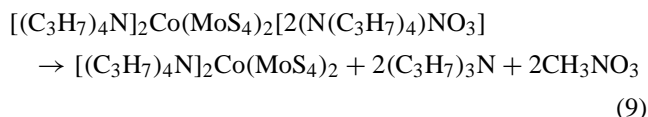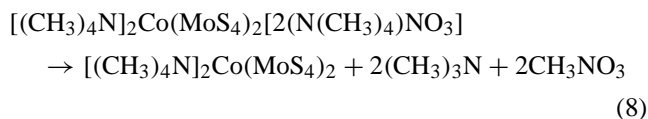$$(NH_4)_2Co(MoS_3)_2 \rightarrow Co(MoS_2)_2S + (NH_4)_2S \qquad (4)$$

The last step occurs at 640–700 K with a weight loss of 17% (theoretical 17.6%) assigned to a further elimination of sulfur, according to the following equation

$$Co(MoS_2)_2S \rightarrow Co(MoS)_2 + 3S^0 \qquad (5)$$
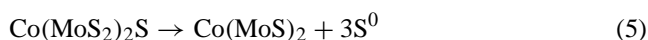
Similarly, during the preparation of the tetraalkylammonium precursors, cobalt nitrate reacts first with tetramethylammonium or tetrapropylammonium thiomolybdates according to the following reactions

$$2[(CH_3)_4N]_2MoS_4 + Co(NO_3)_2$$
$$\rightarrow [(CH_3)_4N]_2Co(MoS_4)_2[2(N(CH_3)_4)NO_3] \qquad (6)$$

$$2[(C_3H_7)_4N]_2MoS_4 + Co(NO_3)_2$$
$$\rightarrow [(C_3H_7)_4N]_2Co(MoS_4)_2[2(N(C_3H_7)_4)NO_3] \qquad (7)$$

when dried at 393 K during the preparation, ammonium nitrate leaves the system forming nitric acid and ammonia

$$[(CH_3)_4N]_2Co(MoS_4)_2[2(N(CH_3)_4)NO_3]$$
$$\rightarrow [(CH_3)_4N]_2Co(MoS_4)_2 + 2(CH_3)_3N + 2CH_3NO_3 \tag{8}$$

$$[(C_3H_7)_4N]_2Co(MoS_4)_2[2(N(C_3H_7)_4)NO_3]$$
$$\rightarrow [(C_3H_7)_4N]_2Co(MoS_4)_2 + 2(C_3H_7)_3N + 2CH_3NO_3 \tag{9}$$

The decomposition of the Co/TMATM precursor occurs in one step in the 460–700 K temperature range with an exothermic peak at 510 K. The weight loss is 55% (theoretical 51.9%) and corresponds to the elimination of $(CH_3)_4N$ and elemental sulfur

$$[(CH_3)_4N]_2Co(MoS_4)_2$$
$$\rightarrow Co(MoS)_2 + 2(CH_3)_4N^+ + 6S^0 \tag{10}$$
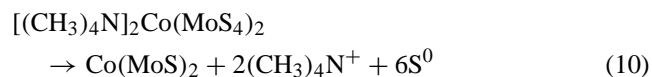
The decomposition of the Co/TPATM occurs also in one step in the 430–680 K temperature range with an exothermic peak at 490 K. The weight loss is 58% (theoretical 56.9%) and corresponds to the elimination of $(C_3H_7)_4N$ and elemental sulfur.

$$[(C_3H_7)_4N]_2Co(MoS_4)_2$$
$$\rightarrow Co(MoS_2)_2 + 2(C_3H_7)_4N^+ + 4S^0 \tag{11}$$
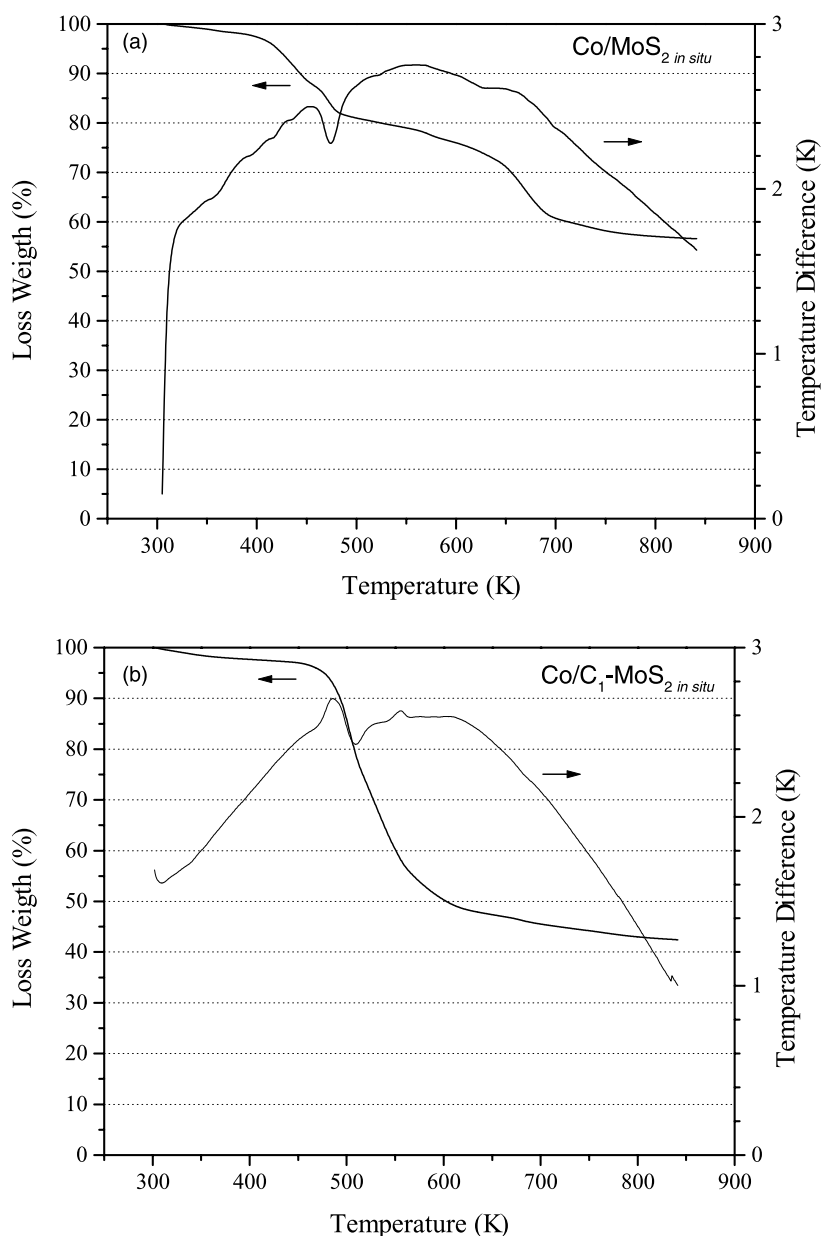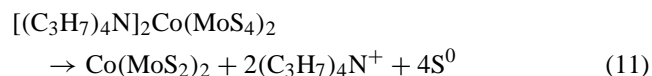

Fig. 2. DTA–TGA curves of the decomposition of (a) Co/ATM, (b) Co/TMATM, and (c) Co/TPATM.
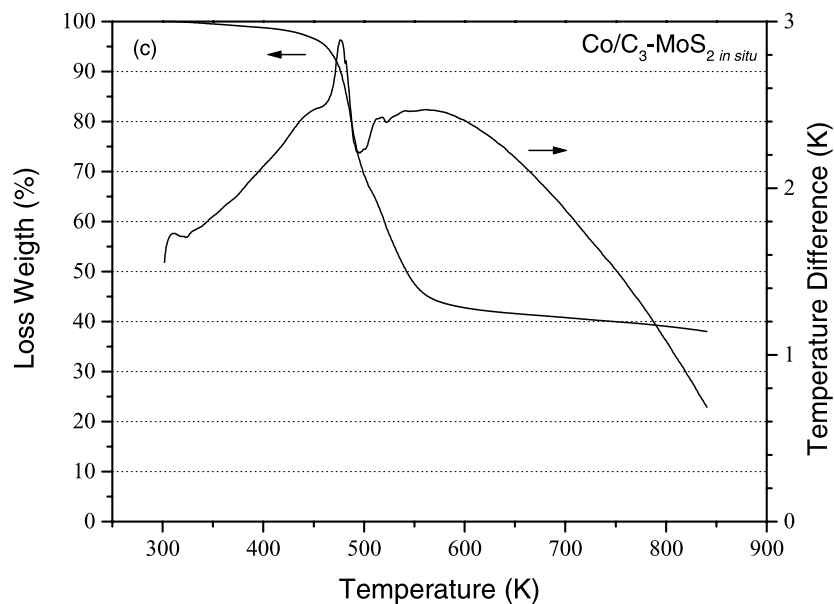
Fig. 2. (*Continued*).

3.2. Elemental analysis

The S/Mo, C/Mo and Co/Mo atomic ratios are reported in Table 1. The elemental analysis was performed for all catalysts after the HDS reaction. For non-promoted MoS_2 catalysts prepared either in situ or ex situ, the S/Mo ratios are always lower than the theoretical value of 2.0. For the cobalt-promoted catalysts, the sulfur content of the in situ activated catalysts is generally higher than the values for their ex situ activated counterparts. The highest S/Mo ratio was obtained for the in situ prepared catalysts formed from Co/TPATM. C/Mo ratios show strong variations depending on the method of activation, the length of the alkyl chain in the precursor or the presence of the cobalt promoter. Indeed, for the in situ activated MoS_2 catalysts, the C content increases markedly with the length of the alkyl chain in the precursor while for their ex situ counterparts, the C amount remains low. For the in situ activated catalysts promoted by Co, the C values are quite similar to those observed for the equivalent series of non-promoted catalysts. A rapid increase of the C content with the length of the alkyl chain in the precursor is observed for the ex situ activated catalysts promoted by Co. Therefore, for the ex situ mode of activation, the interaction of Co with alkyl groups present initially in the precursor seems to promote the formation of a large excess of C or inversely does not block it. The Co/Mo atomic ratio in the experimental analysis is close to the theoretical ratio suggesting that cobalt is well dispersed on MoS_2.

3.3. Surface area and pore size distribution

Specific surface areas for all catalysts are reported in Table 1. Surface areas for the in situ activated samples were measured after the HDS reaction whereas for the ex situ ac-

tivated catalysts surface areas were measured before and after the HDS reaction. The in situ mode of activation results in much higher surface areas than the ex situ preparation. Indeed, the non-promoted C_3-$MoS_{2\,in\,situ}$ catalyst reaches a value of 143 m^2/g whereas for ex situ prepared samples, values are generally lower than 20 m^2/g. The only exception is the C_1-$MoS_{2\,ex\,situ}$ catalyst with a S_{BET} value of 56.7 m^2/g. A similar situation is observed for the co-containing catalysts with a surface area higher after the in situ activation.

For the in situ mode of activation, compared to the equivalent non-promoted catalysts, the promotion by cobalt leads to a decrease in surface area when prepared from the ATM

Table 1
Specific surface area and elementary analysis results for non-promoted and cobalt promoted MoS_2 catalysts prepared using ex situ or in situ modes of activation

Catalyst	Specific surface area ($m^2\,g^{-1}$)		Elemental analysis		
	Before reaction	After reaction	S/Mo	C/Mo	Co/Mo
$MoS_{2\,in\,situ}$	–	59.9	1.8	0.3	–
$MoS_{2\,ex\,situ}$	5.5	8	1.7	0.1	–
$Co/MoS_{2\,in\,situ}$	–	37.4	2.4	0.6	0.35
$Co/MoS_{2\,ex\,situ}$	31.4	14.6	2.2	0.2	0.39
C_1-$MoS_{2\,in\,situ}$	–	75.6	2.5	1.5	–
C_1-$MoS_{2\,ex\,situ}$	62.2	56.7	1.8	0.1	–
Co/C_1-$MoS_{2\,in\,situ}$	–	13.1	2.3	2.1	0.4
Co/C_1-$MoS_{2\,ex\,situ}$	3.1	6.7	2.3	1.4	0.39
C_3-$MoS_{2\,in\,situ}$	–	143	2.0	2.2	–
C_3-$MoS_{2\,ex\,situ}$	17.8	5.1	1.9	0.4	–
Co/C_3-$MoS_{2\,in\,situ}$	–	146	2.6	2.0	0.4
Co/C_3-$MoS_{2\,ex\,situ}$	3.21	18.5	1.9	3.7	0.33

Surface areas were measured before and after the HDS catalytic test for ex situ activated catalysts. The elementary analysis of the catalysts was performed after the HDS reaction.

or TMATM thiosalts or to similar values for the catalysts prepared from TPATM. For the ex situ method, no clear effect of the cobalt promotion on surface area could be noted.

The evolution of the surface area during the HDS test varies with the cobalt promotion and the presence of carbon. For cobalt-promoted systems, the presence of carbon stabilizes the textural properties since, without carbon, $Co/MoS_{2\,ex\,situ}$ loses about 50% of its surface area during the test while $Co/C_3\text{-}MoS_{2\,ex\,situ}$ shows an increase of its surface area, initially quite low. For non-promoted catalysts, the effect seems reversed. While $MoS_{2\,ex\,situ}$ and $C_1\text{-}MoS_{2\,ex\,situ}$ do not present any marked change in surface area before and after the HDS test, the surface area of $C_3\text{-}MoS_{2\,ex\,situ}$ decreases.

The size of the alkyl group affects strongly the development of a porous organization (Fig. 3a and b). For the in situ activated catalysts, while $MoS_{2\,in\,situ}$ presents only a type I isotherm, type IV isotherms can be considered for C_1-$MoS_{2\,in\,situ}$ and C_3-$MoS_{2\,in\,situ}$ (Fig. 3a). The C_3-$MoS_{2\,in\,situ}$ catalyst presents the most developed hysteresis loop with a desorption step above the relative pressure of 0.4 characteristic of a mesoporous organization [11]. The BJH pore size distribution for the in situ activated catalysts reflects this situation. A narrow pore size distribution centered on a diameter of 40 Å was observed for the C_3-$MoS_{2\,in\,situ}$ catalyst (Fig. 4a). This result confirms previous findings showing that increasing the size of the alkyl group in the tetraalkylammonium precursor led to the progressive appearance of a porous
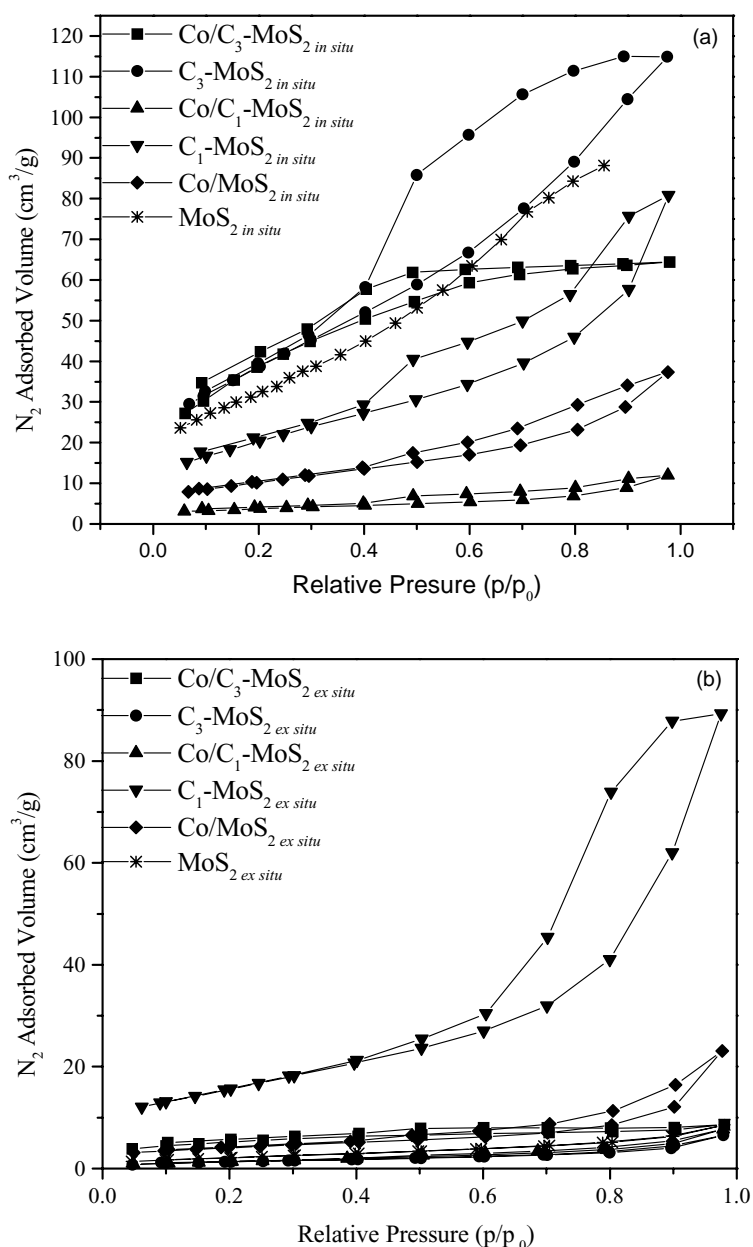

Fig. 3. Adsorption–desorption isotherms for MoS_2 and Co/MoS_2 catalysts formed by (a) in situ activation or (b) ex situ activation.
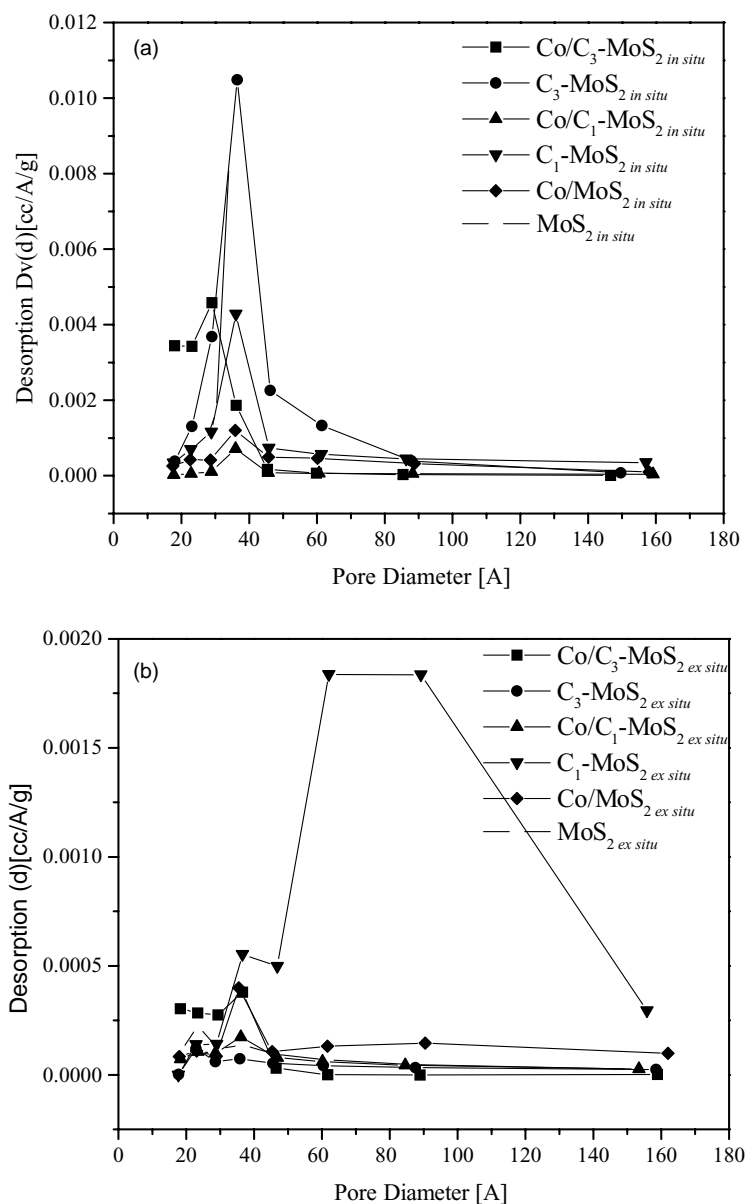
Fig. 4. BJH pore size distribution for MoS_2 and Co/MoS_2 catalysts formed by (a) in situ activation or (b) ex situ activation.

organization [11,16]. The cobalt addition retards strongly the formation of an organized porous system. For instance, while a type IV isotherm is already formed for the C_1-$MoS_{2\,in\,situ}$ catalyst, only a poorly porous system is obtained for the Co/C_1-$MoS_{2\,in\,situ}$ catalysts with a type I isotherm and very low values of N_2 adsorption. In the same way, even if the Co/C_3-$MoS_{2\,in\,situ}$ catalyst presents a type IV isotherm, its hysteresis loop is much less developed than for the C_3-$MoS_{2\,in\,situ}$ solid. Moreover, the BJH pore size distribution for the Co/C_3-$MoS_{2\,in\,situ}$ catalyst shows a much higher proportion of pores lower than 30 Å compared to other in situ activated samples suggesting that the surface area observed for this catalyst compared to its non-promoted counterpart (146 versus 143 m^2/g) is only due to the formation of micropores.

For the ex situ activated catalyst, virtually no porous organization could be observed for all the samples (Fig. 3b). The values of N_2 adsorption are very low. The only exception is the C_1-$MoS_{2\,ex\,situ}$ catalyst with a well-developed hysteresis loop and relatively high values of N_2 adsorption. Consequently, the BJH curves (Fig. 4b) do not exhibit any pore size distributions. Only, the C_1-$MoS_{2\,ex\,situ}$ catalyst presents a very broad distribution centered on pore diameters around 80–100 Å.

3.4. Scanning electron microscopy

The morphology of the catalysts (Fig. 5a–h) shows a strong dependency upon the precursor and the method of activation. The cobalt addition for the in situ activated

MoS_2 catalysts does not provoke any clear modification of the morphology even if a slightly more compact aspect may be noted. On the other hand, comparison between the $MoS_{2\,in\,situ}$ catalyst (Fig. 5a) and the $MoS_{2\,ex\,situ}$ one (Fig. 5c) reveals strikingly that the ex situ method of activation leads to a much denser morphology than the in situ preparation. However, the cobalt addition for the ex situ activated MoS_2 samples leads to a modification of the morphology with a more open aspect (Fig. 5d). The replacement of ATM by a tetraalkylammonium precursor like TPATM involves a strong change in the morphology of the samples (Fig. 5a and e). The C_3-$MoS_{2\,in\,situ}$ catalyst appears very porous with cavities probably resulting from the elimination of gas products during the course of the in situ decomposition process [11,16]. This situation differs completely from the C_3-$MoS_{2\,ex\,situ}$ catalyst which exhibits a more compact structure due probably to a collapse of the porous architecture (Fig. 5g). The cobalt addition for the in situ activated MoS_2 sample prepared from TPATM still results in a very porous solid but cavities appear much smaller than for the non-promoted C_3-$MoS_{2\,in\,situ}$ catalyst (Fig. 5f).

Finally, for Co/C_3-$MoS_{2\,ex\,situ}$, the cobalt addition does not change markedly the morphology of the sample (Fig. 5h).

3.5. Catalytic activity and selectivity

Table 2 reports activity and selectivity results for the HDS of DBT. For the non-promoted catalysts prepared from ATM (without alkyl groups), the in situ activation appears much more efficient in achieving HDS active catalysts than the ex situ preparation. Indeed, the $MoS_{2\,in\,situ}$ catalyst is 3.5 times as active as its ex situ counterpart. The situation is more complicated when catalysts were cobalt-promoted and/or prepared from alkyl-containing precursors. First of all, if only the use of a tetraalkylammonium thiomolybdate instead of ammonium thiomolybdate is considered for non-promoted catalysts, reverse effects were observed between in situ and ex situ methods of activation. For the in situ activation, to use TMATM (C_1) or TPATM (C_3) instead of ATM has a negative effect on the HDS activity since the C_3-$MoS_{2\,in\,situ}$ catalyst is less active than the $MoS_{2\,in\,situ}$ catalyst. These results confirm previous findings showing that the in situ
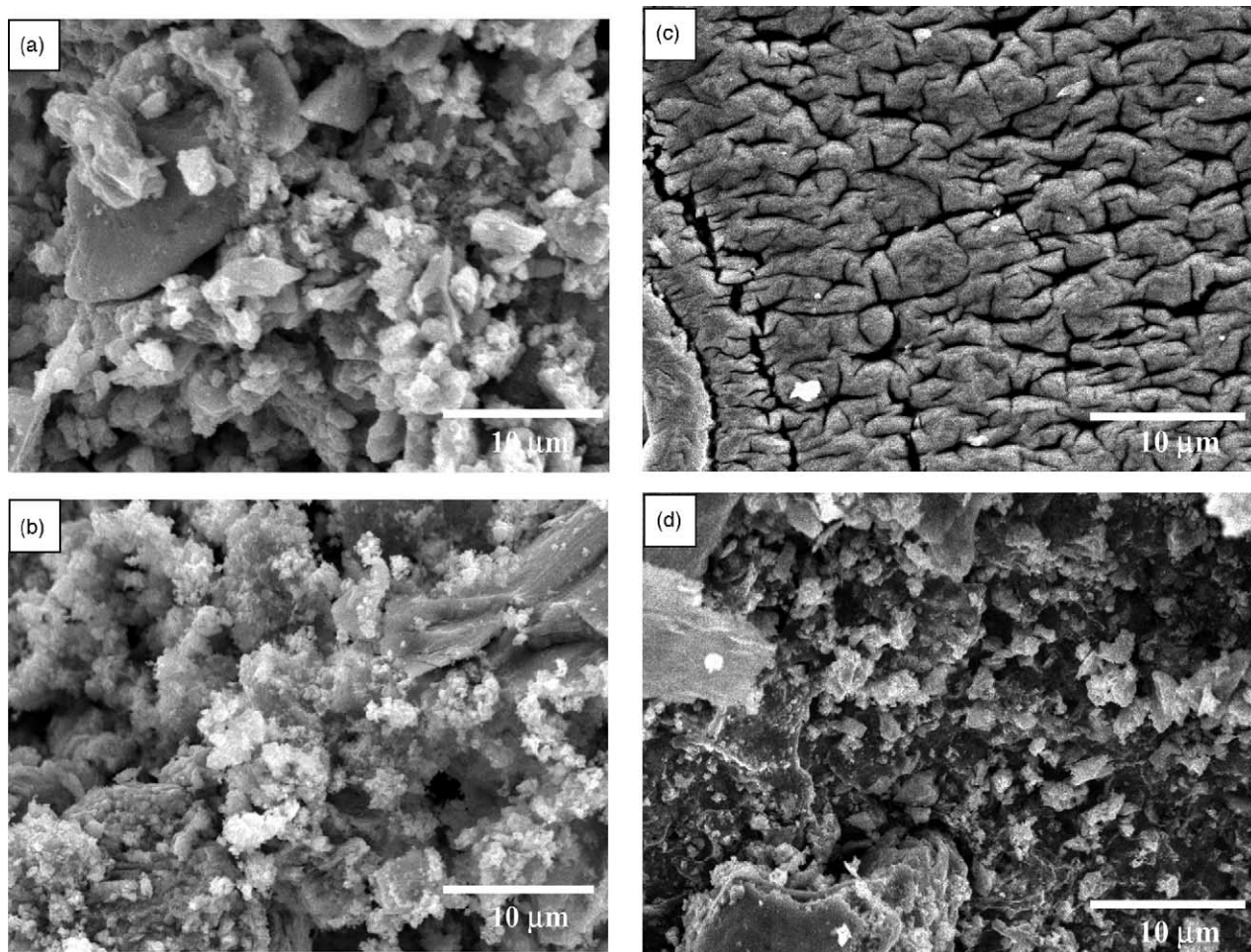

Fig. 5. Scanning electron micrographs of the catalysts: (a) $MoS_{2\,in\,situ}$; (b) Co/$MoS_{2\,in\,situ}$; (c) $MoS_{2\,ex\,situ}$; (d) Co/$MoS_{2\,ex\,situ}$; (e) C_3-$MoS_{2\,in\,situ}$; (f) Co/C_3-$MoS_{2\,in\,situ}$; (g) C_3-$MoS_{2\,ex\,situ}$ and (h) Co/C_3-$MoS_{2\,ex\,situ}$. Samples were all initially DBT tested.
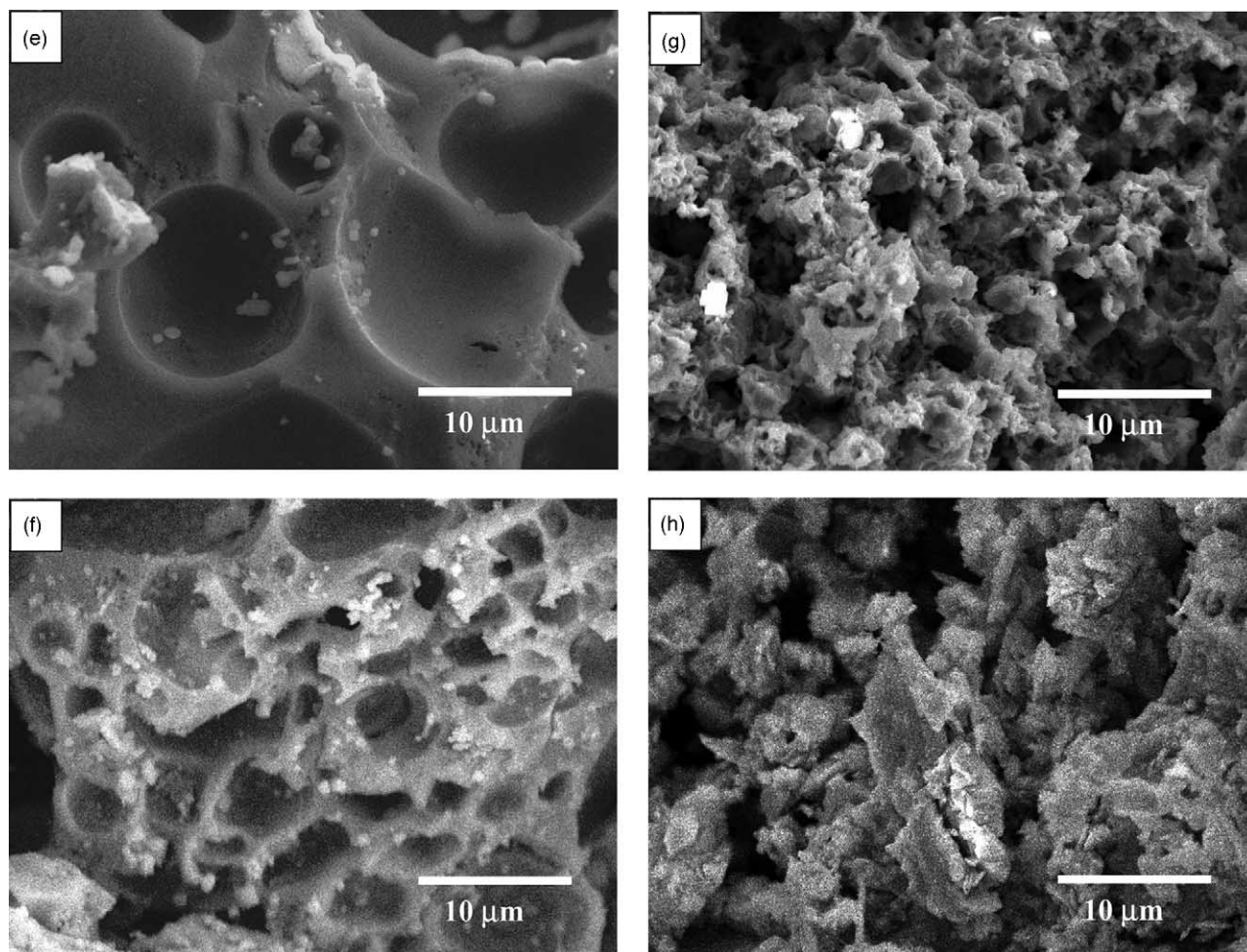
Fig. 5. (*Continued*).

decomposition of tetraalkylammonium precursors do not improve HDS activity for unpromoted catalysts [11]. On the other hand, for the ex situ activation, to use tetraalkylammonium thiosalts has a positive influence since C_3-$MoS_{2\,ex\,situ}$ is twice as active as the $MoS_{2\,ex\,situ}$ catalyst. The advantage of the in situ activation versus the ex situ activation decreases with the increase in the size of the alkyl group in the pre-

cursor. If $MoS_{2\,in\,situ}$ is much more active than $MoS_{2\,ex\,situ}$, C_3-$MoS_{2\,in\,situ}$ is less active than C_3-$MoS_{2\,ex\,situ}$.

The effect of the cobalt addition is very dependent on the method of activation and on the initial presence of carbon (alkyl groups) in the thiosalt precursor. For ex situ activated catalysts, a synergetic effect due to the cobalt addition is observed only if a thiosalt precursor without carbon is used,

Table 2

Initial rates constants, DBT conversion, selectivity for biphenyl (DDS) and phenylcyclohexane (HYD), and HYD/DDS ratio for in situ and ex situ activated catalysts. DBT HDS conversion was measured after 5 h on stream

Catalyst	$k \times 10^7$ (mol s^{-1} g per catalyst)	%DBT conversion	%BiPh	%PhCH	HYD/DDS ratio
$MoS_{2\,in\,situ}$	6.0	34	41	59	1.5
$MoS_{2\,ex\,situ}$	1.7	10	71	29	0.4
Co/$MoS_{2\,in\,situ}$	7.2	34	63	37	0.6
Co/$MoS_{2\,ex\,situ}$	7.6	40	62	38	0.6
C_1-$MoS_{2\,in\,situ}$	5.8	28	40	60	1.5
C_1-$MoS_{2\,ex\,situ}$	3.4	18	55	45	0.8
Co/C_1-$MoS_{2\,in\,situ}$	15	54	68	32	0.5
Co/C_1-$MoS_{2\,ex\,situ}$	2.0	10	89	11	0.1
C_3-$MoS_{2\,in\,situ}$	2.8	15	68	32	0.5
C_3-$MoS_{2\,ex\,situ}$	4.0	21	54	46	0.8
Co/C_3-$MoS_{2\,in\,situ}$	9.5	31	73	27	0.4
Co/C_3-$MoS_{2\,ex\,situ}$	5.0	20	88	12	0.1

the $Co/MoS_{2\,ex\,situ}$ catalyst exhibits a rate constant $k = 7.6 \times 10^{-7}\,mol\,s^{-1}\,g^{-1}$ versus $1.7 \times 10^{-7}\,mol\,s^{-1}\,g^{-1}$ for the $MoS_{2\,ex\,situ}$ catalyst. However, the effect of the cobalt addition is quite weak when using TMATM or rather negative with TPATM. For in situ prepared samples, the combined effect of the cobalt promotion and the initial presence of carbon in the precursor is beneficial. Cobalt addition results in a weak gain in activity if ATM (without alkyl groups) is used, the $Co/MoS_{2\,in\,situ}$ catalyst is only 20% more active than $MoS_{2\,in\,situ}$. On the other hand, a clear synergetic effect is observed if carbon is present in the thiosalt precursor. The Co/C_1-$MoS_{2\,in\,situ}$ catalyst presents the highest HDS activity and is 2.5 times as active as C_1-$MoS_{2\,in\,situ}$. This result is in agreement with previous reports about the beneficial role of C when using tetraalkylammonium precursors for the in situ preparation of CoMo catalysts [16]. This result is in agreement with previous reports about the beneficial role of C when using tetraalkylammonium precursors for the in situ preparation of CoMo catalysts [16]. DBT conversions after 5 h on stream reveal similar results to those observed using initial rate constants. This suggests that catalytic properties do not change during the HDS reaction. One exception is the Co/C_3-$MoS_{2\,in\,situ}$ catalyst which presents a higher initial rate constant than the unpromoted $MoS_{2\,in\,situ}$ catalyst but similar DBT conversions after 5 h on stream. A marked deactivation process occurred for this particular catalyst during the run. This different comportment is due to the high proportion of micropores present on this catalyst. Since cobalt retards the formation of mesopores compared to unpromoted systems, an organized mesoporous organization is not formed yet on this catalyst. As noted before, increasing the size of the alkyl groups to C_5-C_6 results in a well developed mesoporous organization. Moreover, these Co/C_5-$MoS_{2\,in\,situ}$ and Co/C_6-$MoS_{2\,in\,situ}$ catalysts showed a highly stable HDS activity similar to the one observed here for the non porous Co/C_1-$MoS_{2\,in\,situ}$ catalyst [16]. Therefore, the formation of an intermediate microporous solid corresponds to an unfavorable situation during the progressive formation of a porous network (from the non-porous "C_1" catalyst to the highly mesoporous "C_5-C_6" catalysts).

About selectivity results, the cobalt addition favors the selectivity along the DDS pathway for all samples independently of the method of activation. The only exception was the $MoS_{2\,ex\,situ}$ catalyst. Moreover, the use of an in situ method of activation generally results in catalysts with higher hydrogenating properties than ex situ activated solids. However, one exception was once again observed with the C_3-MoS_2 sample.

4. Discussion

The in situ method of activation using tetraalkylammonium thiometallates as precursors to generate non-promoted and cobalt-promoted unsupported MoS_2 catalysts leads to materials presenting high surface area, large amount of

carbon and, in certain cases, a mesoporous organization involving strong changes in selectivity [11,16]. Higher HDS activities were also reported if tetraalkylammonium thiomolybdate precursors are used for the preparation of cobalt-promoted MoS_2 catalysts [16] whereas, for non-promoted catalytic systems, the HDS activity was not necessarily improved with the marked increase in surface area resulting from the in situ activation of carbon-containing thiosalts [11]. Results about the ex situ method of activation have concluded to the formation of MoS_2 solids with very low surface areas [17,18,25]. Therefore, a comparative analysis of the in situ and ex situ methods of activation seems necessary taking into account the cobalt promotion and the use of carbon-containing thiomolybdates instead of ammonium thiomolybdate (ATM).

First of all, as revealed by the DTA–TGA study, the decomposition process observed for the tetraalkylammonium precursors differs from the one determined for ATM. The interaction of alkyl groups in the thiosalt precursors with the tetrathiomolybdate anion, $MoS_4{}^{2-}$ oversimplifies the decomposition pattern since only a single step is really observed in that case. More precisely, this study suggests that the intermediate formation of molybdenum trisulfide-like entities might not occur or, most likely, is strongly minimized. Moreover, it should be noted that above 650 K (T^0 higher than the temperature for the HDS test), a further loss of sulfur could not be avoided and should have a negative effect if higher temperatures of reaction are used [26].

As observed previously [11,16], the in situ activation leads systematically to MoS_2 solids with high surface areas whereas the ex situ preparation results in catalysts with very low surface areas with the noticeable exception of the C_1-$MoS_{2\,in\,situ}$ catalyst exhibiting very large pores. For instance, the $MoS_{2\,in\,situ}$ catalyst presents a specific surface area of $60\,m^2/g$ versus only $8\,m^2/g$ for the $MoS_{2\,ex\,situ}$ catalyst. Indeed, as revealed by the SEM study, the ex situ mode of activation generates very compact solids while a more open structure is achieved with the in situ activation. A possible explanation would be related to a specific role of the hydrocarbon solvent during the in situ preparation. It is well recognized that hydrocarbons can play the role of less tough reducing agents than H_2 during the activation of hydrotreating catalysts [27]. The use of a carbon-containing precursor involves a strong increase in surface area particularly for the C_3-$MoS_{2\,in\,situ}$ catalysts with the concomitant development of type IV isotherms corresponding to the formation of a mesostructure. The SEM analysis reveals a very porous material with a characteristic "Swiss-cheese"-like morphology as observed previously for non-promoted MoS_2 catalysts in situ prepared using thiosalt precursors with long alkyl chains [11]. Such morphology is produced by the vaporization of organic fragments which escape from the material during the process of decomposition. Cavities are formed by the accumulation of gases while channels are created during the escape of these gases giving rise to type IV isotherms.

For the in situ mode of activation, the cobalt addition has a negative effect on textural properties of promoted catalysts since lower surface areas were obtained compared to their non-promoted counterparts. In the same way, as revealed by SEM and nitrogen adsorption studies, cobalt has a retarding effect on the development of type IV isotherms and then on the formation of a mesostructure. For the ex situ method of activation, adding cobalt or using a carbon-containing precursor does not modify really the morphological and textural properties of the as-formed catalysts. Except for the particular case of the C_1-$MoS_{2\,ex\,situ}$ catalyst, the use of a tetraalkylammonium precursor does not involve any increase in surface area. This situation could be surprising if one considers a similar decomposition process for both in situ or ex situ activated catalysts. However, SEM analysis suggests that even if a vaporization of organic fragments had probably occurred, the gas phase activation under H_2S/H_2 led probably to a collapse of the porous architecture. Cobalt promotion does not modify the morphology even if a slight dispersing effect might be probably considered. However, it should be recognized that SEM results cannot be used to rule out any cobalt effect on the morphology of these MoS_2-based catalysts. Transmission electron microscopy (TEM) would be more appropriate to get a qualitative overview of these catalysts. TEM was efficient to demonstrate the enhanced formation of defects sites on cobalt-promoted catalysts [28,29]. This increased number of active sites due to cobalt promotion was later confirmed using TPR and IR spectroscopy [30]. Nevertheless, in the present case, the high amount of C produced during the decomposition of tetraalkylammonium precursors produced "fluffy" zones which reduces the visibility of the MoS_2 slabs. BJH curves (Fig. 4) confirm that a very different morphology was obtained for the ex situ activated solids compared to their in situ prepared counterparts. The ex situ activation produces nearly non-porous solids. Cobalt promotion or the use of carbon-containing precursors does not change this situation.

Even if high specific surface areas could be obtained using the in situ mode of activation particularly with carbon-containing precursors, a direct relationship between the HDS activity and the specific surface areas is not straightforward at all. Indeed, the highest HDS activity was obtained for the C_1-$MoS_{2\,in\,situ}$ catalyst ($15.0 \times 10^{-7}\,mol\,s^{-1}\,g^{-1}$) with only a surface area of $13.1\,m^2/g$ while the C_3-$MoS_{2\,in\,situ}$ catalyst is less active ($9.5 \times 10^{-7}\,mol\,s^{-1}\,g^{-1}$) but with a high surface area. Moreover, similar carbon contents were also observed for these two samples. This result is quite common for anisotropic materials like MoS_2 where no linear correlation between surface area and activity could be obtained. Indeed, only edge sites on the layered slabs of MoS_2 are active while the basal plane is quite inactive [31,32]. This situation is even more complicated by the presence of active sites on defects of the basal planes if MoS_2 slabs are curved [33,34]. However, for Co/C_3-$MoS_{2\,in\,situ}$, it should be underlined that the large proportion of micropores observed for

this catalyst has a negative effect on the HDS activity either by blocking the access of reactants to active sites located in these micropores or by hindering partially the formation of an active phase. Moreover, undoubtedly, the more open morphology of the in situ activated MoS_2 samples would facilitate the interaction of the DBT molecules with the active phase compared to the quite compact ex situ activated MoS_2 catalysts.

Depending on the mode of activation, cobalt addition and the use of a carbon-containing precursor instead of ATM can have opposite effects or could combine together positively. This fact is clearly evidenced by the reversed comportment observed between cobalt synergetic effects and the presence of carbon in the thiosalt precursor if in situ or ex situ activated. For the ex situ preparation, the role of C is quite negative. The cobalt promoting effect seems to be hindered strongly by carbon entities formed during the ex situ decomposition. The cobalt synergetic effect could be completely suppressed like for the Co/C_1-$MoS_{2\,ex\,situ}$ catalyst. The HDS activity for this catalyst suggests that the promoted active phase was not achieved. This result differs strikingly from the clear promoting effect of cobalt if a non-carbon containing thiosalt precursor (ATM) is used. On the other hand, for in situ activated catalysts, the situation is totally reversed. If ATM is used (without C), the cobalt synergetic effect is weak since the $Co/MoS_{2\,in\,situ}$ catalyst was only 20% more active than the $MoS_{2\,in\,situ}$ catalyst. Its activity is not different from the activity expected by a simple addition of the activities of non-interacting MoS_2 and Co_9S_8 phases. Inversely, the cobalt synergetic effect is quite discernible if a carbon-containing thiosalt precursor is used since cobalt-promoted catalysts were about 3 times as active as their non-promoted counterparts. This result points out clearly the beneficial role of the use of a tetraalkylammonium precursors and more generally of carbon in order to achieve highly HDS active catalysts for in situ prepared samples. This beneficial role of carbon could be related to a structural effect leading to the formation of a final $MoS_{2-x}C_y$ active phase with surface carbide-like moieties [12,13,35,36] and/or to a morphological effect leading to more dispersed particles if carbonaceous entities interact during the initial stages of the formation of the transition metal sulfide phase [37]. The structural effect would result from the interaction of C with the molybdenum disulfide phase leading to a partial replacement of surface sulfur atoms located on the edges of MoS_2 slabs by carbon leading to a "sulfocarbide" surface phase. Actually, this structural replacement of sulfur by carbon at the edges of MoS_2 or WS_2 layers was evidenced by Auger spectroscopy for catalysts prepared by in situ activation of tetraalkylammonium precursors [12,13]. This effect was also observed with carbide catalysts interacting with sulfur and could be a general phenomenon [38–41]. The morphological effect would result from the interaction of carbonaceous species blocking the crystalline growth of sulfide particles. This interaction prevents the catalytic system from sintering and maintains a good dispersion of the

active phase. It should be underlined that these two effects, structural and textural, could even occur simultaneously or successively.

Selectivity results reveal that cobalt promotion favors the DDS pathway for the HDS of DBT whatever the method of activation. This result is in agreement with previous results showing that cobalt promotion accelerates the C–S bond rupture steps in the DBT HDS mechanism [42–45]. The in situ method of activation favors generally the selectivity along the HYD pathway. According to the Rim–Edge model [46], this result would suggest a decrease in the stacking of the MoS_2 slabs if in situ activated. A higher dispersion of the active phase could then be envisaged and would be in agreement with results by Glasson et al. [37]. However, this conclusion would be correct only if we assume that the Rim–Edge model could be used for cobalt-promoted catalytic systems while this model was validated only for non-promoted unsupported MoS_2 catalysts. Moreover, the use of tetraalkylammonium precursors does not seem to have a clear effect on the HDS selectivity as long as a well-developed mesoporous organization is not obtained. Indeed, for the C_3-$MoS_{2\,in\,situ}$ catalyst, the appearance of a mesostructure was accompanied by a strong decrease in the HYD/DDS ratio (Table 2) compared to $MoS_{2\,in\,situ}$ and C_1-$MoS_{2\,in\,situ}$. This effect was already observed previously for non-promoted [11] and cobalt-promoted catalysts [16] and results from a confining effect inside the mesopores hindering hydrogenation reactions. Indeed, assuming the same assumptions than those developed for the Rim–Edge model, the flat adsorption through the aromatic ring of the DBT molecule, prerequisite for its subsequent hydrogenation, makes hydrogenation a geometrically demanding reaction. Confinement inside the mesopores would then hamper the flat adsorption of DBT on "rim" sites located on the external layers of the MoS_2 particles. This hindered flat adsorption inside the mesopores led to highly DDS selective catalytic systems.

Mesoporosity can be achieved when using TPATM while only a poorly developed porous system was obtained previously using the same thiosalt precursor [11]. These differing results are related to a slight modification of the experimental procedure to prepare the TPATM precursor. While in the previous study, tetrapropylammonium bromide (TPABr) and ATM were mixed at room temperature, in the present case, the reaction was carried out at 333 K leading to a faster and cleaner process with a lower amount of TPABr impurities. This resulted in a higher final C amount (C/Mo = 3.5) if prepared at room temperature than at 333 K (C/Mo = 2.2). This higher amount of C seems to block the formation of a mesostructure. This result is in agreement with a previous study using a surfactant like cetyltrimethylammonium bromide with ATM [47]. Indeed, in that case, the corresponding tetraalkylammonium thiomolybdate was very rapidly formed but was degraded into a MoS_2 powder with very high C amount but without mesoporosity.

5. Conclusions

The method of activation (in situ or ex situ) and the nature of the thiosalt precursor (with or without C) influences strongly the textural and catalytic properties of the final MoS_2 and Co/MoS_2 catalysts. The use of a tetraalkylammonium thiomolybdate precursor (with C) reduces significantly the formation of an MoS_3-like intermediate. The in situ mode of activation generates high surface area MoS_2-based materials while only low surface areas were obtained using the ex situ preparation. For the in situ method, the initial presence of alkyl groups in the thiosalt precursor can lead to a final MoS_2 mesostructure. However, cobalt addition retards this formation. For the ex situ activation, carbon-containing thiosalt precursors and/or cobalt addition does not modify the final MoS_2 structure.

The synergetic effect of cobalt depends on the nature of the thiosalt precursor and on the mode of activation. For the ex situ activation, the use of a tetraalkylammonium thiomolybdate precursor (with C) has a negative influence and blocks the formation of a promoted active phase. For the in situ activation, the cobalt synergetic effect is enhanced by the use of a carbon-containing thiosalt precursor. These results show the beneficial effect of carbon for the in situ activation of CoMo catalysts.

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