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Genesis of active phase in MoW/Al₂O₃ hydrotreating catalysts monitored by HAADF and *in situ* QEXAFS combined to MCR-ALS analysis.

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Abstract

Alumina supported MoW hydrotreating catalyst was synthesized by using bimetallic H₄[SiMo₃W₉O₄₀] Keggin heteropolyacid (HPA). Catalysts based on monometallic H₄[SiMo₁₂O₄₀] and H₄[SiW₁₂O₄₀] and their mixture were also studied. Genesis of the active phase was studied during atmospheric gas sulfidation by H₂S/H₂ of the catalysts by *in-situ* Quick X-ray absorption spectroscopy (XAS) and High-Angle Annular Dark-Field (HAADF) imaging. The combination of different chemometric tools such as Principal Component Analysis (PCA) and Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) allowed to determine the number of intermediate species, their chemical nature and concentration profiles during sulfidation. It was found that tungsten sulfidation using bimetallic HPA precursor started at lower temperature, compared to W sulfidation in the monometallic and in the mixture of monometallic HPA catalysts. Simultaneous sulfidation of Mo and W atoms in case of the bimetallic molecular precursor can govern the formation of mixed MoWS₂ phase, which formation during activation was evidenced by HAADF.

Keywords: MoW catalyst, Time-resolved XAS, Chemometric methods, Sulfidation intermediates, HAADF.

1. Introduction

Development of more active hydrodesulfurization (HDS) catalysts remains a challenge for the deep refining of lower quality feedstocks. Traditionally, bimetallic catalysts based on Mo or W sulfides, promoted by Ni or/and Co and supported on γ -Al₂O₃ are used in HDS processes. These catalysts exhibit high activity in removing sulfur from thiophene and benzothiophene compounds, and some non-refractory dibenzothiophenes (DBT). However, their activity is significantly lower in the HDS of refractory compounds such as 4,6-dibenzothiophene due to steric hindrance of substituent alkyl groups. To avoid costly developments of more efficient processes, the use of mixed MoWS catalysts has been considered as a solution. A leap to a new level of activity of hydrotreating catalysts was achieved in the early 2000 with the advent of the “Nebula” catalyst, a commercial bulk NiMoW catalyst with improved catalytic performances, at least three times higher than conventional alumina supported catalysts [1]. Beneficial effect was attributed to the trimetallic character and formation of a mixed NiMoWS active phase, which appeared more efficient than their bimetallic NiWS, NiMoS and CoMoS counterparts [2]. The use of unsupported trimetallic catalysts indeed allowed to obtain high content of metals, however, this advantage is at the same time the cause of the main drawback of “Nebula”, its cost.

Keggin structures have been successfully used to replace conventional precursors in the preparation of oxidic precursors of metal sulfide catalysts [3, 4]. The observed better promotion in the sulfided active phase has been attributed to proximity of metals in the oxidic precursors. From a catalytic point of view, the use of mixed metals Keggin-type HPAs may enhance activity due to the introduction of a second metal in the HPA cluster. We recently reported the synthesis of β -H₄[SiMo₃W₉O₄₀] HPA and its use as precursor for hydrotreating alumina supported catalyst [5]. This HPA presents the advantage to introduce simultaneously both metals in the same compound allowing to maintain a Mo-W nanoscale proximity. We have shown that better catalytic properties for DBT HDS and naphthalene hydrogenation have been obtained when using this HPA compared to the use of a mixture of monometallic SiMo₁₂ and SiW₁₂ HPA precursors, in relation with the formation of a mixed Mo_xW_{1-x}S₂ phase [5]. In this paper, genesis of the active phase will be monitored by High-angle annular dark-field imaging (HAADF) and Quick-XAS. Using *in situ* time-resolved characterizations of the sulfidation by H₂S/H₂ of the catalysts by Quick-XAS associated with Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) chemometric

method, we will unravel differences in sulfidation pathways and sulfidation intermediates between supported catalysts prepared from monometallic Keggin HPAs and bimetallic ones.

2. Experimental

2.1. Catalyst preparation

The bimetallic SiMo_3W_9 HPA was synthesized according to the published method [6]. The obtained HPA has been extensively characterized at the solid state by FTIR and Raman spectroscopies, single crystal X-ray diffraction and Mo K and W L_{III} edges XAS in a previous work [5]. Two monometallic SiMo_{12} and SiW_{12} HPAs were also prepared. Catalysts with the same surface density of metals $d(\text{Mo+W}) = 3.9 \text{ at/nm}^2$ were synthesized by incipient wetness method *via* impregnation of $\gamma\text{-Al}_2\text{O}_3$ extrudates ($S_{\text{BET}} = 275 \text{ m}^2/\text{g}$, $V_p = 0.85 \text{ cm}^3/\text{g}$) with aqueous solutions containing the required amounts of HPAs. One bimetallic $\text{SiMo}_3\text{W}_9/\text{Al}$ catalyst was prepared by using the corresponding bimetallic HPA. MoW reference supported catalyst (RefMo_3W_9) was synthesized using as impregnating solution a mixture of monometallic HPAs with the same Mo/W ratio as in the bimetallic $\text{SiMo}_3\text{W}_9/\text{Al}$ one. Finally, $\text{SiMo}_{12}/\text{Al}$ and $\text{SiW}_{12}/\text{Al}$ samples based on the corresponding monometallic HPAs were also synthesized for comparison purposes. After impregnation and maturation, the catalysts were dried at $100 \text{ }^\circ\text{C}$ for 10 h in air atmosphere without further calcination. Chemical compositions of the catalysts, together with the nomenclature at which they are referred to in the paper, are shown in Table 1.

2.2. *In situ* time-resolved measurements

The sulfidation process as well as oxide and sulfide states of the prepared catalysts were studied *in situ* by XAS at the ROCK beamline at SOLEIL synchrotron [7]. The sulfidation was performed in a flow of 10 % H_2S in H_2 at atmospheric pressure. Powdered oxide catalysts were loaded in the cell [8] and were then heated from room temperature (RT) to $400 \text{ }^\circ\text{C}$ with a heating rate of $3 \text{ }^\circ\text{C}/\text{min}$ followed by a plateau of 2 h.

The remotely-controlled edge jumping capability of the beamline was used in order to record XAS spectra simultaneously at different edges: Mo K edge and W L_{I} , L_{II} and L_{III} edges on the same sample during one sulfidation treatment [7]. In that case a monochromator equipped with Si (111) channel-cut was used alternatively with Bragg angle centered around 10.36° (cam amplitude 2.4°) at the W edges and around 5.50° (cam amplitude 0.5°) at the Mo K edge whereas harmonic rejections were ensured changing stripes, from B_4C for W edges to Pd for Mo edge, of both mirrors surrounding the monochromator aligned with a grazing

incidence of 2.5 mrad. For the whole measurements, XAS spectra were measured in transmission mode with ionization chambers as X-Ray detectors. Ionization chambers were filled with a mixture of argon and nitrogen (50:50) for Mo K edge and (73:27) for W L edges.

Mo and W-edges EXAFS regions of the spectra were extracted and analyzed using Athena and Artemis software packages [9]. For Mo K edge, $k^3\chi(k)$ EXAFS signals were Fourier transformed in R-space pseudo-radial distribution functions using a Kaiser–Bessel window between $k_{\min} = 4.8 \text{ \AA}^{-1}$ and $k_{\max} = 10.5 \text{ \AA}^{-1}$ ($E_0=20004.3 \text{ eV}$) and dk window sill parameter equal to 2. For W L_{III} edge, Fourier transforms (FT) of the $k^3\chi(k)$ EXAFS data were carried out from 3.5 to 16.8 \AA^{-1} ($E_0 =10218.8 \text{ eV}$) with a dk parameter equal to 2. Identification of the phases present during the *in situ* sulfidation treatment can be obtained using the MCR-ALS chemometric method as reported in recent time-resolved XAS studies [10-18]. The basic assumption for applying MCR-ALS method is the inner linear structure of the data set, which is fully verified for spectroscopic techniques following the Lambert-Beer law as X-ray Absorption Spectroscopy does. In that case, experimental data are first represented in a matrix form, D , where spectra are arranged as rows. Taking into account the linear structure of the data set, a bilinear decomposition of the matrix D can be done into the matrix containing pure concentration profiles C arranged as columns and the matrix containing pure spectra S^T of the n species of the unknown mixtures according to relation: $D = CS^T + E$, where the matrix E contains the residual variation of the data (typically the experimental noise). The superscript T means the transpose of matrix S , where pure spectra are rows. Matrices C and S^T are responsible for the observed data variance. MCR techniques do not require a priori information concerning the data for resolving C and S^T , except an estimation of the number of pure components. The description of the MCR-ALS methodology applied to XAS has been detailed [10, 13, 15]. The MCR-ALS minimization algorithm developed under Matlab by the group of R. Tauler was used [17]. The methodology recently used is detailed in [18, 19]. MCR-ALS analysis was carried out on normalized XAS data obtained using the *normal_gui* graphical user interface available at the SOLEIL's ROCK beamline and described in [19]. The normalization was carried out over the full collected energy range i.e. ~1100 eV above the Mo K edge, ~ 1300 eV above the W L_{III} edge and ~ 220 eV above the W L_I edge. The spectra of pure species isolated by MCR-ALS at the Mo K and W L_{III} edges can be analyzed as a conventional experimental spectrum: EXAFS can be extracted and corresponding FT can be calculated. Simulations of the so-obtained EXAFS spectra of pure species using Artemis [9] allowed us to subsequently determine the nature of the neighbours in the first and second coordination shells and the distances between the

metallic centers and those neighbours. This information leads to propose possible structural models for the species involved during sulfidation.

2.3. High resolution transmission electron microscopy (HRTEM)

HRTEM was carried out using a Tecnai G2 20 electron microscope with a 0.14 nm lattice-fringe resolution and an accelerating voltage of 200 kV. Freshly sulfided samples were ground under an inert atmosphere and dispersed in ethanol. The suspension was collected on carbon films supported on copper grids and 20 representative micrographs were obtained for each catalyst in high-resolution mode.

High resolution high-angle annular dark-field (HRHAADF) imaging has been performed at 200 kV on a TITAN Themis FEI scanning transmission electron microscope (STEM). The microscope is equipped with a monochromator and a Cs probe corrector. For HAADF acquisition, the spot size was 9 with a screen current of ~50 pA, semi-convergence angle of 21 mrad and camera length of 115 mm, corresponding to collection angles for the HAADF detector between ~50 and ~200 mrad. More than 50 images were observed on each studied catalyst.

3. Results

3.1. *In situ* measurements

Sulfidation of the dried oxidic precursors was followed by continuous and alternate recording of XAS data at both Mo and W edges, with an incremental change in temperature of 6 °C along the full heating ramp from RT to 400 °C. Evolution of the XANES spectra at the Mo K and W L_I edges and Fourier transforms at the Mo K and W L_{III} edges Quick-EXAFS functions are reported in Figure S1 and S2 respectively, for SiX₁₂/Al (X=Mo or W), SiMo₃W₉/Al and RefMo₃W₉ catalysts. In order to emphasize the main transformations and differences characterizing the sulfidation of those samples, Fourier transforms of EXAFS signals recorded at several intermediate temperatures were extracted and gathered in Fig. 1 at the Mo K edge and in Fig. 2 at the W L_{III} edge.

3.1.1. SiMo₁₂/Al

Before H₂S introduction, the position of the edge in the XANES spectra of SiMo₁₂/Al catalyst is characteristic of hexavalent molybdenum species [20]. The observed pre-edge feature is related to transition from 1s toward molecular orbitals in which 4d Mo orbitals are

hybridized with p Mo orbitals due to the presence of a non-centrosymmetric environment for Mo [18] (Figure S1a). In the FT of the spectra before addition of H₂S at RT (Fig. 1a), the signal between 0.5 and 2 Å (not phase corrected) can be assigned to the octahedral coordination of the Mo absorber atom with oxygen atoms [18]. The signal at around 3Å (not phase corrected) can be associated to Mo-Mo and Mo-Al contributions [21-23]. These features have been previously assigned to the formation of the 6-molybdoaluminate Anderson-type heteropolyanion (AlMo₆O₂₄H₆³⁻) in the case of a dried Mo/Al₂O₃ catalyst [18] and of a dried promoted NiMo/Al₂O₃ catalyst [23]. This is in agreement with Raman analysis of SiMo₁₂/Al catalyst that has shown that SiMo₁₂ HPA was not preserved on alumina and decomposed in AlMo₆O₂₄H₆³⁻ Anderson heteropolyanion species [5].

Just after H₂S introduction at RT, Mo atoms remain mainly in oxygen surrounding, the FT of the spectrum being unchanged compared to that obtained for the oxidic precursor at RT (Fig. 1a and Figure S2a). When increasing the temperature, the pre-edge of the Mo XANES spectra disappears with simultaneous shift to lower energy of the edge position, which is characteristic of an exchange of oxygen ligands by sulfur ones accompanied by a reduction of the Mo oxidation state [18]. As expected, evolution of the position and intensity of the peaks in the FT of the spectra indicates gradual modification of the local order around Mo throughout the sulfidation process (Fig. 1a and Figure S2a). On the FT of the spectrum recorded at 100 °C, the contribution of the first oxygen coordination shell corresponding to the Mo-O contribution is shifted from 1.2 to 1.4 Å. In addition, a strong contribution centered at 1.9 Å has appeared. This observation has been previously reported in the literature and was related to Mo-S contribution in oxysulfide species [18, 19]. Moreover, a new peak centered at 2.4 Å can be seen which could be attributed to a Mo-Mo contribution. At 200 °C, the intensity of the Mo-O contribution is almost vanished and the Mo-S contribution centered at 1.9 Å and the Mo-Mo one centered at 2.4 Å become dominant. At 300 °C a new contribution emerges at 2.8 Å corresponding to the Mo-Mo signal in MoS₂ and the Mo-S contribution shifts from 1.9 Å to 1.8 Å which corresponds in non phase-shift corrected FT to the R-space position of the first coordination shell in MoS₂ crystallites. The amplitude of the Mo-S (1.8 Å) and Mo-Mo (2.8 Å) signals increases with increasing the temperature up to 400 °C. At 400 °C the Mo-O peak at 1.2 Å has completely disappeared indicating total reduction of Mo in MoS₂.

3.1.2. SiW₁₂/Al

Before addition of H₂S an intense pre-edge peak on the W L_I edge XANES data (Figure S1b) is observed at RT for SiW₁₂/Al catalyst. According to dipolar selection rules, L_I edge probes the same p empty states than K edges, except that the photoelectron is ejected from the 2s level for the former and from the 1s ones for the later. Accordingly, the intensity of the pre-edge structure at the W L_I edge is associated to hybridization between 5d states and 6p levels gaining intensity for non-centrosymmetric environments around W [24]. The FT of the RT EXAFS spectrum recorded at W L_{III} edge (Fig. 2a and Figure S2b) is characteristic of W oxide species. Indeed the first peaks in the spectra recorded at RT between 1 Å and 2 Å (not phase corrected) are attributed to W-O bonds [25-27], the second peak at ~ 3.4 Å (not phase corrected) being mainly associated to W-W bonds [27]. In contrast to SiMo₁₂/Al catalyst, the Raman spectrum of the oxidic SiW₁₂/Al was similar to that of the corresponding bulk HPA, indicating its preservation on alumina at the dried state [5], in agreement with the more stable structure of H₄SiW₁₂O₄₀ compared to that of H₄SiMo₁₂O₄₀.

Just after addition of H₂S the features of XANES and EXAFS spectra remain unchanged over an extended temperature range. In particular, the pre-edge resonance which vanishing is ascribed for Mo K edge to the exchange of oxygen ligands by sulfur ones is observed at the W L_I edge up to ~ 350 °C (Figure S1b) against 100 °C for SiMo₁₂/Al. The most significant changes in the first coordination shell start after 200 °C (Fig. 2a) but it is clearly seen from Fig. 2a and Figure S2b that, despite the sulfidation treatment, the oxidic phase is still present at 300 °C, in contrast with the results obtained at Mo K edge for SiMo₁₂/Al.

The peak centered at 2 Å corresponding to the W-S coordination in WS₂ [28] appears only after 300 °C, with a second metal-metal contribution at 2.8-3.3 Å (not phase-corrected) attributed to the formation of WS₂ particles [28]. The intensity of the W-S signal keeps on increasing during the plateau under H₂/H₂S at 400 °C (Figure S2b), indicating an incomplete sulfidation of tungsten at the end of the temperature ramp. These results are in agreement with the more difficult sulfidation of tungsten oxide compared to molybdenum oxide, due to stronger W-O bonds and a stronger tungsten-support interaction.

3.1.3. SiMo₃W₉/Al and RefMo₃W₉ – comparison with monometallic catalysts

At the oxidic state, differences are observed in the Mo K edge and W L_{III} edges FT of the SiMo₃W₉/Al and SiX₁₂/Al catalysts (X=Mo or W) (Fig 1a and b). In a previous work Raman analysis of the dried precursors has shown that SiMo₃W₉ HPA was preserved on

alumina in contrast to the aforementioned decomposition in AlMo_6 of SiMo_{12} . This result was confirmed by EXAFS characterization after drying performed simultaneously at the Mo K and W L_{III} edges indicating bimetallic heteropolyanion preservation at the alumina surface [5]. From the strong structural differences between $\text{SiMo}_3\text{W}_9/\text{Al}$ and the monometallic supported catalysts, we assume that different intermediates species for the bimetallic catalyst and the monometallic ones should be involved during activation leading to different sulfidation pathways.

During *in situ* sulfidation, Mo K edge XANES spectra (Figure S1a) and FT moduli of EXAFS spectra (Fig.1 and Figure S2a) exhibit with time different evolution for the $\text{SiMo}_{12}/\text{Al}$ and $\text{SiMo}_3\text{W}_9/\text{Al}$ catalysts, in particular for $T < 300$ °C. At 200 °C, almost all Mo atoms in the $\text{SiMo}_{12}/\text{Al}$ catalyst are in sulfidic form, while an oxidic contribution is still present at this temperature for $\text{SiMo}_3\text{W}_9/\text{Al}$. At 400 °C a higher contribution of the Mo-O signal (1.2 Å) is present for $\text{SiMo}_3\text{W}_9/\text{Al}$ compared to the $\text{SiMo}_{12}/\text{Al}$ catalyst. The second coordination shell located at ~ 3.0 Å at 400 °C which indicates the formation of well-developed Mo(W)S_2 particles is less pronounced for the bimetallic samples. Such decrease in second shell of the bimetallic MoW catalysts could be caused by the presence of W neighboring atoms with opposite backscattering phases in this shell. Actually in our previous work, we clearly evidenced from the EXAFS simulations of signals recorded for both sulfided catalysts after cooling down at RT that the bimetallic catalyst consists in mixed Mo(W)S_2 particles [5]. During the 2h isothermal treatment at 400 °C this Mo-M contribution kept on evolving for both catalysts, ending with a higher Mo-M contribution in $\text{SiMo}_{12}/\text{Al}$ than that in $\text{SiMo}_3\text{W}_9/\text{Al}$.

At the W L_{III} edge, despite the sulfidation treatment, the oxidic phase is still present up to 300 °C on the bimetallic MoW samples as observed on the monometallic $\text{SiW}_{12}/\text{Al}$ one, in contrast to what is observed at the Mo edge, with a sulfidation occurring at lower temperature. However, significant changes in the FT start only after 200 °C in $\text{SiW}_{12}/\text{Al}$ whereas transformation of the oxidic phase in the bimetallic HPA based catalyst $\text{SiMo}_3\text{W}_9/\text{Al}$ begins between 100 and 200 °C (Figure S2b). The peak located between 1.9 and 2.3 Å, which is attributed to the W-S coordination in WS_2 , is present at 300 °C in the $\text{SiMo}_3\text{W}_9/\text{Al}$ catalyst and only at 400 °C in the monometallic one.

As observed on the monometallic catalyst, the intensity of the W-S signal increases faster during plateau for $\text{SiW}_{12}/\text{Al}$ (Figure S2b) than for the bimetallic catalyst. In $\text{SiMo}_3\text{W}_9/\text{Al}$, the second coordination shell observed in the monometallic solid at the end of

the plateau is not present. This feature is still ascribed to the presence of Mo and W backscatterers in the Mo(W)S₂ slabs also confirmed at W L_{III} edges by the analysis of RT fully sulfided phases [5].

The comparison of RT EXAFS spectra of the RefMo₃W₉ catalyst prepared from the mixture in solution of SiMo₁₂, and SiW₁₂ in the proportion 1:3 displays quasi superimposable spectrum at the W L edges to the one reported for SiW₁₂/Al and slight differences in position and amplitude with the Mo K edge EXAFS spectrum of SiMo₁₂/Al. The difference is ascribed to a mixture of 85% AlMo₆ HPA and 15% of MoO₄ species. Indeed, we have previously shown that SiMo₁₂ anions were not preserved on alumina and decomposed in AlMo₆O₂₄H₆³⁻ Anderson heteropolyanion species. The proportion of MoO₄ species observed in the case of the RefMo₃W₉ catalyst is due to the different pH value in solution. Due to the full preservation of the monometallic SiW₁₂ HPA upon preparation of RefMo₃W₉ and formation of more than 85% of AlMo₆, which composes SiMo₁₂/Al, we surmise that sulfidation pathways for the RefMo₃W₉ catalyst will share common intermediates species with the monometallic catalysts. As a matter of fact, as it will be described in the next section, quasi equivalent evolutions are observed in temperature upon sulfidation for the monometallic catalysts and for RefMo₃W₉, specially at the W L_{III} edges (Figure S2b).

3.2. Chemometrics analysis

3.2.1. Mo K edge

As molybdenum is almost completely sulfided before the onset of isothermal treatment at 400 °C for all catalysts, data analysis at the Mo K edge was performed on spectra collected during the heating ramp. As already evidenced in other studies on Mo, CoMo and NiMo based catalysts [18,23,29] several intermediate species are involved in the complex activation process starting from the oxidic precursor and resulting in the sulfided solid. PCA applied to the set of Mo K edge time-resolved XAS data revealed that 4 components are necessary to describe the variance contained in the data irrespective of the analyzed catalysts. This result is in agreement with Rochet et al who also observed 4 components when monitoring the sulfidation of a dried Mo based catalyst supported on δ -alumina and prepared from MoO₃ dissolved in H₂O₂ [18]. According to the matrix rank previously determined by PCA, the MCR-ALS minimization of the Mo K edge data of all SiMo(W)/Al catalysts was thus performed with four components, named hereafter MoK-comp.1, MoK-comp.2, MoK-comp.3 and MoK-comp.4, which concentration profiles are presented in Fig. 3. Fig. 4 and 5 display the Mo K

edge XANES and EXAFS spectra and corresponding FT moduli of the four components determined by MCR-ALS.

We verified that the XANES of the 1st component (MoK-comp.1) obtained by MCR-ALS for all catalysts are superimposable to the XANES of the corresponding oxidic catalysts (Fig. 6a). Similarly, for all catalysts, the XANES of extracted MoK-comp.4 is very similar to the XANES of the sulfided catalyst at the end of the ramp and to that of the pure MoS₂ reference (Fig. 6b). As expected from the use of the mixed solution of monometallic HPAs, the RefMo₃W₉ catalyst shares the same MoK-comp.2 and MoK-comp.3 intermediates than SiMo₁₂/Al and consequently the evolution of concentrations of the four species are rather similar for both catalysts. In contrast, due to the vicinity of Mo and W in the SiMo₃W₉ HPA based catalyst, the intermediate MoK-comp.2 and MoK-comp.3 species isolated upon sulfidation of the bimetallic HPA, together with their evolution of concentrations profiles are different to the ones measured for SiMo₁₂/Al.

First simulation of intermediates was carried out without constraints on the coordination numbers in order to orientate second simulations with constrained coordination numbers, which support possible structural models. Those models take into account the pristine structure of the molybdenum or tungsten based compounds supported on alumina identified through comparison with Raman and EXAFS spectra of pure HPA. Results of those simulations are reported in Table 2.

Scheme 1 displays possible models for MoK-comp.2 for which good agreements were achieved for the fitting of the EXAFS spectra presented in Fig. S3. For SiMo₁₂/Al and RefMo₃W₉, MoK-comp.2 is described as an oxysulfide species with two molybdenum centers at a distance of 2.80 Å. This distance is currently found in Mo(V) based oxysulfide compounds [18]. Each Mo center is bound to one terminal oxygen ($d(\text{Mo}-\text{O}_t) = 1.63 \text{ \AA}$) whereas the distribution of disulfidic ligands ($d(\text{Mo}-\text{S}) = 2.45 \text{ \AA}$) is described with one terminal and one bridging $\{\text{S}_2\}^{2-}$ ligands leading to a mean coordination number for the sulfur shell around Mo of 3. A reminiscence of the pristine AlMo₆ structure is found with the presence of the Mo-Al contribution at 3.53 Å (3.46 Å in bulk AlMo₆). Two oxygen bridging ligands complete the coordination of Mo: one associated to the Mo-O-Al contribution of AlMo₆ and one which could be potentially ascribed to the anchorage of the species at the surface of alumina although the fit does not reveal additional Mo-Al contribution. The fitting of the second intermediate species of SiMo₁₂/Al, MoK-comp3, reveals a higher coordination by sulfide ligands (N=4.0) at 2.40 Å which could be described as a fragment of the chain-like MoS₃ species [30].

For $\text{SiMo}_3\text{W}_9/\text{Al}$, MoK-comp.2 is still described as an oxysulfide species with oxygen bridging ligands at 1.97 Å, terminal sulfide (at 2.10 Å) and disulfide (at 2.41 Å) ligands. However, the striking result coming out from the simulation is the strong similarity with the pristine HPA bimetallic structure, since marked contribution of W at 3.32 Å is still present. We surmise that the sulfidation of the bimetallic HPA starts first from the side of Mo leading potentially to fragmentation of Mo trimeric unit without breaking the link between Mo and W. The partial depolymerization of the HPA at the Mo side could decrease the steric hindrance and release constraints in the distance between Mo and W explaining that a slightly shorter distance is found compared to the pristine HPA for this contribution. Si and Al being backscatters with close atomic numbers, they cannot be distinguished by XAS simulation. Herein the Mo-Si(Al) contribution is located at 3.18 Å which is a rather short distance to be ascribed to the Mo-Si distance in the Keggin structure (at 3.58 Å) [5] except if we consider a strong relaxation of distances due to partial depolymerization. Otherwise, this distance could be ascribed to a Mo-Al distance characteristic of an anchorage of the HPA to the alumina surface [29].

The second intermediate extracted for $\text{SiMo}_3\text{W}_9/\text{Al}$, MoK-comp.3, is a fully sulfided species with two contributions at 2.39 Å and 2.51 Å, which is the fingerprint of a MoS_x like species [18]. The attempt to improve the fit by introducing a Mo-O contribution was unsuccessful.

3.2.2. W L_I and L_{III} edges

As mentioned before, W L_I edge XANES displays more resolved features than W L_{III} XANES for discriminating between sulfide and oxide environment around W, the spectra of W-based pure components and corresponding concentration profiles were determined for the catalysts on the basis of the evolution recorded at the W L_I edge. Considering the slower sulfidation kinetics observed for W-based species and that completion proceeds during the plateau, the MCR-ALS analysis at the W- L_I edge was performed considering the experimental data recorded during heating and isothermal treatment under sulfiding atmosphere (Fig. 7). Due to the fact that the three W L edges were recorded simultaneously, the information extracted at the W L_I edge can be transposed at the other W edges. Consequently, the concentration profiles determined at the W L_I edge were then constrained at the W L_{III} edge to isolate the spectra of intermediates and allowed us to analyze their EXAFS contributions. The obtained spectra corresponding to these pure components are presented in Fig. 8 and 9.

Irrespective of the catalysts, three main components were found for explaining the variance of the data during heating ramp and isothermal treatment under sulfiding atmosphere. W L_{I} XANES of the 1st component isolated by MCR-ALS (Fig. 10a blue curve) is superimposable with the spectrum of their respective catalyst before sulfidation. It displays a general shape with a pre-edge structure characteristic of tungsten surrounded by oxygen atoms observed on the catalysts before sulfidation (Fig. 10a red curve). It is noteworthy that the second component displays also a pre-edge structure in the rising edge suggesting the transformation of the pristine supported HPA into another oxidic phase. XANES spectra of the 3rd components (Fig. 10b blue curve) are well in phase with corresponding spectra of the sulfided catalysts after 2 h duration in H_2S/H_2 (Fig. 10b green curve) and in agreement with the XANES spectrum of the bulk WS_2 reference (Fig. 10b red curve). The rising edge of the 2nd component is shifted at high energy compared to the one of the 3rd component characteristic of tetravalent W species and is located nearly at the same position than the pristine hexavalent W compound. This feature strongly indicates that in the 2nd component, W is still at the hexavalent oxidation state. Results of the fit of W L_{III} EXAFS spectra of the 2nd component are gathered in Table 3.

The FT of the W L_{III} EXAFS spectrum of the second intermediate species (Fig. 8b green curve) determined for SiW_{12}/Al displays short and medium range order contributions which can be simulated using W-O, W-W and W-Si contributions. This is a strong indication that this second intermediate is a partially decomposed HPA. No sulfur contribution has been evidenced from the simulation (Table 3).

The FT of the W L_{III} EXAFS spectrum of the second intermediate species (Fig. 8b green curve) determined for $SiMo_3W_9/Al$ displays only two resolved contributions of almost equal intensity centered at 1.4 Å and 1.9 Å. Those contributions are satisfactorily simulated considering only oxygen contributions at 1.83, 2.06 and 2.43 Å (Table 3). The lack of medium range order contribution, in contrast to what can be observed for SiW_{12}/Al , suggests that the process of depolymerization occurring upon sulfidation is more efficient for the bimetallic supported catalysts. At the Mo K edge, it was evidenced for the second intermediate a Mo-W contribution with a distance close to the one encountered in the bulk HPA. Herein the lack of W-Mo contribution at the W L_{III} edge could result from the existence of this intermediate on a more extended temperature range (from 30 to 400 °C) than the second intermediate at the Mo K edge: the expected high Debye Waller factor resulting from the temperature increase could lead to a vanishing of this contribution at the W L_{III} edge.

3.3. Genesis of the sulfided phase followed by HRTEM

The genesis of the active phase has been followed by TEM and HAADF. The samples were analyzed after sulfidation at different temperatures, without any plateau, in order to monitor the active phase formation during the heating ramp. Indeed, TEM will only provide an overall view of the morphology of the sulfide phase, as Mo and W cannot be discriminated by this technique. Moreover, only sulfide slabs parallel to the electron beam can be visualized. Typical TEM images of the $\text{SiMo}_3\text{W}_9/\text{Al}$ sample sulfided at 150, 250, 300 and 350 °C are presented in Figure S4. After sulfidation at 150 and 250 °C, only some black spots are visible on the micrographs, in agreement with the low sulfidation degree (M atoms in the MS_2 phase) of both metals at these temperatures as determined by XAS (Figure S4a and b). At 300 °C, the typical layered structures of sulfide slabs appear, with an average length of 2.7 nm and an average stacking of 1.2 (Figure S4c). When increasing the sulfidation temperature to 350 °C, the number of slabs increases, from 288 slabs on 20 images at 300 °C to 493 at 350 °C (Figure S4d). The average stacking is not modified, while the average length reaches 3.1 nm, with a decrease of the number of slabs with a length below 2 nm.

HAADF provided more detailed information allowing the visualization of the supported phase with atomic resolution, even if not in sulfide phase and even if the sulfide slabs are perpendicular to the electron beam, in contrast to classical TEM. Moreover, since annular dark field images are formed by collecting electrons scattered at high angles, intensities of the atomic columns in the HAADF images increase with the atomic number Z of the atom as approximately $Z^{1.7}$, thus allowing the discrimination between Mo and W atoms due to the Z difference. After sulfidation at 150 and 250 °C, small aggregates of atoms below 2 nm are observed, with no visible organization (Fig. 11a and b). At 350 °C, sulfided slabs with their characteristic atomic arrangement are visible. Moreover, mixed structures with Mo and W can be identified, W appearing brighter than Mo due to the Z difference, showing that mixed Mo-W slabs are formed at this temperature (Fig. 11c). This finding is fully in agreement with the previous EXAFS analysis performed on the RT fully sulfided phases at the Mo and W L_{III} edges, which evidenced in the second coordination shell of the MS_2 phase the presence of Mo and W atoms.

4. Discussion

We studied the genesis of the active phase during *in situ* sulfidation by H₂S/H₂ of the catalysts prepared from heteropolyanions by Quick-XAS combined to multivariate analysis and by electron microscopy.

EXAFS results, together with published Raman characterization [5], evidenced that the SiMo₁₂ HPA deposited on alumina support is decomposed into AlMo₆ species after drying due to the “buffer effect” of alumina and Al³⁺ extraction from the support as already reported in the literature [31, 32]. Indeed, during impregnation the important parameter is the pH of the solution in alumina pores, which evolves towards the point of zero charge (PZC) of alumina (around 7). In contrast to the SiMo₁₂/Al catalyst, the SiW₁₂ HPA structure is preserved on alumina at the dried state, in agreement with the more stable structure of H₄SiW₁₂O₄₀ compared to that of H₄SiMo₁₂O₄₀ upon pH increases [33, 34]. The EXAFS characterization of the SiMo₃W₉/Al catalyst after drying performed simultaneously at the Mo K and W L_{III} edges indicated mixed heteropolyanion preservation at the alumina surface. For the RefMo₃W₉ catalyst, prepared from the mixture in solution of SiMo₁₂ and SiW₁₂ HPAs in the proportion 1:3, we have observed that the RT EXAFS spectra at the W L edges are quasi identical to the one reported for SiW₁₂/Al and that the RT EXAFS spectrum at the Mo K edge presents slight differences in position and amplitude with the EXAFS spectrum of SiMo₁₂/Al corresponding to transformation of ~15 % of the pristine AlMo₆ HPA into MoO₄ species.

Our study shows that the sulfidation of the MoW alumina supported dried catalysts involves a four-step pathway for Mo and a three-step pathway for W irrespective of the catalysts. The use of the MCR-ALS method applied to the study of Quick-XAS spectra allowed us to isolate the intermediates formed during sulfidation. The sulfidation pathway for the RefMo₃W₉ catalyst presents common intermediates species with the monometallic catalysts. Quasi-equivalent evolutions are observed in temperature upon sulfidation for the monometallic catalysts and for RefMo₃W₉. At the opposite a different behavior is observed for SiMo₃W₉/Al.

Indeed, on the bimetallic SiMo₃W₉/Al mixed HPA based catalyst MoK-comp.2 appears at the same low temperature as on SiMo₁₂/Al (around 30°C). However, third and fourth components begin to be formed at higher temperature, around 200 °C and 250 °C respectively instead of 110 °C and 235 °C for the SiMo₁₂/Al catalyst. It should be noticed that the final sulfide phase is present in parallel with the first three components (in the range of 250 – 300 °C), while MoS₂ in the monometallic sample appeared when the first oxide (MoK-comp.1) and the second component (MoK-comp.2) have completely disappeared (Fig. 3). The evolution of concentration profiles obtained for RefMo₃W₉ (Fig. 7) is quasi equivalent to the

ones observed for SiMo₁₂/Al with a slight delay in the appearance of MoK-comp.3 (+ 29 °C) and MoK-comp.4 (+37 °C).

For all catalysts, WL_{III}-comp.1 progressively decreases in a similar way, and has completely disappeared at 400 °C. WL_{III}-comp.2 evolves quasi similarly in SiW₁₂/Al and RefMo₃W₉, with a maximum at ~ 350-357 °C (Fig. 7). On SiMo₃W₉/Al, this intermediate compound displays a maximum in concentration at a lower temperature than SiW₁₂/Al and RefMo₃W₉ (~ 280 °C). For all catalysts, tungsten requires the 2 h sulfidation plateau to be fully sulfided. However, at 400 °C, the tungsten sulfide contribution reaches 90% and 78% for SiMo₃W₉/Al and RefMo₃W₉, respectively, and 65% for the monometallic SiW₁₂/Al catalyst. The low sulfidation state of tungsten in tungsten containing catalysts is in agreement with the literature [35-37]. By XPS analysis, a sulfidation degree for W of 50% has been reported after sulfidation at 400 °C and atmospheric pressure for 4 h on WO₃/Al₂O₃ [35]. Mangnus *et al.* also showed that WO₃/Al₂O₃ catalysts were only partially sulfided at commonly applied sulfiding temperature, the degree of sulfidation increasing from 24 to 95% upon an increase of temperature from 300 to 600 °C [36, 37]. At 400 °C the degree of sulfidation is equal to 67%. As can be seen from the concentration profiles, the formation of final tungsten sulfide in the monometallic SiW₁₂/Al catalyst begins at 330 °C. The substitution of three W atoms into the structure of the SiW₁₂ HPA by three Mo atoms led to a significant decrease of the onset of WS₂ formation from 330 °C to 160 °C, while the onset of WS₂ formation in the catalyst prepared from the mixture of the monometallic HPAs appears at an intermediate temperature compared to SiW₁₂/Al and SiMo₃W₉/Al with a startup temperature ~ 215 °C. It is interesting to note that in the SiMo₃W₉/Al sample the final WS₂ contribution appearing at 160 °C intensively increases only at 230-250 °C, temperature at which MoS₂ also appears, with further similar evolution of the sulfidation for both metals (Figure S5). It is not the case for the other two samples: indeed, at 300 °C, around 50-60 % of Mo is transformed into MoS₂ while 45-50 % of W is in WS₂ in the SiMo₃W₉/Al catalyst, whereas at the same temperature, WS₂ is not present on SiW₁₂/Al and only at 10% in Ref Mo₃W₉ at this temperature. All these results are strong evidences that the presence of Mo leads to a synergetic effect on W, which is more efficient when a close vicinity between W and Mo exists. The EXAFS fitting result at the Mo K edge reported for MoK-comp.2 of SiMo₃W₉/Al has evidenced the presence of a mixed Mo-W phase with the presence of a Mo-W contribution [5]. Simultaneous sulfidation of Mo and W in SiMo₃W₉/Al seems to be related to the formation of this mixed MoWS₂ phase.

These results are comforted by HAADF, where the morphology of the supported phase was monitored during sulfidation. After sulfidation at 150 and 250 °C, clusters of atoms below 2 nm are observed, with no visible organization, while mixed sulfide slabs with Mo and W were identified after sulfidation at 350 °C, with Mo atoms surrounded by tungsten ones. These results can be correlated with a previous work, where we have observed by HAADF analysis of the $\text{SiMo}_3\text{W}_9/\text{Al}$ sample after sulfidation at 400 °C the formation of a mixed sulfided phase with a core of Mo atoms surrounded by W shell [38]. In contrast HAADF images of the RefMo_3W_9 catalyst prepared from two separate HPAs showed a large majority of monometallic MoS_2 and WS_2 slabs with only few bimetallic particles, in agreement with our EXAFS results [5]. The study of catalytic activities has shown that the $\text{SiMo}_3\text{W}_9/\text{Al}$ sample with a mixed MoWS_2 phase displays enhanced activity in HDS of DBT as well as in naphthalene hydrogenation, compared to the RefMo_3W_9 catalyst [5, 39]. The comparison of activation procedures (gas phase versus liquid phase) confirmed that sulfidation in gas phase led to more efficient catalysts, even in the case of the formation of mixed slabs [38]. The beneficial effect of the mixed MoWS_2 phase was even more pronounced in the case of HDS of a more refractory molecule, 4,6-dimethyldibenzothiophene, which was attributed to the improved hydrogenating properties of mixed sulfides.

5. Conclusion

The MCR-ALS applied to time-resolved Quick-XAS spectra allowed to study the speciation of Mo–W based catalysts supported on alumina. It has been shown that the introduction of molybdenum in the HPA tungsten structure ($\text{SiMo}_3\text{W}_9/\text{Al}$ compared with W_{12}/Al) favors the sulfidation of tungsten. The onset of formation of the fully tungsten sulfided phase appears at a lower temperature than in the monometallic tungsten catalyst (160°C instead of 330 °C) and at 400 °C the sulfidation of tungsten is higher (90% instead of 65%). A 3-stepped route has been evidenced for the tungsten sulfidation involving the transformation of the oxidic catalyst into an oxysulfide species and finally to a mixed MoWS_2 phase. By opposition, molybdenum in the SiMo_3W_9 HPA based catalyst begins sulfidation at the same temperature as in $\text{SiMo}_{12}/\text{Al}$ and is completely sulfided at ~ 380 °C. The main difference for Mo consists in the formation of the second intermediate at a higher temperature for $\text{SiMo}_3\text{W}_9/\text{Al}$ (200 °C) than for $\text{SiMo}_{12}/\text{Al}$ (110 °C). For molybdenum sulfidation a 4-stepped route has been evidenced with the transformation of molybdenum oxide first into oxysulfide, then into intermediate fully sulfided species and finally to the MoWS_2 phase. All the results are in agreement with the simultaneous sulfidation of both Mo and W metals in the

SiMo₃W₉/Al catalyst, with the formation of mixed Mo-W sulfide slabs, which formation was also evidenced by HAADF. On the contrary, the use of RefMo₃W₉ prepared from a mixture of two monometallic HPAs with the same Mo/W ratio as in the bimetallic SiMo₃W₉/Al sample did not allow to observe similar synergetic effects between W and Mo sulfidation. Although a slight decrease in temperature of formation of MoS₂ is observed for RefMo₃W₉ compared to the parent monometallic catalyst, it appears that the formation of a MoWS₂ is limited for this sample, as evidenced by HAADF. This catalyst looks more like a juxtaposition of monometallic sulfide phases.

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Supporting Information Available:

- S1. Quick-XANES evolution of the Mo(W)/Al catalysts during *in situ* sulfidation (a) at the Mo K edge, (b) at the W L_I edge.
- S2. Evolution of FT moduli of EXAFS spectra during *in situ* sulfidation (a) at the Mo K, (b) at the W L_{III} edges.
- S3. EXAFS oscillations at the Mo K edge (a) and the corresponding Fourier transforms (b) of the 2nd component determined by MCR-ALS (solid lines) and of the best model (dotted lines) obtained by fitting of the k^3 weighted EXAFS in *R*-space.
- S4. Representative HRTEM images of SiMo₃W₉/Al sulfided at 150 (a), 250°C (b), 300°C (c) and 350°C (d) as well as distribution of stacking and length of the slabs for the two last activation temperatures.
- S5. Concentration profile of components determined by MCR-ALS for Mo K and W L_{III} edges for SiMo₃W₉/Al catalyst as a function of the temperature during sulfidation.

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