In situ QEXAFS investigation at Co K-edge of the sulfidation of a CoMo/Al_2O_3 hydrotreating catalyst

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In situ sulfidation of a commercial alumina-supported CoMo hydrotreating catalyst (3 wt% Co, 12.3 wt% Mo) has been studied by QEXAFS at Co K-edge. Sulfidation was performed by heating progressively the oxide precursor from room temperature (RT) up to 673 K in a H_2/10% H_2S flow (ramp 4 K/min). XAFS spectra were recorded each 10 K with an acquisition time of only 30 s. The obtained XANES and EXAFS data were compared with those of a Co/Al_2O_3 (2.36 wt% Co) used as reference sample. It is evidenced that sulfidation of Co atoms in a CoMo/Al_2O_3 catalyst starts at room temperature while the sulfidation of a Co/Al_2O_3 catalyst begins at 473 K.

KEY WORDS: hydrotreatment; sulfide catalysts; QEXAFS; sulfidation

In the field of catalysis, sulfided catalysts represent an important class of solids used in refineries for the hydrotreatment of crude oils. Even if sulfides have been utilized since almost 50 years, intense researches are still performed in order to develop more active systems and to improve the understanding of these catalysts. All hydrotreating catalysts contain Mo or W and Ni or Co ions as active components and the most important ones belong to the NiMo, CoMo and NiW families. They are usually prepared by impregnation of a γ-alumina carrier by aqueous solutions of ammonium heptamolybdate or tungstate and Ni or Co nitrates with a subsequent calcination treatment [1]. If these systems are commercially available in the oxidic form, they should be sulfided before reaching their active states and this sulfidation step is particularly important since it determines the catalytic performances of the overall system. Industrially this activation step is conducted *in situ* under hydrogen pressure by the feed itself or with a light gas oil spiked with a sulfur-containing molecule which liberates H_2S at moderates temperatures. Recently, a process has been developed for providing directly to the refiners a fully sulfided catalyst activated with H_2S [2]. Such a process requires a deeper knowledge on the kinetic of the activation of the catalyst. Intensive works were devoted to the physico-chemical characterization of either the initial oxide precursor or the final sulfided phase. From these data, it is now well admitted that the operating active phase consists of small Mo(W)S_2 particles deposited on the support where the Co or Ni atoms are mostly located at the edges of the layered MoS_2 crystallites in the so-called "CoMoS" phase. This particular location of the Co ions explained that most of the studies on the transformation of the oxide form into the sulfided one were devoted to the evaluation of overall sulfur content or to the characterization of Mo element modification. It was only evidenced using Mössbauer spectroscopy [3,4] and EXAFS [5–7]. Kinetics of formation of this active phase was roughly estimated by using stepwise characterizations, similarly to the observations previously made on Mo supported alumina [8], the CoMo catalyst rapidly started to be sulfided at room temperature [9,10]. From the literature, it appeared that for Mo atoms sulfidation starts at RT leading to intermediate species formed by a rapid O–S exchange type mechanism [11]. These transitional O- and S-containing species are then gradually transformed into a completely sulfided state upon the temperature rising [12]. MoS_3 has also been proposed as an intermediate state [13]. The fast sulfidation process has been also demonstrated by the use of QEXAFS at Mo K-edge [13–15] or Ni K-edge on NiMo model catalyst [13]. Concerning the Co state, stepwise XPS experiments obtained on model catalysts CoMo/Al_2O_3/Si(100) by de Jong et al. [16,17] demonstrated that sulfidation starting at 400 K; in our case we observed at room temperature a shift toward lower energies indicating that cobalt already started to react and complete sulfidation seemed to be achieved at 573 K. In order to get kinetic information we applied a quick EXAFS technique. This technique is particularly suitable since it provides a specific probe for the study of Co (even

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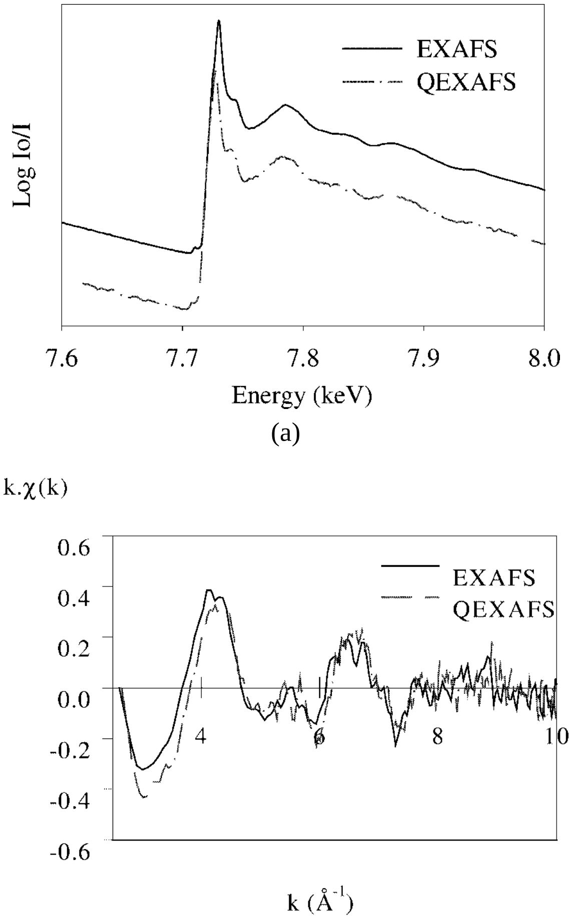
for a commercial catalyst), which is not the case for many other techniques.

The new X-ray synchrotron sources, characterized by the high brilliance of the beam, have opened the door for new types of experiment, especially time-resolved *in situ* studies [18,19]. At the ESRF (European Synchrotron Radiation Facility, Grenoble, France), the IF-CRG beam-line allows time-resolved studies to be performed [20]. In this work, we report the QEXAFS study of the sulfidation of a commercial catalyst under *in situ* conditions analogous to those performed at the laboratory scale. The XAFS measurements have been performed in the transmission mode using the spectrometer installed by the French Collaborative Research Group on the BM32 beam line at the ESRF. The storage ring operated at 6 GeV in the multi-bunch mode (2/3 filling) with a 200 mA current. The activation process is performed similarly to the laboratory scale under H_2/10% H_2S flow from RT up to 673 K (rising temperature 4 K/min, gas flow 50 ml/min). This sulfidation procedure was performed in a dedicated *in situ* furnace. The XAFS cell was adapted from the cell designed by Jentoft et al. [21]. In order to avoid any H_2S consumption due to the reactivity of this gas with the walls of the reactor [22], the heated inner part was protected by a quartz tube of which the diameter has been adjusted to minimize the resulting dead volume. Teflon rings isolated the quartz tube and avoided gas leaks between quartz and stainless steel tubing. Two flow-meters allowed H_2/H_2S or He to be introduced in the cell. A calcined Co/Al_2O_3 sample (2.36 wt% of Co) was also studied for comparison. Samples were pressed as pellets (diameter of 1.8 cm, 2000 $\mathrm{kg\,cm^{-2}}$, thickness below 1 mm, 237 mg for Co/Al_2O_3 and 160 mg for CoMo/Al_2O_3, in order to get an edge jump close to 1.5) and mounted in the sulfidation cell. Quick XAFS measurements were required to obtain kinetic data and to reproduce the sulfidation conditions. Figure 1(a) compares the absorption data in transmission mode for XAFS (45 min) and QEXAFS (30 s). Even if the signal-to-noise ratio is decreased in fast acquisition mode, reliable XAFS information is still obtained (see figure 1(b)). During the sulfidation temperature ramp, we collected one spectrum during 30 s each 10 K. The scan duration is reduced by moving the monochromator at a constant angular speed and recording the data "on the fly". The originality of the set-up is that the start of the record of a spectrum is triggered by an external signal (temperature, voltage, current, etc.) at a value pre-set in a trigger file. In this mode, the external signal can change while recording spectra, and one has to optimize the counting time with respect to the external value and the scan rates. The typical recording conditions in QEXAFS mode are the following ones: energy range 800 eV, energy step 0.5, spectrum recorded in 1–20 s and counting time equals to 0.032 s per point. In our case, we estimated that the best compromise between temperature ramp and quality of QEXAFS data is obtained with a 30 s acquisition, in that case the temperature change of the sample is only 2 K. Under these activation conditions, the sample is under a non-equilibrium state and the data obtained gave an average image of Co environment. However, probably due to the thickness of the pellet and the geometry reactor, we did not notice such sample heterogeneity as observed in the case of Cattaneo et al. [13] who also used apparently longer acquisition time and faster temperature ramp. Experiments have been also performed at increasing or decreasing temperature under inert atmosphere of He in order to get the contribution of thermal effects (such as D–W factors). Figure 2 displays the raw QEXAFS analysis of the *in situ* sulfidation of a Co on alumina catalyst. It demonstrates the stability of the line during the acquisitions.



(a)

(b)

Figure 1. Comparison of XAFS and QEXAFS modes recorded at room temperature at Co K-edge of absorption (a) and EXAFS (b) for CoMo/Al_2O_3 catalyst in its initial oxide form.

A first interpretation is provided by the analysis of the intensity of the white line in the XANES spectra. Co in the oxide form either in Co or CoMo on alumina presents a strong white line due to Co(1s) → Co(4p) transition, whereas in the sulfided state the white line disappears. This effect is a measurement of the change in the partial density of the final states located above the Fermi level [23,24]. Figure 2 illustrates the evolution of the white line during the sulfidation reaction of the Co/Al_2O_3 sample. In order to compare the intensities, the edge jump has been normalized to the room temperature one. Due to the absence of strong white line in the sulfided form, it was not possible to approximate the steps by arct-

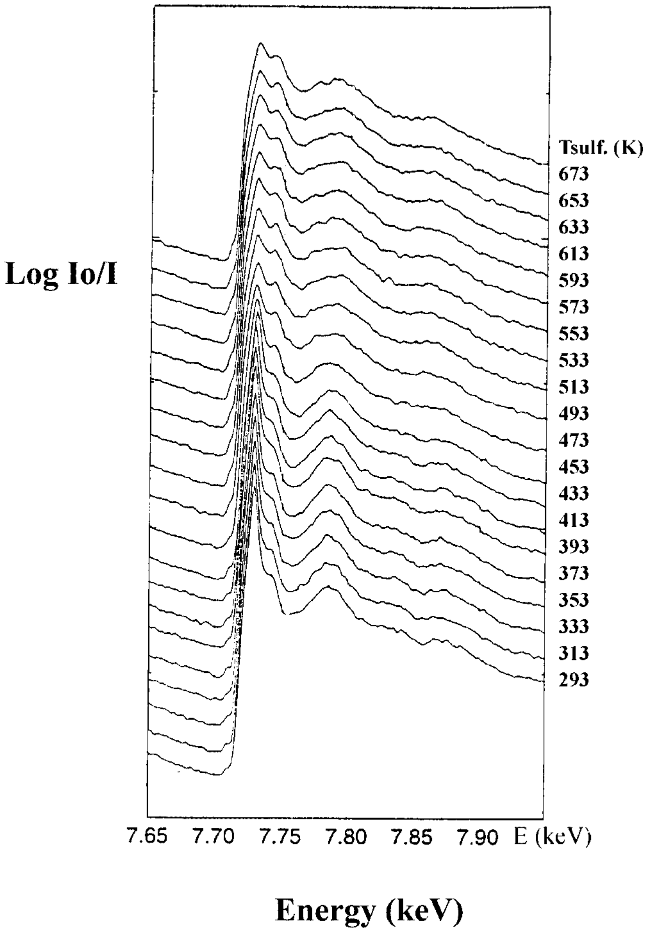


Figure 2. *In situ* QEXAFS at Co K-edge of the sulfidation of a Co on alumina catalyst.

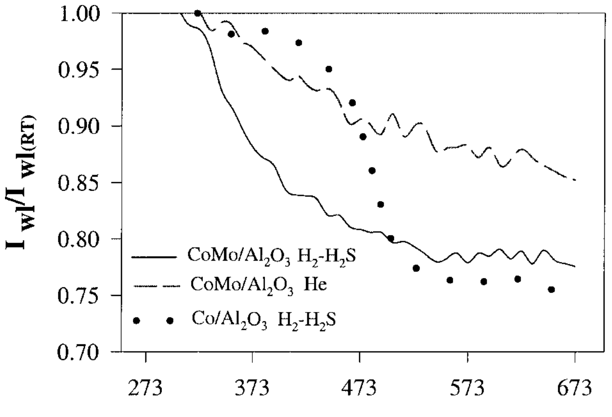


Figure 3. Evolution of white line intensity versus temperature of a $CoMo/Al_2O_3$ catalyst under H_2/H_2S and He. Comparison with Co on alumina sample under H_2/H_2S.

angent and Lorentzian functions, as it was previously done for the L-edge of platinum-based catalysts [25]. White line intensity (difference between the flat absorption before the edge and the maximum of absorption after the edge I_{wl}) was normalized by the white line intensity of the oxide form at room temperature. It has been checked that the results obtained are similar to those obtained after a shape renormalization of the absorption spectra. Comparison of the sulfidation treatment with that performed under He shows that even at room temperature the Co atoms in the CoMo catalyst react with H_2/H_2S (figure 3). Above 523 K, no variation of the white line intensity is observed suggesting that sulfidation of Co is completed. The Co/Al_2O_3 presents a different behavior, white line modification is noticeable and abrupt: modification of Co environment starts at 423 K and finishes at 523 K. Similar results have been obtained with *in situ* NEXAFS studies on Co on alumina samples (10 wt%) [26]. In contrast, XPS results obtained on Co/SiO_2 model catalysts evidenced a fast sulfidation of Co [15]. Measurements performed during cooling of a sulfided CoMo sample under H_2/H_2S from 673 K to RT showed that temperature has no effect on the edge jump of the sulfided CoMo sample. Similar observation can be done after treatment of the EXAFS oscillations. A careful extraction using SEDEM software was applied (with no phase shift correction). Replacement of O atoms by S atoms in the coordination sphere of Co atoms shifted the first peak of the Fourier transform uncorrected from phase shift (figure 4). A program using an automatic extraction of the RDF and the distance of the main peak, including phase shift correction, was also used during the experiments to get an rapid overview of the modification of Co atoms neighboring during the sulfidation process [27]. The figure 5 shows that the first neighbor distance rapidly rises up to the value of Co–S distance in CoMo catalyst, whereas for

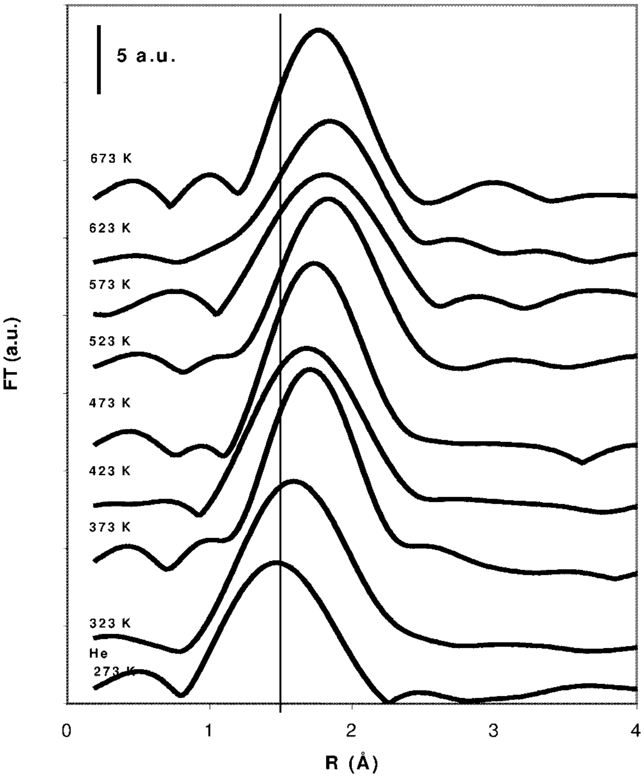


Figure 4. Fourier transforms of the Co K-edge k^3-weighted quick EXAFS functions of an oxide $CoMo/Al_2O_3$ catalyst under He and during sulfidation at rising temperature.

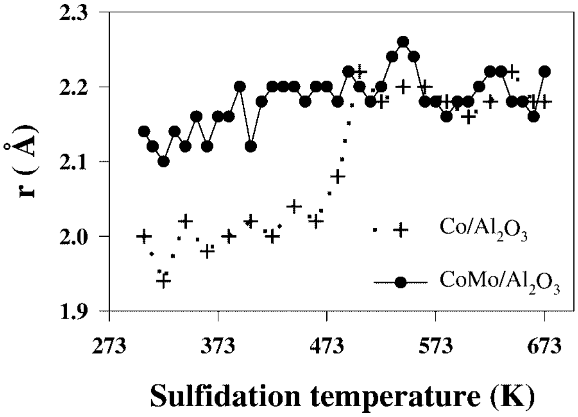


Figure 5. Evolution of the distance of the maximum of the first peak of the FT of EXAFS signal corrected from Co–S phase shift.

Co alone a temperature of 473 K is needed to perform the sulfidation. Both techniques give the same image of a fast sulfidation process for the CoMo catalysts starting at room temperature and a sudden reaction at circa 473 K for the Co on alumina catalysts.

Conclusion

The performance of recent SR sources such as ESRF allows the study of the activation process of catalysts under *in situ* conditions with a fast data acquisition. Time resolved XANES and EXAFS was used to characterize Co environment of a commercial sulfide catalyst during its activation stage and also compared to a Co on alumina catalyst. Simple interpretations of these experiments clearly evidence that the sulfidation mechanisms of Co atoms on alumina or associated with Mo on alumina are very different. Both XANES and EXAFS data show that the sulfidation of Co on CoMo catalysts is a rapid process, whereas for Co alone on alumina sulfidation starts at about 473 K. On-line analysis of XANES and EXAFS can be rapidly performed in order to get the crucial points of a kinetic process which can be further studied by conventional EXAFS.

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