

HR-TEM micrographs were acquired using a 200 kV JEOL-2100F microscope equipped with a digital camera. The samples were embedded within a resin and thin (thickness of 70 nm) sections were cut using an ultramicrotome. These thin sheets were placed in a carbon-coated copper grid and examined under microscope.

The XPS sampling of promoted catalysts after catalytic tests was carried out in an argon-filled glove-box, in order to prevent the aerial oxidation of MoS₂ phase. The samples were grinded and placed onto an indium foil on the sample holder and transferred to the introduction chamber of the spectrometer. The XPS spectra were obtained using a Kratos Axis Supra instrument equipped with an aluminium monochromator source (1486.6 eV) and a hemi-spherical analyzer with a fixed pass energy of 20 eV. The measurement was carried out with a step size of 0.05 eV for Co, 0.1 eV for S and 0.1 eV for Mo and the base pressure of sample analysis chamber was less than 10⁻¹⁴ bar. The binding energy of 284.6 eV for C1s peak was used as an internal standard for calibration (binding energy for Al_{2p} is found to be 74.4 eV). The Shirley type baseline correction was made for the spectra. The recorded spectra were analyzed using a CasaXPS software. The deconvolution of S2p, Co 2p and Mo 3d signals were carried out with respect to the appropriate standard samples (supported oxide and sulfided monometallic catalysts). Standard protocol for quantification of the promoted CoMoS phase was used and briefly discussed here [2,3]. In case of cobalt, three different species were noted: i) Co (II) oxide (Co²⁺) as observed in oxide mono metallic catalyst with a binding energy of 781.5 ± 0.1 eV for Co 2p_{3/2} peak, ii) cobalt sulfide (Co₉S₈), the peak position for Co 2p_{3/2} at 778.1 ± 0.1 eV, and iii) a third contribution of the sulfided catalysts has to be incorporated to suitably fit the spectrum. This is the contribution comes from the “CoMoS” phase and the Co 2p_{3/2} peak position is 778.6 ± 0.1 eV. The Mo 3d spectra of the catalysts were also deconvoluted according to the reported methods [3]. Three different oxidation states of Mo were observed: Mo⁺⁶ (232.2 eV), Mo⁺⁵ (MoO_xS_y, 229.8 eV), and Mo⁺⁴ (MoS₂, 228 eV). These peaks were, respectively, assigned to the oxide, oxysulfide and sulfide phases. Similarly, S 2p peak decomposition shows three components, corresponding to the three different phases: S_{Sulf} (sulfide phase), S_{Ox} (oxysulfide phase) and S_{Sulfates} (completely oxidized phase). Herein, the sulfate phase was formed due to the partial exposure of the sample to air while transferring it to the spectrometer.

$$\text{Degree of sulfidation [\%]} = \frac{\text{Concentration of MoS}_2}{\text{Total Concentration of Mo}} \times 100$$

$$\% \text{at Co in the mixed phase} = \% \text{atCo} \times \% \text{CoMoS}$$

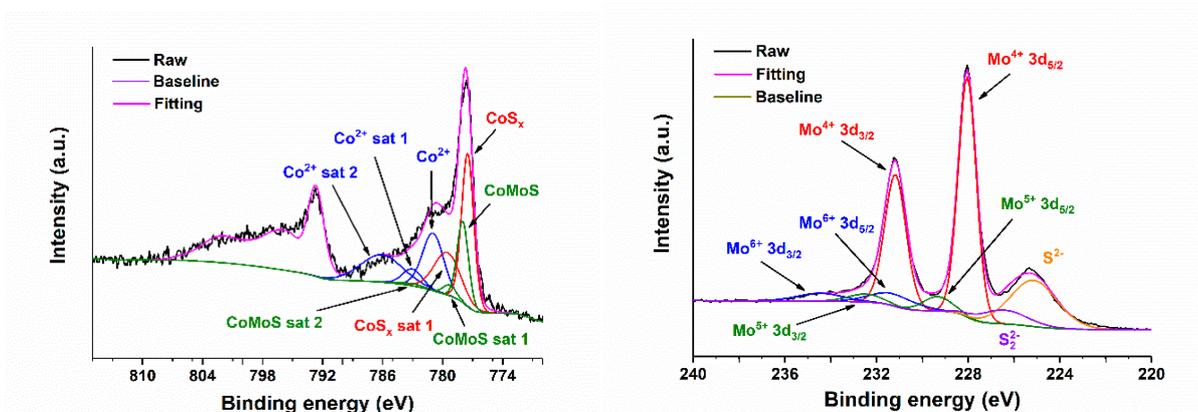


Figure S1. XPS spectral decompositions a) Mo 3d and b) Co 2p (2p_{3/2} region of the spectrum) core level spectrum of spent sulfided CoMo/PANI catalyst chosen as an example.

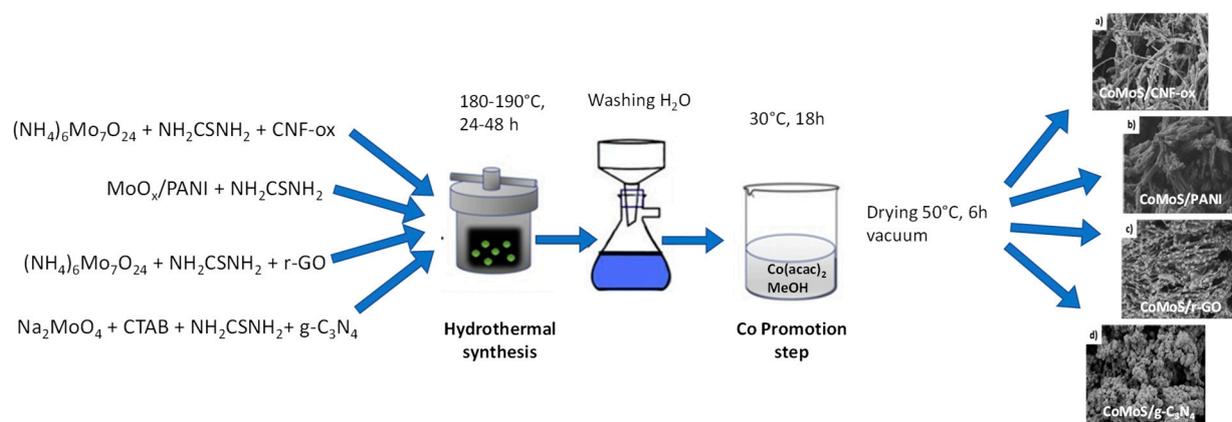


Figure S2. General scheme of the synthesis.

[30] L. Coulier; V.H.J. de Beer; J.A.R. van Veen; J.W. Niemantsverdriet. Correlation between hydrodesulfurization activity and order of Ni and Mo sulfidation in planar silica-supported NiMo catalysts: The influence of chelating agents. *J. Catal.* **2001**, 26-33.

[31] A.D. Gandubert; C. Legens; D. Guillaume; S. Rebours; E. Payen. X-ray photoelectron spectroscopy surface quantification of sulfided CoMoP catalysts relation between activity and promoted sites - Part I: Influence of the Co/Mo ratio. *Oil Gas Sci. Technol.* **2007**, 62, 79-89.