Time resolved In-situ Quick-XAS study of CoMoP additivated catalysts under sulfidation conditions

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The strengthened environmental regulations require the development of more efficient catalysts for hydrotreatment processes. These active catalysts formed during a sulfidation step[1] are generally supported MoS_2 nanoslabs decorated at the edges by Co or Ni, the active phase being named "Co(Ni)MoS". One way to improve the activity of these catalysts is to add dispersing or chelating organic additives which are considered to improve dispersion and delay the sulfidation of the metals to favor their concomitant sulfidation, thereby favoring the formation of the desired mixed phase[2]. The objective of this work is to have a better insight into the role of citric acid and tri-ethylene-glycol (TEG) as additives during the sulfidation step carried out under 15% H_2S/H_2 atmosphere of CoMoP catalysts. For this purpose time resolved in-situ Quick-XAS experiments at both Co and Mo K edge were performed.

The catalysts were prepared by incipient wetness impregnation of an industrial γ-alumina with an aqueous solution of Mo, Co and P precursors to reach 22% wt MoO_3 on the support, with Co/Mo et P/Mo molar ratio respectively 0.4 and 0.55. Citric acid is added in the same initial solution while TEG is post impregnated. Quick-XAS in-situ measurements were performed on ROCK beamline at SOLEIL synchrotron with a dedicated SAXO cell under a 15%H_2S/H_2 gas flow from 25 to 400°C (5°C/min). Thanks to the specificities of the beamline, XAS spectra at both Mo and Co K-edge can be recorded quasi-simultaneously during the activation step[3]. Due the high number of experimental data a methodology combining Principal Component Analysis and Multivariate Curve Resolution with Alternating Least Squares method was used to quantify and extract spectra of intermediate species for the different catalysts[3].

For all the catalyst, we evidenced that the sulfidation of Mo includes two intermediates compounds which are oxisulfide and MoS_3 like species before reaching the final MoS_2 phase at higher sulfidation temperature. The cobalt promoter evolves via a first sulfide component and a final one at higher temperature, which corresponds to a mixture of Co_9S_8 and the mixed CoMoS active phase. The additives modify the nature of the oxide and of the first intermediate species, whereas the final species look similar from a local structure point of view.

We did not evidence any sulfidation delay of Mo and Co when citric acid was added, compared to catalyst without additives. In presence of TEG, the MoS_2 phase was formed at lower temperature, and a complete sulfidation of cobalt was achieved around 200°C instead of ~380°C for the dried catalyst. Finally, one striking point is the formation of the final cobalt species (including the active CoMoS active phase) simultaneously with MoS_3 suggesting that promotion would be achieved before the structuration of the final MoS_2 nanoslab[4].

Combining time resolved in-situ Quick-XAS method and chemometric analysis was found to be a suitable tool to improve our understanding of the activation of hydrotreatment catalysts, which is a key step to rethink new ways to improve their efficiency.

[1] Toulhoat *et al.*, Catalysis by transition metal sulphides, Editions technip, 2013
[2] Pimerzin *et al.*, Applied catalysis B: Environmental 205 (2017) 93-103
[3] V. Briois et al Journal of Physics: Conference Series 712 (2016) 012149
[4] Rochet et al., J. Phys. Chem. C 2017 , 121, 18544-1855t body]