Quality improvement of Carabobo heavy crude oil with Al_2O_3- supported CoW carbide and nitride nanoparticles

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Alumina- supported catalysts based on CoW carbide and nitride nanoparticles were used to improve the quality of *Carabobo* heavy crude oil (in terms of S content, API gravity and asphaltenes stability) trough hydrotreating (HT) reactions. These nanoparticles were prepared by programmed temperature reaction of the supported oxidic precursors of W(Co), varying the (Co/(Co+W)) atomic ratio from 0 to 1, using NH_3 for nitrides or a mixture of CH_4/H_2 for carbides as synthesis gases. XRD results revealed that the oxidic precursors consisted on a $CoWO_4$ monoclinic primitive bimetallic phase, while carbide and nitride were formed as isostructural bimetallic phases of Co_3W_3C and Co_3W_3N, respectively, however, nitride catalysts showed (non-)stoichiometric monometallic species segregation which were identified as hexagonal $W_{4.6}N_4$ and *fcc* CoN, in contrast to carbide- based catalysts where no segregation of this kind was observed. SEM- EDS corroborated the presence of C and N in carbides and nitrides catalysts, respectively. In addition, S was present in presulfided carbide- based catalysts suggesting the formation of mixed structures of cobalt tungsten carbosulfide, which was in accordance to the stacking of planes of the hexagonal WS_2(slabs), identified during HRTEM analysis. However, nitrides did not reveal the presence of S. Presulfided catalysts with the best activities in thiophene hydrodesulfurization (HDS) were selected to be used in the HT of *Carabobo* oil at 320 °C and 70–80 Kg/cm^2. Noteworthy, a synergistic effect was found in all the catalytic systems proposed during thiophene HDS. In addition, API gravity was improved, S content reduced, and changes on asphaltenes chemical properties derived from hydrotreated oil revealed that these catalysts had impact on this fraction of petroleum, corroborating that this catalytic system could be employed as promising alternative HT catalysts for heavy crudes since they can be synthesized using ammonia and methane, which are common products of the petrochemical industry.

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