In this work, density functional theory (DFT), catalytic activity tests, and in-situ X-ray absorption spectroscopy (XAS) was performed to gain detailed insights into the activity and stability of MoS2, Ni-MoS2, and Co-MoS2 catalysts used for hydrodeoxygenation (HDO) of ethylene glycol upon variation of the partial pressures of H2O and H2S. The results show high water tolerance of the catalysts and highlight the importance of promotion and H2S level during HDO.

DFT calculations unraveled that the active edge of MoS2 could be stabilized against S-O exchanges by increasing the partial pressure of H2S or by promotion with either Ni or Co. The Mo, NiMo, and CoMo catalysts of the present study were all active and fairly selective for ethylene glycol HDO at 400 °C, 27 bar H2, and 550-2200 ppm H2S, and conversions of ≈ 50-100 %. The unpromoted Mo/MgAl2O4 catalyst had a lower stability and activity per gram catalyst than the promoted analogues. The NiMo and CoMo catalysts produced ethane, ethylene, and C1 cracking products with a C2/C1 ratio of 1.5-2.0 at 550 ppm H2S. This ratio of HDO to cracking could be increased to ≈ 2 at 2200 ppm H2S which also stabilized the activity. Removing H2S from the feed caused severe catalyst deactivation. Both DFT and catalytic activity tests indicated that increasing the H2S concentration increased the concentration of SH groups on the catalyst, which correspondingly activated and stabilized the catalytic HDO performance. In-situ XAS further supported that the catalysts were tolerant towards water when exposed to increasing water concentration with H2O/H2S ratios up to 300 at 400-450 °C.

Raman spectroscopy and XAS showed that MoS2 was present in the prepared catalysts as small and highly dispersed particles, probably owing to a strong interaction with the support. Linear combination fitting (LCF) analysis of the X-ray absorption near edge structure (XANES) spectra obtained during in-situ sulfidation showed that Ni was sulfided faster than Mo and CoMo, and that Mo was sulfided faster when promoted with Ni. Extended X-ray absorption fine structure (EXAFS) results showed the presence of MoS2 in all sulfided catalysts. Sulfided CoMo was present as a mixture of CoMoS and Co9S8, whereas sulfided NiMo was present as NiMoS.
Original language: English
Keywords: Hydrodeoxygenation, DFT, molybdenum sulfide, XAS, bio-oil
Electronic versions:

MARAC_1_s2.0_S0926860X17305628_main.pdf. Embargo ended: 11/12/2018

DOI: 10.1016/j.apcata.2017.12.008
Source: RIS
Source-ID: urn:7AAE8644A3CF39FA9A780101D7952F9F
Research output: Research - peer-review; Journal article – Annual report year: 2018