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Hydrodeoxygenation (HDO) is proposed as an efficient way to remove oxygen in bio-oil, improving its quality as a more sustainable alternative to conventional fuels in terms of CO\textsubscript{2} neutrality and relative short production cycle [1]. Ni and Ni-MoS\textsubscript{2} nanoparticles supported on ZrO\textsubscript{2} show potential as high-pressure (100 bar) catalysts for purification of bio-oil by HDO. However, the catalysts deactivate in presence of sulfur, chlorine and potassium species, which are all naturally occurring in real bio-oil. The deactivation mechanisms of the Ni/ZrO\textsubscript{2} have been investigated through scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and X-ray diffraction (XRD). Catalytic testing has been performed using guaiacol in 1-octanol acting as a model compound for bio-oil.

Addition of sulphur (0.3 vol% octanethiol) in the feed resulted in permanent deactivation of the catalyst by formation of a catalytically inactive Ni-S phase, as suggested by the very similar spatial distribution of nickel and sulphur signals in STEM-EDX elemental maps (Figure 1) and confirmed by XRD and X-ray absorption spectroscopy (XAS) techniques. Deactivation by chlorine (0.3 vol% chlorooctane) co-feeding was found to be reversible, as the catalyst could regain close to its initial deoxygenation activity upon restoration of a clean feed. SEM-EDX investigations excluded the presence of chlorine species; however, XRD analysis revealed sintering of nickel nanoparticles (Figure 2). Impregnating KCl and KNO\textsubscript{3} on two different batches of catalysts decreased permanently their deoxygenation activity, suggesting the adsorption of potassium at low coordinated nickel sites [2]. The high mobility of potassium under the electron beam [3] prevented the spatial distribution study of this element through STEM-EDX. Moreover, nickel sintering was observed in the KCl poisoned sample and was ascribed once again to the formation of mobile Ni-Cl species upon reaction of HCl with surface oxides [4].

Furthermore, environmental transmission electron microscopy (ETEM) has been used in order to investigate the oxidation of Ni-MoS\textsubscript{2}/ZrO\textsubscript{2} catalyst active phase as a function of different HDO reaction conditions and using methanol as a model molecule for bio-oil.

References


**Figure 1** (a) STEM-HAADF micrograph of a portion of a sulfur poisoned Ni/ZrO$_2$ catalyst with (b) nickel, (c) zirconium and (d) sulfur EDX elemental distributions.

**Figure 2** (Left) SEM-EDX spectrum of the chlorine poisoned catalyst and (right) X-ray diffraction pattern of the same catalyst.