Electron microscopy study of the deactivation of nickel based catalysts for bio oil hydrodeoxygenation - DTU Orbit (08/01/2019)

Electron microscopy study of the deactivation of nickel based catalysts for bio oil hydrodeoxygenation

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 CO2 neutrality and relative short production cycle [1]. Ni and Ni-MoS2 nanoparticles supported on ZrO2 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/ZrO2 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 KNO3 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-MoS2/ZrO2 catalyst active phase as a function of different HDO reaction conditions and using methanol as a model molecule for bio-oil.
BFI (2013): BFI-level 1
Scopus rating (2013): CiteScore 1.55 SJR 0.286 SNIP 0.279
Web of Science (2013): Impact factor 2.161
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 0.52 SJR 0.327 SNIP 0.408
Web of Science (2012): Impact factor 2.495
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
BFI (2011): BFI-level 1
Scopus rating (2011): CiteScore 0.32 SJR 0.286 SNIP 0.168
Web of Science (2011): Impact factor 3.007
ISI indexed (2011): ISI indexed yes
BFI (2010): BFI-level 1
Scopus rating (2010): SJR 0.27 SNIP 0.148
Web of Science (2010): Impact factor 3.259
Web of Science (2010): Indexed yes
BFI (2009): BFI-level 1
Scopus rating (2009): SJR 0.264 SNIP 0.292
Web of Science (2009): Indexed yes
BFI (2008): BFI-level 1
Scopus rating (2008): SJR 0.225 SNIP 0.326
Web of Science (2008): Indexed yes
Scopus rating (2007): SJR 0.236 SNIP 0.117
Web of Science (2007): Indexed yes
Scopus rating (2006): SJR 0.214 SNIP 0.233
Scopus rating (2005): SJR 0.173 SNIP 0.098
Scopus rating (2004): SJR 0.177 SNIP 0.23
Scopus rating (2003): SJR 0.208 SNIP 0.404
Scopus rating (2002): SJR 0.259 SNIP 0.888
Scopus rating (2001): SJR 0.489 SNIP 0.838
Scopus rating (2000): SJR 0.623 SNIP 0.333
Scopus rating (1999): SJR 0.725 SNIP 0.741
Original language: English
Keywords: STEM-EDX, Catalysis, Bio-oil
Electronic versions:
  S1431927614004012a.pdf
DOIs:
  10.1017/S1431927614004012
Source: PublicationPreSubmission
Source-ID: 97570739
Research output: Research - peer-review » Conference abstract in journal – Annual report year: 2014