Detection of minute phase changes occurring over MoS_2 catalysts under H_2O and H_2S by employing modulated excitation X-ray absorption spectroscopy

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Introduction

Catalytic hydrodeoxygenation (HDO) of biomass oxygenates is a key step in removing oxygen from bio-oil where hydrogen is used to exclude oxygen from the bio-oil [1]. Ni and Co promoted MoS_2 is catalytically active for these HDO reactions. Water formed as a by-product during HDO has been reported to deactivate non-promoted MoS_2 based catalysts probably due to oxidation of the sulfided edges of the active phase [2]. In this work, MoS_2, Ni-MoS_2, and Co-MoS_2 supported on $MgAl_2O_4$ and sulfided in 10% H_2S/H_2 have been studied using *in-situ* X-ray absorption spectroscopy (XAS) at the Mo K- and Ni K-edges. *In-situ* XAS has been coupled with modulation excitation spectroscopy (MES) to detect and study the exchange of S with O atoms at the surface sites with high sensitivity.

Methods

The catalysts were prepared by the incipient wetness impregnation on a water tolerant and attrition resistant $MgAl_2O_4$ spinel support [3]. Sulfidation was performed *in-situ* at 400 °C. Quick XAFS spectra at 10 Hz were recorded in transmission mode at the SuperXAS beamline at the Swiss Light Source (SLS, Villigen, CH). Spectra were collected separately at the Mo K-edge (20,000 eV) for all catalysts and also at the Ni K-edge (8,333 eV) for Ni-MoS_2 under the same experimental conditions. By means of a fixed bed quartz capillary reactor with Oxford heater, *in-situ* studies were conducted on these samples. MES experiments were carried out at 400-450 °C by periodically cycling between 3% H_2O/H_2 and 1000ppm H_2S/H_2.

Results and discussion

The features present in the demodulated Mo K-edge XANES spectra of the non-promoted and Co promoted sample treated at 400 °C matched the difference spectrum of MoS_2 and MoO_3 references. Thus, Mo-O bonds were formed by breaking some Mo-S bonds during H_2O/H_2 exposure, while the reverse process was occurring under the consecutive H_2S/H_2 exposure. For Ni-MoS_2, H_2O induced changes were delayed effectively, indicating that the sample was comparatively less affected under these conditions (stabilization by Ni promotion). For a non-promoted catalyst treated at 450 °C, the first two peaks of the demodulated spectra matched the difference spectrum, MoS_2-(MoO_3+Mo), which indicates that reduction of Mo sulfide to metallic Mo took place simultaneously to oxidation under the influence of H_2O/H_2. This was supported by analysis of the corresponding demodulated EXAFS spectra. For Ni-MoS_2, the Ni K-edge XANES and EXAFS spectra extracted from the MES analysis showed that Ni is highly prone to oxidation under the effect of H_2O/H_2 flow thereby reducing the effect of H_2O at Mo.

Conclusions

XANES and EXAFS data extracted by MES analysis showed that the Mo/Ni atoms at the surface of MoS_2 particles exchange sulfur with oxygen when exposed to H_2O, and that they were completely resulfided when H_2S without H_2O was supplied in the feed. A non-promoted sample also showed simultaneous formation of reduced and oxidized phases of Mo under H_2O/H_2. Thus, MES coupled XAS proved to be a very useful technique in unravelling the very small and dynamic phase changes occurring in these HDO active catalysts.

[1] P.M. Mortensen, J.-D. Grunwaldt, P.A. Jensen, K.G. Knudsen, A.D. Jensen, Appl. Catal. A 407 (2011) 1.

[2] M. Badawi *et al.*, J. Catal 282 (2011) 155.

[3] T. M. H. Dabros, A. Gaur, A. D. G Pintos, P. Sprenger, M. Høj, T. W. Hansen, F. Studt, J. Gabrielsen, J.-D. Grunwaldt,. A. D. Jensen, Appl. Catal. A 551 (2018) 106