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Influence of active phase loading in hydrodeoxygenation (HDO) of ethylene glycol over promoted MoS₂/MgAl₂O₄ catalysts

Trine M. H. Dabros^{1,2}, Hendrik Kramer^{1,3}, Martin Høj¹, Jan-Dierk Grunwaldt⁴, Jostein Gabrielsen², Anker Degn Jensen^{1*}.

1 – Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, 2800, Denmark.

2 – Haldor Topsøe A/S, Kgs. Lyngby, 2800, Denmark.

3 – IWT Foundation Institute of Material Science, University of Bremen, Bremen, 28359, Germany.

4 – Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, 76131, Germany.

* aj@kt.dtu.dk

1. Introduction

Catalytic fast hydrodeoxygenation can be used to convert solid lignocellulosic biomass into liquid fuels by combined fast pyrolysis and catalytic hydrodeoxygenation (HDO) [1]. The advantage of this technique is that the pyrolysis vapors can be deoxygenated and stabilized against polymerization immediately when formed, since fast pyrolysis occurs in the presence of an HDO catalyst and hydrogen. Promoted MoS₂ catalysts are active and selective for HDO [2]. Since the cellulosic part of biomass contributes to polymerization and coking [3], a key focus of the catalyst and process development is to investigate HDO of cellulose and hemicellulose derived compounds. Ethylene glycol (EG) represents these compounds and was used as model compound in this work.

2. Experimental

Catalysts (Ni- and Co-promoted MoS₂/MgAl₂O₄) were prepared at different active phase loading by incipient wetness impregnation followed by *in-situ* sulfidation in a fixed bed reactor setup, which was also used for activity testing. In activity tests, 0.5-4.0 g catalyst was loaded into the reactor, and ethylene glycol was fed at ≈ 0.15 mL/min giving a weight hourly space velocity (WHSV) of 2-19 g_{EG}/(g_{cat}·h). Activity tests were run for up to 172 h at 400 °C, a total pressure of 40 barg, 27 bar H₂, and a co-feed of H₂S typically around 550 ppm. Gaseous products were quantified with GC-TCD, while liquid products and unconverted EG were quantified with GC-MS/FID. Fresh and spent catalysts were analyzed with BET, TEM, ICP-OES, XRD, and Raman spectroscopy.

3. Results and discussion

The conversion of EG over the pure MgAl₂O₄ support (WHSV = 9 h⁻¹) showed that it catalyzed coupling reactions such as alcohol condensation, dehydration, and acetalization. The conversion of EG over low (L, 0.8-0.9 wt% Mo) and moderate (M, 2.8-3.4 wt% Mo) loading catalysts showed that Ni- and Co-MoS₂ catalyzed both HDO (giving ethane and ethylene (C₂)) and cracking (giving CO, CO₂, and CH₄ (C₁)). There was a higher selectivity towards HDO as seen from the C₂/C₁ yield ratio of 1.1-1.5, independent of catalyst loading (see Table 1). The moderate loading catalysts showed superior hydrogenation activity (ethane formed rather than ethylene), whereas the low loading catalysts formed a mixture of ethylene and ethane during activity tests (see Table 1). The EG conversion was > 90 % for all catalysts at an EG WHSV of 2 h⁻¹. Catalyst deactivation was observed for the low loading catalysts (WHSV = 2 h⁻¹), and by increasing the WHSV, deactivation could also be observed for the moderate loading catalysts (see Figure 1). Carbon deposition was the main reason for catalyst deactivation, determined by TEM, elemental analysis and Raman spectroscopy.

4. Conclusions

Ni-MoS₂ and Co-MoS₂ supported on MgAl₂O₄ is active and selective for HDO. The MoS₂ based active phase catalyzes HDO, but also cracking, with a C₂/C₁ yield ratio >1. The active phase loading and WHSV influences the hydrogenation activity and the level of deactivation.

References

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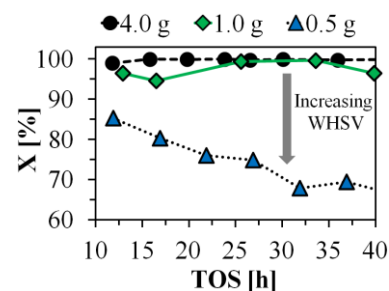


Figure 1. EG conversion (X) versus time on stream (TOS) over moderate loading Ni-MoS₂/MgAl₂O₄ for different EG WHSV (2, 9, and 18 h⁻¹).

Table 1. EG conversion (X) and selected carbon based yields (Y). WHSV = 2 h⁻¹ (for MgAl₂O₄, WHSV = 9 h⁻¹). TOS = 14-20 h. ETA: ethane. ETY: ethylene.

Catalyst	Loading [wt%]	X [%]	Y _{ETA} [%]	Y _{ETY} [%]	Y _{C2} /Y _{C1}
(L) Ni-MoS ₂	Mo:0.83 Ni: 0.17	99	3.4	7.5	1.2
(L) Co-MoS ₂	Mo: 0.88 Co: 0.16	96	2.5	8.2	1.3
(M) Ni-MoS ₂	Mo: 2.83 Ni: 0.58	100	43	0	1.4
(M) Co-MoS ₂	Mo: 3.28 Co: 0.59	100	44	0	1.4
MgAl ₂ O ₄	-	25	0.2	0.9	1.6