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Deactivation of Ni-MoS_2 by bio-oil impurities during hydrodeoxygenation of phenol and octanol

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ABSTRACT

The stability of Ni-MoS_2/ZrO_2 toward water, potassium, and chlorine containing compounds during hydrodeoxygenation (HDO) of a mixture of phenol and 1-octanol was investigated in a high pressure gas and liquid continuous flow fixed bed setup at 280 °C and 100 bar. To maintain the stability of the catalyst, sufficient co-feeding of a sulfur source was necessary to avoid oxidation of the sulfide phase by oxygen replacement of the edge sulfur atoms in the MoS_2 structure. However, the addition of sulfur to the feed gas resulted in the formation of sulfur containing compounds, mainly thiols, in the oil product if the residence time was too low. At a weight hourly space velocity (WHSV) of 4.9 h^{-1} the sulfur content in the liquid product was 980 ppm by weight, but this could be decreased to 5 ppm at a WHSV of 1.4 h^{-1}. A high co-feed of sulfur was needed when water was present in the feed and the H_2O/H_2S molar ratio should be below ca. 10 to maintain a decent stability of the catalyst. Chlorine containing compounds caused a reversible deactivation of the catalyst when co-fed to the reactor, where the catalytic activity could be completely regained when removing it from the feed. Commonly, chlorine, H_2O, and H_2S all inhibited the activity of the catalyst by competing for the active sites, with chlorine being by far the strongest inhibitor and H_2S and H_2O of roughly the same strength. Dissimilar, potassium was a severe poison and irreversibly deactivated the catalyst to <5% degree of deoxygenation when impregnated on the catalyst in a stoichiometric ratio relative to the active metal. This deactivation was a result of adsorption of potassium on the edge vacancy sites of the MoS_2 slabs.

1. Introduction

It has become generally accepted that the oil reserves are depleting due to increased use of fossil fuels throughout the last 100 years [1]. In addition, this has led to a rising concentration of CO_2 in the atmosphere, which is correlated to a greenhouse effect leading to global warming on the Earth [2]. These aspects raise concerns and give incitement for investigation of alternative ways for production of fuels, as well as bulk chemicals. A prospective path to these could be biomass based, as this constitutes a carbon containing resource which can be reproduced within a relatively short time [3,4].

A challenge with biomass is that it has a relatively low energy- and mass-density. This makes transport expensive and constrains its utilization [5]. Hence, it has been suggested to convert biomass into bio-oil by flash pyrolysis and subsequently upgrade this to fuel by hydrodeoxygenation, which is applicable with practically any type of biomass [6]. Hydrodeoxygenation (HDO) constitutes a prospective upgrading route for bio-oil. This is a high pressure catalytic upgrading process where hydrogen is used for exclusion of oxygen [6].

One of the major challenges in the HDO process is to develop an active catalyst which also is sufficiently stable. The latter aspect is challenged by the bio-oil's tendency to form coke and its content of alkali metals, sulfur, chlorine, phosphorus, and other impurities [6–8].

Traditional hydrotreating catalysts, such as Co-MoS_2 and Ni-MoS_2, have been among the most tested catalysts for HDO of bio-oil [6,9–14]. This group of catalysts is already industrially established for hydrodesulfurization (HDS) of crude oil [15–18]. In HDS, the activity of the catalyst has been linked to the availability of edge

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sites on the MoS_2 slabs with two adsorption sites for the sulfur containing compound on vacancy sites and hydrogen on Mo-S [16,19–22]. As the mechanisms for HDS and HDO are similar, this type of sites are believed to be the active sites for HDO as well [23,24]. Promotion with either Co or Ni increases the availability of vacancy sites by lowering the Mo-S bond energy [16,18,20,25,26].

Long term stability of MoS_2 based catalysts during HDO remains to be thoroughly investigated. One of the concerns raised, is the requirement for co-feeding sulfur in order to retain the active sulfide form of the catalyst, but this could potentially contaminate the otherwise sulfur scant bio-oil [6,25,27,28]. Additionally, little is known about the influence of bio-oil impurities on the catalyst stability.

In the present work, the stability of $Ni\text{-}MoS_2/ZrO_2$ is investigated in a series of prolonged continuous flow reactor experiments. The stability was evaluated in the presence of H_2S, H_2O, potassium and organically bound chlorine. For this purpose, a bio-oil model system of phenol in 1-octanol was used. Phenol and phenolic derivatives are a fairly abundant part of bio-oil constituting up to 15 wt% [6], which are quite persistent oxy-compounds to deoxygenate [29]. 1-octanol was chosen partly as a solvent for the phenol, but also to simulate some of the more easily accessible oxygen functionalities which are also found in bio-oil [30], as simple alcohols may constitute up to 4 wt% of the bio-oil [6]. $Ni\text{-}MoS_2/ZrO_2$ was chosen as catalyst, as promotion by nickel previously has been shown to be slightly superior to cobalt promotion for HDO purposes [9,25] and ZrO_2 was previously found as a suitable support for HDO [31–35] and does apparently not suffer from the instability in high concentration of water, as reported for the conventionally used $\gamma\text{-}Al_2O_3$ support for hydrotreating catalysts [9,36,37].

2. Experimental

2.1. Catalyst synthesis

$Ni\text{-}MoO_3/ZrO_2$ (3 wt% Ni, 15 wt% Mo) was prepared by sequential incipient wetness impregnation. The zirconia was supplied by Saint-Gobain NorPro, type SZ6*152 containing 3.3% SiO_2, a specific surface area of 140 m^2/g, and a pore volume of 0.32 ml/g. In the synthesis, the catalyst precursor was dissolved in water equivalent to the pore volume of the support and subsequently mixed with the support. 15 wt% Mo was initially impregnated from a solution of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Sigma-Aldrich, ≥97.0%) in water on ZrO_2 (sieve fraction 300–600 μm) and then dried overnight at 70 °C. $Ni(NO_3){\cdot}\,3H_2O$ (Sigma-Aldrich, ≥96.0%) was dissolved in water and impregnated on the dry Mo-loaded catalyst to a level of 3 wt% Ni and then dried at 70 °C overnight. Finally, the catalyst was calcined by heating to 400 °C at a rate of 10 °C/min in air and held there for 4 h.

The catalysts were sulfided in the continuous flow reactor setup prior to testing by initially heating a portion of the catalyst to 200 °C in N_2 and then heating at a rate of 5 °C/min to 350 °C in a flow of 800 Nml/min H_2 and 0.2 ml/min dimethyl disulfide (DMDS, Sigma-Aldrich, ≥ 99%) at atmospheric pressure. Sulfidation was carried out for 2.5 h at 350 °C. Assuming complete decomposition of DMDS to H_2S the feed concentration of the gas would be: 12% H_2S, 12% CH_4, and 76% H_2.

2.2. Catalyst testing

The experiments were performed in a high pressure gas and liquid continuous flow packed bed setup. The setup was thoroughly described in previously published work from our group [7].

2.5 g of catalyst sieved to 300–600 μm was mixed with 7.5 g glass beads of sieve fraction 210–250 μm to dilute the catalyst bed and thereby obtain better control of the exothermic reactions. The glass bead/catalyst mixture rested on a quartz wool plug in the reactor, which was supported on a crossbar in the reactor.

Evaluation of transport limitations by Mears criterion [38] for the given sieve fraction of catalyst particles revealed that the system was not limited by boundary layer diffusion. On the contrary, internal diffusion limitation was present in some of the experiments. Specifically, conversion of 1-octanol in the most active cases seemed limited. Detailed information of the evaluation of the transport limitations in the different configurations investigated in this study can be found in the electronic supporting information (ESI).

A feed mixture of 50 g/l phenol (Sigma-Aldrich, ≥ 99%) and 2–5 vol% DMDS in 1-octanol (Sigma-Aldrich, ≥ 99%) was used as bio-oil model compound system and generally fed at a flow of 0.2 ml/min. 1-octanol was chosen as co-reactant (despite it is not a usual bio-oil component) due to its relative high boiling point (195 °C at ambient pressure [39]) and ability to mix with phenol in a single homogenous phase. Hydrogen (AGA, 99.9%) and nitrogen (AGA, 99.9%), as internal standard, were fed to the reactor at a flow of respectively 200 Nml/min and 50 Nml/ml, corresponding to 5 times the stoichiometric hydrogen requirement of the feed oil. During the reactions, the reactor was maintained at a constant pressure of 100 bar and the set point temperature of the reactor furnace was 280 °C.

In the experiments with varying weight hourly space velocity (WHSV), the H_2/oil feed ratio was kept constant at 1000 Nml/ml, and N_2 was not co-fed in these experiments. Each feed rate was kept for at least 8 h to ensure representative product samples.

The catalytic activity in an empty reactor was tested in connection with previous work on the same setup as used in this study and was found insignificant [7]. Repeatability was also tested in this study and a relative standard deviation for hydrodeoxygenation activity of 9% was found from a threefold repetition on the setup.

2.3. Product analysis

The liquid product was analyzed using a Shimadzu gas chromatograph GC–MS/FID-QP2010 UltraEi fitted with a Supelco Equity-5 column. Identification was made on mass spectrometer (MS) and quantification was done using a flame ionization detector (FID). External standards were prepared for phenol, cyclohexanol, cyclohexane, methanol, 1-octanol, and octane. The concentration of the remaining peaks were calculated from the FID on the basis of the effective carbon number method [40], where the concentration of a compound was calculated as:

$$C_i = C_{ref} \times \frac{A_i \times \nu_{eff,ref}}{A_{ref} \times \nu_{eff,i}} \tag{1}$$

Here C is the concentration, A the area of the peak in the FID spectrum, and ν_{eff} the effective carbon number. Index i refers to the compound with the unknown concentration and index ref refers to a reference compound where the concentration is known. In all calculations using Eq. (1), octane was used as reference. The effective carbon number was taken from the review by Schofield [40].

The weight hourly space velocity was calculated as:

$$WHSV = v_0 \times \frac{\rho_{feed}}{m_{cat}} \tag{2}$$

Here v_0 is the volumetric feed flow, ρ_{feed} the density of the liquid feed, and m_{cat} the mass of catalyst used.

The conversion (X) was calculated for both phenol and 1-octanol as:

$$X = \left(1 - \frac{C_{out,i} \times v_{out}}{C_{0,i} \times v_0}\right) \times 100\% \tag{3}$$