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Activity and stability of Mo_2C/ZrO_2 as catalyst for hydrodeoxygenation of mixtures of phenol and 1-octanol

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Dedicated to the memory of Haldor Topsøe.

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Mo_2C/ZrO_2 was investigated as catalyst for hydrodeoxygenation (HDO) of phenol in 1-octanol as a simplified bio-oil model system in a fixed-bed setup at 100 bar. Mo_2C/ZrO_2 selectively converted phenol to benzene above 320 °C. During long-term testing, limited stability of the catalyst was observed, with the conversion of 1-octanol and phenol decreasing from 70% to 37% and from 37% to 19%, respectively, over 76 h of operation. Repeating the experiment but also co-feeding 30% water, the catalyst deactivated completely within 12 h of operation. Thermodynamic calculations and in situ XRD analysis showed that Mo_2C is transformed to MoO_2 in the presence of water at the given conditions, and this was probably the source of deactivation in the experiments. Thus, Mo_2C-based catalyst for HDO seems interesting, but requires further stabilization or regeneration of the carbide phase as bio-oil contains high levels of water and water is a by-product during HDO.

1. Introduction

Production of sustainable fuels and chemicals has been identified as one of the biggest challenges of the 21st century [1]. A prospective route to biofuels usable in the current infrastructure is the combination of flash pyrolysis and hydrodeoxygenation (HDO) [2]. A challenge in the field of HDO is to find a suitable catalyst for the reaction [2–4]. Sulfide catalysts such as Ni-MoS_2 and Co-MoS_2 have good HDO activity [2,5,6], but one of the drawbacks is that a sulfur source is required to maintain these in their active form [7,8]. Noble metal catalysts such as Ru and Pd have shown some promise [9,10], but are unfavorable due to their high prices [11]. Reduced metal catalysts such as Ni have been found as attractive alternatives to noble metal catalysts [12–14], but suffer from fast deactivation by many of the impurities found in bio-oil such as sulfur, chlorine, and potassium [15]. A less investigated group of catalysts for HDO is based on transition metal carbides [4,3]. This group of catalysts has received increasing attention in several reactions as their properties have been compared to noble metal catalysts for some reactions [16–18] while being more reactive in reactions involving oxygen and hydrogen [18]. The latter property is of particular interest in HDO. Additionally, Mo_2C has been used as hydrodesulfurization catalyst and is therefore also tolerant to at least sulfur [19–21], which makes it an interesting catalyst for HDO as well. So far, the use of this catalyst for HDO has been demonstrated with propanol [22], fatty acids and vegetable oils [23–26], furfural [27] and phenolic type molecules [28–32].

In this work, the activity for HDO of phenol in 1-octanol over Mo_2C/ZrO_2 has been investigated with special emphasis on stability. This was chosen as a simplified bio-oil system since phenol and its derivatives are generally considered as the more persistent and fairly abundant types of oxy-compounds found in bio-oil [33,34]. Furthermore, they are considered to be potential coke precursors [4], and this was therefore a good candidate as a model compound for stability tests. 1-Octanol was chosen as co-reactant to simulate alcohols in the feed and additionally due to its relative high boiling point and ability to form a single-phase mixture with phenol, but note that C_8 alcohols are not as such part of bio-oil.

2. Experimental

2.1. Catalyst synthesis

15 wt% MoO_3/ZrO_2 was prepared by incipient wetness impregnation with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Sigma–Aldrich, $\geqslant$97.0%) as precursor. The zirconia was supplied by Saint-Gobain NorPro, type SZ6∗152 with an impurity of 3.3% SiO_2, a specific surface area of

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140 m^2/g, and a pore volume of 0.32 ml/g. This was initially grinded to a particle size of 125–180 μm. In the synthesis, the precursor was dissolved in water equivalent to the pore volume of the support and subsequently mixed with the support. After impregnation, the sample was dried at 70 °C for 12 h.

The carbide was produced directly in the setup from the 15 wt% MoO_3/ZrO_2 prior to testing. The sample was heated to 200 °C in N_2 at atmospheric pressure, and hereafter ramped to 550 °C at 0.5 °C/min in 50 Nml/min 20% CH_4 in H_2, and finally held at this temperature for 4 h. A temperature of 550 °C was verified by in situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) to be sufficient for carburization of MoO_3/ZrO_2. This is further described in Section 3.1.

2.2. Catalyst testing

The experiments were performed in a fixed-bed high-pressure continuous-flow reactor setup. The setup has been thoroughly described in a previous publication [15].

2.5 g of the catalyst in a sieve fraction of 125–180 μm was mixed with 7.5 g glass beads in sieve fraction 212–245 μm to dilute the catalyst bed and thereby obtain better control of the reactor temperature for these exothermic reactions. The glass bead/catalyst mixture was suspended on a quartz wool plug in the reactor, which was supported on a crossbar in the reactor.

A feed mixture of 70 g/l phenol (Sigma–Aldrich, ⩾99%) in 1-octanol (Sigma–Aldrich, ⩾99%) was used as bio-oil model compound system and fed at a flow of 0.2 ml/min. Hydrogen (AGA, 99.9%) and nitrogen (AGA, 99.9%) were fed to the reactor at flows of respectively 200 Nml/min and 50 Nml/ml. During the reactions, the reactor was maintained at a constant pressure of 100 bar and the set point of the reactor oven was between 280 and 380 °C.

The temperature dependence was evaluated by combining two experiments of ca. 24 h each, one measuring from 280 to 320 °C and the other from 340 to 380 °C in 20 °C steps. Samples were collected after at least 8 h of operation at each temperature setting to ensure representative samples.

The stability of the catalyst was investigated in a long-term experiment with the feed described above at 300 °C. Furthermore, since real bio-oil usually has a high content of water, the stability test was repeated with a feed with the same proportions of phenol and octanol but with a co-feed of 0.1 ml/min water from a separate liquid feed line, resulting in a liquid feed with about 33 wt% water.

2.3. Product analysis

Analysis of the liquid product was performed using a Shimadzu GC (GC–MS/FID-QP2010 UltraEi) fitted with a Supelco Equity-5 column. Identification was made on the mass spectrometer (MS), and quantification was done using the flame ionization detector (FID) of the analyzer. External standards were prepared for phenol, cyclohexanol, cyclohexane, methanol, 1-octanol, and octane. The concentration of the species corresponding to the remaining peaks was calculated from the FID peak area on the basis of the effective carbon number method [35] as follows:

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

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 with this formula, octane was used as reference. The effective carbon number was taken from the review by Schofield [35].

Gas analysis was performed using a gas chromatograph (GC) fitted with a thermal conductivity detector (TCD, Shimadzu GC-2014), allowing analysis in 20-min intervals. The GC was calibrated for H_2, N_2, CH_4, CO_2, CO, ethane, and ethene.

The conversion, X, was calculated as

$$X = \left(1 - \frac{C_{out,i} \cdot v_{out}}{C_{0,i} \cdot v_0}\right) \cdot 100\% \tag{2}$$

Here C_i is the concentration of compound i and v is the volumetric flow. Index *out* refers to the conditions after the reactor, index 0 refers to the inlet conditions, and i refers to the compound of relevance. The conversions of both phenol and 1-octanol were evaluated.

The yields (Y_i) of relevant products were calculated as

$$Y_i = \frac{C_{out,i} \cdot v_{out}}{C_{0,j} \cdot v_0} \cdot 100\% \tag{3}$$

Index i refers to the compound of relevance, and index j is referring to the initial reactant, phenol, or 1-octanol.

The selectivity (S_i) of a compound (i) was calculated as

$$S_i = \frac{Y_i}{X} \cdot 100\% \tag{4}$$

2.4. Catalyst characterization

The carburization and influence of water in the feed on the catalyst were followed by alternated in situ XAS and XRD. The measurements were carried out at the bending magnetic beamline BM01B (Swiss-Norwegian beamlines) at the ESRF (Grenoble, France). An in situ cell based on a quartz capillary and heated by a gas blower (FMB Oxford) was employed resulting in plug-flow-like conditions [36,37]. The sample, around 5 mg of 15 wt% MoO_3/ZrO_2 (sieved), was loaded in a quartz capillary (0.5 mm diameter, 20 μm wall thickness) between two glass wool plugs. The gases, 50 ml/min, were delivered by mass flow controllers. The outlet gas composition was monitored by MS.

In the carburization step, a mixture of 1 vol% CH_4 and 4 vol% H_2 in He was used. The sample was heated at 5 °C/min from room temperature to 250 °C, then to 550 °C at 2 °C/min, and finally kept at 550 °C for 100 min. The activated sample was then cooled to 300 °C in the carburizing atmosphere.

The stability of the catalyst in a water-containing environment was studied by exposing a fully carburized sample to 5 vol% H_2 diluted in He saturated with H_2O at room temperature, corresponding to a water content of about 2.3 vol%. The sample was kept at 300 °C and under this atmosphere for 2 h.

XRD patterns were acquired using a wavelength of 0.50 Å delivered by a Si(1 1 1) channel-cut monochromator. The diffracted photons were recorded by a two-dimensional CCD detector located at 408.5 mm from the sample. The XRD patterns were integrated from the CCD using the FIT2D software [38]. The XRD patterns used as standards were downloaded from the Inorganic Structure Crystal Database of the Leibniz-Institut für Informationsinfrastruktur [39].

XAS spectra were recorded by continuous scanning at the Mo K-edge in transmission mode, and a Mo foil was used for calibration. The X-ray beam was monochromatized by a Si(1 1 1) double-crystal monochromator and high harmonics rejected by a Au-coated mirror. The beam size on the samples was 3 mm × 0.3 mm (width × height). The analysis of the XAS data was performed using the Athena and Artemis software of the IFFEFIT package [40].

The X-ray absorption near-edge spectra (XANES) were energy calibrated and normalized. Linear combination was used to determine the relative phase composition during the activation and deactivation studies. The fittings were carried out in the range between −20 and 90 eV, relative to the energy of the edge.