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Hydrodeoxygenation of solvolysed lignocellulosic biomass by unsupported MoS_2, MoO_2, Mo_2C and WS_2 catalysts

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ABSTRACT

Hydrotreatment of liquefied lignocellulosic biomass was investigated at 300 °C under the total pressure of 8 MPa in a slurry reactor over unsupported molybdenum (disulphide, dioxide and carbide) and tungsten (disulphide) catalysts. Novel nanostructured urchin-like MoS_2 and inorganic-fullerene MoS_2 interconnected with carbon materials were synthetized and tested, while the influence of metal variation and the sulphide replacement with carbide or oxide was also investigated by using commercially available MoS_2, Mo_2C, MoO_2 and WS_2. Catalysts were structurally characterised by field-emission scanning (SEM) and high-resolution transmission (HRTEM) electron microscopies, energy-dispersive X-ray (EDX) and Raman spectroscopies, as well as X-ray diffraction (XRD). The hydrodeoxygenation (HDO), decarbonylation, decarboxylation and hydrocracking kinetics of depolymerised cellulose, hemicellulose and lignin were determined according to the transformation of their functional groups in liquid phase, and the corresponding gaseous products by an innovative lumped kinetic model based on Fourier transform infrared spectroscopy. Unsupported MoS_2 catalysts showed high hydrogenolysis selectivity, the morphology clearly affecting its rate. A high HDO activity reflected in the mass balance and phase distribution of the upgraded liquid product by reducing tar residue and increasing the yield of oil phase with the gross calorific value of 38 MJ kg^{-1} and oxygen content below 8.5 wt%.

1. Introduction

Utilisation of biomass as a renewable energy source has nowadays gained a great interest in petroleum-importing countries. Biomass is the most attractive sustainable carbon source, and less than 2% of the energy from natural biomass replacement is currently being used [1]. Waste lignocellulosic materials are an especially desirable feedstock, as they are abundant and their origin does not compete with food crops as in the case of the edible oils in biodiesel production or corn for bioethanol. However, solid lignocellulosic biomass is unpractical to transport and store due to its low bulk density, and consequently a low volumetric energy density. To widen its applicability as a fuel, it is particularly desirable to convert it into a liquid product.

Lignocellulosic biomass liquefaction by the solvolysis in cheap renewable solvents such as glycerol, a by-product from biodiesel production, is a promising thermochemical biomass-to-liquid (BtL) conversion route, since it can be performed at significantly lower temperatures in comparison to other thermochemical technologies (e.g. pyrolysis or gasification). Process temperatures, as low as 170 °C, prevent extensive char and gas formation, and consequently lead to a higher liquid product yield and a higher gross calorific value (GCV) of the liquid product in comparison to pyrolysis. Solvolysed lignocellulosic biomass was successfully tested as a fuel in a gas turbine [2], but due to its high viscosity and a high content of chemically bonded oxygen (mass fraction over 40%), it is unsuitable for use as a transportation fuel without preceding upgrade.

Various biomass-derived oils, containing oxygenates such as alcohols, aldehydes, esters and carboxylic acids, can be upgraded to hydrocarbon fuels in the catalytic hydrotreatment process under a high-pressure hydrogen and in the presence of heterogeneous catalysts [3–5]. Beside the hydroprocessing of real bio-oils, chemical mechanisms were intensively studied on model compounds that represent depolymerized cellulose [6,7] and lignin [8,9] components, or simply oxygenates with various types and combinations

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of functional groups [10,11]. Sulphided bifunctional catalysts such as NiMo/γ-Al_2O_3 and CoMo/γ-Al_2O_3 are traditionally used for hydrotreatment, where molybdenum is the active element, and the sulphur vacancies, located at the edges of MoS_2 nanoclusters, are the active sites responsible for hydrodeoxygenation (HDO), while nickel or cobalt serves as a promoter [11,12]. γ-Al_2O_3 support has been widely used because of its high surface area and acidic character, but on the other hand, it is unsuitable for HDO, as it is converted to boehmite (AlO(OH)) in the presence of water at elevated temperatures [5,13–15]. Al_2O_3 support also showed high tendency for coke deposition caused by polymerisation reactions of unstable species on the catalyst surface [16], so the use of neutral (e.g. carbon) supports or the use of unsupported catalysts with either high surface area or sufficient activity seems promising. The use of unsupported MoS_2 is advantageous because of its low price and high selectivity towards HDO [17], while some forms of its diverse morphology might result in a high catalytic activity [18].

The most frequently applied route for the preparation of unsupported MoS_2 catalysts is the decomposition of ammonium thiomolybdates [19–24]. Intensive work was done on the investigations of the preparation conditions contribution to the catalytic activity of the resulting material [19]; by the thermal decomposition of $(NH_4)_2MoS_4$ (ammonium tetrathiomolybdate, ATTM), authors managed to obtain molybdenum sulphides with the specific surface areas of up to $88\,m^2\,g^{-1}$, while the hydrothermal decomposition of ATTM in the presence of an organic solvent was reported to give an amorphous MoS_2 with the surface area up to $368\,m^2\,g^{-1}$ [18,23,24].

In this work, the ammonium thiomolybdates replacement with molybdenum halides or coordination precursors was introduced; specifically, the fine powders of MoI_3 or $CpMoCl_4$ were used for the preparation of molybdenum disulphide with morphology that was not reported up to date. Molybdenum halides are readily transformed into sulphides at the elevated temperature in the reductive atmosphere of $H_2/H_2S/Ar$ gas mixture. In previous work, the urchin-like MoS_2 units formation from MoI_3 precursor was only briefly communicated [25], while this work provides detailed insights into its catalytic activity. In this work, the formation of first MoS_2 inorganic fullerenes, with $\sim$12 nm unit size, interconnected by carbon (MoS_2(IF)/C) is reported from $CpMoCl_4$ precursor. Inorganic fullerenes (IF) are expected to possess a high concentration of surface active sites [26], while the role of carbon is to affix MoS_2(IF) units, preserving the original shape of agglomerates; however, it can also reduce the catalytic activity by blocking the active sites on the IF surface.

The activity and selectivity comparison for various prepared and commercially available unsupported Mo catalysts in oxide, carbide and sulphide form, and commercial WS_2 nanotubes is based on the apparent kinetic rate constants for hydrodeoxygenation, decarboxylation, decarbonylation and hydrocracking of solvolytic oil. Kinetic model was developed and focused on the removal of the main oxygen-containing moieties in liquid phase, and the formation of corresponding gaseous products. The main emphasis of this work is to compare the influence of different morphologies of the unsupported MoS_2 on catalytic performance and to parallel the activity with commercially available NiMo/γ-Al_2O_3 catalysts, reported in previous studies [27]. Molybdenum replacement with tungsten, as well as sulphide substitution with carbide or oxide, was also investigated by commercially available materials.

2. Experimental

2.1. Solvolysis oil

Solvolysed biomass was provided by a company that runs the pilot plant for the liquefaction of the lignocellulosic biomass waste in acidified glycols, strictly following the procedure from the literature [2,28]. The mass fraction of the dry sawdust in the solvolysis oil was 25%, the rest being glycerol and diethylene glycol mixture (1:1 by mass), containing 3 wt% of *p*-toluenesulphonic acid. The liquefied biomass had the gross calorific value (GCV) of $21.9\,MJ\,kg^{-1}$ and the oxygen mass fraction of 43.3%, including the dissolved water (less than $20\,g\,kg^{-1}$). The detailed characterization of the liquefied biomass can be found in our previous study [29], or elsewhere in the literature [2].

2.2. Catalyst preparation and characterisation

MoS_2(IF)/C catalyst was synthesized by the sulphidisation of $CpMoCl_4$ (Sigma–Aldrich, 95 wt%), where Cp represents cyclopentadiene, in the quartz boat inside quartz tube. To prevent the decomposition of material, caused by the contact with moisture or oxygen, it was kept under the argon atmosphere in dry-box, while a glass vessel was used for boat transfer. 850 mg of $CpMoCl_4$ was placed into the boat ($75 \times 16 \times 12$ mm) and carefully transferred to quartz tube (970 mm length; 22 mm diameter). Quartz tube was purged for 30 min with the constant flow of the sulphidising gas mixture ($60\,mL\,min^{-1}$; 2/2/96 vol% of $H_2/H_2S/Ar$; Air Liquide) before a sample was heated to 800 °C with the heat-up rate of $2000\,^{\circ}C\,h^{-1}$. It was then kept at the set temperature for 3 h under the constant flow of sulphidising agent, and subsequently left to cool down to the ambient temperature.

Urchin-like MoS_2 was prepared through the sulphidisation of MoI_3 that was synthesised from $Mo(CO)_6$ (Sigma–Aldrich, 98 wt%) and I_2 (Sigma–Aldrich, 99.99 wt%), following the procedure, reported in our previous work [25]. Bulk MoO_2 (Sigma–Aldrich, 99 wt%), MoS_2 (Sigma–Aldrich, 99 wt%) and WS_2 nanotubes (NanoMaterials, 99 wt%) were used as-received without further purification.

Raman spectra of crystals were measured with Horiba Jobin–Yvon LabRAM HR spectrometer using the 632.81 nm excitation line of the He–Ne laser with the power of 17 mW. To prevent the decomposition of a sample, density filter was applied to reduce the power of the laser to 1.7 mW. An Olympus ×50 long-distance objective was used. Spectra were obtained by accumulating 20 scans with the integration time of 5 s. Spectrometer was calibrated using Si polycrystalline plate as the standard with the characteristic band at $520.6\,cm^{-1}$. Field emission scanning electron microscopy (FE-SEM; Jeol 7600) and high-resolution transmission electron microscopy (HRTEM; Jeol JEM-2100) was used for the characterisation of the morphology and structure of samples, while energy-dispersive X-ray spectroscopy (EDX) analysis was applied to evaluate the carbon distribution over the MoS_2(IF)/C. For elemental analysis, Elementar MICRO cube elemental analyser was used, whereas BET analysis was performed using Micrometrics Gemini IV apparatus with the N_2 gas at −196 °C. X-ray powder diffraction data were collected using XRD equipment (Rigaku, AFC7, Cu Kα1 and Cu Kα2 radiation with 40 kV and 20 mA) over the 2θ range of 10–75°, with the step size of 0.05°, and the counting time of 5 s per step.

2.3. Hydrotreatment reactions

Solvolysed oil hydrotreatment experiments were performed in the cylindrical 300 mL batch stainless steel autoclave (Parker Autoclave Engineers) with the inner diameter of 43 mm and the height of 210 mm (Fig. SD.1). The reactor was equipped with magnetically driven Rushton turbine impeller with the diameter of 30 mm that was located 25 mm above reactor bottom. The reactor was filled with 125 mL of cold reaction mixture containing homogenised solvolytic oil and tetralin (Sigma–Aldrich, $\geq$97 wt%) in a 3:1 mass ratio. The mass fraction of the catalyst in the reaction mixture for