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Research article

Effect of Li-LSX-zeolite on the in-situ catalytic deoxygenation and denitrogenation of *Isochrysis* sp. microalgae pyrolysis vapours

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ABSTRACT

In this work, we report for the first time the use of Li-LSX-zeolite as catalyst for the catalytic pyrolysis of biomass (*Isochrysis* sp. Microalgae). Li-LSX-zeolite showed a good catalytic performance, principally for bio-oil denitrogenation (mainly in form of NH_3), and good activity for olefins and aromatics production. At 500 °C, 11.8% aromatics and 23.1% aliphatics were produced. The increase of temperature led to transfer of C to the gas phase, coke formation on the catalyst surface and decrease in N-compounds in the bio-oil. The increase of the catalyst to biomass ratio from 0 to 3:1 resulted in the aromatics being five-fold those non-catalytically obtained and in a higher cracking power that reduced the bio-oil to 23% at expenses of olefins rich gas. However, a linear correlation between coke formation and aromatic yield was observed as the catalyst to microalgae ratio was increased. Therefore, the experimental results indicate that Li-LSX-zeolite could be used as catalyst for in-situ denitrogenation of microalgae bio-oil and for enhancing aliphatics and aromatics formation to be blend in gasoline and diesel and olefins in gas phase.

1. Introduction

Microalgae have great potential as feedstock for bioenergy production because of their high productivity, fast growth rate, capability to fix CO_2 and for being not in competition with food crops. The raw microalgae can be pyrolysed to get a liquid bio-oil, which still contains a large fraction of the microalgae initial energy [1]. Oxygen and nitrogen compounds represent the main limitation for the bio-oil implementation as biofuel, and methods/catalysts able to reduce O and N content in the bio-oil during or after its production must be developed. Catalytic pyrolysis is a process in which a catalyst is used to promote deoxygenation of the bio-oils through simultaneous dehydration, decarboxylation and decarbonylation reactions [2–5]. Among these catalysts, zeolitic materials such as ZSM-5 zeolite, have been found to be very active to deoxygenate pyrolysis vapours and to produce aromatic hydrocarbons [6–9].

The simultaneous in-situ deoxygenation and denitrogenation of microalgae pyrolysis bio-oils is somehow a new research topic, with few works available in literature, since nitrogen is typically removed via hydro-processing [10,11]. Despite this, bio-oils hydro-processing consumes large amount of H_2 and the development of in-situ oxygen and nitrogen removal techniques (during pyrolysis) would be a more cost-effective alternative. But also, catalytic pyrolysis has attracted interest for the conversion of biomass into light olefins [12,13].

Isochrysis sp. has been identified among the microalgae species that are suitable candidates for multiple-product algae-crop, due to their variety of fatty acids that offer a wide scope for several bio-products in a biorefinery approach [14]. However, only few studies are available on *Isochrysis* catalytic pyrolysis [15–17]. Dong et al. [15] studied the direct production of light olefins (C_2–C_4) of up to 11 wt% from *Isochrysis* catalytic cracking at 550–650 °C in presence of modified ZSM-5, being neutral lipids the principal contributor to olefin production. On the other hand, Wang et al. [17] investigated the direct and indirect (after removal of lipids) pyrolysis of *Isochrysis* at 475 °C. Defatted *Isochrysis* yielded higher total pyrolysis oil (41.3 wt%) than direct microalgae pyrolysis (36.9 wt%). However, there was also an increase for N-heterocyclic compounds and phenols and a decrease for hydrocarbons in defatted microalgae pyrolysis oil [17]. In a previous work, we investigated the effect of Ni-Ce derived catalysts on the *Isochrysis* microalgae pyrolysis, being Ni-Ce/ZrO_2 the most effective in terms of mass and energy bio-oil yield with 25.5 wt% and 77%, respectively.

In this work, a low silica X type (LSX) zeolite (Li-LSX-zeolite) was evaluated for the first time as catalyst for the in-situ catalytic pyrolysis of *Isochrysis* sp. This zeolite is generally used for the air separation process at industrial scale for oxygen production. However, its catalytic activity on the biomass depolymerisation and its deoxygenation and denitrogenation potential has never been studied so far. Recently, bifunctional catalysts with both acid and base sites have been shown to be

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effective in the conversion of biomass to hydrocarbons and on the removal of oxygen. The low Si/Al and the presence of Li suggest that Li-LSX-zeolite could promote oxygen removal and produce olefins and aromatics as other acidic zeolites [7]. Since Li cations preferentially adsorb nitrogen over oxygen [18], its affinity to nitrogen could be beneficial for the denitrogenation of microalgae bio-oils.

High surface microsilica has also shown to be active on catalytic pyrolysis of biomass, where the use of microsilica resulted in increased yield (from 6 to 15 wt%) of dehydration acid-promoted products such as anhydrosugars, compared to standard silica [19].

The aim of this work was therefore to study the activity of Li-LSX-zeolite as potential catalyst for the catalytic pyrolysis of microalgae, evaluating their predisposition to in-situ bio-oil denitrogenation, deoxygenation and to evaluate the potential production of aromatics and olefins under different process conditions. Microsilica was also evaluated for comparison.

2. Experimental

2.1. Raw material

Isochrysis sp. was obtained from Varicon Aqua solutions in liquid form as biomass feedstock. The biochemical compositions (carbohydrates, lipids and proteins) of microalgae provided by the company can be found in the producer website [20]. The algae were pre-dried in an oven at 50 °C for 2 weeks to remove all moisture content and then pulverised and sieved into a particle size of < 180 μm.

2.2. Catalysts preparation and characterization

Li-LSX-zeolite was acquired from Shanghai Hengye Chemical Industry Co. Ltd. The catalyst was crushed and sieved into a particle size of < 180 μm. Then, it was calcined at 550 °C for 5 h in a muffle furnace. Physical properties of the catalyst were analysed using a Micromeritics Gemini VII instrument. The sample (0.5 g) was outgassed at 200 °C for 12 h before running the N_2 physisorption isotherms at −195 °C. The surface area was determined by using the standard Brunauer–Emmett–Teller (BET) equation.

Temperature programmed desorption of ammonia (NH_3-TPD) was carried out to determine the acidity distribution and acid strength of the catalysts. For that purpose, a ChemBET TPR/TPD equipment from Quantachrome Instruments fitted with a thermal conductivity detector (TCD). Firstly, 50 mg of sample was degassed under helium flow in quartz U-tube at 200 °C for 2 h and then cooled down to room temperature in the same flowing helium atmosphere. After that, the sample underwent NH_3 adsorption by flowing 25 ml min^{-1} of a gas mixture of ammonia (10%) in helium at 50 °C until saturation was reached. Then, the sample was exposed to helium gas (25 ml min^{-1}) at the same temperature for 2 h to remove any physically bound ammonia from the surface. Then, the desorption study was carried out under helium flow by heating the sample from 50 to 900 °C at a heating rate of 10 °C min^{-1}.

The determination of the weak and strong acid sites by pyridine desorption was carried out at the Quantachrome Materials Characterisation Laboratory in Florida (USA) using a Chemstar Chemsiorption Instrument. The Li-LSX-zeolite was degassed at 100 °C for 1 h in flowing helium. The sample was then temperature programmed up to 500 °C at a heating ramp of 10 °C min^{-1} and held at that temperature (2 h) to remove bound species and activate the sample. Finally, the sample was cooled down to 120 °C in an atmosphere of flowing helium. Next, the sample was saturated with pyridine at 120 °C to minimize the physisorption of the pyrydine. The temperature-programmed desorption (TPD) was performed by heating the sample at 10 °C min^{-1} up to 500 °C.

Presence of Lewis and Brønsted acid sites was evaluated by Pyridine-FTIR. Pyridine adsorption was carried out at 150 °C using a Harrick made Praying Mantis cell attached to a PerkinElmer Spectrum GX instrument. The pyridine adsorbed on Lewis and Brønsted acid sites gives characteristic FTIR bands at 1450 and 1540 cm^{-1}, respectively.

2.3. Microalgae and products analysis

2.3.1. Proximate and elemental analysis

The moisture, volatile matter and ash content of the pre-dried microalgae were determined according to ASTM standards (D2016-74, E872-82, and D1102-84). The elemental analysis (C, H, N) of the dried microalgae and reaction products (bio-char and bio-oil) was carried out using Exeter CE-440 Elemental. The oxygen content was calculated by difference (O = 100–C + H + N). The high heating value (HHV) of the microalgae and of the different fractions was calculated according to Eq. (1), which is a correlation reported to be valid for solid and liquid fuels [21].

$$HHV\left(\frac{MJ}{kg_i}\right) = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (1)$$

where C, H, O, N, S and A represent carbon, hydrogen, oxygen, nitrogen, sulphur and ash contents of *i*.

2.3.2. Thermogravimetric analysis

A thermogravimetric analyser (TA Q500) was used to determine the moisture and volatile matter contents of the microalgae using N_2 as carrier gas. The temperature programme consisted in heating the sample in nitrogen gas from 20 to 105 °C with a ramp of 15 °C min^{-1} and maintaining the sample at 105 °C for 15 min to evaluate the moisture content (MC). Then, the temperature was risen to 800 °C with ramp of 20 °C min^{-1} and hold for 30 min to evaluate the volatile matter. Next, the temperature was cooled to 550 °C under nitrogen atmosphere and held at this temperature for about 30 min under air flow to establish the ash content. Finally, the fixed carbon content (FC) was calculated by difference (FC = 100 − MC − VM − Ash). Finally, the system was cooled down to 30 °C at 50 °C min^{-1}. The ash content of the sample was determined from the amount of solids that remains at the end of the combustion step, meanwhile the fixed carbon was calculated by subtracting the ash content remaining at the end of the run.

2.3.3. Bio-oil and gas analysis (GC–MS and MS)

The chemical composition of the bio-oil samples was analysed using Gas Chromatography – Mass Spectrometry (GC–MS), GC 8000 series equipped with VG Trio 1000. The column (length: 30 m, inner diameter: 0.25 cm; film: 0.25 μm) is temperature limited from 40 to 300 °C. So, the oven was programmed at 40 °C for 10 min, then ramp at 5 °C min^{-1} to 200 °C and hold for 15 min, ramp at 10 °C min^{-1} to 240 °C and hold for 15 min, ramp at 10 °C min^{-1} to 260 °C and hold for 10 min. Helium was used as carrier gas with constant flow rate of 1.7 ml min^{-1} and an injector split ratio at 1:20 ratio. The end of the column was directly introduced into the ion source detector of VG Trio 1000 series. Typical mass spectrometer operating conditions were as follows: transfer line 270 °C, ion source 250 °C, electron energy of 70 eV. The chromatographic peaks were identified according to the NIST library to identify bio-oil components.

The term rel.% C that appears in Tables 3, 6 and 7 refers to the relative % of the compounds from the GC–MS analysis, which has been reported in terms of relative carbon % by considering the average molecular weight (MW) and C number of the main compounds in each functional group. The formula used is the following: rel.% C = (rel $\%_n$ * average C $number_n$) / average MW_n; where $_n$ represents the average of the main compounds for each functional group.

Gasoline and diesel fractions were distributed according to their distillation temperatures ranges as follows: gasoline (< 190 °C), diesel cut 1 (190–290 °C), diesel cut 2 (290–340 °C) and vacuum gas oil