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Catalytic pyrolysis of natural algae over Mg-Al layered double oxides/ZSM-5 (MgAl-LDO/ZSM-5) for producing bio-oil with low nitrogen content

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HIGHLIGHTS

- MgAl-LDO/ZSM-5 composites were prepared with both properties of basicity and ZSM-5.
- MgAl-LDO/ZSM-5 were used as catalysts for bio-oil production in the pyrolysis of the algae.
- The bio-oil obtained with MgAl-LDO/ZSM-5 has low O/C molar ratio and high HHV.

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ABSTRACT

Cyanobacteria were catalytically pyrolyzed over Mg-Al layered double oxide/ZSM-5 composites (MgAl-LDO/ZSM-5) to produce bio-oil. MgAl-LDO/ZSM-5 with a Mg/Al molar ratio of four was proved to be the best catalyst. Under the optima condition that the final temperature was 823 K, heating rate was 10 K/min and catalyst/algae mass ratio was 0.75, a maximum yield of liquid (41.1%) was achieved at 823 K with a heating rate of 10 K/min and a catalyst/algae mass ratio of 0.75, which was much higher than the one obtained without catalyst. The element analysis results proved that this bio-oil had much lower O/C molar ratio and higher HHV. The GC–MS results showed that the bio-oil had less nitrogenous compounds. MgAl4-LDO/ZSM-5 was proved to be an applicable and effective catalyst to obtain bio-oil from catalytic pyrolysis of water-blooming algae.

1. Introduction

Recent years, water blooms have continued to appear in many inland water in China, which causes serious damage of the environment as well as the security of drinking water. However, water blooms also could provide abundant raw materials for biomass energy. For example, algal biomass harvested only from water blooms of Dianchi Lake in China could reach up to 13,600 tons (dried weight) every year. If the calculated yield of bio-oil production from water blooms was 50%, the potential bio-oil output could reach about 6800 tons (Hu et al., 2013). The main transfer methods of algae to energy chemicals include gasification, liquefaction and pyrolysis (Chen et al., 2015). Pyrolysis typically refers to the thermal decomposition of algae into a mixture of gases, liquid, and chars (Marcilla et al., 2013). More recent researches have proved that pyrolysis of some algae can produce bio-oil with higher quality than that produced from traditional lignocellulosic biomass (Maddi et al., 2011; Pragya et al., 2013). Miao et al. (2004) reported that the bio-oil produced from fast pyrolysis of microalgae contained lower oxygen content and a higher heating value of 29 MJ/kg than those of bio-oils from wood, which made it more suitable to substitute for heavy fuel oil than bio-oils from lignocellulosic biomass.

However, water-blooming cyanobacteria which contains three major components—carbohydrates, proteins and lipids, have much higher nitrogen content than lignocellulosic biomass. Because of its high nitrogen content (about 10%), the bio-oil obtained by direct pyrolysis of algae consists of high nitrogenous compounds, which impedes the direct use as transportation fuel (Jena and Das, 2011). Catalytic pyrolysis is one of the promising technologies to adjust the components of bio-oils and upgrade the quality of bio-oil (Adjaye and Bakhshi, 1995).

Molecular sieves are famous catalysts used in pyrolysis in recent years. Among various zeolites, HZSM-5 has gained more attention for its capability of deoxygenation to the pyrolysis product. A study on catalytic pyrolysis of *Nannochloropsis sp.* residue

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over HZSM-5 by Pan et al. (2010) revealed that the oxygen content of the bio-oil from direct pyrolysis (30.09%) decrease efficiently to 19.53% in the bio-oil with HZSM-5 (catalyst/ biomass ratio of 1:1), and the heating value of the bio-oils also increased obviously. And HZSM-5 also showed its special effect of the selectivity on aromatic hydrocarbons (Wang and Brown, 2013; Williams and Horne, 1995). Thangalazhy-Gopakumar et al. (2012) found that in the catalytic pyrolysis of algae over HZSM-5, 25% of the carbon yield in the bio-oil was aromatic hydrocarbons. Despite the fact that HZSM-5 has some advantages in shape-selectivity, easy coke deposition which resulted in the low yield of bio-oil and the rapid deactivation of it had also been found (Lin et al., 2015). In a research of upgrading a fast pyrolysis bio-oil with HZSM-5 (Sharma and Bakhshi, 1993), hydrocarbons yield of 12–15% were reported but high coke production and rapid deactivation of HZSM-5 were also observed. Moreover, HZSM-5 has minor effect on denitrogenation especially when the dosage was not excess enough. In Pan's work (2010), the oxygen content of bio-oil had been lowered by using HZSM-5, but the nitrogen content did not change.

On another hand, basic materials especially metal oxides have also been used in catalytic pyrolysis of biomass to alter the composition of bio-oils. CaO and MgO was the most popular catalysts used in pyrolysis. Pütün (2010) demonstrated that MgO decreased the oxygen content of the catalytic bio-oil from 9.56% to 4.90%, and more long-chain alkanes and alkenes had been converted to lower molecular weight materials with the short chain and alkyl substituted forms. Lu et al. (2010) reported that in the catalytic pyrolysis of poplar wood, adding CaO increased the concentration of hydrocarbons and cyclopentanones which could improve the heating value of bio-oils.

Layer double oxide (LDO), which obtained by calcined layer double hydroxides (LDH), has these properties such as thermal stability, basicity, higher dispersion and larger surface area than common metal oxide. MgAl-LDO was effective in the decarboxylation of Jatropha curcas oil, which produced more hydrocarbons and decreased more oxygen contained in the liquid than Al_2O_3 (Romero et al., 2015). Loaded LDO on zeolite might prepare a catalyst with both properties of base and zeolite. NiAl-LDH/ZSM-5 showed better selectivity of benzaldehyde in the benzoin ethyl ether reaction (Xie et al., 2011). In the pyrolysis-gasification of polypropylene using several nickel-based catalysts, both NiAl-LDO and Ni/ZSM-5 showed high catalytic performance in H_2 production, and NiAl-LDO exhibited good ability for the prevention of coke formation while Ni/ZSM-5 showed some deactivation after reaction (Wu and Williams, 2009). And in the study of CO hydrogenation to hydrocarbons using CuO-CoO-Cr_2O_3/HZSM-5 as catalyst, the catalyst showed higher CO conversion than the separated bed of Cu-Co-Cr and HZSM-5 and it also had a slow deactivation than HZSM-5 (Yan et al., 2008).

In this study, a series of Mg-Al layered double oxide/ZSM-5 composites (MgAl-LDO/ZSM-5) were obtained from MgAl-LDH/ZSM-5 precursors. Catalytic pyrolysis of cyanobacteria were studied over LDO/ZSM-5 with different Mg/Al ratio. The effects of the pyrolysis parameters on products distribution were investigated as well.

2. Experimental section

2.1. Materials

The raw material, microalgae (mainly cyanobacteria), was collected in the summer of 2014 from Taihu Lake, China, and dried directly. Before use, the dried algae were ground into powder (about 80 mesh), kept at 378 K for 24 h. The ultimate analysis of the microalgae was 48.97 wt.% carbon, 7.19 wt.% hydrogen, 11.43 wt.% nitrogen, 28.463 wt.% oxygen and 3.947 wt.% others. And the HHV of the algae was 21.243 MJ/kg, which was calculated by the formula (Friedl et al., 2005) as followed: HHV (MJ/kg) = $(3.55\ C^2 - 232\ C - 2230\ H + 51.2\ C \times H + 131\ N + 20{,}600) \times 10^{-3}$.

HZSM-5 powder ($SiO_2/Al_2O_3 = 25$) was purchased from Nanjing refinery Co., Ltd. Magnesium nitrate hexahydrates, aluminum nitrate nonahydrates and urea were purchased from Sinpharm Chemical Reagent Co., Ltd. And HZSM-5 was calcined at 823 K for 4.5 h before use.

2.2. Catalysts preparation and characterization

MgAl-LDH/ZSM-5 was prepared by loading LDH on HZSM-5 with hydrothermal synthesis. A typical preparation process was as follows: an accurately weighed amount of HZSM-5 was added into a mixed aqueous solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ under vigorous stirring at room temperature. After a certain period of time, an aqueous solution of urea (n_{urea}: $n_{Mn+} = 3.3$) was added into the flask. Then the mixture was heated at 378 K for 1 h and then transferred into a Teflon-lined autoclave and aged at 393 K for 24 h. After cooling to room temperature, the precipitate was filtered and washed with deionized water, then dried at 338 K and the precursor MgAl-LDH/ZSM-5 was obtained. The precursor was milled to 80 mesh and calcined at 823 K for 4 h to obtain MgAl-LDO/ZSM-5 composite before use. In this paper, MgAlx-LDO/ZSM-5 is labeled as catalysts with different Mg/Al molar ratio (x = 2–4). MgAl4-LDO, MgO/ZSM-5 and Al_2O_3/ZSM-5 were also prepared by the same method.

X-ray powder diffraction patterns were obtained on Bruker D8-discover using monochromatic Cu Kα ($\lambda = 1.5406$ Å) radiation. The instrument was operated at 40 kV and 30 mA with 2θ scanning speed at 8°/min and scanning range between 5° and 80°. N_2-adsorption analysis was obtained on a 3H–2000PS1 specific area & pore size analysis instrument (BeiShiDe Instrument Company). The samples were degassed at 473 K for 5 h under vacuum prior to the analysis and the specific surface areas were determined by multi-point BET method.

2.3. Catalytic pyrolysis of algae

The pyrolysis experiments were operated in a self-made apparatus. A typical run procedure was as follows. 5 g cyanobacteria was mixed directly with certain amount of the catalyst and then packed in a stainless steel tube (300 mm height × 25 mm diameter). N_2 was used as the carrier gas and the flow rate was 40 mL/min. The reactor was firstly swept by N_2 for more than 10 min before heating to remove air completely. Then the reactor was heated to 823 K at 10 K/min and kept for 30 min to ensure that the biomass was pyrolyzed completely. The condensable gas was cooled by a condenser and collected. After reaction, the mass of liquid and solid residue were weighed respectively to calculate their yields, and the yield of gas was calculated by overall mass balance. The liquid obtained in our experiments was a mixture of oily phase (upper) and aqueous phase (lower) which was separated by centrifugation and weighed respectively. The effects of catalyst/biomass mass ratio, final pyrolysis temperature and heating rate were also studied by single-factor experiments.

2.4. Products analysis

The liquid obtained by pyrolysis was separated into oily phase (referred here as bio-oil) and aqueous phase. The components of bio-oil were analyzed by GC/MS using Agilent 7890B/5977A equipped with HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). NIST library was used to identify