



Bio-fuel production from the catalytic pyrolysis of soybean oil over Me-Al-MCM-41 (Me = La, Ni or Fe) mesoporous materials



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ARTICLE INFO

Article history:

Received 16 January 2013

Accepted 30 June 2013

Available online 10 July 2013

Keywords:

Soybean oil

Pyrolysis

Me-Al-MCM-41 (Me = La, Ni or Fe)

Bio-fuel

ABSTRACT

In order to obtain a fuel with properties similar to fossil fuel, the catalytic pyrolysis of soybean oil was accomplished over Me-Al-MCM-41 (Me = La, Ni or Fe) mesoporous catalysts. The catalysts were synthesized by hydrothermal method and characterized by X-ray diffraction (XRD). Pyrolysis experiments were performed in a tubular reactor at the constant conditions of temperature 450 °C, weight hourly space velocity (WHSV) 6 h⁻¹ and reaction time 4 h in the absence and presence of the above catalysts. The catalytic activity of the catalysts was studied on the base of the yields and composition of the pyrolysis products. All the pyrolysis products were distilled and classified into three categories according to the distillation temperature (DT) of fossil fuel. (a) Green gasoline (DT ≤ 50 °C); (b) Green diesel (50 °C < DT < 150 °C); and (c) Tar (DT ≥ 150 °C) under vacuum of 100 Pa. The liquid products were examined by Gas chromatography–Mass spectrometry (GC–MS) and elemental analysis, and the tar component was analyzed by the Fourier transform infrared (FTIR). Among the catalysts, the catalyst Ni-Al-MCM-41 showed the best activity which yielded 57.9 wt% bio-fuel, with 9.1 wt% and 48.8 wt% selectivity toward green gasoline and green diesel respectively. Some fuel properties of the diesel fraction were also tested according to the national standard methods in China (GB) and compared with the fuel specification in China. The results showed the bio-fuel obtained from the pyrolysis experiment under Ni-Al-MCM-41 has a good prospect to serve as an alternative for the traditional fossil fuel.

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1. Introduction

The production and composition of fossil fuels have caused environmental pollution and energy crisis. Therefore, there is a pressing need for the development of renewable energy sources as useful fossil fuel substitutes [1,2]. In this respect, bio-fuel has been proposed as an alternative for the fossil fuel. Bio-fuel can be produced from a variety of renewable sources, among these, triglyceride produced from plants and animal fats is thought to be a great potential source for the fuel production because of its similar chemical composition with the traditional fossil fuel [3]. However, now the major challenge is how to efficiently convert the materials into proper fuel.

Extensive researches [4–6] have been done in the past years on bio-fuel production using various technologies. One particular interesting method is pyrolysis [6–11]. The technology was first introduced during the first and second war, the Chinese researchers [12] produced the motor fuels from tung oil through an industrial batch-process. In the pyrolysis process, the triglyceride was heated

in an inert atmosphere at temperature ranging from 400 to 500 °C with a residence time of 10–30 s [13]. The products obtained were liquid, gas and coke. Furthermore, in order to increase the yield of bio-fuel while reducing the yield of undesirable products such as coke, gaseous products and tar, different catalysts have been added into the pyrolysis process [14–16]. Among these catalysts, the zeolites as cracking catalysts have shown great prospect for their unique porous structure and the hydrothermal and thermal stability. In this context, the mesoporous materials Mobil Composition of Matter No. 41 (MCM-41) have been used as catalysts for the vegetable oil cracking, since its large pore size is much closer to the molecule size of the hydrocarbon fuels. However, the pure silica MCM-41 presents weak acid intensity, poor ion-exchange ability and hydrothermal stability due to the absence of active sites. Many researchers have tried to increase the acidity and catalytic activity by introducing Al into the framework. Twaiq et al. [15] investigated the catalytic pyrolysis of palm oil in the presence of Al-MCM-41 with different Si/Al ratios. It was shown that the catalytic activity increased with the aluminum content up to an optimum level and the higher Al content decreased the crystallinity. In addition, with the incorporation of various metals, the catalytic activity could be improved further. Some catalysts, such as Fe-MCM-41 and Fe (Cu, Zn)-Al-MCM-41 have shown good catalytic

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Table 1
Typical fatty acids in the soybean oil.

Fatty acids	Soybean oil (area %)
Palmitic acid	12.5
Stearic acid	2.9
Oleic acid	34.8
Linoleic acid	49.2
Others	0.6

activity on the degradation of plastic materials [17] and the pyrolysis of wooden based biomass [18] respectively. Whereas, these catalysts have never been used in the pyrolysis of triglyceride.

Thus, in this paper, the catalyst Al-MCM-41 with a Si/Al = 80 ratio was chosen as a parent catalyst, and transition metal incorporated materials Me-Al-MCM-41 (Me = La, Ni or Fe) were synthesized hydrothermally. The aim of this study was to investigate the potential to bio-fuel production from the pyrolysis of soybean oil over these synthesized catalysts. All the catalytic pyrolysis experiments were studied in terms of the yield of the bio-fuel as well as the composition of the products. Some physical–chemical fuel properties were also reported in this research.

2. Materials and methods

2.1. Materials

Soybean oil was chosen as the raw material in the pyrolysis experiment. The oil was obtained from commercial sources without further purification. The relative amount of the fatty acids in the soybean oil was experimentally determined with methyl esterification by the Agilent gas chromatograph–mass spectrometry (GC7890A-MS5975C), summarized in Table 1. To determine the C, H and O contents of the starting material, elemental analysis was performed on a Vario MACRO cube Elemental Analyzer. It principally consisted of 76 wt% C, 11 wt% H and 13 wt% O. The oxygen content was determined by the difference.

2.2. Catalysts

The catalyst Al-MCM-41 (Si/Al = 80) and transition metal incorporated Me-Al-MCM-41 (Me = La, Ni, Fe) were prepared according to the method reported in the literature [19]. The catalysts were synthesized according to the molar ratios: SiO₂:MeO = 80; SiO₂:Al₂O₃ = 80; SiO₂:Hexadecyl trimethyl ammonium Bromide (CTAB) = 0.2; SiO₂:H₂O = 140. Prior to experiment, all the catalysts were pelleted, crushed and sieved to give the particle size of 0.28–1 mm. The hexagonal structure of the catalysts was confirmed by XRD. It was recorded by a PANalytical powder diffractometer using Cu-K α radiation (40 kV, 40 mA) in the range of 0.5–10°.

2.3. Experiment procedure

Fig. 1 shows the simplified diagram of the continuous system used in this study for the pyrolysis of soybean oil. The pyrolysis experiments were performed in a stainless steel (#316) tubular reactor with a length of 60 cm and an internal diameter of 10 mm. Prior to experiment, the reactor was filled with nitrogen to remove oxygen, and the reactor was heated by an electric furnace. Once the temperature inside the reactor had reached a steady state, the soybean oil was injected into the reactor through a peristaltic pump drop by drop. The soybean oil was pyrolyzed and vaporized in the reactor. Then, the vapor passed through the catalyst bed resulting in a catalytic pyrolysis reaction. Subsequently, the vapor entered into a cooling system which was with a sufficient volume. Two phases were obtained in the condenser, the aqueous and the organic phase.

The aqueous fraction was separated by a syringe, and the organic phase was collected for further analysis. The residue in the reactor was weighed to give the coke yield.

For the parameters investigation, the maximum yield of bio-fuel was gained at the temperature of 450 °C, weight hourly space velocity (WHSV) 6 h⁻¹ and reaction time of 4 h under atmospheric pressure. In order to investigate the catalytic activity of the catalyst, the experiments were conducted under the above conditions. All the pyrolysis results were studied in terms of the yield and the composition of the pyrolysis product.

2.4. Product analysis

The composition of the liquid product was determined by GC7890A-MS5975C. Samples were injected with a split ratio of 20:1 at 280 °C. A capillary column HP-5 (30 m \times 0.25 mm \times 0.25 μ m) was used, the temperature started at 50 °C (5 min), increased with the gradient of 3 °C min⁻¹ up to 280 °C (5 min). All the peaks were determined with help of NIST library.

The carbon and hydrogen contents of the products were determined on a vario MACRO cube Elemental Analyser, and the oxygen content was given by mass balance.

The initial liquid product gotten from the pyrolysis process was normally dark in color because of some tar component in it. And the component always cannot be detected by the GC method. Considering this, the liquid products were divided into three categories according to the distillation temperature (DT) of fossil fuel in China: (a): Gasoline (DT \leq 205 °C); (b): Diesel (205 < DT < 370 °C); and (c): Tar (DT \geq 370 °C). In order to avoid the polymerization reactions, the distillation experiments were conducted in a simple vacuum (100 Pa) distillation system, the corresponding distillation temperature were: (a) green gasoline (DT \leq 50 °C); (b) green diesel (50 < DT < 150 °C); and (c) tar (DT \geq 150 °C) respectively. The sum of green gasoline and green diesel was defined as bio-fuel in this paper. In addition, the functional groups of tar component were studied by the Bruker Tensor27 Fourier transform infrared (FTIR). In order to study the potential use of the bio-fuel, some fuel properties were carried out by standardized procedures: density according to GB/T19147-2003, viscosity according to GB/T265-1988 on a viscosity determination device; heating value according to GB/T384 on an oxygen bomb calorimeter.

3. Results and discussion

3.1. Characterization of the catalysts

The X-ray diffractogram is a common method to study the crystal structures. Based on the position of the diffraction peak center, the crystal plane and crystal structures could be determined. The low angle X-ray powder diffractions patterns of MCM-41, Al-MCM-41 and Me-Al-MCM-41 (Me = La, Ni, Fe) catalysts have been given in Fig. 2.

As can be seen from Fig. 2, the XRD pattern of MCM-41 exhibited a strong peak in the 2θ range 1.8–2.2 due to (1 0 0) plane reflection lines, and two small weak peaks in the 2θ range 3.5–4.2 due to (1 1 0) plane and (2 0 0) plane reflections. All these indicated the formation of a well-ordered mesoporous material, and these peaks are generally indexed according to the hexagonal regularity of MCM-41 [20]. On the other hand, the appearance of the above peaks in Al-MCM-41 and La (Ni, Fe)-Al-MCM-41 catalysts suggested that the hexagonal array of mesopores in MCM-41 was sustained after the incorporation of Al and La (Ni, Fe) in the framework. However, the insertion of metal ions in the samples resulted in a partial destruction of the hexagonal ordering, as can be seen from the reduction in peak intensity and broadening of (1 0 0) plane of Al-MCM-41 and La

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