



Research paper

Catalytic cracking of rosin over acid-activated montmorillonite catalysts

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ABSTRACT

A series of acid-activated montmorillonite were prepared and evaluated as catalysts for the catalytic cracking of rosin. All the samples were characterized by X-ray diffraction (XRD), Fourier transform-infrared spectroscopy (FT-IR), nitrogen adsorption-desorption, temperature-programmed desorption of NH₃ (NH₃-TPD), scanning electron microscopy (SEM) and thermal analysis (TGA-DSC). Their catalytic performances were evaluated by the cracking of rosin in a batch reactor. The experimental results showed that acid-activated montmorillonite catalysts were active in the catalytic cracking of rosin. The acidic value of the non-essential oil products significantly declined from 163.05 mg/g to 0.43 mg/g and the main component in the non-essential oil and essential oil was the C₁₃ compound. The acid treatment of montmorillonite improved the specific surface area and the amount of surface Si-OH⁺ groups. The moderate (Brønsted) acidity on the acid-activated montmorillonite might be responsible for the cracking of rosin.

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1. Introduction

Over the past decades, the depletion of non-renewable fossil fuels has brought a growing concern about the sustainable supply of energy. Simultaneously, stricter environmental regulations than ever before have been made in many countries and even worldwide to prevent global warming. In this context, the strict limitation on the emission of CO₂ generated from the combustion of fossil fuels is dispensable (Gupta et al., 2014; Huber et al., 2006; Vyver et al., 2011). Therefore, much attention has been devoted to applying green catalytic processes to convert renewable biomass to useful chemicals and clean fuels (Liu et al., 2012; Wang et al., 2013; Zhang et al., 2010a,b; Zhou et al., 2008; Zhou et al., 2011). For example, bioethanol and biodiesel as so-called first-generation biofuels have been developed (Klemm et al., 2005). However, their production from sugars, starches, and vegetable oils easily induces fierce competition among food supply, land usage, and carbon emissions (Palkovits, 2010). Such problems have stimulated the interest in developing new feedstock from non-food biomass for producing fuels and chemicals (Romani et al., 2013; Sims et al., 2011; Wu et al., 2012).

Lignocellulosic residues and wastes in agriculture and forestry, can all be used as non-food biomass to produce biofuels. These biomass feedstocks require virtually no additional land and have few impacts on crop production and food supply. For example, straw and sugar cane bagasse have been studied by some researchers to produce the

biofuels and other bio-materials (Griffin, 2011; Jeong and Oh, 2011; Kobayashi et al., 2011). Nevertheless, in addition to lignocellulosic residues and wastes, any other sources abundant in organic compounds can also be used. Here, it is worth noting that rosin, the exudate of pines and conifers, has an estimated annual yield of more than 1 million tons. Clearly, rosin does not compete with the food chain. As such, it can serve as an alternative feedstock for the production of fuels and chemicals (Coll et al., 2001).

Rosin is a mixture of rosin acids (ca. 90%) and neutral organic compounds (ca. 10%). The 10% of rosin acids are the closely related pimaric-type resin acids with non-conjugated double bonds. Approximately 90% of the rosin acids are of the abietic-type resin acids with conjugated double bonds and a single carboxylic group, such as abietic acid, palustric acid or neoabietic acid (Enos et al., 1968). Due to these conjugated double bonds and the carboxyl group, rosin and its derivatives have been widely used in adhesive agents, coatings, printing inks, papermaking, rubber, paints, soap, food additives and biomaterials (Liu et al., 2008; Liu et al., 2009). Only a few studies have been conducted on the conversion of rosin into fuels and chemicals. Several catalysts such as heteropoly acids and metal oxides have been reported for the cracking of rosin (Hao and Ha, 2000).

Montmorillonite (Mt) is one of the most common 2:1 type clay minerals and often exists on the form of a bentonite deposit (Bergaya and Lagaly, 2013; Zhang et al., 2010a,b). It is well-documented that the treatment of bentonite with mineral acids increases its surface acidity. In this way, the resultant acidic bentonite has improved adsorption and catalytic performances. Usually, acid treatment of bentonite leads

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Table 1

The catalytic performance of natural and acid-activated montmorillonite in the cracking of rosin.

Samples	Acidic value of non-essential oil (mg/g)	Yields of essential oil (%)	Yields of non-essential oil (%)
None	113.27	33.56	52.35
Phosphotungstic acid	2.07	6.0	75.40
Silicotungstic acid	6.12	5.50	76.20
Montmorillonite	108.52	31.24	53.21
Mt-2.5	0.61	14.0	57.0
Mt-3.5	0.43	17.0	54.0
Mt-4.5	0.54	16.0	57.0
Mt-5.5	1.01	14.0	57.0

Reaction conditions: temperature: 240 °C, rosin amount: 100 g, the weight ratio of rosin/montmorillonite: 10, the weight ratio of rosin/heteropoly acid: 100, reaction time: 4 h.

to the replacement of the original exchangeable cations in the interlayer space of montmorillonite by hydrogen ions. In addition, the leaching of aluminium from the central octahedral sheet in the layer of montmorillonite can take place. Even the layer can be partly or completely broken (Zhou, 2011; Zhou and Keeling, 2013). The extent of the changes varies with the acid type, the concentration of acid, temperature and time used for the acid treatment. Acid-treated bentonite of the montmorillonite type has been used as a solid acid catalyst for a variety of hydrocarbon cracking processes (Liu et al., 2004; Manos et al., 2002; Mao et al., 2009). However, the catalytic effects of clay minerals on rosin cracking have been rarely reported. In the present work, for the catalytic cracking of rosin, a series of acid-activated montmorillonite with different contents of H⁺ ions in the interlayer was prepared and tested as the catalyst. The structure and surface properties of the acid-activated montmorillonite catalysts and their correlations with their catalytic performances in the catalytic cracking of rosin were then studied.

2. Experimental

2.1. Materials

Rosin (C₁₉H₂₉COOH, acid value, 163.05 mg/g) was obtained from Chunan Huayuan Economic and Trade Co. Ltd., China. The acid value presented for the carboxylic acid of rosin was determined by Chinese Industrial Standards (CIS: GB/T 8146-2003). The rosin used as a raw material for this work contains 90% resin acids, and the other 10% is composed of fatty acids and neutral compounds. The bentonite was purchased from Zhejiang Changan Rengheng Science and Technology Co., Ltd., China. The cation exchange capacity (CEC) of Ca-bentonite was 80 meq/100 g, and other chemicals (analytic purity) were commercially available and used without further purification.

2.2. Catalyst preparation

Natural bentonite was up-graded by sedimentation to remove impurities like grit before use. Typically, 10 g of material was vigorously

stirred in 1 l of distilled water and then kept for sedimentation for 24 h. The fraction corresponding to 2/3rd of the uppermost portion of the supernatant was separated and dried at 50 °C for 48 h, then dried residue was powdered and sieved to 150 mesh particle size.

The purified bentonite, mainly montmorillonite (10 g), was dispersed in 40 ml 4 M H₂SO₄ and refluxed at 80 °C for 4 h. Then the slurry was cooled, filtered and washed thoroughly with distilled water, till the pH of the leaching solution was 2.5, 3.5, 4.5 and 5.5, respectively. The montmorillonite was dried at 120 °C for 6 h. The activated montmorillonite was designated as Mt-2.5, Mt-3.5, Mt-4.5 and Mt-5.5.

2.3. General procedure

The catalytic reaction was carried out in a 250 ml four-neck round-bottomed flask, equipped with a magnetic stirring bar, a nitrogen inlet, a dropping funnel, and a fractionating column connected to a liquid dividing head. 100 g of rosin and 10 g of the catalyst were introduced into the flask. The reaction temperature was kept at 240 °C for 4 h. During the reaction, the distillate was collected slowly in a receiver flask attached to the liquid dividing head for analysis. After the reaction, the mixture was cooled to room temperature and the catalyst was filtered and then the essential oil and the reaction system were analyzed by a gas chromatograph equipped with a capillary column (30 m) and a flame ionization detector (FID).

Identification analysis of the reaction system was conducted on an Agilent 6890/GCT-Premier GC–mass spectrometer equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 mm) and a flame ionization detector (FID). The following temperature program was used for the analysis: 80 °C for 2 min, 250 °C at 10 °C/min, 250 °C for 20 min.

2.4. Material characterization

The X-ray diffraction (XRD) measurements were collected using a PANalytical X'Pert PRO diffractometer between 2° and 80° (2θ) with a scanning rate of 0.1 °/s, employing Cu Kα radiation (λ = 1.54056 Å). The nature of the surface species was determined by Fourier transform-infrared spectroscopy (FT-IR). The FT-IR spectra were registered using a Thermo Nicolet 6700 spectrometer in KBr pellets. The samples were dried at 110 °C, mixed with KBr and exposed to infrared light. The pellets were immediately measured after preparation under ambient conditions in the mid-infrared area. The spectra were the result of averaging 32 scans in wavelengths ranging from 4000 to 400 cm⁻¹. The surface areas were determined by N₂ adsorption at 77 K using a Micromeritics ASAP 2020 instrument. The samples were outgassed in vacuum for 12 h at 110 °C prior to nitrogen adsorption. The specific surface area was calculated using the BET method based on adsorption data in the partial pressure (P/P₀) range of 0–0.1 and the pore diameter and pore volume were determined from desorption isotherms using the BJH method.

The temperature-programmed desorption of NH₃ (NH₃-TPD) was employed to determine the strength of acid sites. The sample (about

Table 2

Analytical results of main constituents of non-essential oil in cracked rosin.

Number	Compound	Formula	Relative content (%)
1	3,3,6-Trimethyl-2,3-dihydro-inden-1-one	C ₁₂ H ₁₄ O	3.52
2	1,2,3,4-Tetrahydro-2,5,8-trimethyl-naphthalene	C ₁₃ H ₁₈	22.07
3	1,3,4,5,6,7-Hexahydro-1,1,5,5-tetramethyl-(2S)-2H-2,4a-methanonaphthalene	C ₁₅ H ₂₄	2.61
4	2-Butyl-3-hexyl-1H-indene	C ₁₉ H ₂₈	5.74
5	1,1,4a-Trimethyl-1,2,3,4,4a,9,10,10a-octahydro-2-phenanthrenol	C ₁₇ H ₂₄ O	2.95
6	7-Ethenyl-4,7-dimethyl-1,2,3,4,4a,4b,5,6,7,8,10,10a-dodecahydro-1-methyl-phenanthrene	C ₁₉ H ₂₈	2.29
7	6-Ethyl-1,1,4,4-tetramethyl-7-(1-methylethenyl)-1,2,3,4-tetrahydro-naphthalene	C ₁₉ H ₂₈	10.03
8	1,2,3,6,7,8-Hexahydro-1,1,6,6-tetramethyl-4-(1-methylethyl)-indene	C ₁₉ H ₂₈	2.78
9	5,6,8,9-Tetrahydrobenz(a)anthracen-11(10H)-one	C ₁₈ H ₁₆ O	7.25
10	3-Methoxyestra-1,3,5(10),8,14-pentaen-17-one	C ₁₉ H ₂₀ O	1.99

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