Research article

Production of aromatic hydrocarbons from catalytic pyrolysis of lignin over acid-activated bentonite clay

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ARTICLE INFO

ABSTRACT

Natural bentonite clay (mainly sodium-rich montmorillonite) both purified and acid activated using HCl, H_2SO_4, and H_3PO_4 acids were applied to the catalytic fast pyrolysis (CFP) of lignin. The modifications in crystalline structure and acidity of the activated clay were investigated via XRD, N_2-adsorption-desorption, FTIR, TGA and NH_3-TPD analysis. The activity and selectivity of the clays were evaluated for lignin conversion in down- flow micro reactor in the temperature range 500–650 °0C in flowing Nitrogen (oxygen-free). The yields of high value added monocyclic aromatics such as BTX (benzene- toluene- xylenes) and naphthalene were increased by catalytic upgrading using HCl-activated bentonite clay. The selectivity for o&p-xylenes, naphthalene, and methyl naphthalene were greatly enhanced using HCl-activated bentonite in the temperature range 550–650 °C. The catalyst: lignin ratio 3:1 and the nitrogen flow rate 75 ml/min, at 600 °C were the optimum conditions.

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1. Introduction

Lignin is the promising viable and bio-renewable alternative for the fossil resources to produce the aromatic raw chemicals utilized in the petrochemicals industries such as BTX, Phenol, and naphthalenes. This is due to the polymeric structure of lignin-based mainly on aromatic units, and its abundance as a waste product from pulping process and in agriculture residue (e.g. straw and bagasse) [1–6].

In the last decade, several research studies have been reported in literature dealing with catalytic fast pyrolysis of lignin using acidic microporous Zeolite catalysts such as HZSM-5, HB, HY, and H-mordenite [7–13]. HZSM-5 exhibited the highest selectivity for aromatics production [8,14–17]. This was attributed to the shape and size selectivity of the pores in the crystalline structure together with the presence of a great number of Bronsted acid sites distributed in the pores. This indicates that the selectivity for the aromatics production is dependent on the pore size and crystal structure [15, 18]. In addition to the acid sites strength and distribution in the zeolite. Thus, non-porous or non-acidic Si—C materials do not exhibit activity in the pyrolysis of lignin [19].

It is well known that the complex reactions involved in the lignin catalytic pyrolysis such as decarboxylation, cracking, isomerization, and oligomerization are strong acid catalyzed reactions [20–25].

On the other hand, the microporous HZSM-5 zeolite, in spite of being very active in lignin pyrolysis, it has some drawbacks such as the rapid deactivation due to coke deposition and pore blocking. This is due to the formation of partially deoxygenated intermediates which undergo repolymerization to be precursors for coke deposition inside the pores [2,7,9,26,27]. In this concern, H-USY is an acidic zeolite, with low Si/Al ratio than H-ZSM-5, high surface area, and larger pore size, was proved to more selective to monocyclic aromatic hydrocarbons in the catalytic fast pyrolysis of lignin [11,16]. Further, it produces much less coke deposit and high yield of aromatics from lignin (>70%). This was ascribed to the large pore size which enables large molecules, in the pyrolysis vapors to fit in and undergo the conversion reactions, avoiding, to large extent, the coke deposition.

Mesoporous materials such as molecular sieves (Al-MCM-41, HMS, and SBA-15) with large pore size & surface area than ZSM-5 zeolite have attracted attention for their anticipated potential for avoiding rapid catalyst deactivation via pores blocking in CFP of lignin [13,28]. However, these materials indicated lower activity than the acidic zeolites [19], mostly because of the lack of strong Bronsted acid sites. Recently, MCM-48 as the mesoporous material was tested by Lee et al. [29], in the CFP of lignin due to their high resistivity against pore blocking; hence it has three-dimensional channel structure [30–32]. Increasing the acidity of such catalysts increased its activity. Thus Al-MCM-48 exhibited much activity than Si-MCM-48 [29]. Also loading Al, Zirconia on the pores of MCM-48 proved to raise the activity in the CFP of lignin [33]. These observations suggest that it would be beneficial to provide the mesoporous SiC materials

with strong Bronsted acid sites to promote desired reactions with less chances of catalyst deactivation.

Natural bentonite clay is a lamellar aluminosilicate mesoporous material. This material has a crystalline structure made out of alumina octahedral sheet sandwiched between two tetrahedral sheets of silica. The interlayer space in such structure is occupied with replaceable cations, for example, Na^+, k^+, Ca^{+2}. Acid activation of bentonite clay with inorganic acids results in the replacement of the exchangeable cations with H^+ ions of the acid. This treatment leads to the dealumination of the structure and increasing the clay specific surface area and adsorption capacity [34–36]. Thus, the acid activation creates strong Bronsted acid sites between the interlayer spaces.

The objective of this paper is to evaluate the aromatic hydrocarbons production (especially BTX) by the catalytic fast pyrolysis of lignin over bentonite clay (montmorillonite) as naturally occurring and acid activated with mineral acids HCl, H_2SO_4, and H_3PO_4. Furthermore, to investigate the influence of tuning the nature of the active sites on the catalyst surface on the aromatic yields and selectivities. This study may potentially provide an approach for the production of BTX and the development of aromatic compounds from lignin.

2. Experimental

2.1. Materials

The alkaline lignin used through this study was purchased from sigma- Aldrich, the chemical composition of alkaline lignin was C: 46.24%; H: 3.32%; O: 50.213; S: 0.225%. The naturally occurring bentonite clay (Bihar bentonite [37]) used in this study is mainly ascribed to montmorillonite, which is composed of stacked alumino-silicate layers.

2.2. Catalysts preparation

2.2.1. Preparation of acidic bentonite activated by HCl
HCl-acidified bentonite was prepared by adding 50 g of the clay to 500 ml of HCl of 1 M concentration and refluxing at 110 °C under the atmospheric pressure in a round-bottomed flask equipped with a reflux condenser for four hours. The resulting clay suspension was then rapidly quenched by adding 500 ml ice-cold water. The content was then filtered, repeatedly washed with distilled water until all chloride ions disappear, dried in an oven at 100 °C, calcined at 550 °C for 4 h and ground in a mortar pastel to powder form [38].

2.2.2. Preparation of acidic bentonite activated by H_2SO_4
H_2SO_4 acidified bentonite was prepared by wet impregnation method. Typically 50 g of bentonite sample was mixed with 1 M H_2SO_4 solution with stirring for 1 h at room temperature. The slurry was filtered off and washed several times with hot distilled water. The residual solid was dried at 100 °C for 12 h in an oven. The dried sample was calcined at 550 °C for 4 h in air [39].

2.2.3. Preparation of acidic bentonite activated by H_3PO_4
H_3PO_4 acidified bentonite was prepared by impregnation of 50 g of bentonite sample in 1 M H_3PO_4 solution with stirring for 1 h at room temperature. The impregnated sample dried at 100 °C for 12 h, calcined at 550 °C for 4 h [40].

2.3. Characterization of catalysts

XRD analysis of pure bentonite sample as well as acid treated samples were carried out using a Philips PW-1050-25 diffractometer fitted with PW-1965-40 and PW-2100-00 using goniometers employing Ni-filtered Cu. Ka radiation at 500 KV and 30 mA, in order to confirm the crystal structure. The scans were taken at a 4–80⁰ 2θ range. X-ray fluorescence (XRF) was recorded using a Bruker (S4 EXPLORER) operated at 20 mA and 50 kV. The Brunauer, Emmett, and Teller (BET) surface area

of the catalysts was measured using Quanta chrome AS1Win, Quanta chrome Instrument v_2.01. Prior to such measurements, all samples were perfectly degassed at 200 °C for 6 h before experiments. The specific surface area (ABET) was determined from the linear part of the adsorption curve. The pore diameter distribution was calculated from the desorption branch using BJH formula. FTIR analysis was performed using Nicolet IS-10 FTIR over the wave number 4000–400 cm^{-1}. Temperature-programmed desorption (TPD) studies were obtained using an adsorption unit Micromeritics, (Chemisorb-2705) equipped with TCD detector. 500.0 mg catalyst sample was pretreated under helium flow at 500 °C for 30 min and allowed it to cool up to 100 °C, and at this temperature the gas was switched to 5% NH_3 in helium with a flow rate of 20 ml/min for 30 min and subsequently purged with helium gas at 100 °C for 1 h to remove the physisorbed NH_3. NH_3-TPD curves were obtained from 100 °C to 800 °C with a ramping rate of 10 °C/min and hold at 800 °C for 30 min. Thermo gravimetric analysis (TGA) was done by means of a thermo gravimetric analyzer (TG–DSC TAQ600).

2.4. Catalytic activity

The lignin was ground before pyrolysis and sieved (<200 mesh, 75 mm). Then, lignin and the catalyst were mixed physically with lignin/catalyst weight ratio from 1:1 to 1:4. Catalytic fast pyrolysis was investigated in a down-flow fixed-bed quartz reactor. The reaction cell is 25 cm tall and 3 cm in diameter. For each run, 4 g of a mixture of lignin and catalyst was loaded into the reactor with 3 g glass beads. The reactor was kept under nitrogen (O_2 free) flow for 1 h to remove the extraneous air from the reactor. As soon as the oven was heated to the desired temperature, the reactor was inserted suddenly to the oven for achieving the fast pyrolysis. A constant stream of N_2 (O_2–free) was introduced in the reactor to assure the withdrawal of the products and keeping the inert atmosphere during pyrolysis. At the end of the experiment, the reactor was cooled and purged for 10 min. with N_2.

The liquid products were collected in dry ice/ethanol trap and gaseous products collected in air bag. Agilent 7890 Gas chromatograph was used to separate pyrolysis product. The column used was HP-5 column (30 M × 0.32 mm × 0.23 μm). Helium was used as a carrier gas and the split ratio was 50:1. The oven program was started at 40 °C with ramp 2 °C/min to 50 °C and then ramp with 10 °C/min to final temperature 260 °C and hold at this temperature for 20 min. The injector temperature was 300 °C. The separated compounds were then analyzed using an Agilent 5975 mass spectrometer (MS) detector. The mass spectra were operated in electron ionization (EI) mode at 70 ev and obtained from m/z 50 to 650 °C most aromatic monomers were identified by GC/MS spectra according to NIST library and the previously published data [41,42] and gaseous products analyzed by porapak `Q 80/100 column (6 ft. × 1/8 in.), using TCD. The area % of the GC–MS chromatogram was considered as an estimate of the product distribution in the liquid products. Thus, all the chromatographic peak areas obtained were averaged from duplicate runs and presented as percentage values. This estimate is useful for relative comparison of the compounds produced under different operating conditions [43,44] and different catalysts.

The solid residue in each experiment was immediately removed from the heating zone and cooled to room temperature in N_2 flow. The yield of solid implies the amount of solid left after pyrolysis was determined gravimetrically. The liquid yield was calculated as remaining after quantification of the gases and solids [11]. The overall weight yields (Y wt%) were calculated based on the equation:

$$Ywt\% = \left(\frac{\text{mass of gas, liquid or solids products}}{\text{mass of feed}} \right) \times 100$$

Aromatic selectivity is defined as the moles of carbon in the product divided by the total moles of aromatic carbon [19].