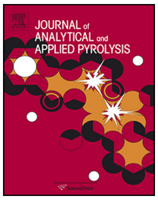
Journal of Analytical and Applied Pyrolysis 121 (2016) 318–328

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap



Catechol production from lignin by Al-doped mesoporous silica catalytic cracking

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ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 27 April 2016
Accepted 9 August 2016
Available online 12 August 2016

Keywords:
Lignin
Hydrothermal catalytic cracking
Catechol
Aluminosilicate catalyst

ABSTRACT

Two synthesized mesoporous aluminosilicate catalysts were tested for their performance in the lignin hydrothermal cracking to benzenediol derivatives, and especially to catechol (1,2-benzenediol), compared to non-catalytic cracking. In this study, Al-doped MCM-41 catalysts were synthesized by direct and post-synthesis methods while Al-doped SBA-15 was prepared by post-synthesis method. The catalytic performance of these synthesized mesoporous aluminosilicate catalysts was compared with microporous HZSM-5 in terms of their selectivity for catechol production. All the tested catalysts gave markedly higher catechol selectivity than the non-catalytic reaction. The acidity and porosity of the catalyst played an important role in the selectivity for catechol. The highest selectivity for catechol (35.5%) was achieved from lignin hydrothermal cracking at a low temperature (300 °C) for 30 min with the Al-MCM-41 catalyst prepared by post-synthesis method, and at a catalyst to lignin weight ratio of 0.75.

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1. Introduction

Catechol (1,2-benzenediol) is mainly used as an intermediate for the synthesis of pharmaceuticals, agrochemicals and other formulations. In addition, catechol is a precursor to various flavors, such as vanillin or eugenol, which are used in the food, perfume and personal care product industries [1]. Traditionally, catechol is mainly produced in industry by the alkaline hydrolysis of *o*-dichlorobenzene, 2,4-sulphonic-5-phenol or *o*-chlorophenol [2]. However, these processes have many drawbacks, such as a serious environmental pollution, rigorous reaction conditions, large operation complexity, high production cost and a low yield of catechol. Recently, it was reported that catechol can also be prepared through other routes, including the wastes from the biomass, wood, paper, petrochemical and textile industries [3].

Lignin is the second most abundant component of biomass and is a major waste by-product from the pulp and paper plant, wood and food industries. Lignin is bio-synthesized from monomeric substitute phenyl propylene units, coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, as lignocelluloses. Because the cellulose, hemicellulose and lignin are incorporated in plant structures as fiber, a variety of producing technologies have been investigated to separate lignin. Six commercial grade lignin generating methods are alkaline (soda), kraft, sulfonate, organosolv, steam explosion (hydrothermal) and dilute acid lignin. The soda (alkaline) process is the pulping method, which uses sodium hydroxides as the chemical reagents [4]. The recovery of valuable chemicals from industrial lignin wastes would represent a tremendous opportunity for material conservation and pollution prevention. Moreover, lignin is considered as a major natural aromatic source because of its aromatic polymer structure [5]. Therefore, lignin has been considered a promising feedstock to produce renewable aromatic compounds and catechol through pyrolysis and hydrothermal cracking process [6–8]. However, the transformation of lignin to aromatic compounds or catechol by direct hydrothermal cracking has too low a yield, and so catalytic cracking is often performed to improve the aromatic yield [6,9].

Previously, the evaluation of alkaline lignin pyrolysis has examined zeolite catalysts with different acidities and pore sizes, which revealed that the maximum aromatic hydrocarbon yield was achieved using the H-USY catalyst at 650 °C [6]. The production of gasoline-range hydrocarbons from Alcell® lignin using HZSM-5 as the catalyst in a fixed bed reactor gave the highest yield of liquid (43 wt.% of hydrocarbon) at 550 °C [10], while the pyrolysis

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http://dx.doi.org/10.1016/j.jaap.2016.08.011
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of four different lignin sources using H-ZSM5 and CoO/MoO_3 catalysts revealed that the H-ZSM5 catalyst was the most effective for the conversion of lignin into aromatic hydrocarbons[11].

In addition, a few reports of catalyst-mediated dehydroaromatization of 1,2-cyclohexanediol to produce catechol have been published [12–18]. The noble metal based catalysts [12] provided a high yield of catechol, such as78%, 80% and 95% yields over Pt/C [13], K/Pd/C [14] and Pd-Rh alloys catalysts [15], respectively. However, these catalysts have a high cost and are hard to regenerate due to the high temperature combustion of the carbonaceous support [1]. The supported transition metal oxide catalysts, and particularly the supported nickel oxide ones [6,16,17], typically provide relatively high yields of catechol, for example an 85% yield of catechol was obtained over tin or alkali metal Al-doped Ni/kieselgur catalysts [18], and these are often higher than the yields obtained from the noble metal catalysts. The lower cost, easier regeneration and high performance catalytic activities of these nickel based catalysts, compared to the noble metal ones, make them more attractive for commercial application.

The Mobil Composition of Matter No. 41 (MCM-41) mesoporous material has been used as a catalyst for biomass cracking because it has a large surface area and large pore size that are much closer to the molecular size of the biomass polymer. However, the pure silica MCM-41 displays a weak acidity and poor ion-exchangeability due to the absence of Al active sites [19–22]. Many researchers have tried to increase the acidity and catalytic activity by doping Al into the tetrahedral framework. Analysis of the catalytic pyrolysis (400 °C) of palm oil using Al-MCM-41 with different Si/Al ratios revealed that the catalytic performance was increased with increasing Al contents but that a large amount of Al decreased the hexagonal crystallinity. However, Al-doped MCM-41 catalysts have never been used in the lignin hydrothermal cracking to produce catechol. Moreover, the hydrothermal cracking conditions used previously in lignin or biomass cracking were performed at high temperatures (400–650 °C).

Thus, in this research, Al-MCM-41 catalysts synthesized by different Al doping methods were evaluated as catalysts for alkaline lignin transformation to catechol in direct comparison to that for theHZSM-5 and Al-SBA-15 catalysts. This study is carried out by water green catalytic cracking process (without harmful organic solvent) at lower temperature. The first aim of this study was to investigate the effect of the Al loading level and mesoporous support on the selectivity of catechol and lignin conversion from lignin hydrothermal cracking over these synthesized catalysts. Secondly, the selected catalyst was then used to determine the optimal condition for lignin hydrothermal cracking, in terms of the temperature, time and catalyst amount, so as to maximize the catechol selectivity and lignin conversion.

2. Experimental

2.1. Chemicals

Alkali lignin (P-370959, Aldrich), which has molecular weight ~10,000 and weight composition of C:H:N:S ratio 61:6:1:2, was chosen as the raw material for catalytic cracking. Tetraethyl orthosilicate (TEOS; Fluka) was used as the silica precursor in the synthesis of the silica mesoporousMCM-41 and SBA-15 materials. The tri-block copolymer pluronic P123 ($EO_{20}PO_{70}EO_{20}$; Aldrich) and cetyltrimethylammonium bromide (CTAB; Calbiochem) were used as a mesoporous template. Aluminiumisopropoxide (AIP; Merck) and sodium aluminate ($NaAlO_2$; Riedel-de Haen) were used as aluminium sources. Ammonia solution (25% NH_3; Merck) was used as pH adjustment agent in the synthesis of MCM-41. Hexane (Merck) and toluene (Carlo Erba) were used as solvents in the preparation of Al-loaded MCM-41. The commercial HZSM-5 with Si/Al ratio 14 (Aldrich) was employed to compare catalytic performance with synthesized Al-doped mesoporous silica catalysts.

2.2. Preparation of the catalysts

2.2.1. Synthesis of the Al-MCM-41 catalysts

The mesoporous silica (MCM-41) was synthesized in house based on a modified procedure as reported previously [23]. The CTAB (2.4 g) was dissolved in 120 g of deionized water (DW) to which 25% (w/v) NH_3 (10.2 g) was added and the mixture was stirred for 0.5 h prior to the addition of TEOS (9.3 g) with constant stirring. The white solution was aged for 18 h at room temperature and then the gel was filtered, washed with a 20:80 (v/v) mixture of ethanol: DW and dried at 60 °C overnight. The template was removed by furnace calcination at 550 °C in air for 5 h to give the calcined MCM-41.

All Al-MCM-41 samples were prepared at a Si/Al molar ratio of 10.5 (10 wt.% Al) by direct and post-synthesis methods. For the direct synthesis, the materials were synthesized by two processes. In the first process, the Al-MCM-41 sample was synthesized in the same manner as that for the MCM-41 above, except the TEOS (9.3 g) was mixed with AIP (0.46 g) before adding to the $CTAB/NH_3$ mixture and after adding the mixture was aged at room temperature for 18 h. This synthesized sample was denoted as Al-MCM-41 (DA). In the second process, the material was prepared in the same manner as that for the Al-MCM-41 (DA) except the 18 h aging stage was replaced with hydrothermal treatment at 100 °C for 5 d to yield the Al-MCM-41 (DHT) samples. For the post-synthesis method of making Al-loaded MCM-41, the calcined MCM-41 (1.0 g) was added to the solution containing AIP (0.76 g) dissolved in either hexane or toluene (100 mL) and stirred at room temperature for 12 h. The solid

Table 1
Physicochemical and textural properties of the synthesized catalysts.

Catalyst	BET surface area[a] (m^2/g)	Total pore volume[b] (cm^3/g)	Average pore diameter[c] (nm)	Acid amount (mmol/g)[d]	Si/Al mole ratio in catalyst[e]
HZSM-5	320	0.12	0.6	0.45	14.6
MCM-41	1100	0.86	2.4	0.18	–
Al-MCM-41 (DA)	941	0.75	2.4	0.62	18.7
Al-MCM-41 (DHT)	886	0.79	2.4	0.59	19.6
Al-MCM-41 (PH)	751	0.49	2.4	0.95	4.4
Al-MCM-41 (PT)	776	0.51	2.4	1.12	4.2
SBA-15	874	1.14	9.2	0.24	–
Al-SBA-15	469	0.90	9.2	0.72	10.1

[a] Calculated from the BET method.
[b] Determined from the BJH pore size distribution method for mesoporous materials and *t*-plot method for microporous material.
[c] Calculated from the BJH method for mesoporous materials and MP-plot for microporous material.
[d] Acid capacities were obtained directly by acid-base titration.
[e] Calculated from ICP-QMS.

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