



# Selectively catalytic upgrading of bio-oil to aromatic hydrocarbons over Zn, Ce or Ni-doped mesoporous rod-like alumina catalysts



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## ARTICLE INFO

### Article history:

Received 8 March 2016

Received in revised form 5 May 2016

Accepted 1 June 2016

Available online 2 June 2016

### Keywords:

Mesoporous alumina

Metal doping

Catalytic upgrading

Bio-oil

Aromatic hydrocarbon

## ABSTRACT

Zn, Ce or Ni metal was doped on mesoporous rod-like  $\text{Al}_2\text{O}_3$  prepared by using cationic surfactant cetyltrimethyl ammonium bromide (CTAB) assisted hydrothermal method for in-situ catalytic upgrading of bio-oil derived from the fast pyrolysis of sunflower stalk. The morphology, crystal structure, surface area, reduction behaviour and acidity of the as-prepared catalyst were characterized. Uniform rod-like  $\gamma\text{-Al}_2\text{O}_3$  particles with a surface area as high as  $412\text{ m}^2/\text{g}$  and an average mesopore diameter of  $3.51\text{ nm}$  were obtained at a CTAB/Al molar ratio of 0.5 and Zn, Ce or Ni metal was found to be able to homogeneously disperse on it. The catalysts with 2.5 wt.% metal (Zn, Ce or Ni) loading amount exhibited the high catalytic activity and selectivity for upgrading of bio-oil with high content of oxygenated components to aromatic hydrocarbons, especially benzene, toluene and xylene (BTX). The total relative maximum hydrocarbon amount of 92% in the upgraded bio-oil was obtained by using 2.5 wt.% Ni/ $\text{Al}_2\text{O}_3$ . Four-cycle reusability test indicated that the metal-doped microporous rod-like  $\gamma\text{-Al}_2\text{O}_3$  alumina catalysts had long-term stability in their performance. Moreover, the regeneration of spent catalysts (4th reuse) by calcination at  $650^\circ\text{C}$  in air for 30 min recovered their activity perfectly. It is expected that such metal-doped rod-like alumina catalysts can be applied as bio-oil upgrading catalysts in a practical process.

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## 1. Introduction

Nowadays, with the rapid consumption of fossil fuel resources and the expanding energy demand, biomass is considered as one of alternative and green energy resources due to its sustainable and renewable property [1]. Thermochemical technologies such as torrefaction, gasification and pyrolysis have been developed for the conversion of biomass to fuels [2]. Fast pyrolysis is an effective way to produce bio-oil from biomass. However, pyrolysis bio-oil always contains a large amount of oxygenated compounds such as acids, ketones, phenols, alcohols, aldehydes, sugars and others, and cannot be applied directly in the engine and other machines. It needs to be upgraded by converting oxygenated compounds to hydrocarbons to increase its heating value and chemical stability [3].

To date, various upgrading techniques have been developed. Hydro-deoxygenation (HDO) is a catalytic hydrotreating process by using hydrogen under high pressure [4]. However, the consumption of a large amount of hydrogen and high operation pressure increases the cost in an industrial process. To solve this problem, upgrading of bio-oil using solid acid catalysts such as zeolites at ambient pressure was proposed [5]. Veses et al. [2] found that HZSM-5 is good catalyst with high activity for the removal of oxygen element in oxygenated compounds, producing rich aromatic hydrocarbons in the upgraded bio-oil. However, the small micropore structure with a pore size of  $5.1\text{ \AA} \times 5.6\text{ \AA}$  limits large oxygenated compounds in bio-oil entering [6]. Mochizuki et al. [7] found that rapid catalyst deactivation easily occurs for the zeolites with relatively small pores owing to the pore blockage by coke deposition. Moreover, many unwanted polycyclic aromatic hydrocarbons such as naphthalene and phenanthrene are also easily generated on such zeolite catalysts.

Mesoporous materials have been considered as the most promising and alternative catalysts for upgrading bio-oil [8]. The large pores in these materials can provide enough mass transfer

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channels for reactants and products, avoiding the pore blockage due to the possible coking and molecule polymerization. Lu et al. [9] found that mesoporous  $ZrO_2$  and  $TiO_2$  based catalysts can effectively transform oxygenated compounds such as phenols, sugars and acids with large molecular sizes to hydrocarbons via cracking and deoxygenating reactions such as dehydration, decarboxylation and decarbonylation. However, due to the low surface area ( $\sim 80 \text{ m}^2/\text{g}$ ), the highest hydrocarbon content in the upgraded bio-oil was only 13%. To solve this problem, mesoporous silica with high surface area ( $\sim 280 \text{ m}^2/\text{g}$ ) was applied so that the hydrocarbon content in the upgraded bio-oil was increased up to 23.4% [7]. To achieve higher hydrocarbon content, various transition metals such as Co, Ni, Zn, Fe, Ga and Mo and some noble metals such as Pd, Pt and Ru have been doped on catalyst supports for adjusting the acidity and promoting deoxygenation effectivity and an improving anti-coking ability [10]. Vichaphund et al. [11] found that the metal loaded on HZSM-5 had higher ability for the generation of monocyclic aromatic hydrocarbons (MAHs) such as benzene, toluene and xylenes (BTX) via oligomerization and aromatization. Wang et al. [12] modified catalyst by Zn to improve the coking resistance property. In our previous work [13], Cu was loaded on mesoporous MCM-41 and KIT-6 materials for the upgrading of bio-oil. It is found that these mesoporous catalysts with pore size in the range from 2 to 5 nm exhibited a high selectivity to aromatic hydrocarbons ( $\sim 85\%$ ). Due to the large pore size, some lignin-derived oxygenated compounds were found to be also effectively transformed to monocyclic aromatic hydrocarbons (MAHs).

$\gamma\text{-Al}_2\text{O}_3$  should also be one of the most effective catalyst and catalyst support for the upgrading of bio-oil owing to its high surface area, large pore size and high acidity for pre-cracking of large bio-oil molecules. However, direct application of traditional  $\gamma\text{-Al}_2\text{O}_3$  always results in severe coke formation, leading to the deactivation of catalyst. To date, only a few studies on metal-loaded  $\gamma\text{-Al}_2\text{O}_3$  for the catalytic upgrading of bio-oil have been reported [14,15]. In this study, mesoporous rod-like  $\gamma\text{-Al}_2\text{O}_3$  was prepared by hydrothermal synthesis method, in which cationic surfactant cetyl-trimethyl ammonium bromide (CTAB) was applied to control the morphology, surface area, and pore size by adjusting CTAB/Al molar ratios. Three kinds of metals, i.e., Zn, Ce and Ni were separately doped on the as-prepared  $\gamma\text{-Al}_2\text{O}_3$  for in-situ catalytic upgrading of bio-oil derived from the fast pyrolysis of sunflower stalk. The objective of this study is to improve the performance of mesoporous  $\gamma\text{-Al}_2\text{O}_3$  based catalysts in term of effective converting oxygenated compounds to hydrocarbons, especially aromatic hydrocarbons and reducing the coke deposition on the catalyst during reaction. It is expected that high hydrocarbon amount can be obtained in the upgraded bio-oil by using these catalysts.

## 2. Experimental

### 2.1. Biomass materials

Dried sunflower stalk particles with a size of 1–2.8 mm was used as biomass feedstock in this study. The proximate and ultimate analysis results and ash compositions of this biomass were reported elsewhere [19].

### 2.2. Catalyst preparation

Mesoporous alumina was prepared by hydrothermal synthesis with initial molar compositions: 1.0Al: 0.1–0.75CTAB: 5.28urea: 70  $\text{H}_2\text{O}$ . In a typical synthesis process, 10.72 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Wako, Japan) and 9.06 g of urea (Wako, Japan) were dissolved in 36 mL of deionized water under vigorous stirring at 35 °C for 30 min. Then, a certain amount of CTAB (Wako, Japan) was added into the

solution and remained at 35 °C under vigorous stirring until homogeneous solution was formed. The mixture was then poured into a Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. Finally, the white precipitate was filtered, washed with deionized water, dried at 105 °C in oven and then calcined at 750 °C in air for 2 h. The mesoporous alumina sample was denoted as  $\text{Al}_2\text{O}_3\text{-X}$ , where X represents the molar ratio of CTAB/Al.

Metal (Zn, Ce or Ni)-doped  $\text{Al}_2\text{O}_3$  was prepared by impregnation method. In a typical impregnation process, a certain amount of as-prepared  $\text{Al}_2\text{O}_3$  powder was added into the aqueous solutions of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Wako, Japan) and stirred at room temperature for 2 h. Thereafter, the slurry was dried at 80 °C, followed by calcination at 650 °C in air for 2 h.

### 2.3. Catalyst characterization

Specific surface area (BET method), pore volume and mesopore size distributions (BJH method) of the catalyst were determined by  $\text{N}_2$  adsorption-desorption which conducted at  $-196^\circ\text{C}$  using a Quantachrome instrument (NOVA 4200e, USA). XRD pattern was determined by a X-ray diffractometer (XRD, Rigaku Smartlab, Japan) in the  $2\theta$  range of  $30\text{--}90^\circ$  with a scanning step of  $0.02^\circ$  using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ). Surface morphology of catalyst was observed with a scanning electron microscope (SEM, SU8010, Hitachi, Japan) coupled with energy dispersive X-ray detector (EDX). Reduction behaviour and acidity of the catalyst were carried out by  $\text{H}_2$ -Temperature-programmed reduction ( $\text{H}_2$ -TPR) and  $\text{NH}_3$ -Temperature-programmed desorption ( $\text{NH}_3$ -TPD), respectively, using a BET-CAT catalyst analyzer (BEL, Japan). Before  $\text{H}_2$ -TPR and  $\text{NH}_3$ -TPD measurements, all samples were preheated at 750 °C for 1 h under He flow for removal of moisture and some impurities within sample structure. The amount of coke deposited on catalyst after reaction was determined using a thermogravimetric analyzer (TGA, DTG-60H, Shimadzu, Japan) with a heating rate of  $10^\circ\text{C}/\text{min}$  until a temperature of 800 °C under air flow.

### 2.4. In-situ catalytic upgrading of bio-oil

The schematic diagram of the experimental setup for in-situ catalytic upgrading of bio-oil derived from the fast pyrolysis of biomass was reported elsewhere [13]. In a typical run, 0.1 g of biomass particles and 0.6 g of catalyst powders were separately packed with quartz wool in the fixed bed reactor. During the reaction  $\text{N}_2$  gas flow ( $100 \text{ cm}^3/\text{min}$ ) was used as the carrier gas. Prior to the experiment, reactor was purged by  $\text{N}_2$  gas flow for about 10 min in order to move out the inside air. The fast pyrolysis reaction temperature, reaction time and heating rate were fixed at 565 °C, 4 min and  $1000^\circ\text{C}/\text{min}$ , respectively, which are the optimum conditions to obtain the highest bio-oil yield in our preliminary experiments. The liquid product was trapped by acetone in ice-cooling bottle and the non-condensed gas was purified and collected in a gas bag for further analysis.

### 2.5. Analysis of bio-oil and gas products

The obtained bio-oil was analyzed by using a gas chromatography (GC-2010 Plus, Shimadzu, Japan)/mass spectrometry (GCMS-QP2010 Ultra, Shimadzu, Japan) with Ultra ALLOY+ 5 capillary column. The bio-oil sample was automatically injected into the column whose temperature was increased from 50 to 300 °C with a ramp rate  $10^\circ\text{C}/\text{min}$  and hold at 300 °C for 10 min. The ionization chamber of MS setup was set at 200 °C. Various peaks in chromatogram corresponding to various compounds such as aromatics, aliphatics, ketones, phenols sugars, acids, aldehydes, furan and others were identified by comparison with the built-in NIST spectral library. Here, the products with boiling points lower than 300 °C

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