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High selectivity and stability of Mg-doped Al-MCM-41 for *in-situ* catalytic upgrading fast pyrolysis bio-oil

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ABSTRACT

In-situ catalytic upgrading of bio-oils derived from the fast pyrolysis of cellulose, lignin or sunflower stalk over Mg-doped Al-MCM-41 was investigated in details. It is found that Mg species with doping amounts ranged between 0.25 and 10 wt.% was well dispersed on Al-MCM-41, and that doping Mg on Al-MCM-41 effectively adjusted the acidity and basicity of the catalysts, resulting in significant improvement of bio-oil quality. Mg/Al-MCM-41 exhibited high selective conversion of bio-oils derived from cellulose, lignin or sunflower stalk to high value-added aromatic hydrocarbons via catalytic cracking, deoxygenation and aromatization. In the upgraded bio-oil, the relative total hydrocarbon amount reached up to approximately $\geq$80%, which consisted of aromatic hydrocarbon approximately 76% and aliphatic hydrocarbon approximately 4% for all feedstocks. The selectivity to the monocyclic aromatic hydrocarbons (MAHs) such as benzene, toluene and xylenes (BTXs) increased while the coke formed on the catalyst decreased with the increase in Mg doping amount. 1 wt.% Mg/Al-MCM-41 resulted in the highest relative total hydrocarbon amount in the upgraded bio-oil at lower catalytic deoxygenation temperature, and showed stable reusability for at least 5 cycles. It is expected that Mg/Al-MCM-41 can be widely applied for bio-oil upgrading in a practical process.

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1. Introduction

Aromatic hydrocarbons such as benzene, toluene, xylenes (BTXs), ethylbenzene, indenes and naphthalenes are considered as the basic chemicals in the petroleum chemistry, which can be also produced from renewable biomass source [1]. Fast pyrolysis of biomass has gained more extensive attention in recent years since it is one of the most promising technologies for bio-oil production with high yield [2]. However, the bio-oil obtained usually contains a large amount of oxygenated compounds such as phenols, ketones furans, acids and sugars so that it has some undesirable properties such as corrosiveness, instability, immiscibility and low heating value [3]. As such, it is necessary to improve the bio-oil quality by converting those oxygenated compounds to hydrocarbons such as BTXs chemicals.

Catalytic cracking with deoxygenation of bio-oil is considered as a promising method since it has many advantages such as no H_2 consumption, and cheap and facile operating condition at atmosphere pressure [4]. Many zeolites have been applied as solid acid catalysts for oxygen removal from bio-oil [5–7]. However, some bulky oxygenates were found to be difficult to pass through the small channel of zeolite, resulting in many oxygenate compounds remaining in the final bio-oil [8]. In particular, during lignin pyrolysis, large oxygenated molecules such as guaiacols, syringols, dimethoxyphenol and trimethoxyacetophenone are always formed, which cannot enter into the zeolite pores. Yu et al. [9] found that lignin-derived syringols cannot be effectively converted to aromatic hydrocarbons due to size exclusion or pore blockage. Park et al. [10] reported that low mass transfer rate is one of the problems by using HZSM-5 with micropore structure in the upgrading process. On the other hand, the strong acidity of zeolite easily leads to the coke formation, resulting in the blocking of pores and rapid deactivation of catalyst [11]. Thus, choosing suitable pore structure and avoiding the coke formation on the catalyst are necessary for developing effective catalyst for deoxygenation of bio-oil.

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Several mesoporous catalysts with adjustable uniform pore size in the range of 2–15 nm, have been developed in order to allow the interaction of large oxygenated molecules in the bio-oil with active sites in the pores [12,13]. MCM-41 is one of mesoporous materials with higher surface area, larger pore size and more accessible reaction sites than the traditional zeolites [14]. Its Brönsted and Lewis acidities can be also adjusted by aluminum incorporation. Adam et al. [15] found that the use of Al-MCM-41 resulted in the reduction of the carbonyl and acid yields, and the increase of hydrocarbons amount, especially aromatic hydrocarbons in the final upgraded bio-oil. Iliopoulou et al. [16] also reported that Al-MCM-41 is a promising catalyst for production of high quality bio-oil. However, it is found that high amount of coke always deposited on this catalyst due to its specific properties such as high acidity and large pore volume. Moreover, even though high acidity and large pore of catalyst are benefit for the deoxygenation and mass transfer, it usually results in the formation of higher polycyclic aromatic hydrocarbons (PAHs) amount in bio-oil via further aromatization and alkylation of MAHs. It should be noted that PAHs are not desirable products due to their carcinogenicity. Especially, PAHs can serve as the precursors of coking, causing catalyst deactivation [17]. To solve these problems, various metals were doped on such catalysts. Vichaphund et al. [18] doped Ni, Ga, Mo, Pd or Co on HZSM-5 and found that the synergy of metal and HZSM-5 slightly improved anti-PAHs formation ability. Zheng et al. [19] used mesoporous Mo_2N/γ-Al_2O_3 for the catalytic fast pyrolysis of lignin, and found that the highest aromatic hydrocarbon yield reached 17.5%. Recently, alkali and alkaline earth metals (AAEM) were considered as the base catalyst for catalytic upgrading of bio-oil because of their high activity, abundant and low cost [20]. Lin et al. [21] confirmed that CaO can be applied for the catalytic deoxygenation reactions, which result in significant decreasing of oxygenated compounds such as laevoglucose, formic acid, and acetic acid in the bio-oil. Stefanidis et al. [22] used the basic MgO catalyst as an alternative of solid acid catalysts for *in-situ* upgrading of bio-oil, and found that MgO exhibited high decarboxylation ability to reduce acid components in bio-oil with releasing of CO_2 gas. To date, only a few studies were reported on the doping of alkali earth metals such as Mg on mesoporous support for the selective productions of MAHs and PAHs [23].

In this study, Mg-doped Al-MCM-41 was prepared as an acid–base bifunctional mesoporous catalyst for upgrading of bio-oils derived from the fast pyrolysis of cellulose, lignin or sunflower stalk. The prepared catalyst was characterized using surface area and porosity measurements, X-ray diffraction (XRD), scanning electron microscopy with energy dispersive X-ray Spectroscopy (SEM-EDX), transmission electron microscopy (TEM), UV–Vis diffuse reflectance (UV–Vis) and NH_3-Temperature-programmed desorption (NH_3-TPD), CO_2-Temperature-programmed desorption (CO_2-TPD) techniques. The product distributions in the upgraded bio-oils from different biomass feedstock were investigated by using Mg/Al-MCM-41 with different Mg loading amounts at different reaction temperatures. The reaction pathways for catalytic upgrading of bio-oils to aromatic hydrocarbons were proposed. Furthermore, the reusability of catalyst was tested for 5 cycles in the cases without regeneration as well as with regeneration. To the best of our knowledge, such catalysts have not been reported in literature so far. It is expected that such catalysts can be widely used for production of high value-added chemicals such as BTXs from bio-oils.

2. Experimental

2.1. Biomass feedstock

Cellulose and lignin were purchased from Wako Pure Chemical Company (Japan) and Tokyo Chemical Industries (Japan), respectively. Sunflower stalk collected from Aomori, Japan was milled to a size in the range of 0.5–1 mm. Prior to analysis, all these biomass feedstocks were dried at 105 °C for 12 h without any further treatment. Their proximate, ultimate analysis and thermal decomposition range were shown in Table S1 and Fig. S1, respectively. The details of biomass characterization can be found elsewhere [24].

2.2. Catalyst preparation

2.2.1. Synthesis of Al-MCM-41 catalyst

Al-MCM-41 (Si/Al = 30) was synthesized by sol-gel method following the procedure described in literature [25]. Here, tetraethyl orthosilicate (TEOS, Wako, Japan), aluminum isopropoxide (AIP, Wako, Japan) and cetyltrimethylammonium bromide (CTAB, Wako, Japan) were employed as silica source, aluminum source and structure-directing template, respectively in the synthesis. In a typical procedure, a certain amount of AIP was dissolved in 260 mL of deionized water, 32.4 mL of ethanol and 21 mL of ammonia solutions under vigorous stirring at 35 °C for 1 h. Then, 7.3 g of CTAB was added in the resultant clear solution and maintained at 35 °C under vigorous stirring until the template was fully dissolved. Thereafter, a certain amount of TEOS was added and stirred for 2 h. This procedure resulted in a precursor gel with a molar composition of $0.1TEOS:0.002AIP:0.02CTAB:2.4NH_4OH:5.2EtOH:14.4H_2O$, which was transferred to a Teflon-lined stainless steel autoclave and heated at 100 °C for 24 h. Finally, the precipitated white product of MCM-41 was filtered, washed with deionized water, dried at 105 °C in oven and calcined at 550 °C in air atmosphere for 4 h.

2.2.2. Preparation of Mg-doped Al-MCM-41 catalyst

Mg doped Al-MCM-41 s with various doping amounts (0.25–10 wt.%) were prepared by impregnation method. In brief, a certain amount of $Mg(NO_3)_2{\cdot}6H_2O$ (Wako, Japan) was dissolved in the deionized water and stirred until a homogeneous solution was obtained. Then, the Al-MCM-41 powder was added in the mixture and stirred at ambient temperature for 2 h. Thereafter, the slurry was dried at 80 °C and calcined at 650 °C in air atmosphere for 2 h. For comparison, pure mesoporous MgO material was also selected as a catalyst for the upgrading of bio-oil in this work. The mesoporous MgO was synthesized using hydrothermal method as described in the literature [26]. Prior to performance test, all the catalysts were pelleted, crushed and sieved to a particle size of 1–2.8 mm.

2.3. Catalyst characterization

2.3.1. Surface area and porosity measurements

N_2 adsorption/desorption isotherms were measured at −196 °C using a Quantachrome instrument (NOVA 4200e, USA). Before the N_2 sorption measurement, the catalyst was degassed under vacuum condition at 200 °C for 2 h. The specific surface area and pore size of catalyst were calculated by Brumauer–Emmett–Teller (BET) method and Barrett–Joyner–Halanda (BJH) method, respectively.

2.3.2. X-ray diffraction (XRD)

XRD pattern of catalyst structure was recorded using an X-ray diffractometer (XRD, Rigaku Smartlab, Japan) in 2θ range of 25–85° with a scanning step of 0.02° at each point using Cu Kα radiation (λ = 0.1542 nm).

2.3.3. Acidity and basicity measurements

The acidity and basicity of catalyst were evaluated by NH_3-Temperature-programmed desorption (NH_3-TPD) and CO_2-Temperature-programmed desorption (CO_2-TPD), respectively using a BET-CAT catalyst analyzer (BEL, Japan) equipped with a

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