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Hydrodeoxygenation of lignin-derived bio-oil using molecular sieves supported metal catalysts: A critical review

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ABSTRACT

It is an economical and environment-friendly method to produce renewable and sustainable oil by upgrading pyrolysis bio-oil containing phenolics. Among all upgrading methods, the hydrodeoxygenation (HDO)-based method of converting bio-oil into renewable fuels is one of the most promising and interesting technologies for the bio-oil refining, which can produce renewable fuels that have comparable quality to conventional fossil fuels. A high hydrogen pressure is usually required for HDO process when using the traditional hydrotreating catalysts. In recent years, molecular sieves supported noble metal and/or transition metal catalysts have been introduced in the reaction of lignin-derived bio-oil upgrading.. This paper summaries the HDO catalysts such as noble metal and transition metal catalysts that are supported on microporous molecular sieves, mesoporous molecular sieves and porous molecular sieves, as well as the HDO activities and the HDO reaction pathways. The investigation of hydrodeoxygenation of phenolic model compounds in bio-oil over various metal(s)/molecular sieves is crucial to understand catalyst behavior for the hydrodeoxygenation process and to illuminate the reaction pathways of hydrodeoxygenation.

1. Introduction

Fossil fuels consumption has increased significantly since the industrial revolution, which causes serious environmental pollutions, such as water pollution, air pollution and soil pollution. With the increasing emission volume of environmentally harmful gases the phenomenon of greenhouse effect and global warming emerging are gradually resulted [1]. In addition, fossil oil is non-renewable resource, which will be eventually used up with the increasing demand of fuels for the society's development, therefore renewable resources enjoy great prospect of serving as a new type energy and chemicals in the foreseeable future [2]. Biomass provides a promising stock for producing renewable fuels and chemicals, especially for liquid fuels [3,4].

Lignocellulosic biomass and other types of biomass such as sugars, algae biomass and vegetable oils biomass, are available as the feed stock for the production of biofuels [5–8]. The main components of biomass feed stock varies in accordance with the kind of biomass, type of tissue, stage of growth and growing conditions of the plant [9]. For example, in lignocellulosic materials, the main components are cellulose, hemicellulose, lignin and extractives [10]. However, for algal biomass, the main components are lipids, carbohydrates and proteins [1,11].

Up to now, three generations of biofuels have been discovered, which can be depicted as the first, the second and the third generation of biofuels [12]. The first generation biofuel is mainly composed of vegetable oil, biodiesel and bioalcohol [12]; the second generation biofuel is derived from cellulosic plant matter such as switch grass, corn stover, or trees [13]; the third generation biofuel is mainly produced by decomposition of cellulosic feed stock using algae or bacteria [14]. In recent years, the market share of first generation biofuels (bioethanol and biodiesel) blending with conventional fuels has been increased. However, it should be noticed that biomass which is in rich of lignocellulose can be grown together with cereal crop in nonagricultural lands, such as alkali soils, therefore it will conflict with the sustainable utilization of good land for food production, namely, it will not compete with the food supply for mankind [15,16].

Renewable biomass-based liquid fuel differs from petroleum with its higher content of oxygen [17], as shown in Table 1. Typically, carbon accounts for 30–60% dry biomass weight, oxygen accounts for 30–40%, and hydrogen accounts for 5–6%, which is depended on the ash content in actual situation. Sulfur, nitrogen and chlorine, which can be found in some types of biomass, account for less than 1% of the

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Table 1
Comparison of properties of bio-oil with those of heavy fossil fuel [18].

Oil from	Pyrolysis of wood	Heavy fossil fuel
Elemental composition (%)		
C	58	86.1
H	7	11.8
O	40	–
N	0.2	0.1
Viscosity (cP)	100	180
Water content (wt%)	15–30	< 0.1
Distillation residue (wt%)	Up to 50	1
Heating value (MJ/Kg)	19	40

biomass weight [1,18]. The carbohydrate portion of biomass is composed by cellulose and hemicellulose (shorter polymers of various sugars, such as xylose, arabinose and galactose), whereas the portion of non-carbohydrate is constituted by lignin (propyl-phenol polymer) [1,5,19,20]. In the plant, cellulose and hemicellulose play a part in providing structural and mechanical strength, while the lignin plays the role in maintaining the stability of these structures [21]. These three essential components form a structure with very complex and insoluble three-dimensional network, making the lignocellulosic biomassmore difficult to be converted than vegetable oils or sugars [5].

The processes of liquefaction and fast pyrolysis are mainly developed to directly convert biomass feedstocks into liquid products which generally called bio-oils [22–24]. The biomass-derived oils are composed by up to more than 400 different kinds of oxygenated hydrocarbons including acids, aldehydes, alcohols, ketones, esters, ethers, phenols, furans and carbohydrates [25,26]. Due to the high content of oxygenated compounds, bio-oils as fuels are subjected to some unfavorable properties, such as low heating value (less than 50% of fossil fuel), chemical and thermal instability, high density and viscosity, immiscibility with hydrocarbon fuels and corrosiveness [15,20,27,28]. The obtained bio-oils are generally presented as dark brown organic liquids which have a special smoky odor [29,30]. Typically, the bio-oils which are derived from fast pyrolysis of biomass contain higher oxygen content, lower heating value and higher acidity than liquefaction oils [31]. Therefore, significant modification is needed before bio-oils can be used widely as a transportation fuel. The bio-oils can enjoy increased volatility and thermal stability as well as reduced viscosity through oxygen removal and molecular weight reduction [32].

The high diversity of chemical compounds in biomass feedstocks makes the catalytic upgrading of bio-oil a complex reaction system. The mainly reported reactions taking place during cracking and hydrodeoxygenation of biomass-derived chemicals over zeolite include cracking, decarbonylation, decarboxylation, hydrocracking, hydrodeoxygenation, hydrogenation, and polymerization [33–35]. Examples of these reactions are given in Fig. 1.

Catalytic cracking and catalytic hydrotreating are two main routes are proposed for partial or total elimination of oxygen atoms from bio-oils. The stoichiometric equations for these processes are summarized as follows [36]:

$$\text{Hydrodeoxygenation: } C_6H_8O_4 + 4H_2 \rightarrow C_6H_8 + 4H_2O \quad (1)$$

$$\text{Cracking: } C_6H_8O_4 \rightarrow C_{4.5}H_8 + H_2O + 1{\cdot}5CO_2 \quad (2)$$

Due to that hydrogen is not required during the reaction process and the reaction is proceeded under atmospheric pressure, catalytic cracking is regarded as an important and cost-effective alternative [37,38]. However, there are some drawbacks that need to be overcome, such as the poor hydrocarbons yields, the extensive coking during catalytic cracking, and the high content of phenolic compounds in the fuels obtained. Hydrodeoxygenation normally occurs with elimination of oxygen as water and hydrogenation-hydrocracking of large molecules. It usually proceeds at high temperature, under high hydrogen pressure, and over heterogeneous catalysts. The reaction of hydrodeoxygenation can lead to production of hydrocarbons in the diesel range [36]. Catalytic hydrodeoxygenation is supposed to be one of the most efficient pathways for lignin-derived bio-oils upgrading [39], moreover the catalysts for hydrodeoxygenation are various.

As traditional catalysts for hydrodesulfurization and hydrodenitrogenation of petroleum products, sulfide CoMo and NiMo/γ-Al_2O_3 catalysts have been applied in catalytic upgrading of bio-oils derived model compounds and the real bio-oils [40,41]. However, sulfided catalysts are subjected to disadvantages such as contaminating the final products as sulfur may be dissolved into the reaction liquids, water-induced catalyst deactivation, and coke accumulation [42]. Noble metal catalyst or catalysts of noble metal supported on such supporters as Pd/C, Pt, Ru, Rh/SiO_2-Al_2O_3, Pt/zeolites also exhibite high activities during the hydrodeoxygenation of lignin-derived compounds [43–46]. However, the high price of noble metals limits the wide industrial application of these catalysts.

Further studies found that support materials with different physical and chemical properties are of great influence to the catalytic activity of these catalysts. This is due to that the hydroconversion of aromatics and/or O-containing compounds over the bifunctional catalysts involves the reactions of (de)hydrogenation on metallic centers, and isomerization/cracking on acid centers [47]. Researchers have investigated many kinds of supports including alumina, silica, Kaolin, active carbon, and molecular sieves and so on [47–52]. Their different acidities and pore constructions make a diverse catalytic activities for hydrodeoxygenation of bio-oil [53–55]. The appropriate acidity of the support is necessary to hydrodeoxygenation of high oxygen content compounds. A relatively large pore size of mesoporous zeolite is helpful for reactants and intermediates to overcome the limitations of diffusion and adsorption on metal active sites [51].

The acid-base properties of the support play an essential role in mediating the product distribution in the HDO of bio-oil [56]. For example, heavy alkanes with carbon number larger than 35 are mainly manufactured due to C-C coupling of fatty ester intermediates using vegetable-oil as feed and basic MgO as the catalyst [57]. In comparison, supports with appropriate acidity can significantly promote liquid hydrocarbon production by enhancing dehydration/hydrogenation of the alcohol intermediates. However, strong acidity of support can cause severe cracking to lighter hydrocarbons [58].

Molecular sieve with various pore structures and acidity strength is a huge family of inorganic materials, wherein molecular based on silicon oxide with various pore structures is a representative. In recent years, molecular sieve has been widely used as the support of hydrodeoxygenation catalyst for bio-oil upgrading, especially for lignin derived bio-oil refining [55,59,60]. In the following section, the hydrodeoxygenation of lignin-derived bio-oil using molecular sieves supported metal catalysts as well as the reaction pathways within will be discussed.

2. Molecular sieves as support of HDO catalyst

Among the heterogeneous catalysts, zeolite is the most widely used one [61–63]. Zeolite has the ability of separating molecules mixtures from each other by differing their structures [64]. Zeolite has environmentally-friendly feature and adjustable strong acidity due to Lewis and Bronsted acid sites. Moreover, the excellent thermal robustness and well manageable pore sizes make it a suitable catalyst or support for industry reaction such as cracking, fluid catalytic cracking(FCC), isomerization and alkylation of various hydrocarbon molecules [65]. Zeolite has large surface area due to its unique topological structure, morphology and chemical composition. With capacity of partitioning reactants from products and modulating the electronic performance of the active sites, as well as excellent thermal and hydrothermal stability, high adsorption capacity, electric fields and limiting effects within the pores, zeolite can enhance the pre-activation of reactants and inter-

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