The relationship between acidity, dispersion of nickel, and performance of Ni/Al-SBA-15 catalyst on eugenol hydrodeoxygenation

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ABSTRACT

Catalytic hydrodeoxygenation (HDO) is considered as one of the most efficient methods for lignin-derived bio-oils upgrading. To reveal the relationship between the characters of Ni/Al-SBA-15 and the catalytic activity of eugenol hydrodeoxygenation in aqueous phase, Al-SBA-15 with different Si/Al ratios were synthesized using acid free method and corresponding Ni/Al-SBA-15 catalysts were prepared by incipient wetness impregnation method. The physicochemical characteristics were obtained by advanced instruments. The highest degree of nickel dispersion on Al-SBA-15 was obtained when the Si/Al ratio was 132 and the corresponding smallest average active nickel particle diameter is 38 nm. The adsorption and dispersion of nickel onto Al-SBA-15 was significantly relevant with the ratios of Brønsted acid site to Lewis acid site as well as the ratios of weak acid site to strong acid site. HDO experiments were carried out over Ni/Al-SBA-15 with different Si/Al ratios. 16Ni/S2-R catalyst with high quantity of acid sites and good dispersion of nickel showed high catalytic activity during hydrodeoxygenation of eugenol. A possible reaction mechanism was concluded based on the reaction results.

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1. Introduction

Lignin is a three dimensional amorphous biopolymer, which is composed by various methoxylated phenylpropanoid building blocks. A large amount of lignin has been produced as byproduct from biomass pretreatment processes in the pulp-and-paper industry [1,2]. Massive lignin residue is of high application value instead of being abandoned as waste or burned as fire materials for cooking [3]. In consideration of the composition of lignin, hydrocarbons with five to nine carbon atoms can be obtained through various depolymerization methods [4]. However, due to the large quantity of phenols and oligomers existing in the liquid phase after depolymerization, lignin-derived bio-oil is not suitable to be used as fuel for engines of vehicles directly [5,6]. It is necessary to further upgrade lignin-derived phenols. Of all existing upgrading methods, catalytic hydrodeoxygenation (HDO) in aqueous phase is

considered as one of the most efficient methods for the lignin-derived bio-oils upgrading due to its lower reaction pressure, reaction temperature and energy consumption demand [7,8].

Various of catalysts, such as sulfide catalysts [9], base metal catalysts [10,11], noble metal catalysts [12] and bimetallic catalysts [13,14], have been widely applied in the HDO process for lignin-derived bio-oil upgrading. The sulfur-free catalysts containing transition metals as active metal species have attracted increasing attention in HDO of lignin-derived bio-oils. Among transition metals, the d electron band of Ni is wider and its energy density near the lattice plane is higher compared with other transition metals [15]. Besides, Ni has the lowest unoccupied molecular orbital (LUMO) [16]. Owe to these outstanding properties of Ni-based catalysts have strong H_2 absorbing ability and good catalytic performance [17]. More active hydrogen species can be supplied during the hydrogenation reactions over Ni-based catalysts. Moreover, Ni-based catalysts are regarded as one of the most potential catalysts being applied to bio-oils upgrading in industry owe to its low cost [10,18].

The hydrodeoxygenation process of lignin-derived phenols involves hydrogenation reaction and isomerization/cracking reactions. Hydrogenation reaction mainly occurs at metallic centers,

while isomerization/cracking reactions mainly take place on acid sites of catalyst supports [19]. Therefore, catalyst supports with different physicochemical properties have significant impact on hydrodeoxygenation of lignin-derived phenols. Main catalyst supports for HDO of lignin-derived bio-oils include microporous molecular sieve (eg. ZSM-5, Beta and HY) [20–22], mesoporous molecular sieve (eg. MCM-41and SBA-15) [23], porous molecular sieve and oxides [24–26]. Acidic supports, which play an important role in removing oxygen from oxy-compounds by dehydration, have been widely used for HDO of lignin-derived phenols [27,28]. As one of mesoporous materials, Al-SBA-15 has highly ordered two-dimensional hexagonal *p6mm* symmetric channel-type mesopores, wider pore size and thicker pore walls and improved thermal and hydrothermal stability, which has attracted extensive attention [29,30]. Al-SBA-15 has been applied as a catalyst support for phenols hydrodeoxygenation. Most of existing researches focus on the catalytic activity of metal based Al-SBA-15 catalysts. However, the effect of acidity on active metal dispersion of metal based Al-SBA-15 catalysts and on the catalytic activity of eugenol hydrodeoxygenation has not been deeply discussed.

The acidity of catalysts and metal dispersion on catalysts supports have significant impact on the activity of catalysts [31,32]. Khokarale et al. reported that a high dispersion of the Fe and Ni on the ZrO_2 could result in a higher catalytic activity of Fe–Ni/ZrO_2, so as to better catalyze the hydrodeoxygenation of methyl lactate into methyl propionate [33]. Hewer et al. found that the combination of acidic sites of the supports as well as good dispersion of metal species can lead to a higher hydrodeoxygenation yield [32]. Sankaranarayanan et al. found that a synergetic effect between the acid sites of supports and the metallic active phases enhanced the hydrodeoxygenation of anisole [34].

In this study, Al-SBA-15 with different Si/Al ratios were direct synthesized without adding acid, which can be used for preparation of Ni-based catalyst. Meanwhile, eugenol as one of the typical phenols in the liquid phase after lignin depolymerization was chosen as the model compound for hydrodeoxygenation reaction. The acidity of Al-SBA-15, dispersion of nickel on Al-SBA-15, and performance of eugenol hydrodeoxygenation in aqueous phase over Ni/Al-SBA-15 catalyst were studied. In addition, the possible mechanism of metal dispersion on Al-SBA-15 as well as the possible reaction pathway were proposed.

2. Experimental/materials and methods

2.1. Materials

Pluronic P123, aluminium nitrate 9-hydrate ($Al(NO_3)_3 \cdot 9H_2O$, analytical pure), eugenol (99%), *p*-cresol (≥99.7%) and nickel nitrate hexahydrate (98%) were purchased from Aldrich company. Tetraethyl orthosilicate (TEOS, analytical pure) was purchased from Sinopharm Chemical Reagent Company. Dodecane (analytical pure) was purchased from Tianjin Kermel Chemical Company. All the chemicals were directly used without further processing.

2.2. Preparation of Al-SBA-15 supported Ni catalysts

Mesoporous Al-SBA-15 with different theoretical Si/Al ratios of 10, 30, 50 and 70 are respectively named as S1, S2, S3 and S4 for short in this paper. The synthesis processes can be described as follow [35]. Firstly, 80 mL of deionized water was added into a glass beaker containing 1.0 g of P123 and stirred for 2 h at room temperature to obtain a clear solution. Secondly, 1.23, 0.41, 0.246 or 0.176 g of aluminum nitrate 9-hydrate was put into the solution obtained in the first step and fully dissolved under magnetic stirring. Thirdly, 7.3 mL of TEOS was put into the above clear solution

obtained at the second step, resulting in mixture, and then vigorous magnetic stirring was kept for 15 h. After that, the temperature of the mixture was raised to 313 K and kept for another 24 h. Subsequently, the mixture was transferred to a 100 mL autoclave, sealed, and put in an oven at 363 K for 2 days. Then, the autoclave was cooled by tap water and the solid precipitate was recovered by filtration, washed with distilled water for several times, and then put into an oven for drying at 333 K overnight. Finally, the precursors were put into a muffle furnace with the temperature raising to 373 K for 2 h at a heating rate of 3 K/min, and then raising to 823 K for 5 h at a heating rate of 3 K/min.

Ni/Al-SBA-15 with different Si/Al ratios and 16% nickel are named as 16Ni/S1, 16Ni/S2, 16Ni/S3 and 16Ni/S4 for short in this paper, respectively. These samples were synthesized by incipient wetness impregnation method and the corresponding synthesis process is showed as follow. At the first step, 2.889 g of nickel nitrate hexahydrate was weighed and dissolved in certain amount of water, and then the solution was mixed with 3 g of Al-SBA-15 powder in a beaker. Subsequently, the obtained mixture was sealed with para film and stayed at room temperature overnight. Then, the samples were put into an oven at 333 K for 12 h. Finally, the samples were put into a muffle furnace with temperature raising from room temperature to 823 K at a heating rate of 3 K/min and then held at 823 K for 4 h in the muffle furnace at atomosphere. Prior to reaction, the catalysts were reduced under hydrogen-nitrogen mixture (hydrogen to nitrogen ratio: 3 : 7) at 823 K for 2 h, with gas flow rate of 60 mL/min.

2.3. Catalyst characterization

X-ray diffraction (XRD) measurements of Al-SBA-15 and Ni/Al-SBA-15 were carried out on a Bruker D8 Advance diffractometer using Cu Kα as radiation source (λ = 1.5147 Å) within the range of 2θ = 20° −70° and 0.5° - 8°, respectively.

Nitrogen adsorption-desorption isotherms were detected on a Micromeritics ASAP 2460 sorptometer. Before detection, the samples were put into sample cell and outgas process was performed at 423 K for 3 h. Brunauer-Emmett-Teller (BET) method was used to calculate the total specific surface area of sample, while *t*-plot method was used to calculate the external specific surface area and the micropore volume of sample. The mesopore diameter of sample was determined by non-local density functional theory (NLDFT) method from adsorption branch.

Scanning electron microscopy (SEM) was conducted on a Hitachi SU 3500 microscope. Transmission electron microscopy (TEM) analysis was carried out on a Hitachi FB-2100 FIB electron microscope with an accelerating voltage of 100 kV.

The contents of Si, Ni and Al in Al-SBA-15 samples were determined by X-ray fluorescence spectrometer (XRF, Axios PW4400, Panalytical).

Fourier transform infrared spectrum (FTIR) was obtained through a Nicolet 410 spectrometer. The samples were mixed and ground thoroughly with KBr, then pressed into a thin circular disc for conventional IR determination. The spectrums were recorded in a transmission mode. Thermo Nicolet was used to record the infrared spectra of pyridine adsorption (Py-FTIR) of samples. The samples were pretreated before FTIR test. In order to remove the physically adsorbed water in samples, the obtained disc was dehydrated by heating at 723 K for 2.5 h under vacuum condition, followed by collection of background of IR spectrum. Afterwards, the temperature of sample was raised from room temperature to 403 K and then pyridine vapor was admitted into the cell for 20 min, resulting in a second spectrum. Then, the cell was heated to 603 K and evacuated at that temperature for 0.5 h, so that another spectrum was collected after the sample was cooled down to