Energy 81 (2015) 33–40

Contents lists available at ScienceDirect

Energy

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

Catalytic hydrodeoxygenation of 2-methoxy phenol and dibenzofuran over Pt/mesoporous zeolites

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ARTICLE INFO

Article history:
Received 18 March 2014
Received in revised form
13 November 2014
Accepted 20 November 2014
Available online 16 December 2014

Keywords:
Pyrolysis
Bio-oil
2-Methoxy phenol
Dibenzofuran
Hydrodeoxygenation
Pt/mesoporous zeolites

ABSTRACT

The hydrodeoxygenation of 2-methoxy phenol and dibenzofuran, which are representative model compounds of bio-oil, was performed using two different Pt/mesoporous zeolite catalysts, Pt/mesoporous Y and Pt/mesoporous MFI. The reforming of 2-methoxy phenol and dibenzofuran via catalytic hydrodeoxygenation was investigated using a batch reactor at 40 bar and 250 °C. The characteristics of the catalysts were analyzed by N_2 adsorption-desorption, X-ray diffraction, and NH_3 temperature programmed desorption. Pt/mesoporous zeolite catalysts containing both strong acid sites and mesopores showed the higher conversion of 2-methoxy phenol than Pt/SiO_2 and Pt/Si-MCM-48 with no acid sites, $Pt/\gamma\text{-}Al_2O_3$, and a mixture of mesoporous Y and Pt/SiO_2, indicating the importance of both Pt and strong acid sites for high catalytic activity. Among the two Pt/mesoporous zeolite catalysts tested, the conversion of 2-methoxy phenol to cyclohexane over Pt/mesoporous Y was much higher than that over the Pt/mesoporous MFI. This was attributed to the better textural properties, such as surface area, pore volume and micropore size, compared to those of Pt/mesoporous MFI. The catalytic conversions of dibenzofuran obtained using two Pt/mesoporous zeolite catalysts were similar and the main products were 1,1′-bicyclohexyl, cyclopentylmethyl-cyclohexane and cyclohexane. In addition, the reaction mechanisms of 2-methoxy phenol and dibenzofuran over Pt/mesoporous zeolite were suggested.

1. Introduction

Bio-oil is considered as a potential replacement for conventional fossil fuels, and its production from the pyrolysis of biomass has been studied extensively [1–9]. Among the biomass materials used for pyrolysis, lignocellulosic biomass, e.g. wood, is abundant and its pyrolysis has attracted considerable attention. On the other hand, the fuel quality of bio-oil is inferior to that of conventional petroleum-derived liquid fuels because of its low energy density and poor chemical stability.

A range of catalytic reforming methods have been developed to improve the quality of bio-oil. Atmospheric-pressure catalytic cracking over zeolite catalysts and high-pressure hydrodeoxygenation (HDO) are the two most widely used catalytic reforming methods. Atmospheric-pressure catalytic cracking over zeolite catalysts normally results in a low oil yield and high oxygen content but aromatic compounds can be produced. On the other hand, the HDO process can reduce the oxygen content of oil considerably while increasing the heating value. Therefore, HDO can normally produce bio-oil with better quality than the catalytic cracking process [10].

A range of catalysts have been used in the HDO of bio-oil. Supported transition metal catalysts, such as $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$, have been applied in earlier studies [6–8]. These catalysts

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http://dx.doi.org/10.1016/j.energy.2014.11.058
0360-5442/

were pre-sulfided to enhance their activities. Recently, non-sulfided noble metal (e.g. Pt, Ru and Pd) catalysts have been used instead of sulfided catalysts, showing excellent catalytic activity for HDO [10–16]. Various support materials, such as carbon, TiO_2, ZrO_2, HY, and ZSM-5 have been studied to replace Al_2O_3 [10–12,17,18].

It was recently reported that mesoporous materials, such as aluminum incorporated mesoporous silica SBA-15 (Al-SBA-15), facilitated the diffusion of reactants into the pores [19]. On the other hand, there has been little research on the application of mesoporous materials as a support material so far. In particular, few studies have reported the use of mesoporous zeolites containing both mesopores and micropores as the support materials. A series of catalysts based on mesoporous zeolites are expected to have higher catalytic activity than those based on mesoporous silica because they have better hydrothermal stability and higher acidity than other mesoporous materials [20]. Therefore, it is important to apply various mesoporous zeolites with different structures to the HDO of bio-oil and compare the resulting product distributions to develop suitable catalysts for the upgrading of bio-oil.

To better understand the fundamental principles of the HDO of bio-oil, the characteristics of the catalysts need to be investigated through the HDO of the representative model components of bio-oil, such as 2-methoxy phenol, phenol, anisole, and dibenzofuran, before applying these catalysts to the HDO of real bio-oil. For example, Elliot and Hart [21] carried out the HDO of 2-methoxy phenol over Ru/C and Pd/C catalysts to produce 2-methoxycyclohexanol as the major product. Gutierrez et al. [14] conducted the HDO of 2-methoxy phenol over ZrO_2-supported noble metal catalysts and reported that the activities of noble metal catalysts were similar to or higher than that of sulfided $CoMo/Al_2O_3$. Nimmanwudipong et al. [16] suggested a mechanism for the HDO of 2-methoxy phenol over Pt/Al_2O_3. Zhao and Lercher [17] produced cyclohexane from 2-methoxy phenol using bifunctional Pd/C and HZSM-5 catalysts.

The present study examined the possibility of using two different types of mesoporous zeolites (mesoporous Y and mesoporous MFI) as the catalyst supports for the HDO of bio-oil. The catalytic activity for HDO is expected to be enhanced due to the use of mesoporous zeolites (mesoporous Y and mesoporous MFI) as the catalyst supports because they contain both strong acid sites and mesopores. Two types of platinum supported on mesoporous zeolites (Pt/mesoporous Y and Pt/mesoporous MFI) were prepared as bifunctional catalysts and applied to the HDO of bio-oil. As a model compound, 2-methoxy phenol was selected because it represents a large number of substituted phenolics observed in bio-oils derived from lignin. In addition, dibenzofuran was used because it is regarded as one of the most representative furan compounds. The changes in catalytic activity for HDO were thoroughly investigated as a function of reaction conditions and the catalyst types to understand the role of mesopores and micropores, and synergy between acid and platinum sites. In addition to the catalytic activity, an analysis of the liquid product under various reaction conditions assists in proposing the reaction mechanism for HDO.

2. Experimental

2.1. Reactant

Commercial 2-methoxy phenol (TCI, 98%) and dibenzofuran (Sigma–Aldrich, 98%) were used as the model bio-oil components without further purification.

2.2. Catalyst preparation

Mesoporous Y and mesoporous MFI zeolites were synthesized using the method reported elsewhere [22–25]. For the synthesis of mesoporous Y, 1.67 g of HY zeolite (CBV720, Zeolyst) was added to 50 ml of 0.09 M tetramethyl ammonium hydroxide (TMAOH, Aldrich) solution. Subsequently, 0.83 g of hexadecyltrimethylammonium bromide (CTAB, 98%, Aldrich) was added and the resulting solution was stirred for 30 min. The solution was then treated hydrothermally for 20 h in a Teflon-lined autoclave maintained at 150 °C. The precipitate was recovered by filtration and washed with water. After drying overnight at 75 °C and calcining for 8 h at 550 °C (heating rate = 1 °C/min), mesoporous Y zeolite was finally obtained. For the synthesis of mesoporous MFI, an amphiphilic organosilane, [(3-trimethoxysilyl)propyl] dodecyldimethylammonium chloride (TPDAC) ($[(CH_3O)_3SiC_3H_6N(CH_3)_2C_nH_{2n+1}]Cl$, $n = 12$), was used as a mesopore-directing agent. SiO_2 and γ-Al_2O_3 was purchased from Sigma–Aldrich. H-MFI (Si/Al = 15) was obtained from Zeolyst. Si-MCM-48 was synthesized using the method reported elsewhere [25]. An aqueous solution of $Pt(NH_3)_4(NO_3)_2$ was used as a precursor solution to impregnate 0.5 wt% Pt on various supports (mesoporous Y, mesoporous MFI, SiO_2, γ-Al_2O_3, H-MFI and Si-MCM-48) using the incipient wetness method. After impregnation, the catalysts were calcined at 500 °C for 3 h in a nitrogen atmosphere, and then reduced at 500 °C for 3 h under a hydrogen atmosphere.

2.3. Catalyst characterization

A surface area analyzer (TriStar, Micromeritics) was used to obtain the N_2 adsorption/desorption isotherms. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method over the relative pressure (P/P_0) range of 0.05–0.20. The pore size distribution was obtained using the Barrett–Joyner–Halenda (BJH) method.

The crystalline structure of the catalysts was analyzed by X-ray diffraction (XRD, Rigaku D/MAX-2200 Ultima) in reflection mode using Cu-Kα radiation (1.541 Å) at 30 kV and 40 mA. The temperature programmed desorption of ammonia (NH_3-TPD) was performed using a chemisorption analyzer (BELCAT, BEL Japan Inc.) equipped with a thermal conductivity detector to compare the characteristics of surface acidity on the catalysts.

To examine the surface area and dispersion of platinum, hydrogen chemisorption measurements (Quantachrome, ChemBet 3000) were performed using an excess pulse technique. 0.4 g of the catalyst sample was first purged in flowing N_2 (50 cc/min) to remove moisture and then reduced by flowing N_2 containing 5 vol.% H_2 (50 cc/min) at 400 °C for 1 h. Residual H_2 was removed by a N_2 flow (50 cc/min) at 400 °C for 1 h, and the chemisorption uptake was then measured at room temperature. A pulse of H_2 with a known volume was injected into a He carrier stream, and the amount of H_2 chemisorbed by the sample was determined from the difference in the thermal conductivity detector (TCD) response before and after passage across the detector.

2.4. HDO of model bio-oil components

The HDO experiments were performed using a high-temperature high-pressure batch reactor fabricated by Hanwool Incorporation. 0.4 g of the reduced catalyst and 40 ml of a model bio-oil solution was introduced to the reactor. Decane was used as a solvent for the model solutions. 2-methoxy phenol solution of 7.5 wt% and dibenzofuran solution of 3.0 wt% were used as the model bio-oil solutions. The reactor was purged three times with hydrogen gas and then filled with 40 bar hydrogen gas. The reactor temperature was increased to 250 °C at a rate of 5 °C/min. At 250 °C, stirring began at a rate of 400 rpm, at which point, the HDO reaction was considered to have started. Preliminary studies showed that 250 °C was the best reaction temperature for the conversion of