



Deoxygenation of guaiacol and woody tar over reduced catalysts



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ABSTRACT

The effect of various reduced catalysts for the upgrading of bio-oil produced by fast pyrolysis in a small batch reactor was evaluated using reduced Ni/SiO₂, Co/SiO₂, Pt/SiO₂, Pd/SiO₂, and conventional sulfided CoMo/Al₂O₃ catalysts. All of the reduced catalysts were prepared by incipient wetness impregnation. Hydrodeoxygenation (HDO) reactions carried out in the H₂ pressure range of 1–5 MPa and temperature range of 300–350 °C using guaiacol and woody tar as model compounds for fast pyrolysis oil demonstrated that at 300 °C, higher guaiacol conversion was achieved with the reduced Co/SiO₂, Ni/SiO₂, and Pd/SiO₂ catalysts compared with the conventional sulfide CoMo/Al₂O₃ catalyst. However, only the reduced Co/SiO₂ catalyst exhibited high HDO activity and selectivity toward aromatics in the guaiacol HDO reaction. The reduced Co/SiO₂ catalyst also exhibited high HDO activity and selectivity toward aromatics in the HDO of woody tar, indicating that this catalyst may be active for direct deoxygenation of phenol yielding mostly benzene. Thus, the reduced catalysts, especially the Co/SiO₂ catalyst, can be considered to be potential candidates for use as HDO catalysts with improved activity and selectivity.

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1. Introduction

The use of renewable energy resources represents one of the best means of reducing the dependence on petroleum energy [1]. Biomass is renewable and available for use as biofuel throughout the world. Due to the negligible content of sulfur and ash, biomass is considered a clean energy source that produces less emission of harmful pollutants than conventional fossil fuels do. Biomass is also greenhouse gas neutral given that the CO₂ emitted from fuels is recycled by photosynthesis. Several biomass conversion technologies have been proposed for producing biofuel, and some have already been commercialized. The existing techniques include fast pyrolysis followed by hydroprocessing, gasification followed by Fischer–Tropsch synthesis and hydroprocessing, and biochemical conversion using dilute acid pretreatment with simultaneous saccharification and co-fermentation. Recently, the fast pyrolysis process for producing bio-oil has gained special recognition because of its economic advantages relative to other biomass-to-liquid conversion processes such as gasification–FT synthesis (FT-oil) and biochemical (bio-ethanol) processes. Fast pyrolysis is economically advantageous because it requires a very short reaction time (a few seconds or less) and a moderate reaction temperature (around 500 °C) [2]. However, bio-oils produced from fast pyrolysis cannot be used directly as transportation fuels because of their high oxygen (30–40 wt%) and water (15–30 wt%) contents.

Further improvement of bio-oil is thus necessary prior to its practical application as transportation fuel [3,4].

Hydrodeoxygenation (HDO) is a promising way to decrease the oxygen content of bio-oil. This reaction has conventionally been applied in conjunction with commercial hydrodesulfurization (HDS) catalysts, i.e., sulfided CoMo/Al₂O₃ or NiMo/Al₂O₃ catalysts [5]. These sulfided CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are widely utilized in oil refineries during hydrotreatment processes. However, removal of sulfur from the active sites of these sulfide catalysts during the reaction [6] may result in product contamination, which is a major disadvantage to the use of these catalysts. Moreover, the catalysts must be continuously replenished with sulfur to prevent desulfiding and consequent loss of activity. In addition, the presence of sulfur-containing compounds has a negative impact on the reaction rate of deoxygenation owing to competitive adsorption of sulfur- and oxygen-containing compounds. Furthermore, the alumina (Al₂O₃) support used with these catalysts is known to be active for coke formation [7–9] and unstable in the presence of large amounts of water [10,5]. Thus, water present in the pyrolysis oil along with the water generated during the HDO reaction may have an adverse effect on the lifetime of the catalyst [11,12]. In addition, compounds produced from the thermal degradation of lignin, such as guaiacol (2-methoxyphenol) and alkyl guaiacols, tend to form heavy hydrocarbons and coke, which reduce the activity of the catalyst [9,13]. Centeno et al. reported that the performance of the conventional catalysts can be improved by the use of a less acidic support such as active carbon or silica. The design of new catalysts that are active at the low temperatures needed to prevent coke formation is an alternative approach for the HDO of fast

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pyrolysis oils. The use of noble metal catalysts that can be prepared on supports such as silica (SiO₂), zirconia (ZrO₂), titania (TiO₂), and active carbon, all of which are more tolerant to water than Al₂O₃, is an attractive option [14,15]. Andrey and co-workers reported that carbon deposition on a silica-supported HDO catalyst was substantially lower than that on an alumina-supported HDO catalyst, thus silica-based supports should be considered as potential candidates for the design of HDO catalysts with improved stability [16]. However, one of the disadvantages of these noble metal catalysts is the requirement for high metal loadings to be active. In a previous study, it was demonstrated that the selectivity of both sulfided catalysts and noble metal catalysts for aromatic hydrocarbons, which are useful compounds for a high octane booster, was very low [17–23]. To achieve improved economic incentive, aromatic hydrocarbon selectivity, and stability, the design of new catalysts for the hydrotreatment of pyrolysis oil is highly desirable.

In the present study, the HDO reactions of the model compound, guaiacol (GUA) (which is a main component of bio-oil) and real woody tar are evaluated in the presence of several metal catalysts using a small batch reactor. In particular, the effects of metal species, the hydrogen pressure, and the guaiacol content on the HDO activity and selectivity are investigated with the objective of generating large amounts of aromatic hydrocarbon.

2. Experimental

2.1. Catalyst preparation

The monometallic Co, Ni, Pd, and Pt catalysts investigated in this study were prepared by the pore-filling incipient wetness method. A SiO₂ granule (Q-10; Fuji Silysia Chemical Ltd., BET surface area: 192 m² g⁻¹, pore volume: 1.03 mL g⁻¹) sample was sieved to yield a 150–250 μm powder and calcined at 550 °C before use. The sieved SiO₂ powder was then impregnated with the aqueous solution containing the metal precursor. The precursors were Co(NO₃)₂·6H₂O (Wako Pure Chemicals, purity: >99.5%), Co(CH₃COO)₂·4H₂O (Wako Pure Chemicals, purity: >99.5%), Ni(NO₃)₂·6H₂O (Wako Pure Chemicals, purity: >99.9%), [Pd(NH₃)₄]Cl₂·xH₂O (N.E. CHEMCAT, Pd: 40.16%), and [Pt(NH₃)₄]Cl₂·xH₂O (N.E. CHEMCAT, Pt: 55.71%). The impregnated samples were dried at 110 °C for 12 h and then calcined at 300 °C (Pd, Pt catalyst) or 450 °C (Co, Ni catalyst) for 4 h in static air. The metal loading of these catalysts was 1 wt% (Pd, Pt) or 20 wt% (Co, Ni) on a SiO₂ weight basis (as metallic). A commercial CoMo/Al₂O₃ catalyst was used as a sulfided catalyst.

2.2. Catalyst characterization

The specific surface area of the support was determined by N₂ physisorption using a surface area analyzer (BELSORP-28SA, BEL Japan, Inc.). Prior to the analysis, the sample was heated overnight under vacuum, at 200 °C to eliminate the volatile species adsorbed on the surface.

Metal dispersions of the catalysts were analyzed on the basis of the amount of chemisorbed CO, which was measured using a pulse method (Ohkura Riken, R-6015). The catalysts were reduced in situ in a H₂ stream, at 300 °C (Pd, Pt catalyst) or 450 °C (Co, Ni catalyst), for 4 h, followed by purging with He at the same temperature for 3 min, then cooling to 50 °C. Subsequent to these pretreatments, a sequential 10% CO/He pulse was injected into the sample at 50 °C until no more CO was adsorbed onto the sample.

The acidity of the catalysts was investigated by NH₃ adsorption using an NH₃ calorimeter (CSA-450G, Tokyo Riko Co., Ltd.). The catalysts were evacuated at 300 °C for 2 h and cooled to 50 °C to measure the heat of NH₃ adsorption on the acid moieties.

2.3. Catalytic testing of guaiacol or woody tar

The HDO reaction was carried out in a small (80 ml) batch reactor. 0.137 g of the calcined catalyst was charged into the pre-reactor and then reduced in a stream of H₂ (purity: >99.995%) at 300 °C (Pd, Pt catalyst) or 400 °C (Co, Ni catalyst) for 4 h. Only the commercial CoMo/Al₂O₃ catalyst was sulfided at 360 °C for 2 h in a stream of 5% H₂S/H₂. These pretreatment conditions were suitable for each catalyst. After pretreatment, the respective catalysts were charged into the batch reactor with 5.48 g of reactant [5% guaiacol (Sigma, purity: >99%)/*n*-tetradecane (Aldrich, purity >99%), 5% phenol (Sigma–Aldrich, purity: >99.5%)/*n*-tetradecane (Aldrich, purity: >99%), 5% benzene (Wako Chemicals, purity: >99.5%)/*n*-tetradecane (Aldrich, purity: >99%), 5% cyclohexene (Wako Chemicals, purity: >99%)/*n*-tetradecane (Aldrich, purity: >99%) or 50% woody tar (Naratanka Kogyo Co., Ltd.)/*n*-hexadecane (Aldrich, purity: >99%)] in a glove box. Hydrogen gas (purity: >99.995%) was then charged into the batch reactor at an initial pressure of 1–5 MPa. The batch reactor was heated to 300–350 °C and maintained at that temperature for 1–3 h.

The compounds in the liquid phase were identified using a GC/MS (6890N/5795; Agilent Technologies) equipped with an HP-1 fused silica capillary column (50 m × 0.2 mm, film thickness of 0.11 μm). The temperature profile was as follows: heating for 3 min at a constant temperature of 40 °C, subsequent heating to 200 °C at 5 °C/min and to 320 °C at 10 °C/min, and then maintaining the temperature at 320 °C for 10 min. Quantification of the compounds was performed with a GC/FID (6890N; Agilent Technologies) equipped with an HP-1 fused silica capillary column (60 m × 0.25 mm, film thickness of 0.25 μm). The temperature profile used was as follows: constant heating for 3 min at 40 °C, subsequent heating to 200 °C at 5 °C/min and to 320 °C at 10 °C/min, and then maintaining the temperature at 320 °C for 30 min. The guaiacol conversion and the product distribution were calculated from analysis of the liquid phase. The conversion, rate of deoxygenation, and yield for each experiment were calculated as follows:

$$\text{GUA conversion (\%)} = \left(1 - \frac{n_{\text{GUA}}^{\text{final}}}{n_{\text{GUA}}^0}\right) \times 100 \quad (1)$$

$$\text{HDO (\%)} = \left(1 - \frac{n_{\text{Alcohol}} + n_{\text{Ketone}} + n_{\text{phenol}} + n_{\text{Others}}}{2 \times n_{\text{GUA}}^0}\right) \times 100 \quad (2)$$

where n_{GUA}^0 is the initial amount of guaiacol (mol), $n_{\text{GUA}}^{\text{final}}$ is the final amount of guaiacol (mol), and n_i is the amount of *i* (alcohol, ketone, phenol, and others) product at the exit of the reactor.

3. Results and discussion

3.1. Catalyst characterization

The characteristics of the catalysts were evaluated on the basis of BET-surface area analysis, CO-chemisorption, and NH₃-adsorption. The surface area of the catalysts is shown in Table 1. The surface area of Ni/SiO₂ and Co/SiO₂ was clearly lower than that of Pd/SiO₂ and Pt/SiO₂, which is attributed to blocking of the small pores of Ni/SiO₂ and Co/SiO₂ given that the metal loadings of Ni/SiO₂ and Co/SiO₂ were higher compared to that of the Pd/SiO₂ and Pt/SiO₂ samples. The dispersion of the metal on the surface of the catalyst is recorded in Table 1. Notably, the metal dispersion followed a trend similar to that of the surface area of the catalysts. The dispersion of Ni/SiO₂ and Co/SiO₂ was clearly lower than that of Pd/SiO₂ and Pt/SiO₂. Fig. 1 shows the heats of adsorption of NH₃ on the various catalysts versus the amounts of NH₃ adsorbed, as determined via NH₃ calorimetry. The extent of adsorption of small basic molecules (such as NH₃) is commonly used to

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