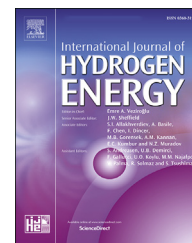




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Nickel supported on low-rank coal for steam reforming of ethyl acetate

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ABSTRACT

Ethyl acetate is a volatile organic compound (VOC) that has emerged as a major environmental pollutant and also one of representative components of bio-oil. In this study, mostly metallic Ni particles (size: <10 nm) were finely dispersed on low-rank coal (LRC) by the ion-exchange process. Catalytic steam reforming of ethyl acetate (EA) was performed over Ni supported on Eco LRC (Ni/Eco) to reduce EA emissions and simultaneously produce H₂. EA reforming over 17.7 wt% Ni/Eco at 400 °C results in H₂ yield of 70%–80%; this is comparable to that achieved with reforming over commercial Ni/Al₂O₃. Advantageously, metallic Ni particles are dominant over Ni oxides on LRC, and therefore, the pre-reduction step routinely required for an alumina-supported catalyst can be skipped. Furthermore, deactivation by coking is slower with Ni/Eco than with Ni/Al₂O₃ during long-term operation, probably because of the smaller particle size and preferential adsorption on the coal support.

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Introduction

Ethyl acetate (EA), one of the most common volatile organic compounds (VOCs), is emitted from many industrial processes such as painting, wastewater treatment, dry cleaning, printing, and coating. VOC release to the environment causes air pollution that has thus far been minimized by mostly using expensive combustion techniques [1]. When VOCs are reformed after being concentrated to >1000 ppm, they can serve as a valuable syngas for H₂ production, which is of particular importance nowadays [2–4]. In addition, ethyl acetate is a representative ester group of bio-oil and a catalyst

suitable to its reforming is necessary for the upgrading [5]. Xue et al. performed autothermal reforming over Ni_xLa_{10-x}O_y/Al₂O₃ to investigate the feasibility of hydrogen production from waste cooking oil. Bavisar et al. also studied the steam reforming of ethyl acetate, as one of a model components in the bio-oil aqueous fraction, using Ni/Al₂O₃ catalyst [6,7].

Nickel catalyst deposited on metal oxides such as alumina or silica has been used for the catalytic steam reforming of hydrocarbons [8,9]. However, nickel is often deactivated by coking; furthermore, it offers low flexibility in terms of compositional and structural modification [10]. In addition, it should be reduced to be active. Recently, low rank coals and

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their pyrolysis products (chars) have been prepared as catalytic supports, and applied to various reactions. It has been studied by Gunma University in Japan. The enhanced kinetics was found by applying low rank coal supported catalysts to steam reforming of volatile compounds like tars during pyrolysis of eucalyptus, Japanese cypress, sewage sludge and pre-composted pig manure [11–15]. The coal-supported catalysts have also showed catalytic activity for the decomposition of volatile nitrogen species (VNSs) into N_2 [14]. The nano-scale Ni particles are uniformly dispersed in the coal support, but start to aggregate at $T > 650$ °C. The chars produced by thermal decomposition of coal or biomass have relatively high BET surface area of 300 m^2/g or more and have been also applied as catalyst supports for tar reforming and water-gas shift reactions [16–21]. Low-rank coal (LRC) contains numerous oxygen atoms (up to 35 wt%), normally in the form of carboxyl and hydroxyl groups, that can disperse metal cations via the ion exchange process [22–25]. Pyrolysis then results in a coal-supported catalyst with nanodispersed particles [26]. These coal-supported catalysts can skip the pre-reduction step which is required for typical alumina-supported catalysts, since coals act as reductants while oxidized to CO_2 . Research on coal-supported catalysts is still at an early stage. There are not many reports on the characterization of coal-supported catalysts until now. Extensive characterization on microstructure (TEM and SEM), pore structure (BET), and chemical composition (XRD, XPS, and TPR) is performed in this study.

Reforming catalysts are deactivated with time owing to carbon deposition, and therefore, it is recommended that they be used under excess steam condition [5]. In practice, coke removal is required periodically. A coal support may slow down coking-related deactivation [16,27,28]. A coal support also affords other advantages compared to conventional alumina. The catalytic behavior of coal can be tailored by modifying its porosity by thermal and chemical activation and its chemical composition by addition/removal of the heteroatomic functional groups [29]. Coal can be gasified or combusted at the end of its lifespan to recover coal energy and expensive active materials such as transition metals and platinum group metals (PGMs) [11], thereby avoiding difficult recycling processes and the disposal of waste catalysts [14]. It is known that in some cases, carbonaceous coal can itself exhibit catalytic activity over discontinuous surface sites, defects, and functional groups [29,30]. In addition, LRC is inexpensive, being more than 50 times cheaper than the activated alumina. Coal matrix is not structurally affected by acids and bases as well as by high temperatures. However, it may be reactive under oxidation and hydrogenation at high temperatures [31].

This work describes the steam reforming of EA over Ni catalyst supported on Eco LRC (Ni/Eco) [1]. The steam reforming was performed under a wide range of conditions to assess the utilization of the reforming catalyst and its feasibility for H_2 production. Specifically, the influence of reaction temperature, amount of nickel loading, gas hourly space velocity (GHSV), and steam-to-carbon ratio (S/C) on the activity was analyzed. Ni/Eco was then compared with alumina-supported catalysts in terms of catalytic performance and long-term stability.

Experimental

Materials

The reactant gas (1000 ppm EA in N_2) was supplied by RIGAS. Indonesian Eco LRC was used as the catalytic support; its proximate and ultimate analysis is given in Table 1. $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, $(NH_4)_2CO_3$, and ammonia solution were purchased from Samchun Chemicals for catalyst preparation. Commercial 18 wt% Ni/ Al_2O_3 (R110, Alfa-Aesar) and 58 wt% Ni/ Al_2O_3/CeO_2 (N186, JGC) catalyst were used for the purpose of comparison.

Catalyst preparation and characterization

Eco coal was pulverized and sieved to achieve a particle size of 0.5–1.0 mm. Ni supported on Eco coal catalyst (Ni/Eco) was prepared by the ion-exchange process [13]. First, a hexaamine nickel carbonate ($(NH_3)_6NiCO_3$) solution was prepared by mixing nickel carbonate hydroxide ($NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$), ammonium carbonate ($(NH_4)_2CO_3$), and ammonia in distilled water. The concentration of Ni precursor solutions was controlled between 0.1 and 1.4 M (Ni metal basis) for preparation of 5.1 wt %, 8.9 wt%, 10.6 wt%, and 17.7 wt% Ni/Eco catalysts. A proper amount of NH_3 solution was added to reach $pH = 10$ –11. Subsequently, 60 g Eco coal was immersed into the solution, and the mixture was stirred for 6 h at room temperature. The resultant coal was filtrated, washed, and dried at 107 °C for 24 h under N_2 . Finally, the Ni-loaded coal was pyrolyzed at 650 °C for 30 min to produce Eco coal-supported Ni catalyst (Ni/Eco).

Proximate analysis of the samples was performed using the TGA-701 thermogravimeter (LECO Co., USA) to determine the moisture, ash, volatile matter, and fixed carbon contents. A CHN-2000 elemental analyzer (LECO Co., USA) was used to determine the elemental composition of C, H, N, S, and O. The nickel content of Ni/Eco was analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES; Thermo Scientific iCAP 6500 duo). Transmission electron microscopy (TEM, FEI Tecnai G2-20 S-twin, 200 kV, LaB6) was used to observe the dispersion of nickel particles in the support. The surface morphology of the samples was determined by scanning electron microscopy (SEM, Hitachi S-4800). Nitrogen adsorption-desorption isotherms were measured using a typical volumetric setup (ASAP 2020, Micromeritics). The catalysts were characterized by X-ray diffraction (Rigaku, DMax 2500 PC, Japan) and X-ray photoelectron spectroscopy (Kratos, AXIS NOVA, UK). Temperature-programmed reduction (TPR) was measured using BEL-CAT-BASIC (Belcat Japan, Inc.). For TPR, ~0.04 g of sample was loaded and cleaned at 150 °C under Ar gas. Then, the sample was reduced with increasing temperature up to 900 °C (ramp rate = 10 °C/min) under 30 cc/min 10% H_2 .

Catalytic activity measurements

Steam reforming was conducted in a continuous-flow fixed-bed quartz tube reactor (ID = 10 mm) under atmospheric pressure [32]. The reactor was placed in a tubular furnace. A thermocouple was inserted through the top and placed just above the catalyst. In each run, 0.1 g of catalyst (a length of

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