



Catalytic performance of manganese-promoted nickel catalysts for the steam reforming of tar from biomass pyrolysis to synthesis gas

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ABSTRACT

We investigated the performance of Ni + MnO_x/Al₂O₃ catalysts in the steam reforming of tar from the pyrolysis of cedar wood. Performance of Ni + MnO_x/Al₂O₃ catalyst with optimum composition was much higher than those of the corresponding monometallic Ni and MnO_x catalysts. This tendency is also supported by the activity test in the steam reforming of toluene as a model compound of tar. Based on the catalyst characterization results, the surface of Ni metal particles was partially covered with MnO_x, and the interaction between Ni metal and MnO_x can play an important role on the enhancement of the catalytic activity and the suppression of coke deposition in the steam reforming of tar. Excess MnO_x addition decreased the catalytic activity by decreasing the number of the surface Ni atoms.

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1. Introduction

Conversion of biomass to synthesis gas is an important process for the production of liquid fuels by Fischer–Tropsch synthesis and chemicals by methanol synthesis, which is related to the network of C1 chemistry [1]. The production of synthesis gas from biomass is usually carried out in a non-catalytic system [2]. In the non-catalytic system, biomass is gasified with air at high temperature in order to decrease the tar formation [2]. When the catalyst is applied to the biomass gasification system, the catalysts should contribute to the decrease of tar concentration in the produced gas by catalytic conversion and the decrease of reaction temperature [3].

Our group has reported that Rh–CeO₂ based catalysts exhibits high performance in the catalytic gasification of biomass with oxygen [4,5] using a fluidized bed reactor. On the Rh–CeO₂ based catalysts, the interaction between Rh metal and CeO₂ can be related to high catalytic performance [6]. In the case of the practical and industrial gasification process, air must be used as a gasifying agent because the production of oxygen needs very large and expensive facility. In the gasification of biomass with air, the product gas become diluted with nitrogen and is not suitable to the further conversion of synthesis gas to liquid fuels and chemicals,

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where process needs to be pressurized. In contrast, the gasification of biomass with steam reforming of tar derived from the biomass pyrolysis can suppress the dilution of the product gas. In these reaction systems, catalysts should exhibit high activity and resistance to coke deposition in the steam reforming reaction [3], in particular, high resistance to coke deposition can be related to the enhancement of the catalyst stability [7]. As reported previously, Ni is one of the suitable components for the steam reforming of various organic compounds, and the effect of supports and additive oxides and metals with Ni has been investigated. We have reported that the addition of CeO₂ to Ni catalysts enhanced the catalytic performance in terms of the activity and the suppression of coke formation. On the Ni + CeO₂/Al₂O₃ catalysts prepared by the co-impregnation method, the formation of the Ni–CeO₂ nanocomposite could give large interface between Ni metal and Ce oxide surface, and this was connected to high catalytic performance [8–12]. In addition, we have recently reported that the addition of Fe to Ni/Al₂O₃ catalysts promote the steam reforming reaction, and this property is caused by the Ni to Fe alloy formation [13]. On both Ni + CeO₂/Al₂O₃ and Ni–Fe/Al₂O₃ catalysts, it is thought that an important point is that the presence of redox species such as cerium oxide and iron neighboring to the Ni surface. During the redox cycle the oxygen can easily transfer to the carbonaceous species and facilitates to form gas and thus it cleans the catalyst surface.

In the present article, the modification of Ni/Al₂O₃ with Mn is attempted, because Mn species have high redox property like Ce

species. In particular, we investigated the performance of Ni + MnO_x/Al₂O₃ catalysts prepared by co-impregnation method in the steam reforming of tar derived from the pyrolysis of cedar wood. In addition, we tested the catalysts in the steam reforming of toluene as a model compound of tar in the biomass gasification process [14,15]. As reported previously, the reactivity of aromatic compounds is lower than that of other compounds contained in the biomass tar, and high catalytic activity of the steam reforming of toluene can be connected to high activity of the steam reforming of tar [16,17]. The catalysts were characterized by temperature programmed reduction with H₂, X-ray diffraction, and H₂ chemisorption, and the catalytic performance is discussed on the basis of characterization results.

2. Experimental

2.1. Catalyst preparation

The support material of α -Al₂O₃ was prepared by the calcination of γ -Al₂O₃ (KHO-24, Sumitomo Chemical Co., Ltd., 133 m² g⁻¹, grain size 2–3 mm) in air at 1423 K. After calcination, it was crushed and sieved to particle sizes between 0.3 mm and 0.5 mm. The Ni + MnO_x/Al₂O₃ catalysts were prepared by a co-impregnation method using the mixed aqueous solution of Ni(NO₃)₂·6H₂O (WAKO Pure Chemical Industries, Ltd., 98.0%) and Mn(NO₃)₂·6H₂O (Soekawa Chemical Co., Ltd., 99.9%). After the impregnation, the samples were dried at 383 K for 12 h followed by the calcination at 773 K for 3 h under air atmosphere. The loading amount of Ni was 12 wt.%. The additive amount of MnO_x was represented as MnO₂ in the range of 10–40 wt.% because the reduction degree of the Mn species was dependent on the additive amount.

As a reference, the Ni + CeO₂/Al₂O₃ catalyst with 12 wt.% Ni and 15 wt.% CeO₂ was prepared by the co-impregnation method. The conditions for drying and calcining were the same as the case of Ni + MnO_x/Al₂O₃, which were based on the previous report [9].

2.2. Biomass

Cedar wood was ground with a ball mill to about 0.1–0.3 mm size. The moisture content of the cedar wood was 7.2%. The dry basis composition by weight was C 50.8%, H 6.0%, O 41.8%, N 0.2%, and ash 1.1%. The elemental analysis was carried out by the Japan Institute of Energy.

2.3. Activity test in the steam reforming of tar derived from the pyrolysis of cedar wood

The details of the procedures for the activity test in the steam reforming of tar and the diagram of the reactor have been described in our previous report [9]. Catalytic performance was evaluated using a laboratory-scale continuous feeding dual bed reactor. The biomass feeder consisted of a conical glass vessel with a screw valve at the bottom, allowing continuous feeding of biomass particles by vibrating the vessel with an electric vibrator. Nitrogen was used for transporting the biomass particles to the primary bed. Steam was supplied by the evaporation of water fed by a syringe pump. The cedar wood powder (0.1–0.3 mm) was supplied from the top of the reactor to the hot zone and thus it rapidly pyrolyzed mainly to gaseous tar and solid products. Solid products including char and ash were accumulated at the bottom of the primary bed. The dual bed reactor system prevented the contact of char and ash to catalyst. Gaseous products such as volatile tar and gases were introduced to the secondary catalyst bed together with steam in

order to proceed the steam reforming reactions on the catalyst surface.

The details of the reaction conditions are as follow; feeding rate of biomass was 60 mg/min which provided the feeding rate of C, H, and O in 2360, 3350 and 1450 μ mol/min, respectively excluding the moisture content. The feeding rate of added steam was 1110 μ mol/min. The molar ratio of feeding steam including biomass moisture to feeding carbon was estimated to be 0.57. The feeding rate of N₂ was 60 mL/min (2680 μ mol/min). The tests were performed under atmospheric pressure. The amount of catalyst was 0.5 g. We evaluated the catalytic performance over the catalyst after the reduction pretreatment at 773 K for 0.5 h using 30 mL/min of H₂. The sample of effluent gas was collected by a syringe and analyzed by a gas chromatograph (GC). The concentration of CO, CO₂, and CH₄ was measured by FID–GC (Gaskuropack 54) equipped with a methanator and that of H₂ was determined by TCD–GC (MS-13X). The flow rate of the effluent gas was measured by a bubble flow meter. The formation rate of the gaseous products was based on the concentration obtained from the GC analyses and the flow rate of the effluent gas from the bubble flow meter. The yield of carbon-containing gaseous products (CO, CO₂, CH₄) was calculated by the formation rate normalized by the total carbon supplying rate of the biomass. The amount of char formed from the pyrolysis of the cedar, which was accumulated in the primary bed, can be measured after the activity test. Amount of coke deposited on the surface of catalysts can be also determined after each activity test. The amount of coke and char was determined by the amount of CO₂ formed in the combustion after the reaction test, and the yield was calculated by the ratio to the total carbon amount in the fed biomass. As a result, the yields of gaseous products and solid products (coke and char) were available. In contrast, the amount of residual tar is difficult to determine because tar is easily condensable in the reactor system and a part of tar cannot be collected. Therefore, the yield of tar is obtained by the subtraction of carbon-based yield of gaseous and solid products from the total. We also evaluated the catalytic performance in terms of both the yield of residual tar and the formation rate of CO + H₂ + 4CH₄ for the comparison, where 4 times of CH₄ is based on the reaction formula of CO hydrogenation to methane (CO + 3H₂ → CH₄ + H₂O). The performance was evaluated for 15 min in the activity test. The formation rate of the gaseous products was almost stable during 15 min on all the catalysts used in this study.

2.4. Steam reforming of toluene as model compound of tar derived from biomass

Steam reforming of toluene was carried out using a fixed-bed reactor. The reactor was made of a quartz tube (4 mm i.d.). The reaction temperature was monitored by a thermocouple, which was inserted into the outlet of the catalyst bed. The catalyst weight was 0.1 g, which provided the bed thickness of 7 mm. Before experiment the catalysts were reduced in flowing H₂ and N₂ (H₂/N₂ = 30/30) at 773 K for 0.5 h. After the reactor was purged with N₂, the steam and toluene were supplied through vaporizing chamber. In the vaporization chamber, the water and toluene were vaporized and the carrier gas N₂ sweeps out the vapor to the catalyst bed. The molar ratio of steam to carbon was S/C = 3.4 and W/F = 0.03–1.1 g h/mol. In this case, F represents the total flow rate of the reactant gas and N₂ carrier gas. The reaction temperature was 873 K. The sample of effluent gas was collected by a syringe and analyzed by a gas chromatograph (GC). The concentrations of CO, CO₂, and CH₄ were measured by FID–GC (Gaskuropack 54) equipped with a methanator and that of benzene and toluene was measured by FID–GC (DB-1) and that of H₂ was determined by TCD–GC (MS-13X). The flow rate of the effluent gas was measured by a bubble flow meter. Toluene conversion is calculated

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