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Promoting effect of trace Pd on hydrotalcite-derived Ni/Mg/Al catalyst in oxidative steam reforming of biomass tar

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ABSTRACT

Promoting effects of trace noble metals (Pd, Pt, Au, Ru, Rh and Ir) on the activity and stability of the Ni catalyst prepared from the hydrotalcite-like compounds containing Ni, Mg, and Al were investigated in steam reforming and oxidative steam reforming of tar derived from pyrolysis of biomass. The optimum loading of Pd was 0.05 wt% (0.05PdNi catalyst; molar ratio of Pd/Ni = 0.0023), and this catalyst showed higher performance than the other noble-metal-added catalysts with the same noble metal/Ni molar ratio. Characterization results indicated that the addition of 0.05 wt% Pd enhanced the reducibility of Ni species and the dispersion of Ni metal particles simultaneously, which can be attributed to the highest catalytic performance. The monometallic Ni catalyst (0PdNi) totally lost the catalytic activity due to the oxidation of catalytically active Ni metal particles by oxygen after two hour stability test in oxidative steam reforming. In contrast, the oxidation of Ni metal particles did not occur on 0.05PdNi catalyst, and the 0.05PdNi catalyst showed stable catalytic performance during the two hour stability test, which can be due to the formation of highly dispersed Pd atoms on the surface of Ni metal particles on the 0.05PdNi catalyst as suggested by Pd *K*-edge EXAFS analysis.

1. Introduction

Gasification of biomass into syngas is expected to be used in various fields such as power generation and the production of hydrogen and liquid fuels through C1 chemistry (e.g., methanol and Fischer–Tropsch oil) [1–6]. Various methods for the conversion of biomass to syngas have been known and reviewed [1,2,5,6]. One of the methods is the combination of the pyrolysis of biomass and the subsequent catalytic steam reforming of the tar derived from the pyrolysis at low temperature. Here, this method is denoted as "pyrolysis + reforming". The merit of this pyrolysis + reforming is that the very high temperature needed in the case of non-catalytic steam gasification is not necessary [1,2]. In the pyrolysis + reforming method, one of the key points is the development of metal catalysts with high performance in the steam reforming of the tar from biomass pyrolysis, and the catalyst development has been summarized in reviews [7–9]. It has been reported that Ni or Co catalysts and the catalysts modified with various kinds of additives and supports are effective to the steam reforming of the tar and its model compounds [10–39]. One demerit of this pyrolysis + reforming is that external heat supply is required because the steam reforming of tar is a highly endothermic reaction. In the case of natural gas conversion technology, the steam reforming of methane has been shifted to the autothermal reforming of methane where oxygen is introduced to the reactor, and exothermic reaction of methane with oxygen is combined with the endothermic steam reforming of methane [40,41]. This enables the effective heat supply from the exothermic reaction to the endothermic reaction. Furthermore, the catalyst development for the introduction of oxygen together with methane and steam to the catalyst bed, which is denoted as oxidative steam reforming, has been attempted in order to suppress the hot spot formation at the catalyst bed inlet. The Ni catalyst effectively modified with small amount of suitable noble metals has been developed for this oxidative steam reforming of methane [42–51].

In the present study, we attempted the oxidative steam reforming of biomass tar, where oxygen is introduced to the catalyst bed together with steam and the tar from the pyrolysis of biomass. Besides, the presence of oxygen can significantly reduce the amount of the deposited coke on the catalysts surface, which is one of the main causes of catalyst deactivation [52–54]. Nickel based catalysts have been extensively studied in the pyrolysis + reforming

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system for the conversion of biomass to syngas because of its high reforming activity and low cost [7,10–13,16,18,19,23,26,28–39,55]. However, Ni metal species can be oxidized by oxygen and lose their reforming activity in the oxidative steam reforming of biomass tar like the case of that of methane [46,51,56–58]. A possible method for the suppression of the oxidation of Ni metal species is the modification of Ni catalysts with a trace of noble metal. Modification of Ni catalyst for the steam reforming of methane with a trace of noble metal has been reported to be very effective to the enhancement of the catalyst reducibility [51].

Hydrotalcite-like compounds (HTlcs) are suitable precursors for preparing well-dispersed and thermally stable metal particles as active components for catalysts [59]. It has been reported that Ni/Mg/Al catalyst prepared by the calcination and reduction pretreatment of Ni-Mg-Al HTlcs has nanocomposite structure of Ni metal particles supported on Mg(Ni, Al)O (MgO-like phase containing Al and Ni) particles with a similar size to the Ni particles [60]. In particular, the nanocomposite structure can be connected to the high performance in the steam reforming of biomass tar [18,22,23,60]: high dispersion of Ni metal particles was maintained by the presence of Mg-Al-O mixed oxides among Ni metal particles [60]; the amount of coke was decreased by cohesive contact between Ni metal particles and the oxide particles [60]; Ni particles was re-dispersed by calcination–reduction process for regeneration [15,23]. Ni/Mg(Ni, Al)O catalysts also exhibited high stability at the steady operation in steam reforming of methane [61,62]. However, it was totally deactivated just after first steam purging in the daily start-up and shut-down operation (DSSO) because of the oxidation of Ni metal by steam. In contrast, dipping 0.05 wt% of Ru, Rh, and Pt and 0.1 wt% of Pd on Ni/Mg(Ni, Al)O catalysts inhibited the deactivation even after four-cycled DSSO. This can be interpreted by the formation of noble metal-Ni alloys on the surface of Ni particles, and the hydrogen spillover effect of noble metal or noble metal-Ni alloy significantly enhanced the reducibility of Ni particles and the suppression of the oxidation [61,62]. Moreover, alloying Ni with trace noble metals has also been reported to be effective to increase the performance of Ni catalysts in oxidative steam reforming of methane in various aspects such as activity, resistance to Ni oxidation, suppression of hot-spot formation and resistance to coke deposition [42–51]. The effect of noble metals such as Pt, Ru, Rh, and Pd has been investigated on Ni/CeO_2/Al_2O_3 catalyst in the pyrolysis + reforming of cedar wood [13,14]. Pt was found to be the most effective additive to enhance the catalytic performance and this can be explained by the Pt-Ni alloy formation. In contrast, the effect of Pd, Ru, and Rh addition to Ni/CeO_2/Al_2O_3 catalyst was not so effective and this behavior can be explained by the result that Pd, Ru and Rh species interacted with CeO_2 rather than Ni.

In this work, the Ni catalyst prepared from hydrotalcite-like compounds containing Ni, Mg, and Al by the calcination and reduction, which has been reported to be effective to the steam reforming of biomass tar, was used as a reference catalyst. The modification of the Ni catalyst with a trace of noble metals was attempted in order to develop the catalyst for the oxidative steam reforming of the tar. We optimized a noble metal component and the additive amount of the noble metal. The catalyst was characterized and the relation is discussed between the characterization results and the catalytic performances in oxidative steam reforming of tar.

2. Experimental

2.1. Catalyst preparation

A hydrotalcite-like compound containing Ni, Mg and Al was prepared by co-precipitation method as described previously [60]. An aqueous solution containing the nitrates of Ni^{2+}, Mg^{2+}, and Al^{3+} (Wako Pure Chemical Industries, Ltd.) was dripped slowly into a beaker containing an aqueous solution of sodium carbonate under stirring at room temperature. Simultaneously, an aqueous solution of sodium hydroxide (2 M) was dripped into the beaker to maintain the pH at 10 ± 0.5. The resulting suspension was then kept at room temperature for 24 h. The resulting precipitate was filtered, washed several times with deionized water and dried at 383 K for one night. The resultant was ground to fine powders and calcined at 1073 K for 5 h in a static air atmosphere to give Ni/Mg/Al mixed oxide powder. The molar ratio of Ni/Mg/Al was 9/66/25 and the amount of Ni corresponded to 12 wt%.

Noble metals (Pd, Pt, Au, Ru, Rh and Ir) were added to the Ni/Mg/Al mixed oxide powder by the impregnation method. To per gram of Ni/Mg/Al powder 5 ml aqueous solution of noble metal precursors ($PdCl_2$, $H_2PtCl_6 \cdot 6H_2O$, $HAuCl_4 \cdot 4H_2O$, $RuCl_3 \cdot nH_2O$, $RhCl_3 \cdot 3H_2O$, and H_2IrCl_6) was dripped for 1 h at room temperature, followed by evaporation of water in air at 343 K and drying at 383 K for one night. The samples were ground to fine powders and calcined at 1073 K for 5 h in a static air atmosphere again. The obtained material was pressed to a disk, crushed and sieved to particles with 30–60 mesh size (Φ 0.3–0.6 mm). The loading amount of Pd was 0–0.5 wt% and the molar ratio of Pd/Ni was 0–0.023. The loading amount of other noble metal was set to the molar ratio of noble metal/Ni = 0.0023. Catalysts in this work are denoted as *x*PdNi, where *x* means the weight percentage of Pd to total weight of the catalyst.

2.2. Biomass

Cedar wood (ground to about 0.1–0.3 mm in size) was used as the biomass feedstock for all the experiments. The moisture content of the cedar wood was 7.2%. The dry-based composition by weight was C 50.8%, H 6.0%, N 0.2%, O 41.8%, and ash 1.1%. The elemental analysis of cedar wood was carried out by the Japan Institute of Energy.

2.3. Catalytic reaction

Oxidative steam gasification of biomass was conducted using a laboratory-scale continuous feeding dual-bed reactor under atmospheric pressure. The scheme of the reactor was similar to that in our previous report and is shown in supporting information (Fig. S1) [11]. The biomass was introduced into the primary bed, and pyrolyzed to form gaseous and solid products at the reaction temperature which was measured by the thermocouple located at the outside of the reactor. The solid product, which is called char, was accumulated in the primary bed. Steam was supplied by a syringe pump into the primary bed. The gaseous products mainly composed of volatile tar, H_2, CO, CO_2, and CH_4 were introduced to the secondary catalyst bed together with steam and carrier gas N_2. Oxygen was introduced near the inlet of catalyst bed during the oxidative steam reforming by a thin tube which was also used for determination of coke amount [11].

The activity tests were carried out at 773 K. The amount of the catalyst used was 0.3 g. The catalyst was reduced with H_2/N_2 (30/30 ml/min) mixed gas at 1073 K for 0.5 h, and these conditions were the same as the ones optimized for 0PdNi catalyst [60]. The reduction gas was purged with N_2 (60 ml/min (2.5 mmol/min)), and then biomass (60 mg/min), water (555 μmol/min), and oxygen (0, 350 or 555 μmol/min) were further fed to the reactor in order to start the activity test. The molar ratio of feeding rate of externally-added O_2 /feeding rate of externally-added steam/feeding rate of carbon in the biomass is represented by ex-O_2/ex-H_2O/C in each experimental result. The effluent gas went through an iced water