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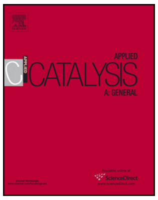

Comparative study on steam reforming of model aromatic compounds of biomass tar over Ni and Ni–Fe alloy nanoparticles

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ABSTRACT

Steam reforming of tar model compounds (benzene, toluene and phenol) was carried out using Ni–Fe/Mg/Al catalysts prepared by calcination and reduction of hydrotalcite-like precursor. Ni–Fe/Mg/Al (Fe/Ni = 0.25) catalyst showed higher activity (~twice conversion rate based on catalyst weight) and better resistence to carbon deposition (~one order smaller amount of deposited carbon) than Ni/Mg/Al. The difference in the weight-based rate and carbon deposition amount between catalysts with and without Fe was large when benzene or toluene was used as a substrate and high steam/carbon (S/C) ratio was applied. On the other hand, when phenol was used as a substrate, relatively large amount of carbon derived from decomposition of phenol was deposited on Ni–Fe/Mg/Al catalyst even with high (3.8) S/C ratio. The catalyst loses some activity for steam reforming of toluene when treated with phenol (untreated catalyst: ~80% conversion of toluene (rate 51 μmol $g^{-1}{}_{\text{-cat}}$ s^{-1}); treated catalyst ~60% (rate 38 μmol $g^{-1}{}_{\text{-cat}}$ s^{-1})), probably because of the deposited carbon from phenol. Kinetic studies and O_2- or H_2O-TPO studies showed that phenol was strongly adsorbed on Fe site as well as Ni site, and the adsorbed phenol could be converted into carbonaceous species under the reaction conditions. On the other hand, the adsorbed phenol on Ni site underwent steam reforming, and the reaction was promoted by Fe.

1. Introduction

Steam reforming of aromatics has received more and more attentions relating to the gasification of biomass to synthesis gas and hydrogen [1–10]. The product gases are used as a gaseous fuel for power generation and they are converted to liquid fuels and chemicals by Fischer–Tropsch and methanol syntheses. One of the problems in the gasification of biomass is a trouble caused by tar by-product. Tar is a mixture of various condensable organic compounds and it is derived from the pyrolysis reaction of cellulose, hemicellulose and lignin which are the main components of biomass. The components of tar include aromatics, oxygen-containing compounds, complex poly-aromatic hydrocarbons and so on [3,11,12]. In particular, aromatics tend to be major at higher gasification temperature. Therefore, toluene, phenol and so on have been used as model compounds of the biomass tar. One of the effective methods to remove the biomass tar from the effluent gas is the catalytic steam reforming of the tar compounds. The catalyst for the tar removal in the gasification processes requires high activity and stability including carbon deposition behavior. Various catalysts have been investigated such as Ni [13–56], Co [13,17–22,57–64], Fe [65–67], noble metal [13,18,21,25,68–75] and natural mineral catalysts [76–78] using tar model compounds such as oxygenates [13–21,41,57,74], hydrocarbons (typically toluene) [22–40,50–56,58–60,66,67] and phenols [65,67–74,76–78] or biomass-derived tar itself [36,38,40,42–50,60–64,74,75]. As a catalytically active component, Ni has high potential for the steam reforming reactions due to the low cost and high activity. Low stability and coke formation are problems of Ni catalysts, and the effect of additives and supports have been investigated to overcome these problems. The attempts include the modification of Ni with some oxide species such as Ce, Mn and La oxides [29,32,39,43–47], and the effects include activity increase and suppression of coke formation. In particular, suppression of coke formation was evident for most cases (up to one order smaller amount than that without modification). The use of redox-active support materials such as CeO_2-based oxides and perovskite oxides has been also tested [17,18,33,34,37,41,42]. The effect of formation of Ni–Fe

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alloy by Fe addition to Ni catalysts has been also investigated. It has been reported that olivine-supported Ni catalyst shows high performance such as high resistance to carbon deposition (<0.1% selectivity to carbon at 1073 K reaction) in the steam reforming of toluene [26,28]. Fe_2O_3–Al_2O_3-supported Ni catalyst was tested for toluene steam reforming and good stability was reported (time on stream 26 h at 923 K with little loss of activity) [30]. Perovskite catalysts containing both Ni and Fe have been intensively studied [51–56]. Oemar et al. investigated the effect of Fe addition to perovskite La–Ni oxide catalyst, and higher stability and activity of Fe-added catalyst was observed in 8 h reaction of toluene at 923 K [52]. We have reported that Ni–Fe/α-Al_2O_3 catalyst was evaluated in the steam reforming of biomass tar [50]. The addition of Fe to Ni/α–Al_2O_3 enhanced catalytic activity and catalyst stability. Ni–Fe/α-Al_2O_3 (Fe/Ni = 0.5) showed the best catalytic performance: tar conversion became 86% from 64% by addition of Fe; the catalyst life was more than three times longer than that of Ni/α-Al_2O_3. Characterizations of used Ni–Fe catalysts in many systems showed that significant amount of Fe was in the metallic state and formed Ni–Fe alloy. The surface of Ni–Fe alloy particles can be the active site with the high performance. However, the particle size of Ni–Fe alloy tends to be large (>20 nm), and uniformity of the Fe/Ni ratio in each alloy particle was very low. We have very recently prepared Ni–Fe bimetallic catalysts by using a hydrotalcite-like precursor containing Ni and Fe ions [50]. In the catalyst with Fe/Ni = 0.25 after reduction (denoted as Ni–Fe/Mg/Al (Fe/Ni = 0.25)) the alloy formation was verified, and the particle size of Ni–Fe alloy was much smaller (ca. 10 nm) than that on Ni–Fe/α-Al_2O_3. The Fe/Ni ratio of each Ni–Fe alloy particle was much more uniform (0.17–0.22 from TEM-EDX) than that in Ni–Fe/α-Al_2O_3 (0.06–2.6 on the sample with Fe/Ni = 0.5). The Ni–Fe/Mg/Al catalyst consisted of the uniform Ni–Fe alloy nanoparticles (ca. 10 nm) and MgO-based solid solution (ca. 13 nm), and this structure can suppress the sintering of the oxide and aggregation of metal particles. Moreover, Ni–Fe/Mg/Al (Fe/Ni = 0.25) showed higher steam reforming activity regarding biomass-derived tar, toluene and phenol than Ni/Mg/Al, Ni–Fe/Mg/Al with other Fe/Ni ratios and Ni–Fe/α-Al_2O_3 [38,50]: for example, the conversion of phenol increased from 11% (Ni–Fe/α-Al_2O_3 (Fe/Ni = 0.5)) to 47% (Ni/Mg/Al) and 71% (Ni–Fe/Mg/Al (Fe/Mg = 0.25)) [50]. However, the decrease of deposited carbon amount from biomass tar by Fe addition to Ni/Mg/Al was not sactifactory (carbon yield: 5.7% → 4.0%), while the amount of deposited carbon from toluene over Ni–Fe/Mg/Al was much smaller (1/50) than that over Ni/Mg/Al. The kinetics and the carbon deposition behavior are not investigated in detail. Therefore in this work we conducted the analysis of the kinetics of the steam reforming reaction and carbon deposition behavior during the reforming reaction of toluene, benzene and phenol. We found that carbon deposition from phenol on Fe species limits the excellent performance of Ni–Fe/Mg/Al catalysts.

2. Experimental

2.1. Catalyst preparation

The procedures of the catalyst preparation were the same as those reported in the previous paper [38,50]. Ni–Fe/Mg/Al catalysts were prepared from hydrotalcite-like precursors containing Ni^{2+}, Mg^{2+}, Fe^{3+} and Al^{3+}. Ni–Fe–Mg–Al hydrotalcite-like precursors were prepared by co-precipitation of the nitrates of metal components. A mixed aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ (WAKO Pure Chemical Industries, Ltd., 98.0%, 99.0%, 99.0% and 99.9%, respectively) was added to an aqueous solution of Na_2CO_3 (WAKO Pure Chemical Industries, Ltd., 99.5%) under stirring at room temperature and a constant pH of 10 ± 0.5. The pH of the solution was adjusted with an aqueous solution (2 M) of NaOH (Soekawa Chemical Co., Ltd., 99.0%). The resulting suspension was kept at room temperature for 24 h. The precipitate was filtered, washed several times with distilled water, and dried at 383 K for 12 h. The precipitate was ground to fine powders and then calcined at 1073 K for 5 h in a static air atmosphere. The obtained material was pressed to a disk, then crushed and sieved to particles with 30–60 mesh size (0.3–0.6 mmφ). The molar ratio of (Ni + Mg)/(Fe + Al) was fixed at 3. The molar ratio of Fe/Ni in Ni–Fe/Mg/Al was adjusted to be 0.25 or 1.0.

For comparisons, three catalysts derived from Ni–Mg–Al, Fe–Mg–Al and Mg–Al hydrotalcite-like compounds were also prepared and denoted as Ni/Mg/Al, Fe/Mg/Al and Mg/Al, respectively. They were prepared by co-precipitation of the nitrates of corresponding metal components, followed by drying and calcination at 1073 K for 5 h. The contents of Ni and Fe in Ni/Mg/Al and Fe/Mg/Al, respectively, were 12 wt%. The composition and the characterization data in the previous paper [50] of the prepared catalysts are summarized in Table S1.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were performed on an Ultima IV diffractometer (Rigaku) using Cu Kα radiation (λ = 0.154 nm) generated at 40 kV and 40 mA. The diffraction pattern was identified by comparing with those in the Joint Committee of Powder Diffraction Standards (JCPDS) database.

2.3. Steam reforming of toluene, benzene and phenol

Steam reforming of model compounds of tar derived from biomass was carried out using a fixed-bed reactor. The used reactants were toluene, benzene and phenol (WAKO Pure Chemical Industries, Ltd., 99.5%, 99.8% and 99.0%, respectively). 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 30–100 mg, which provided the bed thickness of 3–7 mm. Before the experiment, the catalysts were reduced in flowing H_2 and N_2 ($H_2/N_2 = 30/30\ \mathrm{ml\,min^{-1}}$) at 1073 K for 0.5 h to transform Ni^{2+} species in Mg(Ni,Al)O periclase phase to well-dispersed Ni particles [50]. After the reactor was purged with N_2, reactants were supplied through the vaporizing chamber. In the vaporization chamber, water and reactant were vaporized at 573 K and the carrier gas N_2 sweeps out the vapor to the catalyst bed. The standard feeding rate of reactants and carrier gas was toluene/H_2O/N_2 = 0.75/8.9/26.8 $\mathrm{mmol\,min^{-1}}$ and 0.38/4.4/26.8 $\mathrm{mmol\,min^{-1}}$, benzene/H_2O/N_2 = 0.90/8.9/26.8 $\mathrm{mmol\,min^{-1}}$ and 0.45/4.4/26.8 $\mathrm{mmol\,min^{-1}}$ and phenol/H_2O/N_2 = 0.80/9.4/26.8 $\mathrm{mmol\,min^{-1}}$ and 0.40/4.7/26.8 $\mathrm{mmol\,min^{-1}}$. The conditions with lower concentration of substrate were applied to the reactions in earlier sections of this study (Figs. 1 and 2). The contact time in the steam reforming reaction is calculated to be W/F = 0.01–0.05 $\mathrm{g\,h\,mol^{-1}}$. Here, F represents the total flow rate of the reactant gas and N_2 carrier gas and W represents the catalyst weight. For the tests with higher W/F than 0.05 $\mathrm{g\,h\,mol^{-1}}$, the feeding rate was decreased with the molar ratio constant. The reaction temperature was 873 K. This temperature was lower than those in typical studies of tar removal [10]. Lower temperature for tar removal not only increases the efficiency of total system of biomass gasification, but also highlights the difference between catalysts in the performances, especially the resistance to coke formation. The sample of effluent gas was collected by a heated syringe and analyzed by a gas chromatograph (GC). The concentrations of CO, CO_2, and CH_4 were measured by FID-GC (Gaskuropack 54) equipped with a methanator. The concentrations of toluene, benzene and phenol were measured by FID-GC (DB-1) and that of H_2 was determined by TCD-GC (MS-13X). The flow rate of the effluent gas was measured by a bubble flow meter. The main reaction schemes in