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Steam reforming of biomass tar model compound at relatively low steam-to-carbon condition over CaO-doped nickel–iron alloy supported over iron–alumina catalysts

J. Ashok, S. Kawi*

Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 119260, Singapore

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ABSTRACT

CaO doped iron–alumina-supported nickel–iron alloy catalysts were tested in a fixed-bed reactor for steam reforming of toluene as a biomass tar model compound at a relatively low steam-to-carbon (S/C) ratio of 2. The influence of doping CaO to iron–alumina support was also explored for the steam reforming reaction. Ni supported on a CaO(1.5)–Fe_2O_3–Al_2O_3 support (Ni/Ca(1.5)–Fe–Al) gave superior catalytic performance in terms of activity and stability over other catalysts. Ni/Ca(1.5)–Fe–Al gave a toluene conversion of more than 80% for a period of 22 h testing at a S/C ratio of 2. XRD analysis showed that the Ni–Fe alloys formed were stable throughout the reforming reaction. It was observed from XPS results that the surface of the reduced Ni/Ca(1.5)–Fe–Al catalyst was enriched with Fe species compared to other catalysts. These enriched surface Fe species play the role of co-catalysts by increasing the coverage of oxygen species during the reforming reaction to enhance the reaction of toluene and to suppress coke formation. The temperature-programmed surface reaction (TPSR) with water reveals that the Ni/Ca(1.5)–Fe–Al catalyst can activate water molecule at relatively lower temperature over other CaO doped catalysts. TGA analysis on spent catalysts reveals that all CaO-containing catalysts generally result in lower carbon formation rates as compared to Ni/Fe–Al catalyst.

1. Introduction

Catalytic steam reforming of biomass tar to produce H_2-rich synthesis gas is increasingly attractive because of the rising interest in utilizing biomass derived from forest, agricultural, and municipal solid waste materials as a renewable energy source [1–5]. However, one of the most critical problems in utilization of biomass via gasification and/or pyrolysis at low temperature (500–650 °C) is the formation of tars, an undesirable reaction that is an impediment to the commercialization of the biomass utilization process. In addition, these tars are largely aromatic hydrocarbons, such as benzene, toluene, and naphthalene, which harness large amounts of energy, thereby lowering the energy content of the product gas. These tars also cause operational problems when cooled and condensed in heat exchangers, lowering heat transfer efficiencies, plugging pipes, and so on. Therefore, efficient conversion of biomass tars is crucial in the biomass gasification and/or pyrolysis processes. Among many processes [6,7], catalytic steam reforming of biomass tar is a considerably attractive approach for tar removal during biomass gasification and/or pyrolysis processes since it produces syngas, which is a high-value gas product [8–10]. Hence, it is greatly essential to develop highly effective catalysts that are capable of converting the biomass tar to synthesis gas.

Among the effective supported metal (such as Ni, Co, Rh, Pt, Pd, etc.) catalysts [11–13], Ni-based catalysts have been widely investigated for the steam reforming of biomass tar because of its low cost, abundance and high activity [14–16]. However, the major drawback for Ni catalysts is their rapid deactivation due to the coke deposition [17]. In the process of developing highly effective Ni-based catalysts, several approaches reported include modification of Ni with other metal oxides [18–20], alloying with other transition metals [21–25], identification of suitable support [26,27] and modification of support with other metal oxides [18,28]. Among them, alloying of Ni with other metals is one of the promising approaches in recent times to improve the catalytic performance in terms of activity, stability and coke resistance. One such suitable modifier is Fe [22–24,29–31]. Ni–Fe bimetallic catalysts have been reported to be effective for the catalytic reforming of methane, iso-octane, biomass tar, and tar model compounds [29–34]. Our previous studies [22,23] have also shown that improved performance in steam

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* Corresponding author. Tel.: +65 6516 6312; fax: +65 6779 1936.
E-mail address: chekawis@nus.edu.sg (S. Kawi).

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reforming activity for Ni–Fe catalysts is due to the presence of an intimate interaction between Fe and Ni, which results in the formation of a Ni–Fe alloy. Tomishige et al. [24] also obtained a similar conclusion for Ni–Fe/Al_2O_3 catalyst in cellulose gasification. In addition, Tomishige et al. [29,31] has also recently reported that the presence of uniform Ni–Fe alloy particles in Ni–Fe/Mg/Al catalysts enables a high catalytic performance in the steam reforming of toluene and phenol. As has been reported [22–24], Fe plays the role of a co-catalyst. Since Fe has a higher oxygen affinity than Ni, the addition of Fe to Ni catalysts can increase the coverage of oxygen atoms during the steam reforming reactions. This increment in oxygen coverage is vital in enhancing the performance of Ni–Fe alloy species in steam reforming of tar.

Additionally, in order to improve the catalytic performance further, modification of catalyst support has also been suggested in literature. Catalysts with basic properties tend to decrease the rate of coke formation in many reforming reactions, such as steam reforming of toluene [18,30], CO_2 reforming of methane [35–37], steam reforming of methane [37], steam reforming of ethanol [38,39], which in turn leads to reduced catalyst deactivation over time and helps to increase the stability of the catalyst. Furthermore, calcium oxide (CaO) is widely known to be a CO_2 sorbent, assisting the production of hydrogen-rich gas [40,41] in biomass gasification for hydrogen production. This option has recently gained tremendous attention due to the low cost and abundance of CaO [42,43]. CaO can play the vital roles of not only CO_2 sorbent, but also tar reforming catalyst [43]. Removing CO_2 from the gasification reaction as soon as it is formed alters the equilibrium composition of the produced gas and promotes the production of gas rich in hydrogen [42]. In steam reforming of ethanol, the addition of CaO to Ni catalyst could prevent the formation of crystalline carbon which is more difficult to be removed, resulting in higher catalyst stability. Moreover, it was reported that Ca addition promoted water adsorption and provided abundance of adsorbed OH groups on Ni catalyst which could facilitate the C—C break, resulting in higher ethanol conversion [38,39]. It has been reported [44–48] that the surface properties of Ni/Al_2O_3 systems could be improved by introduction of alkaline earth metal oxides (MgO and CaO) due to the increase of steam-carbon reaction and the neutralization of the acidity of the support to suppress cracking and polymerization reactions. In biomass gasification, it was also reported that basic nature of a catalyst is favorable for tar decomposition catalysts since higher catalyst basicity can enhance the catalyst activity [49].

Recently, we have reported [22] Ni–Fe alloy supported over Fe_2O_3–Al_2O_3 catalysts for steam reforming of toluene (SRT) at 650 °C. In that study, we have observed that Ni/Fe_2O_3–Al_2O_3 catalyst calcined at 900 °C (Ni/Fe–Al) is able to activate water molecule more effectively at lower temperatures than other catalysts calcined at lower temperatures. Building on the strength of this catalyst, we explored Ni/Fe–Al catalyst system further in this study at a considerably low steam-to-carbon (S/C) ratio of 2. In order to improve the catalytic performance further, we doped Ni/Fe–Al catalysts system with various amounts of Ca species to obtain Ni–Fe alloy supported over CaO–Fe_2O_3–Al_2O_3 system. The thus-obtained catalysts were investigated for their catalytic performance for steam reforming of toluene (SRT) as a biomass tar model compound at a reaction temperature of 500–800 °C and at S/C ratio of 2. Steam reforming of toluene proceeds according to the reactions as shown below, followed by water gas shift reaction.

$$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2 \quad (S/C = 1) \tag{1}$$

$$C_7H_8 + 14H_2O \rightarrow 7CO_2 + 18H_2 \quad (S/C = 2) \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

Other reactions such as dry reforming, hydrodealkylation, carbon formation by toluene decomposition and cracking are also included in this process.

2. Experimental

2.1. Catalyst preparation

CaO–Fe_2O_3–Al_2O_3 mixed oxides (nominal Ca:Fe:Al molar ratios of 0:1:2, 0.5:1:2, 1:1:2, 1.5:1:2 and 2:1:2) were prepared using a co-precipitation method. In a typical preparation method, nearly saturated solutions of nitrates (ferric nitrate, calcium nitrate and aluminum nitrate) were homogeneously mixed in the required molar ratios. The pH value of the solution was slowly adjusted to ~10 with 2 M aqueous ammonia solution, and the solution was then stirred continuously for another 1 h to complete the precipitation process. The precipitated solution was dried in an oven at 100 °C for 24 h and then calcined at 900 °C for 4 h in an air atmosphere. The as-prepared catalyst supports were labeled as Ca(x)–Fe–Al, where x represents the molar composition of Ca species.

The 10 wt.% Ni supported catalysts were prepared by a simple wetness impregnation method wherein an aqueous solution containing the required amount of $Ni(NO_3)_2{\cdot}6H_2O$ was mixed with the requisite amount of support material to yield the respective Ni weight percent needed. The mixtures were then dried under constant stirring at 80 °C and further dried at 100 °C for another 24 h before they were calcined in air at 700 °C for 4 h. The thus-prepared catalysts were labeled as Ni/Ca(x)–Fe–Al, where x represents the nominal molar composition of Ca species in CaO–Fe_2O_3–Al_2O_3 support.

2.2. Catalyst characterization

The surface areas of the freshly calcined catalysts and their supports were measured by N_2 physical adsorption at −196 °C in an ASAP 2020 instrument. The specific surface area was calculated by applying the Brunauer–Emmett–Teller (BET) method. The actual compositions of all the calcined catalysts were measured using Scanning Electron Microscope coupled to an Energy Dispersive Spectroscopy (SEM-EDX, Jeol, JSM-6701F). The samples were degassed under vacuum condition to remove impurities. Platinum coating (about 10 nm thickness) was carried out at 20 mA for 40 s. The X-ray diffraction (XRD) pattern of each catalyst was measured on a Shimadzu XRD-6000 diffractometer using Cu Kα radiation. The catalyst was placed on an aluminum slide and scanned from 2θ of 20° to 80° at a ramp rate of 2°/min. The beam voltage and current used were 40 kV and 30 mA, respectively. H_2 temperature-programmed reduction (TPR) measurements for fresh catalysts were performed on a Quantachrome ChemBET-3000 instrument. Prior to the TPR measurement, 0.04 g of catalyst was outgassed in He for 1 h at 300 °C to remove any moisture and then cooled to room temperature. Then 5% H_2/N_2 gas was introduced to the catalyst while the furnace temperature was increased at a heating rate of 10 °C/min to 1000 °C. The CO chemisorption was done in the Quantachrome ChemBET-3000 instrument. Prior to the CO pulse chemisorption measurement, the sample (W = 50 mg) was reduced at 700 °C for 1 h under H_2 gas before it was cooled to 0 °C in a helium flow of 80 mL/min. The CO chemisorption was measured at 0 °C by introducing pulses of CO using 5% CO/He with a loop volume of 250 μL. The pulses were continued until no further uptake of CO was measured. Temperature programmed desorption (TPD) of CO_2 profiles were analyzed using mass spectroscopy (Thermostat GSD300). 100 mg of catalyst sample was used in each analysis. Prior to the adsorption of CO_2, the sample was reduced at 700 °C for 1 h under H_2 gas environment. After