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Investigation of Ni/Fe/Mg zeolite-supported catalysts in steam reforming of tar using simulated-toluene as model compound

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ABSTRACT

Catalytic performance of Ni/zeolite, Ni-Fe/zeolite, and Ni-Fe-Mg/zeolite catalysts were investigated in steam reforming of toluene as a biomass tar model compound to explore promotional effect of MgO and Fe on Ni/zeolite support. The Ni-Fe-Mg/zeolite catalysts with optimum metallic composition showed higher catalytic performance over corresponding monometallic Ni and Fe catalysts and Ni-Fe/zeolite (bimetallic) catalysts. Addition of Mg to Ni-Fe/zeolite catalyst enhanced the tar reforming reactions and increased the carbon deposition tolerance. The results suggest that Ni-Fe/zeolite and Ni-Fe-Mg/zeolite catalysts have great potential for application in the steam reforming of biomass tar.

1. Introduction

In recent years, the utilization of biomass as a renewable and sustainable energy source, particularly the application of municipal solid waste in gasification, has attracted tremendous technical interest [1]. The hydrogen-rich syngas can be used as a fuel for many downstream applications. However, one of the most critical issues in biomass gasification is the formation of tars [2]. Biomass tars cause serious hazards to equipment in downstream applications due to their low condensation temperatures, resulting in activity reduction and an increase in the frequency of maintenance requirements [3]. Therefore, tars should be extensively removed from the effluent stream of biomass gasification [4].

Many processes have been developed to eliminate tar from the syngas stream [5]. The techniques employed are mainly physical and chemical technologies [6,7]. Among these techniques, catalytic steam reforming of biomass tar has attracted many interests as a viable means for reducing biomass tar in the effluent gas of biomass gasification [8]. This technique produces high-value syngas.

The chemical reactions carried out during the tar formation process involve a complex mixture of hydrocarbon decomposition equilibrium reactions. These decomposition reactions involve steam reforming, steam dealkylation, hydrocracking, hydrodealkylation, dry reforming, carbon formation, and many cracking reactions [9].

The Ni/SiO$_2$ catalysts have been investigated in methanol, ethanol, and for tar reforming resulting in improved syngas yield [10,11].

Catalytic steam reforming has been stated as being a potential technique in tar removal from gaseous products by transformation of tar into hydrogen and carbon monoxide in the presence of steam [2]. The catalytic tar reforming of tar using iron-, cobalt-, and nickel-based catalysts, dolomites, olivine, and catalyst-loaded zeolites has been extensively studied in the catalytic reforming of tar at temperatures in the range of 600–900 °C [2]. Zeolite provided good catalytic activity in the catalytic cracking of tar. A small amount of coke is formed over zeolite-supported catalysts [2]. It has been reported that the Y type of zeolite was capable of removing 100% of tar in catalytic cracking at high-temperature syngas when using 1-methylnaphthalene as a model of the tar compound [2]. The transition metal-impregnated or exchanged zeolite catalysts were applied for partial and deep oxidation of hydrocarbons [2]. The results showed that the transition metal cations improved zeolite activity for hydrocarbon conversion. The hydrocarbon conversion phenomenon is explained by developing strong zeolite acidity and proper oxygen chemisorption [2].

The global search for new feedstocks to supply hydrogen is on the rise. One of the main feedstocks targeted for hydrogen production through reforming is municipal solid waste (MSW) [12]. It is also, one of the promising low-cost raw materials for hydrogen production, by eliminating MSW-derived tar, is the refused derived fuel (RDF) [13].

The thermal processing of RDF produces a high quality syngas with robust H_2 and CO molar ratio in the effluent gas stream [14]. This valuable syngas can be further used in a variety of applications such as combustion in a micro-turbine for power generation and downstream applications such as Fischer-Tropsch synthesis [15].

The overall goal of this research was to understand the role and mechanism of Ni-Fe-Mg/zeolite catalyst on tar cracking. To the best of our knowledge, Ni-Fe-Mg/zeolite catalyst have not been investigated before.

2. Materials and methods

2.1. Materials and catalyst preparation

Iron (Fe) and nickel (Ni) over zeolite catalysts were prepared by the incipient impregnation method of catalysis [10,14,15]. Aqueous solutions of nickel nitrate tetrahydrate and iron nitrate hexahydrate were used as metal precursors [16]. Different molar ratios of these precursors to zeolite were used, leading to different metal weight concentrations (3–9 wt%). The excess water was initially evaporated at 105 °C. The samples were dried overnight at 105 °C and calcined under air at 500 °C for 4 h before storage for later use. Magnesium (Mg) catalyst over zeolite was prepared by the sequential incipient impregnation method. Aqueous solution of magnesium nitrate tetrahydrate was used as metal precursor. The calcination process was similar to calcined nickel and iron.

The mechanism of Ni-Fe-Mg/Zeolite catalyst on tar cracking is:

Steam reforming: $\quad C_nH_m + nH_2O \rightarrow nCO + \dfrac{n+m}{2}H_2$
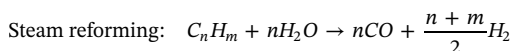
2.2. Catalyst characterization

2.2.1. Programmed reduction (TPR) analysis

The temperature-programmed reduction (TPR) analysis was performed on Autochem 2920 from Micromeritics. Prior to TPR measurement, 0.07 g of catalyst was outgassed in helium for 1 h at 300 °C to remove any impurities, followed by cooling of the sample to room temperature; 10% H_2/Ar gas was then introduced to the catalyst as a reductive gas while the furnace temperature was increased at a heating rate of 10 °C/min to 1000 °C. The flow rate of H_2/Ar was 30 ml/min. The final furnace temperature was held for 30 min. The consumption of H_2 was monitored continuously with TCD gas chromatograph equipped with a dry ice trap in order to remove H_2O from the effluent gas. The amount of H_2 was measured using the peak area in TPR profiles. Due to the different reduction degrees of Ni/zeolite catalysts, the dispersion degree of Ni (D%) and the average particle size of Ni in reduced form (d_{Ni}) were mainly calculated using the following equations [6]:

$$D\% = \frac{1.17X}{W \times f}$$

And

$$D_{Ni} = \frac{97.1}{D\%}$$

Where X is the H_2 uptake by the catalyst in μmol/g-catalyst, W is the weight percentage of active Ni, and f is the fraction of NiO reduced into Ni (reduction degree).

2.2.2. Temperature-programmed desorption (TPD) analysis

The qualitative and quantitative basicity strength of nickel and iron on zeolite were performed by the most common method in the literature, namely, TPD of CO_2. CO_2-TPD profiles were analyzed using a Micromeritics autochem 2920. One hundred mg of Ni-zeolite and Ni-Fe/zeolite were tested by the adsorption of CO_2 at 50 °C for 30 min. The samples of monometallic and bimetallic catalysts were purged in helium for 30 min. Desorption of CO_2 was carried out during the heating stage of the samples. The heating range was 30 °C–1000 °C. The heating ramp rate was set to 10 °C/min.

2.2.3. X-ray diffraction (XRD) analysis

The crystallographic analysis of mono, bi, and promoted catalysts were carried out using a D8 DISCOVER X-ray diffractometer (Bruker Optics, Inc., Billercia, MA). This instrument is used to study the crystallinity behavior of mono, bi, and promoted catalysts. The diffraction spectra were recorded in a 2θ angle range of 10°–70° with a PSD detector at a scanning rate of 0.014°/s. Cu Kα radiation (λ = 1.54 Å) produced at 40 mA and 40 kV was used as the X-ray source.

2.3. Catalytic activity test

The catalytic reaction was carried out in a fixed bed reactor with an inner diameter of 4 mm and a length of 400 mm. Sample amounts of 0.03 g and 0.07 g were investigated in each test and held by quartz wool placed in the middle of the reactor. In the catalytic steam reforming test that was performed, toluene composition in the affluent stream was 320 μmol. This toluene concentration was attained by diluting the toluene feed stock using nitrogen and H_2O in the steam reforming. Prior to the chemical catalytic reaction, the catalyst was reduced in 30 ml/min of hydrogen at 873 K for 6 h. After reduction, the system was purged with 120 ml/min nitrogen while the temperature was kept at the desired temperature of 873 K. Water and toluene were vaporized at a close temperature range. The temperature difference is only 100 °C; therefore, both were preheated and mixed in a preheater at 400 °C. This mixed solution was used to ensure the proper dilution of toluene to create a homogeneous phase of nitrogen and toluene before approaching the reactor chamber. This homogeneous phase is controlled to maintain the vapor state. The reaction products were then passed through a cold trap to condense unreacted toluene and moisture in the effluent stream. The non-condensable gas products were collected using gas sampling bags and analyzed using a GC-TCD type of gas chromatography (7890A) unit from Agilent technologies. The qualitative and quantitative analyses were carried out using the chromatogram of the produced gases. The chromatogram reflects the peak areas for all produced gases which were then converted to a volume percentage through a calibration curve. The gas chromatography is equipped with a thermal conductivity detector. The thermal conductivity detector is mainly used to detect all inorganic gases. The total flow rate of the product gases was measured using a needle bubble flow meter. The conversion of toluene was evaluated in terms of the carbon balance, which was calculated using the following formula [15]:

$$X\ toluene\,(\%) = \frac{nCO + nCO_2}{7 \times nr\ in} \times 100$$

where n is molar flow rate of each gas.

3. Results and discussion

3.1. Characteristics of catalysts

3.1.1. TPR analysis results

The TPR showed that NiO has a reduction peak at 470 °C. This peak has a dramatic decrease after the NiO was supported on zeolite and a new peak was detected at temperatures above 550 °C (Fig. 1). The latter peak was ascribed to the physical interaction between zeolite and NiO, resulting in the increase of reduction temperature. Therefore, Ni and NiO coexist on the surface of zeolite under the annealing temperature of 550 °C. From the TPR study as shown in Fig. 1, all the mon, bi and promoted bimetallic catalysts are reduced at the temperature range between 300 and 700 °C. Therefore, in this work, all catalysts were reduced under H_2 flow at 700 °C for 6 h before use. It is noted that, the doping of nickel with iron seems to decrease the monometallic catalysts