Steam reforming of model gasification tar compounds over nickel catalysts prepared from hydrotalcite precursors

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ABSTRACT

Nickel catalysts derived from hydrotalcite-like compounds, with 10 and 20 wt.% NiO loading, were prepared and tested in steam reforming of different tar model compounds: benzene, toluene and naphthalene. Naphthalene was used in toluene solution. The catalysts were evaluated in terms of activity with temperature and deactivation with time, using a steam/carbon ratio of 1.5. The catalysts presented similar behavior, with slightly higher conversions for the catalyst with 10% NiO in benzene and toluene reforming. H_2 formation was much lower than that predicted by thermodynamics, with CO_2 as the main product at low temperatures and CO at high temperatures. Naphthalene is much more difficult to be converted, and inhibits the toluene reforming. Both catalysts showed good stability with time on stream despite the high amount of carbon deposit and Ni sintering. The amount and morphology of the coke are dependent on the nature of aromatic compound.

1. Introduction

The depletion of the fossil fuel reserves and the global warming issues lead to an increasing interest in a sustainable development. Biomass is considered the renewable energy source with the highest potential to contribute to the energy needs of modern society [1]. The gasification for producing syngas is regarded as one of the most promising options for utilizing biomass. The syngas can be not only directly used for power generation in gas turbines but also catalytically converted to methanol, liquid hydrocarbons via Fischer–Tropsch synthesis and other chemical products [2].

One of the most critical problems in the biomass gasification process is the presence of tars in the produced gas. Tar is a complex mixture of aromatic hydrocarbons that causes condensation and plugging problems in the downstream process equipment, engines and turbines, and deposition on the catalyst surface [3].

Since the middle of the 1980s, research on tar reduction has been carried out mainly by catalytic cracking due to the advantages of converting tar into useful gases and adjusting the composition of the product gases [2]. Several reviews have been published on different catalysts for tar conversion, including natural minerals, alkali metal catalysts and Ni-based catalysts [3–8].

Nickel catalysts, mainly supported on alumina, have been extensively studied for steam reforming of tar because of their high activity and low cost; however, a rapid deactivation due to carbon deposition has been generally observed. To improve the catalytic performance of Ni catalysts in steam reforming of tars, several ways are being employed, such as changing the support and/or adding promoters. For example, alkali earth oxides MgO and CaO improve the surface properties of the Ni catalysts and enhance their resistance to carbon deposition [9,10]. Kong et al. [11] studied a series of supported Ni catalysts in CO_2 reforming of toluene and reported that Ni/MgO presented the best catalytic performance due to the strong interaction between NiO and MgO and the high dispersion of Ni particles in the basic environment.

Hydrotalcite-like compounds (HTLCs) or layered double hydroxides, also known as anionic clays, have a lamellar structure with alternating positively charged mixed metal hydroxide sheets and negatively charged interlayer anions along with water molecules [12]. Thermal treatments of HTLCs give a stable, high surface area, homogeneous mixture of oxides with very small crystal size, which by reduction results in high metallic dispersion. Ni–Mg–Al mixed oxides prepared from hydrotalcite precursors have been successfully used as catalysts for various reactions, including reforming and oxidation of methane [13,14] and ethanol reforming [15].

One of the challenges in laboratory studies of tar conversion is the use of real gasification streams because the complexity of tar composition makes it difficult to understand the reaction mechanisms. Therefore, most studies use tar model compounds, such as benzene, toluene and naphthalene, but only few works compare their reactivities. Coll et al. [16] investigated the steam reforming of five tar model compounds with commercial nickel catalysts and found the following order of reactivity: benzene > toluene ≫ anthracene > pyrene > naphthalene. They also observed that the tendency towards coke formation grew as

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the molecular weight of the aromatic increased. On the other hand, Jess [17] reported that benzene is a more stable compound; the thermal cracking of aromatic hydrocarbons was evaluated in the presence of hydrogen and steam and the order of reactivity obtained was: toluene ≫ naphthalene > benzene, without use of any catalyst.

In this context, the objective of this work is to study steam reforming of model tar compounds over nickel catalysts prepared from hydrotalcite precursors, comparing the activity for conversion of three different aromatics: benzene, toluene and naphthalene. We have evaluated how the nature of the aromatic compound affects the catalyst performance, product distribution and coke formation.

2. Experimental

2.1. Catalyst preparation

Hydrotalcite-like compounds were prepared by coprecipitation from aqueous solutions at room temperature, as described in [15]. An aqueous solution containing appropriate amounts of nitrate precursors (Al/(Ni + Mg + Al) = 0.25 and [Ni + Mg + Al] = 1.5 M) was added dropwise to a vigorously stirred solution containing Na_2CO_3 and NaOH ($CO_3^{2-}/Al^{3+} = 0.375$ and $OH^-/Al^{3+} = 6.3$). The gel formed was aged for 18 h at 60 °C. The resulting solid was filtered, washed with distilled water (90 °C) until pH 7 and dried overnight at 100 °C.

The Ni,Mg,Al-mixed oxides were produced by calcination of HTLCs under flowing air (60 mL min^{-1}), using a heating rate of 10 °C min^{-1}, from room temperature to 500 °C and keeping at this temperature for 2 h. The NiO loading in calcined samples was 10 and 20 wt.% (10NiHT and 20NiHT).

The structural, textural and reducibility properties of the prepared catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption (BET specific surface area) and temperature-programmed reduction (TPR), presented in a previous paper [15].

2.2. Catalytic tests

The catalytic tests were performed at atmospheric pressure in a fixed bed Inconel reactor (9 mm ID). 300 mg of catalyst was used and placed between quartz wool and the bed was filled with silicon carbide. The catalysts were reduced in situ at 1000 °C for 2 h before reaction.

The liquid reactants were fed by HPLC pumps into an evaporator at 180 °C, diluted by 50 vol.% of N_2, and then carried out to the reactor. The S/C (steam/carbon) ratio was 1.5 with gas hourly space velocity (GHSV) of 20,000 h^{-1}. Naphthalene was used in solution with toluene (10 wt.% of naphthalene).

All products were analyzed online by a Shimadzu GC-2014 gas chromatograph. H_2, CO, CO_2 and CH_4 were determined by TCD with molecular sieve and Carboxen columns, while aromatic hydrocarbons were detected by FID with an Equity column.

Aromatic conversion can be defined by Eq. (1):

$$X(\%) = \frac{C_{aromatic}^{in} - C_{aromatic}^{out}}{C_{aromatic}^{in}} \times 100 \tag{1}$$

where $C_{aromatic}^{in}$ and $C_{aromatic}^{out}$ are aromatic molar flow rates of the inlet and outlet gases. Gas product composition was calculated using Eq. (2) and benzene yield was determined by Eqs. (3) and (4) for toluene and naphthalene reforming, respectively:

Product composition (%)

$$= \frac{\text{mole of each gas product}}{\text{total moles of gas products } (H_2 + CO + CO_2 + CH_4)} \times 100 \tag{2}$$

$$Y_{benzene}(\%) = \frac{6 \times C_{benzene}^{out}}{7 \times C_{toluene}^{in}} \times 100 \tag{3}$$

$$Y_{benzene}(\%) = \frac{6 \times C_{benzene}^{out}}{7 \times C_{toluene}^{in} + 10 \times C_{naphthalene}^{in}} \times 100. \tag{4}$$

2.3. Catalyst characterization after reaction

The formation of coke on the catalysts was analyzed by thermogravimetric analysis (TGA) in equipment TA Instruments SDT Q600. The used catalysts were heated to 1000 °C with a rate of 10 °C min^{-1} in air flow (50 mL min^{-1}).

The morphology of the coke formed on the catalysts was analyzed by scanning electron microscopy (SEM) using a Hitachi TM-1000 equipment. The acceleration voltage was 15 kV, using backscattering electron.

X-ray powder diffraction (XRD) patterns of the used catalysts were recorded in a Rigaku Miniflex II, with a monochromator using Cu Kα radiation (30 kV and 15 mA) over a 2θ range from 5 to 90°, with step of 0.05° and 2 s by step.

3. Results and discussions

Firstly, blank tests were performed with each tar model compound, where the reactor was filled with only silicon carbide. The results are displayed in Fig. 1 in terms of aromatic conversion. Benzene is more reactive over the whole temperature range, while naphthalene is much less reactive at high temperatures (>850 °C). The higher reactivity of benzene in thermal conversion is in contrast to the results of Jess [17], who obtained the following order of reactivity: toluene ≫ naphthalene > benzene. It is worth noting that the Jess experiments were performed in the presence of hydrogen, which can be favoring hydrodealkylation reactions. The toluene conversions are identical in reforming of toluene or naphthalene/toluene solution, which is coherent with thermal cracking. The main product in gas phase was CH_4, followed by CO and CO_2; H_2 formation was only significant in reaction with benzene. Benzene yield increases with temperature, reaching 26% in toluene reforming and 18% in naphthalene/toluene reaction at 900 °C. Thus, benzene is a key component in thermal cracking of toluene and naphthalene, as observed by Jess [17].

Many parallel and consecutive reactions can take place during steam reforming reactions and the product distribution is a result of the
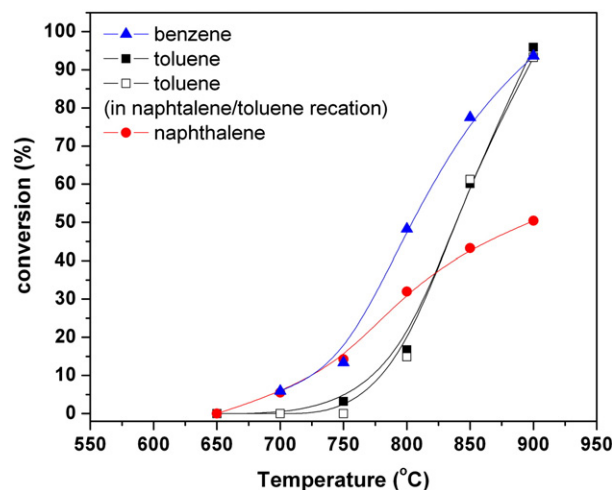

Fig. 1. Blank tests performed with Inconel reactor filled with SiC during steam reforming of benzene, toluene and naphthalene/toluene.