Steam reforming of tar from a biomass gasification process over Ni/olivine catalyst using toluene as a model compound

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Abstract

A Ni/olivine catalyst, previously developed for biomass gasification and tar removal during fluidized bed steam gasification of biomass, was tested in a fixed bed reactor in toluene steam reforming as a tar destruction model reaction. The influence of the catalyst preparation parameters (nickel precursor, calcination temperature and nickel content) and operating parameters (reaction temperature, steam to carbon S/C ratio and space-time) on activity and selectivity was examined showing a high toluene conversion and a low carbon formation compared to olivine alone. The steam reforming of toluene was found to be of zero order for water and first order for toluene. Activation energy required for Ni/olivine was determined to be about 196 kJ mol^{-1} in accordance with literature. Catalyst activity and stability and its resistance against carbon formation were discussed on the basis of X-ray diffraction (XRD), transmission electron microscopy (TEM) and temperature programmed oxidation (TPO) results. Characterization before test (XRD, temperature programmed reduction (TPR), Mössbauer spectroscopy) have shown the presence of NiO–MgO solid solution, formed on the surface of olivine support, which explains the efficiency of the catalyst calcined at 1100 °C. After test, Ni–Fe alloys were observed (TEM, Mössbauer spectroscopy). It was suggested that magnesium oxide enhanced steam adsorption, facilitating the gasification of surface carbon and that Ni–Fe alloys prevented carbon deposition by dilution effect.

1. Introduction

Since the constant increase in petroleum price, use of biomass as a partial replacement for fossil fuels via biomass to liquid (BTL) or biomass to gas (BTG) processes is more and more intended. The value of biomass can be increased via thermal, biological or physical processes. Thermochemical conversion technologies are especially useful to produce fuels, chemicals, combined heat and power with high-energy efficiencies. Among them, biomass gasification has attracted a lot of interest by producing a gas rich in CO and H$_2$ used for methanol or Fischer-Tropsch synthesis, chemicals production or electricity generation (turbine, gas engine or fuel cells). Previous studies, in pilot [1] as well as in demonstration scale [2], have demonstrated that biomass steam gasification, in the dual fluidized bed gasifier (fast internally circulating

fluidized bed gasifier: FICFB), was an efficient process used to produce a nearly nitrogen-free (<2%), hydrogen-rich product gas.

However, one of the most crucial problems in biomass gasification technology [3] is the removal of tar, which is a mixture of condensable aromatic compounds [4]. Tar can condense or polymerize into more complex structures in exit pipes, heat exchangers or on particulate filters, leading to choking and attrition. This can result in a decrease of total efficiency and an increase in the cost of the process. Tar elimination from the gasification product is necessary before additional usage in any application.

Tar removal technologies can be divided into two approaches: hot gas cleaning after the gasifier (secondary methods), and treatments inside the gasifier (primary methods). The secondary methods include tar cracking, either thermally or catalytically, or mechanical separation using cyclones, filters or scrubbers. Although these methods have proven to be effective, treatments inside the gasifier are gaining more attention as they may eliminate the need for downstream

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cleanup. The different approaches of primary treatment are: (a) proper selection of operating parameters, (b) use of bed additive/catalyst and (c) gasifier modifications [5].

For both secondary and primary methods, the catalytic steam reforming process is a very attractive technique for tar destruction [4]. Calcined dolomites are the most widely used non-metallic catalysts for tar conversion [6–15], but their low attrition resistance renders them inappropriate for use in fluidized bed reactors. An effective solution for tar reforming was proposed by Corella [16], consisting of a calcined dolomite guard bed to decrease tar content, followed by a fixed bed Ni catalyst reforming reactor operating at about 800 °C. Olivine, another naturally occurring mineral, has demonstrated activity in tar conversion similar to that of calcined dolomite [15,17]. Its advantage, in comparison with dolomite, is a high attrition resistance, allowing its direct use as a primary catalyst in fluidized bed gasifiers.

Ni catalysts have been used extensively for biomass gasification tar conversion [12,16,18–21] because of their high tar destruction activity, along with the added advantages of methane reforming and water gas shift activity, allowing adjustment of the H_2/CO ratio of the product gas. Some studies [22,23] have also shown that nickel catalyzes the reverse ammonia reaction, reducing the amount of NH_3 in gasification product gas. This is particularly important if it is used in a gas turbine, as NO_x can be formed easily from NH_3.

Two main limitations for Ni catalysts should be stressed. Because of the attrition phenomena in fluidized bed reactors, the use of Ni catalysts was generally as a secondary catalyst in separate fixed bed reactors, although recently some authors have developed or studied nickel catalysts for fluidized bed use [24–28]. The second limitation of nickel catalysts is the rapid deactivation, caused by carbon formation on the catalyst surface. This can be substantial when the tar level in the product gas is high.

Previously, a Ni/olivine catalyst was developed [29,30], characterized [31,32] and used in the FICFB gasifier as a primary catalyst showing activity in tar destruction and methane reforming [33]. To understand better the parameters influencing its activity, a study using simplified model conditions was required. Toluene was used as a model tar compound as it represents a stable aromatic structure found in tar formed during high-temperature processes [4].

The goal of the present work was to demonstrate the efficiency of a Ni/olivine catalyst for tar reforming, as well as its resistance to deactivation by carbon deposition in a fixed bed laboratory reactor. The efficacy of catalyst was tested as a function of different preparation parameters (calcination temperature, nickel precursor) and different operating conditions (reaction temperature, S/C ratio and space-time). Kinetic parameters were evaluated for the optimized catalytic system and special attention was paid to catalyst stability, especially stability linked to carbon formation.

2. Experimental

2.1. Catalyst preparation

2.1.1. Olivine support

Natural olivine was acquired from an Austrian mine (Magnolithe GmbH). It was delivered after calcination at 1600 °C over 4 h, followed by crushing and sieving to obtain particle sizes between 400 and 600 μm. This olivine will be referred to initial olivine. Its composition (30.5 wt% of Mg, 7.1 wt% of Fe and 19.6 wt% of Si), obtained by atomic absorption (CNRS Centre in Vernaison), resulted in the mean global formula $(Mg_{0.94}Fe_{01})_2SiO_4$ (without taking into account the minority elements: Ni, Ca, Al, Cr, lower than 0.2 wt% each). In fact, as shown in [34], natural olivine contains mainly the phase of $(Mg_{0.94}Fe_{0.06})_2SiO_4$ with small quantities of its oxidation products: $MgSiO_3$, and iron oxides (~3 wt% of iron in the form of $MgFe_2O_4$ and probably α-Fe_2O_3). The specific surface area of olivine is very low (<1 $m^2\,g^{-1}$). Reducibility of this initial olivine calcined in the same conditions as the Ni/olivine catalyst was described previously [34].

2.1.2. Ni/olivine catalyst

In order to study the effect of the preparation parameters, a series of Ni/olivine catalysts were synthesized with various nickel precursors and contents, and calcined at different temperatures. Ni/olivine catalysts were prepared by wet impregnation of initial olivine using an excess of nickel salt (nitrate, chloride or acetate) aqueous solution. After solvent evaporation, the sample was dried overnight at 100 °C and calcined at various temperatures (400, 900, 1100 or 1400 °C) over 4 h, using a temperature increase slope of 3 °C min^{-1}. The concentration of the nickel nitrate solution was modified in order to obtain catalysts containing from 1.5 to 5.7 wt% of nickel after calcination at 1100 °C [30].

The different preparation ways resulted in the series of Ni/olivine catalysts described in Table 1.

2.2. Steam reforming of toluene (SRT)

2.2.1. Experimental bench and operating conditions

The scheme of the experimental bench used for toluene steam reforming is shown in Fig. 1. Experiments were carried out at atmospheric pressure in a fixed bed quartz reactor (6.6 mm i.d.) placed in a furnace. The catalyst bed was held by quartz wool in the uniform temperature zone. The temperature was monitored by a thermocouple placed outside of the reactor near the catalyst bed. The furnace temperature was controlled with a Microcor III PR temperature controller. The catalyst was initially activated under the reactants gas mixture during 30 min at 750 °C and then tested for 7 h at a given temperature. The temperature range (560–850 °C) of the experiments was chosen to cover all possible conditions that may occur in practice in the FICFB gasifier.

For the feed gas mixture, argon was used as a diluent gas. Its flow was regulated by mass flowmeter. Water and toluene were introduced by syringe pumps into a vaporization furnace (120 °C), and then carried to the reactor by argon flow.