



Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

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



Fernanda M. Josuinkas^a, Cristina P.B. Quitete^b, Nielson F.P. Ribeiro^a, Mariana M.V.M. Souza^{a,*}

^a Escola de Química – Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Bloco E, sala 206, CEP 21941-909 Rio de Janeiro/RJ, Brazil

^b Petrobras, CENPES, Processo de Conversão de Biomassa, Rua Horácio Macedo, 950, Cidade Universitária, CEP 21941-915 Rio de Janeiro/RJ, Brazil

ARTICLE INFO

Article history:

Received 18 August 2012

Received in revised form 29 September 2013

Accepted 6 January 2014

Available online 1 February 2014

Keywords:

Tar

Steam reforming

Hydrotalcite

Nickel

Coke

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. H₂ formation was much lower than that predicted by thermodynamics, with CO₂ 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.

© 2014 Elsevier B.V. All rights reserved.

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 CO₂ 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

* Corresponding author. Tel.: +55 21 25627598; fax: +55 21 25627596.
E-mail address: mmattos@eq.ufrj.br (M.M.V.M. Souza).