Applied Catalysis A: General 536 (2017) 1–8

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Perspective

Application of Brazilian dolomites and mixed oxides as catalysts in tar removal system

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ARTICLE INFO

Article history:
Received 26 November 2016
Received in revised form 27 January 2017
Accepted 14 February 2017
Available online 16 February 2017

Keywords:
Tar
Steam reforming
Coking
Thermodynamic simulation

ABSTRACT

Two different classes of catalysts, three dolomites with different origins and two Ni- based mixed oxides containing cerium or lanthanum, were used on tar removal by steam reforming. Mixed oxides presented higher toluene conversion than dolomites, which lost activity due to hydration and carbonation. Mixed oxides were quite active for toluene steam reforming, obtaining high conversions for long periods, 16 h at 700 °C and 70 h at 800 °C. Despite the good activity, the samples showed high coke content after reaction, probably caused by the low steam/carbon ratio. The coked catalyst can be completely regenerated by steam. Thermodynamic simulation of coking tendency showed that carbon is formed at low temperatures even at high steam/carbon ratios.

1. Introduction

Gasification has been a widely studied technology for syngas production, focusing on bubbling and fluidized gasifiers, using biomass, sewage sludge and forest residues as the main feed [1–3]. The gas produced on gasification contains CO, H_2, CO_2, CH_4, aliphatic hydrocarbons, olefins, tar, some contaminants (ex.: H_2S and NH_3), and other compounds. Tar is a class of compounds with molecular weight higher than benzene and can cause a lot of operational problems. Due to the several possibilities to take advantage of this gas to produce chemicals, fuels and electricity, the gas composition should be adjusted and some cleaning procedures are needed [4].

Downdraft fixed bed gasifiers produce typically 20–100 gNm^{-3} of tar, containing phenols, aldehydes and furfurals, while for updraft fixed bed, the content is about 0.1–1.2 gNm^{-3}, with mainly naphthalene, phenanthrene, pyrene, toluene, indene and phenols [4,5]. On the other hand, fluidized gasifiers produce a tar content of 10–25 gNm^{-3}, with predominance of the following components: toluene, phenol, naphthalene, methylnaphthalene, phenanthrene, pyrene, benzopyrene and anthracene [5]. Toluene is the main component in a typical composition of biomass tars [6]; moreover, benzene is generally not included in tar [7]. Our experience with a circulating fluidized bed (CFB) pilot plant operating with sugarcane bagasse showed that large quantities of tar accumulates in the coldest points of plant, such as lines, heat exchangers, vessels and pumps, so the whole plant should be kept warmed and many unwanted stops are necessary to clean the high amount of deposited tar.

It is very common to add catalysts on the gasifier bed, like some minerals, as dolomite, olivine, calcite, magnesite, and kaolin, to improve the removal of tar [8–11]. Dolomite presented higher tar conversion than calcite and magnesite [10] and also than olivine [11]. The gas in the gasifier exit is at high temperature (above 750 °C) and humidity (20–60%), so tar removal by steam reforming is a good option [12]. Biomass gasification can generate about 20–200 ppm of H_2S [13]; despite its low concentration, it can cause poisoning on nickel catalysts used on steam reforming.

Our recent studies showed that the catalysts can be easily damaged by coke formation in the presence of high levels of tar on gasification streams [14–17]. The gasification conditions must be optimized to reduce tar content; the alternatives are to increase the gasification temperature, use a guard bed or develop catalysts for gas cleaning more resistant to coking. This work focuses on the last two alternatives.

One way to increase the lifetime of catalysts is through the use of two reactors in series for tar removal [18]; the first running as a guard bed using a low cost catalytic material, as dolomites. Dolomites can retain a portion of H_2S and HCl and promote tar cracking, but they are significantly active only above 800 °C [10]. Besides mineral catalysts, other catalysts can be used for tar removal, as metallic supported [14–20] or bulk catalysts. Bulk cat-

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http://dx.doi.org/10.1016/j.apcata.2017.02.014