Perspective

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

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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.

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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 sugar-

cane 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-

alysts, as perovskites, have been employed when it is necessary thermal and coking resistance, as reported by Mawdsley et al. [21] for autothermal reforming of isoctane on $La_{0.8}Sr_{0.2}M_{0.9}Ni_{0.1}O_3$ (where M = Cr, Mn and Fe). Steam reforming of toluene was evaluated on $La_{1-x}Ce_xNiO_3$ perovskite catalyst (x = 0, 0.2 and 0.4) by Soongsprasit et al. [22], showing that the catalyst with higher Ce content presented higher toluene conversion (87% at 800 °C). Ce substitution on La in perovskite lattice inhibited carbon formation and sintering [14,16,22,23].

The objective of this study is to evaluate an ensemble of catalysts that could be used for tar removal; for this proposal, some Brazilian dolomites and prepared mixed oxides were tested on steam reforming of toluene, a tar model compound. Although a lot of dolomites have been reported for tar removal, they largely varied in composition and catalytic properties depending on their origin. Most studies only evaluated dolomites at high temperatures (above 750 °C); in our work the catalytic activity of dolomites was evaluated at temperatures below 650 °C, aiming the use as a guard bed in a CFB gasification pilot plant. The use of perovskites containing nickel and some promoters in their formulation, like cerium and lanthanum, seems interesting, because they can increase the resistance to coking, and have excellent thermal stability. The perovskite formulations chosen here have not been reported in the literature yet, for this reaction.

2. Experimental

2.1. Catalyst preparation

Two perovskite catalysts with theoretical formula of $Ce_{0.4}Ni_{0.6}AlO_3$ (P1) and $La_{0.2}Ni_{0.8}AlO_3$ (P2) were prepared by coprecipitation method using metal nitrates as precursors and 14.5%m/m NH_4OH solution as precipitation agent. The precipitation was conducted with slow agitation at room temperature for 1 h after nitrate addition, with pH control at 9–11. Then, the samples were filtered and washed with water until pH 7, followed by drying overnight at 120 °C. The calcination was performed in two steps: at 500 °C for 4 h and at 900 °C for 5 h, in static atmosphere.

Other three catalysts were used for comparison: dolomites from different Brazilian mining companies (D1, D2 and D3). They were calcined at 900 °C for 4 h in static atmosphere. Table 1 shows the identification of the catalysts and their elemental composition.

2.2. Catalyst characterization

The chemical composition of the catalysts was determined by X-ray fluorescence (XRF) using a Rigaku Primini spectrometer, equipped with X-ray generator tube of palladium.

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

The textural characteristics, such as BET specific area, pore volume and average pore diameter (BJH method), were determined by N_2 adsorption-desorption at −196 °C in a Micromeritics ASAP

2400. Prior to the analysis the samples were pretreated at 400 °C in vacuum.

Temperature programmed reduction (TPR) was performed using a Micromeritics Autochem II. The gas used was 10% H_2 in Ar, with a flow of 40 mLmin^{-1}, and the temperature increased to 1000 °C using a rate of 10 °C min^{-1}. Firstly the samples were pretreated with 40 mLmin^{-1} of Ar at 400 °C. The hydrogen consumption was monitored by thermal conductivity detector (TCD).

Thermogravimetric (TG) analysis of dolomites was performed in Mettler Toledo (TGA/SDTA 851E) using 40 mLmin^{-1} of N_2, from 25 to 1000 °C, with rate of 10 °Cmin^{-1}. The melting point was analyzed on TG/DSC Netzsch at 25–1400 °C, using 50 mLmin^{-1} of N_2, and rate of 10 °Cmin^{-1}.

The coke content of the used catalysts was also determined using TGA, with the same conditions of temperature and heating rate, under 40 mLmin^{-1} of synthetic air. The morphology of coke was analyzed by scanning electron microscopy (SEM), using a JEOL JSM6490LV equipment with secondary electrons.

The hydrogen chemisorption capacity was used to obtain a measure of the Ni dispersion and particle size, using Micromeritics ASAP 2010C, in a hydrogen pressure range from 0.002 to 260 mmHg and 35 °C. The catalysts were previously reduced at different temperatures, from 800 to 1000 °C, with pure hydrogen.

The basicity of the samples was determined by temperature programmed desorption of CO_2 (CO_2-TPD) using thermogravimetric (TG) balance of Mettler Toledo (TGA/SDTA 851E). The method consisted of the following steps: (1) Pretreatment with 40 mL min^{-1} of Ar from 25 to 400 °C at 20 °C min^{-1}, for 30 min; (2) Cooling until 25 °C with 40 mL min^{-1} of Ar at 15 °C min^{-1}; (3) Adsorption of CO_2 with 40 mL min^{-1} at 25 °C for 30 min; (4) Purge with 40 mLmin-1 of Ar, at 25 °C for 60 min; (5) Desorption of CO_2 with 40 mLmin^{-1} of Ar from 25 to 900 °C at 5 °C min^{-1}; (6) Cooling to room temperature. CO_2 signal was monitored by mass spectrometer, Pfeiffer Vacuum GSD 320 T1 Thermostar, using the fragment m/e- = 44. The total basicity was calculated using the weight loss of desorption period (100–900 °C).

2.3. Catalytic tests

The steam reforming of toluene was performed in a microactivity unit (PID Eng&Tech) using a fixed bed Inconel reactor (9 mm of internal diameter). It was used 300 mg of catalyst placed between quartz wool and the bed was filled with silicon carbide. The P1 and P2 catalysts were reduced in situ at 850 °C for 2 h before reaction.

Toluene and water were pumped separately, vaporized at 180 °C before entering the reactor and mixed with 50%N_2, used as a carrier. The flow rate was 100 mLmin^{-1}, with weight hourly space velocity (WHSV) of 20,000 mLg^{-1}h^{-1}, steam/carbon (S/C) molar ratio of 1.5 and temperature of 400–800 °C. Stability tests were performed with the same WHSV and two different S/C ratios and temperatures: (i) S/C = 1.5, 700 °C during 16 h for P1 and P2 catalysts, and (ii) S/C = 3.0, 800 °C during 70 h for P2 catalyst.

All products were analyzed online by Shimadzu GC-2014 gas chromatograph with two TCDs, one for analysis of the H_2 and the other for CO, CO_2, and CH_4, and a flame ionization detector (FID) for toluene and benzene analysis.

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

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

where $C_{toluene}^{in}$ and $C_{toluene}^{out}$ are toluene molar flow rate of the inlet and outlet gases.

Table 1
Catalyst description and composition.

Catalysts		Elemental Composition (wt%)
D1	Dolomite MP	Ca: 34, Mg: 25, Fe: 3.4, Mn: 2.1, Si: 1.2
D2	Dolomite Pr	Ca: 50, Mg: 16, Si: 1.2, Fe < 0.1
D3	Dolomite O	Ca: 51, Mg: 16, Fe < 0.1
P1	$Ce_{0.4}Ni_{0.6}AlO_3$	Al: 34, Ce: 21, Ni: 5.8
P2	$La_{0.2}Ni_{0.8}AlO_3$	Al: 28, La: 22, Ni: 17