Short communication

Coking resistance evaluation of tar removal catalysts

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ABSTRACT

The tendency towards coke formation on nickel catalysts supported on hexaaluminates of barium, lanthanum and lanthanum/cerium was evaluated by two different methods: model reaction of cyclohexane dehydrogenation and thermogravimetric analysis using a synthetic gas composition. The ratio between hydrogenolysis and dehydrogenation rates provided a good indication of the potential for coke formation on the catalyst and is correlated to the nickel particle size. Thermogravimetric analysis was performed using a synthetic mixture containing H_2, CO, CO_2 and CH_4, and also in the presence of C_2H_4. The catalyst supported on barium hexaaluminate presented lower coking rate and higher activity in toluene steam reforming, with preferential formation of filamentous carbon.

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1. Introduction

The gasification of biomass is considered a promissory route to produce a synthesis gas rich in hydrogen and carbon monoxide, which can be used not only in gas turbines for power generation, but also for synthesis of various products, including fuels and lubricants, through the proper removal of contaminants, being tar one of them [1–3].

Tar is a mixture of aromatic hydrocarbons that depends on biomass composition and gasification conditions. Catalytic route is an alternative to clean the gas from tar. Several catalysts are proposed in the literature for the catalytic removal of tar, and the most cited are supported nickel catalysts and basic solids, as dolomite and olivine. These materials, however, have limitations due to coking and deactivation by the presence of sulfur and/or ammonia [2–5].

The main challenge in the development of catalysts for gas cleaning is the formation of coke, especially serious in tar removal because of the gas composition, which contains aromatics and olefins, known as coke precursors [6,7]. One way to minimize coke formation is through catalyst formulation, including the type of metal and support, presence and type of promoter and metallic dispersion [8].

Therefore, a relevant question is to find methods to evaluate coking resistance of these catalysts, aiming at the improvement of formulations. Lobo and Trimm [9] performed coking studies using several compounds, as cis-2-butene, ethylene, methane, ethane and propane. They found that deposition from olefins is autocatalytic and accelerated by hydrogen, while carbon formation from paraffins is comparatively slow. Additionally, ethane was used in some works to determine the coking rate, since higher hydrocarbons are more reactive in steam reforming than methane [10,11]. However, it is important to study coke formation using a similar gas composition to that obtained in the gasification, because H_2, H_2O and CO_2 can act on the mechanism of coke removal, as reported previously [12].

The use of hexaaluminates in the development of high temperature catalytic systems has been of interest primarily due to their large surface areas, refractory properties, and resistance to sintering [13]. Hexaaluminate-based catalysts have been widely used in combustion, partial oxidation and reforming reactions [13,14]. Our previous studies showed that nickel catalysts supported on hexaaluminates presented high activity for tar reforming and resistance to coke formation [11,15].

This work used two approaches, model reaction of cyclohexane dehydrogenation and thermogravimetric analysis using a synthetic gas composition, in the evaluation of coking resistance of nickel catalysts supported on barium, lanthanum and lanthanum/cerium hexaaluminates, and these catalysts were tested in steam reforming of toluene (a tar model compound).

2. Experimental

2.1. Catalyst preparation

The nickel catalysts were prepared by incipient impregnation of the hexaaluminate supports with a solution of nickel nitrate (Vetec) in an appropriate concentration to obtain contents of approximately 6 and 14 wt.% of NiO. Barium, lanthanum and lanthanum/cerium hexaaluminates were prepared by the coprecipitation route [11,15]. The prepared catalysts will be labeled as 6NiO-LaCeAl, 6NiO-LaAl, 6NiO-BaAl and 14NiO-LaCeAl.

2.2. Characterization of fresh catalysts

The hydrogen chemisorption capacity was used to obtain a measure of the specific Ni surface area, using Micromeritics ASAP 2010C, in a hydrogen pressure range from 0.002 to 260 mm Hg and 35 °C. Before the experiments, the catalysts were pretreated with hydrogen flow at 500 °C for 2 h.

The catalytic dehydrogenation of cyclohexane was conducted in a microactivity reactor using hydrogen as a gas carrier and a saturator where cyclohexane was maintained at 10 °C. The activities were measured at 300 °C and several hydrogen flows (18, 37, 58 and 76 mL min^{-1}) under atmospheric pressure. The reduction was carried out at 550 °C with hydrogen (40 mL min^{-1}) for 2 h. The gas product was analyzed by a chromatograph, using a Al_2O_3/KCl Plot column. It was considered as first order kinetics to obtain the dehydrogenation and hydrogenolysis rates (Eq. (1)).

$$R = W/\nu = (1/k)\ln(1/(1-X)) \tag{1}$$

where R is the reaction rate (mol g_{cat}^{-1} s^{-1}), W is the catalyst mass (g), ν is the H_2 flow (mL min^{-1}), k is the specific rate constant and X is the conversion for each reaction.

Coking rate was determined by thermogravimetric analysis using TGA-DTA 851 Mettler Toledo. The experiments consisted of the following steps: 1—catalyst drying under 80 mL min^{-1} of nitrogen, with temperature increase up to 400 °C; 2—decrease of temperature to 100 °C that was kept for 30 min; 3—gas exchange to a reducing mixture (10% H_2 in Ar), at 40 mL min^{-1}, saturated with water at 15 °C, and temperature increase to 650 °C for 1 h; 4—gas exchange to a synthetic mixture of GAS 1 (21.5% H_2, 27.3% CO, 42.9% CO_2 and 8.3% CH_4) or GAS 2 (21% H_2, 27% CO, 42% CO_2, 8% CH_4 and 2% C_2H_4), saturated with water at 15 °C. The coking experiment was performed using a dynamic segment, from 350 to 700 °C with a heating rate of 5 °C min^{-1}, considered as the reaction step. The methodology was based on coking studies of Borowieck et al. [16], and the gas composition is similar to that produced in a circulating fluidized bed gasifier [17].

2.3. Catalytic tests

2.3.1. Activity tests

The steam reforming of toluene was performed on a microactivity unit at atmospheric pressure, 500 °C and steam/carbon (S/C) molar ratio of 1.9, with gas hourly space velocity (GHSV) of 612,000 mL g_{cat}^{-1} h^{-1}. Nitrogen passed through water and toluene saturators kept at 15 and 0 °C, respectively. Before reaction, the catalysts were reduced in situ at 650 °C for 2 h. The analysis was performed by a gas chromatograph with FID for toluene analysis.

2.3.2. Stability 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 used 300 mg of the catalyst placed between two pieces of quartz wool and the bed was filled with silicon carbide. The catalysts were reduced in situ at 650 °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 mL min^{-1}, with GHSV of 20,000 mL g_{cat}^{-1} h^{-1}, steam/carbon (S/C) molar ratio of 1.9 and temperature of 650 °C. All products were analyzed online by a 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. After 16 h on stream, the catalyst reactivation was performed maintaining only the steam and nitrogen flows for 1 h; after that, the same S/C was established.

Toluene conversion, gas product composition and benzene yield were calculated as shown in Quitete et al. [11].

2.4. Characterization of used catalysts

Elemental analysis (CHN) was performed in some samples, using a ThermoFinnigan FLASH EA1112 equipment. The used catalyst was burned and gases were analyzed in a gas chromatograph.

The morphology of the carbon species present in the used catalysts was examined by scanning electron microscopy (SEM), using a JEOL JSM6490LV equipment with secondary electrons.

3. Results and discussion

3.1. Characterization of fresh catalysts

Data from hydrogen chemisorption and cyclohexane dehydrogenation is shown in Table 1. Some properties of these catalysts, like textural characterization and crystalline phases, have been previously studied [11,15]. All catalysts were prepared using two different loadings of NiO (6 and 14 wt.%), but it was observed that catalysts with higher contents of NiO are more susceptible to coking (whisker carbon formation), using a synthetic mixture (5% ethane, 10% H_2 and 75% N_2) saturated with water, with exception of 14NiO-LaCeAl [11]. Because of this, 14NiO-LaCeAl was the only catalyst with higher Ni loading included in this present evaluation.

For LaCeAl catalysts the nickel dispersion is almost independent of the nickel loading, because CeO_2 hinders the interaction between nickel and support [18], explaining the high value of the metallic area for 14NiO-LaCeAl. In general, metallic dispersion decreases with nickel content, which was confirmed for nickel catalysts supported on hexaaluminates of lanthanum and barium [11,15].

The dehydrogenation reaction of cyclohexane is considered in the literature as insensitive to geometric and electronic factors [19]. The main reaction products are benzene and hydrogen, produced by dehydrogenation, and methane by hydrogenolysis, favored in the studied conditions. Thus, the benzene formation rate (dehydrogenation reaction) provides an estimate of the metallic area. The 6NiO-BaAl catalyst presented the highest dehydrogenation rate, in accordance with its biggest metallic area.

Dehydrogenation rate does not follow exactly the order of the metallic area, probably due to reducible characteristics of nickel catalysts supported on hexaaluminates, which presented a main reduction peak up to 600–700 °C [11,15,20,21]. As chemisorption technique used 500 °C in the reduction step (due to limitations of the equipment), it could be insufficient to reduce all NiO into metallic Ni.

The hydrogenolysis rate provides an indication of the potential for coke formation on the catalyst [19]. Hydrogenolysis reaction of cyclohexane requires a large number of adjacent nickel sites (large metal particle size), which occurs with reduction of metallic dispersion, affecting the resistance to whisker carbon deposition [22–25]. The ratio between

Table 1
Results of hydrogen chemisorption and dehydrogenation reaction.

Catalyst	Metallic area (m^2 g$_{Ni}^{-1}$)	Metallic dispersion (%)	Average Ni particle size (nm)	R_D [a]	R_H [b]	R_H/R_D
6NiO-BaAl	70	11.0	9.4	156	25	0.16
6NiO-LaCeAl	38	5.7	17	117	26	0.22
6NiO-LaAl	48	7.3	13	101	19	0.19
14NiO-LaCeAl	34	5.2	19	82	33	0.40

All data were calculated based on the designed Ni loading.
[a] R_D = dehydrogenation rate (10^4 mol g_{cat}^{-1} s^{-1}).
[b] R_H = hydrogenolysis rate (10^4 mol g_{cat}^{-1} s^{-1}).