



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 H₂, CO, CO₂ and CH₄, and also in the presence of C₂H₄. 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 H₂, H₂O and CO₂ 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.

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