



Steam reforming of tar using toluene as a model compound with nickel catalysts supported on hexaaluminates



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ABSTRACT

Hexaaluminates of lanthanum, lanthanum/ cerium and calcium were prepared by coprecipitation method and used as supports for nickel catalysts, with 6 and 14 wt% of NiO. After calcination at 1200 °C the hexaaluminate supports consisted of different crystalline phases, including α -alumina, perovskites and oxides, with specific surface areas of 14–18 m² g⁻¹. All the catalysts exhibited nickel reduction peaks in the range of 360–500 °C. Coking rates measured in thermogravimetric experiments using a synthetic mixture were directly correlated with Ni particle sizes. Catalysts with lower Ni dispersion exhibited lower initial toluene conversion at 650 °C. Ce-containing catalysts presented higher stability during 16 h of toluene steam reforming, which is coherent with their higher resistance to coke formation.

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1. Introduction

The utilization of biomass has attracted increasing attention as an alternative energy resource because of depletion of fossil fuel reserves and concerns with environmental issues. The gasification for producing syngas is regarded as one of the most promising options for utilizing biomass [1]. In addition to syngas, biomass gasification also produces some contaminants, such as fly ash, hydrogen sulfide, ammonia, and tars. The nature and amount of the contaminants are related to the biomass composition, the process conditions and type of gasification reactor [2–4].

Tar is defined as the condensable fraction of organic gasification products, largely consisting of aromatic compounds [5]. These tars can cause several problems, such as condensation and plugging on the downstream process equipment, engines and turbines, and deposition on the catalyst surface [5,6]. Tar content can vary from about 0.5 to 100 gm⁻³; however, most applications of product gases require a tar content lower than 0.05 gm⁻³ [1].

Tar may be removed using the catalytic steam reforming process, because the gas produced in gasification has a high temperature ($T > 750$ °C) and a high moisture content (20–60%), favoring the steam reforming [2,3]. Several catalysts have been proposed in the literature for the catalytic removal of tar; the most mentioned

are commercial nickel catalysts and nickel supported on aluminas or dolomites. However, these materials have limitations due to coke formation, sintering and deactivation by the presence of hydrogen sulfide and/or ammonia [5–8]. The coke formation is particularly severe when reforming aromatic hydrocarbons; therefore, development of supported Ni catalysts which have both high activity and coking tolerance is necessary. 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.

Hexaaluminate compounds offer potential advantages as catalytic supports, including high surface areas and resistance to sintering and deactivation in high-steam environments [9]. The hexaaluminates crystallize in either β -Al₂O₃ or magnetoplumbite structure, which consist of alternative stacking of a spinel block and a mirror plane; the structure type is determined by the charge and radius of the large cations in the mirror plane layer [10,11]. The hexaaluminates have the general formula AB_xAl_{12-x}O₁₉, where A represents an alkaline, alkaline-earth or rare-earth metal ion and B a transition-metal ion with similar size and charge as aluminum [12]. They have been used in combustion, partial oxidation and steam/CO₂ reforming reactions, as catalysts [10–13] or catalyst supports [9,14–16]. For example, Xu et al. [13] prepared a series of A-modified hexaaluminates, ANiAl₁₁O₁₉ (A = Ca, Sr, Ba and La) for CO₂ reforming of methane, and reported a high catalytic activity with no Ni sintering and coke deposition during 18 h at 780 °C. The advantage of supporting nickel on hexaaluminates, instead of

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