



Carbon formation and its influence on ethanol steam reforming over Ni/Al₂O₃ catalysts

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Abstract

Ethanol steam reforming was studied over Ni/Al₂O₃ catalysts. The effect of support (α - and γ -Al₂O₃), metal loading and a comparison between conventional H₂ reduction with an activation method employing a CH₄/O₂ mixture was investigated. The properties of catalysts were studied by N₂ physisorption, X-ray diffraction (XRD) and temperature programmed reduction (TPR). After activity tests, the catalysts were analyzed by scanning electron microscopy (SEM) and thermogravimetric analysis (TG/DTA). Ni supported on γ -Al₂O₃ was more active for H₂ production than the catalyst supported on α -Al₂O₃. Metal loading did not affect the catalytic performance. The alternative activation method with CH₄/O₂ mixture affected differently the activity and stability of the Ni/ γ -Al₂O₃ and the Ni/ α -Al₂O₃ catalyst. This activation method increased significantly the stability of Ni/ α -Al₂O₃ compared to H₂ reduction. SEM and TG/DTA analysis indicate the formation of filamentous carbon during the CH₄/O₂ activation step, which is associated with the increasing catalyst activity and stability. The effect of temperature on the type of carbon formed was investigated; indicating that filamentous coke increased activity while encapsulating coke promoted deactivation. A discussion about carbon formation and the influence on the activity is presented.

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1. Introduction

In a few decades, the continuous rise of energy demand and the shortage of petroleum reserves may result in a critical situation, with exponential increase in energy cost. Hydrogen fuel cells are the most promising systems for energy production, since they are more efficient and environmentally clean than conventional thermal machines.

Natural gas is still the main source of hydrogen, due to its abundance. However, the development of alternative routes for hydrogen production employing renewable sources is of great interest due to economic and environmental reasons. In this context, ethanol steam reforming has attracted the attention of many researcher groups in the last years. It may become an important industrial process, especially for sugarcane producing countries. It is a cleaner process than methane steam reforming, because the CO₂ “free” cycle, which is generated in

the reforming of ethanol and consumed by sugarcane photosynthesis.

Many studies have suggested Ni as the most suitable metal [1–4] for ethanol steam reforming. Although comparative studies [4–6] have shown better performance on basic supports, such as MgO and La₂O₃, alumina in γ or α phase is interesting due to its industrial use. The high surface area of γ -Al₂O₃ provides higher metal dispersion, while α -Al₂O₃ presents better mechanical resistance.

The coke deposition on Ni/Al₂O₃ catalysts is the main cause for deactivation during ethanol steam reforming [3,4]. The routes for carbon formation include Boudouard reaction, methane decomposition and polymerization of ethene, the latter originated from ethanol dehydration over Al₂O₃ acidic sites. Carbon deposition is thermodynamically unfavorable at high temperatures and higher water/ethanol ratios [7–9].

The direct deactivation of catalysts occurs predominantly by covering active phases, due to encapsulating carbon. Nevertheless, carbon may deposit over catalysts without deactivation [10], in a mechanism that includes: carbon deposition over metal surface, migration of carbon containing species to the

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