



Ni–Fe catalysts derived from hydrotalcite-like precursors for hydrogen production by ethanol steam reforming

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ABSTRACT

Nickel–iron mixed oxides derived from reevesite, a hydrotalcite-type compound, were tested in steam reforming of ethanol for hydrogen production. The influence of iron content (Ni/Fe ranging from 3 to 1) and the calcination temperature of the catalyst precursor (773 and 1073 K) on the catalytic performance were investigated. Both parameters were essential to optimize the reforming performance. Increasing the amount of iron in the reevesite precursors affected both the chemical and activity properties of the derived mixed oxide catalysts. Iron displays a positive role in nickel-based catalysts due to the enhancement of catalytic activity and hydrogen selectivity induced by the improved dispersion of nickel and the alleviation in carbon deposition. The calcination temperature led to variations in phase composition consisting of Ni(Fe)O_x solid solution and NiFe₂O₄, which affected the final size and dispersion of nickel species formed during the reaction. The best catalyst, with a Ni/Fe ratio of 1 and calcined at 773 K, rendered high and stable hydrogen and carbon dioxide selectivity of up to ca. 60% and 40%, respectively, low methane content, and consisted of a Ni(Fe)O_x + NiFe₂O₄ mixture with high surface area and small Ni⁰ crystallites. A higher percentage of crystalline NiFe₂O₄ attained at high calcination temperature (1073 K) associated with a lower carbon deposition resistance and probably Ni⁰ sintering brings about lower activity and fast deactivation. The improved performance over catalysts calcined at lower temperature and with lower Ni/Fe ratio is motivated by the effect of iron on the structural and electronic properties of the mixed oxides, thus inducing a slow formation of metallic nickel particles and coke deposits. Features like high surface area, higher iron content, lower reducibility of nickel species and small nickel crystallite size well dispersed on the surface of the catalyst with high iron content lead to a higher activity in ethanol dehydrogenation, acetaldehyde decarbonylation and reforming, and WGS.

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1. Introduction

Today, over 80% of world primary energy comes from three fossil fuels (petroleum, natural gas and coal) [1–3]. However, fossil fuel reserves are decreasing rapidly due to the continuous increased demand and they are not replaced as fast as they are consumed. Besides, about 98% of carbon emissions derive from fossil fuel combustion, thus, the damaging environmental effect of fossil fuel utilization is also crucial [4,5]. Therefore, the world's over-demand of energy, the crisis of fossil fuel depletion, the continuous increase in oil prices, and the environmental degradation have focused current efforts on the development of new and renewable fuel alternatives. Energy sources, like sun, wind, geothermal, hydraulic, nuclear, hydrogen, and biomass have been taken into consideration

[4]. Among these options, solar, wind and biomass are promising but are generally site-specific and more sporadic [6]. In contrast, hydrogen is expected to play an important role in future energy scenarios [2,7].

At present, the catalytic steam reforming is the most mature and well-established technology for hydrogen production [8]. Particularly, half of the world's hydrogen production derives from the most cost-effective steam reforming of natural gas (also referred as methane steam reforming) [4,8,9]. However, natural gas is a fossil fuel and its utilization to produce hydrogen does contribute to greenhouse gas emissions [6] unless a carbon dioxide capture and sequestration process is implemented in the reforming plant. In this context, there is a growing interest in the search of renewable alternatives to produce hydrogen. Among the various feedstocks, ethanol is very attractive as it can be produced by fermentation of different sources like agricultural wastes, forestry residue materials, and organic fractions of municipal solid wastes, and additionally, it contributes to nearly net-zero CO₂ emissions [10]. From

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