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Hydrogen production by thermocatalytic decomposition of methane over Ni-Al and Ni-Cu-Al catalysts: Effect of calcination temperature☆

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Abstract

Thermo catalytic decomposition of methane using Ni-Al and Ni-Cu-Al catalyst prepared by fusion of the corresponding nitrates is studied. The effects of catalyst calcination temperature on the hydrogen yields and the characteristics of the carbon obtained are studied. The role of copper has been also analyzed. Whatever the calcination temperature, all the catalysts show a high and almost constant hydrogen yield without catalyst deactivation after 8 h on stream, which confirms the good performance of this kind of catalysts. The presence of copper enhances the hydrogen production and the best results were obtained using catalysts calcined at 600 °C. Cu has a strong influence on the dispersion of Ni in the catalysts and inhibits NiO from the formation of nickel aluminate even at high calcinations temperatures, which facilitates the formation of the metallic Ni active phase during the subsequent catalyst reduction step. All catalysts tested promote the formation of very long filaments of carbon a few tens of nanometers in diameter and some micrometers long. The structural properties of these carbon filaments highly depend on the presence of Cu:Ni-Cu-Al catalysts promote the formation of a well-ordered graphitic carbon while Ni-Al catalysts enhance the formation of a rather turbostratic carbon.

Keywords: Hydrogen production; Ni catalysts; Calcination temperature

1. Introduction

Hydrogen is an emerging alternative to conventional fuels to reduce CO_2 emissions. It is considered a clean energy source and its market demand is steadily increasing [1–3]. It is generally accepted, that in the near-to-medium term hydrogen production will rely on fossil fuels, primarily natural gas. At present reforming of hydrocarbons is the technique most widely used for hydrogen production, generally using catalysts based on metals like Ni [4–6], Cu [7] or Co [8], but this production could be considered clean only applying techniques of capture and storage of the CO_2 obtained during the process.

In the near-to-medium term, hydrogen will be produced in small-to-medium decentralised installations located near to use in order to minimise the important concerns derived from hydrogen transport. If methane is reformed in these "on site" installations, the transport of the CO_2 produced to a sink will increment significantly the cost of the hydrogen production. In this scenario, thermo catalytic decomposition of natural gas, TCD, with carbon being captured as a solid of added value product appears as a very interesting alternative to steam reforming [9].

Feasibility of TCD in economical terms is very sensible to the carbon selling price which depends on the properties of the carbon obtained. The quality of carbon produced from TCD largely depends on the operation conditions and the type of catalyst used. Using metal-based catalysts lead to the production of carbon forms of high quality whose high selling price would compensate the high cost of the catalyst. Several prior studies on methane decomposition using mainly transition metals have been reported in the literature [10]. TCD of methane using Ni and Ni-Cu catalysts to produce hydrogen and novel carbonaceous materials was first reported by Muradov [11] and Parmon et al. [12]. Although other many metals have been tested for TCD, most of the reported studies have used Ni and Ni-Cu catalysts [13–18].

In a previous work [19], it has been shown that the catalyst life mainly depends on the morphology of the deposited carbon which appears either as long filaments a few nanometres in diameter emerging from Ni particles or as uniform coatings. Formation of filaments enlarges the catalyst life. The influence

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