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Effects of reaction conditions on hydrogen production and carbon nanofiber properties generated by methane decomposition in a fixed bed reactor using a NiCuAl catalyst

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ABSTRACT

In this paper, the results obtained in the catalytic decomposition of methane in a fixed bed reactor using a NiCuAl catalyst prepared by the fusion method are presented. The influences of reaction temperature and space velocity on hydrogen concentration in the outlet gases, as well as on the properties of the carbon produced, have been investigated. Reaction temperature and the space velocity both increase the reaction rate of methane decomposition, but also cause an increase in the rate of catalyst deactivation. Under the operating conditions used, the carbon product is mainly deposited as nanofibers with textural properties highly correlated with the degree of crystallinity.

1. Introduction

Hydrogen production by means of catalytic decomposition of methane (CDM) into hydrogen and deposited carbon ($CH_4(g) \rightarrow C(s) + 2H_2(g)$) is an interesting alternative to conventional hydrogen production processes, such as steam reforming (SR) and partial oxidation (PO), which result in high CO_2 emissions [1–4].

The carbon properties resulting from CDM are largely dependent on the operating conditions and the type of catalyst used. Methane decomposition using Ni and Ni–Cu catalysts to produce hydrogen and novel carbonaceous materials has been widely reported [5–23]. Activity tests using other transitions metals, such as Fe [24–26] and Co [27,28], have also shown good catalytic performance in CDM.

From these studies, a widely accepted general mechanism of catalyst behaviour and carbon nanofiber formation has been proposed [29,30]. The main steps involved in the CDM process are (i) methane chemisorption on the leading face of a catalyst particle, (ii) dissociation of a chemisorbed CH_4 molecule through progressive breaking of the four C–H bonds, (iii) aggregation of adsorbed atomic hydrogen into molecules, followed by gas phase emission, (iv) atomic carbon aggregation into encapsulated carbon, leading to progressive catalyst deactivation, or atomic carbon diffusion through the bulk catalyst from the leading face to the trailing face, driven by the existing pronounced concentration gradient, and (v) carbon nucleation followed by the formation and growth of carbon nanofibers in the trailing face of the catalyst particle.

In previous works by our research group with nickel-based catalysts, different parameters related to catalyst preparation have been studied. These include the effects of catalyst composition, the presence of Cu as a Ni dopant additive, methods of catalyst preparation [31], the effects of calcination temperatures [32] and the use of different textural promoters [33–35]. From these studies it was concluded that the nickel catalyst prepared by the fusion method using Al_2O_3 as textural promoter and Cu as additive, denoted as NiCuAl with an atomic ratio of 78:6:16, displayed the best performance based on hydrogen production, the amount of carbon deposition as long nanofibers and long catalyst life without deactivation. Furthermore, this simple preparation method, based on a mixture of the respective nitrates, allowed for preparation of catalysts showing similar results to those obtained for catalysts prepared by co-precipitation. The performance of the NiCuAl catalysts in CDM was also assessed in fluidized bed reactor tests, showing the feasibility of this process for the production of large amounts of hydrogen and carbon nanofibers (several hundred grams per day) [36].

Optimization of catalyst performance was achieved in a further study carried out in thermobalance exploring the carbon yields, deposition rates, and changes in the structural properties of the nickel and deposited carbon as a function of the operating temperature and the partial pressures of hydrogen and methane [37].

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