



Optimization of bimetallic dry reforming catalysts by temperature programmed reaction

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ARTICLE INFO

Article history:

Received 4 April 2012

Received in revised form 5 June 2012

Accepted 22 June 2012

Available online 1 July 2012

Keywords:

Dry reforming

CO₂ reforming

Ni–Pt

Ni–Pd

Temperature programmed reaction

Zirconia

ABSTRACT

Catalytic reforming of CH₄ with CO₂ was investigated on mono and bimetallic Pd(or Pt)–Ni based samples supported on Al₂O₃ and ZrO₂. A simple temperature-programmed procedure was used to study both reforming and coke formation via CH₄ or CO decomposition. Catalysts supported on zirconia are more active than alumina-supported samples. The addition of Pt or Pd to Ni/ZrO₂, preferably by co-impregnation, prevents coke formation. The co-impregnated Ni–Pd/ZrO₂ catalyst looks the most promising for a possible industrial application.

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1. Introduction

The catalytic reforming of CH₄ with CO₂, rather than steam, for the production of synthesis gas (CO+H₂) has attracted a considerable interest in the past 20 years for both environmental and commercial reasons. In fact it reduces CO₂ and CH₄ emissions, which are greenhouse gases, and it yields, in the product gas, a lower H₂/CO ratio (H₂:CO:1:1 or less) compared to steam reforming (H₂:CO:3:1). This synthesis gas with a high CO concentration is a suitable feed for Fischer–Tropsch plants and for the synthesis of acetic acid, dimethyl ether and oxoalcohols [1]. An additional advantage of dry reforming is in those cases in which the reactants are simultaneously available at low cost, or even at negative prices [2]. The major problem preventing commercialization of the CO₂ reforming is finding a suitable catalyst that will not deactivate under the conditions needed for this reaction. In fact, due to the endothermic nature of the process, high temperatures (~1100 K) are required to reach high conversions. Besides this process works in presence of high concentrations of carbon-containing compounds. These conditions lead to quick deactivation of the catalyst due to carbon deposition, which originates mainly from two

reactions, i.e., methane decomposition (CH₄ → C + 2H₂) and carbon monoxide disproportionation (2CO → C + CO₂). Although in literature the authors agree that carbon formation is the primary reason for the catalyst deactivation, disagreement exists on the source of the carbon. In fact, in principle, all three carbon-containing species present in the reforming reaction (CH₄, CO and CO₂) can contribute to carbon deposition. Some authors [3,4] reported that CH₄ decomposition is the main source of carbon, others showed that carbon originates mainly from CO [5,6].

To solve the problem of coking the following points were investigated: (i) the increase of the H/C content of the feed through the addition of water (coupling with steam reforming); (ii) the increase of the O/C content of the feed through the addition of oxygen (coupling with partial oxidation); (iii) the use of a catalyst which minimize the rate of coking.

Typically, supported Ni or noble metals are reported as potential catalysts for the CH₄/CO₂ reforming. It has been shown [7] that Pt-based catalysts have high activity in the dry reforming reaction and are less sensitive to carbon deposition compared to Ni-based catalysts, but the latter is the metal most widely studied because of its high activity and low price, pointing to possible industrial application. The addition of alkali or alkali earth dopants to nickel [8,9], or the use of supports with basic characteristics [10,11] were reported as methods to minimize carbon deposition. Some authors [12–20] have investigated the effects of bimetallic samples in the dry reforming of methane. A very recent review has summarized some examples of the catalysts for methane steam reforming

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