



Precursor influence and catalytic behaviour of Ni/CeO₂ and Ni/SiC catalysts for the tri-reforming process

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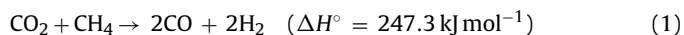
ABSTRACT

The aim of the work described here is to evaluate the catalytic performance in the tri-reforming process of Ni/CeO₂ and Ni/ β -SiC catalysts prepared by using four different nickel salts (nitrate, acetate, chloride and citrate). Metal particles supported over ceria had bigger particle sizes (leading to lower metal–support interactions) than those supported on β -SiC. It was also demonstrated that the metal salt used in the preparation of Ni-based catalysts had a marked influence on the size of the nickel particles. Larger particles with a worse catalytic behaviour were obtained when nickel chloride and nickel citrate were used as the precursors of Ni supported species. Methane consumption rate and H₂/CO ratio in the effluents were influenced by the type of support and salt precursor used in the preparation of the catalysts. CO₂-TPD proved that catalysts based on ceria as the support presented more basic sites, which was related to a decrease of the H₂/CO molar ratio in the effluents coming from the reactor. High methane consumption rate and good catalytic stability were obtained when nickel nitrate and nickel acetate were used to prepare Ni/ β -SiC catalysts. The results showed that these latter catalysts can be considered as promising ones for the tri-reforming process.

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1. Introduction

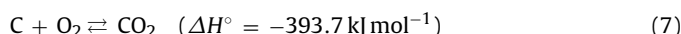
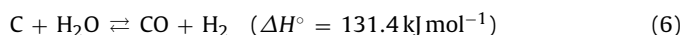
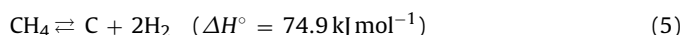
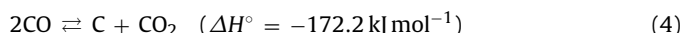
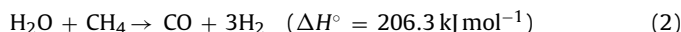
Interest in the use of CO₂ as an important source of carbon for the synthesis of fuels and chemical products has significantly increased in recent years as a consequence of the public concern about its negative effects on the atmosphere. Among the different processes proposed that allow this specie to be transformed in valuable compounds, dry reforming of methane in the presence of CO₂ yielding synthesis gas (Eq. (1)) should be highlighted according to the number of works reported in the literature [1–3]



Despite of that, the high cost and limited availability of noble metal catalysts, such as Pt, Rh, and Ru used in this process [4–6] limits its commercialisation. For many years, nickel-based catalysts have been proven to be the most suitable ones for hydrocarbon reforming. Following this idea, nickel supported on oxides, such as Al₂O₃, MgO, TiO₂, ZrO₂, SiO₂, CeO₂ and La₂O₃ have been extensively investigated [7–10] as catalysts for the reforming of CH₄ by CO₂. However, drawbacks as the deactivation of the catalyst by carbon formation and the high energy consumption required as a result

of the endothermic nature of the process should be considered in future developments.

The tri-reforming process proposed by Song [11] could avoid these problems. This process consists of a synergetic combination of dry reforming (Eq. (1)), steam reforming (Eq. (2)) and partial oxidation (Eq. (3)) of methane. Tri-reforming process presents three major advantages: H₂/CO molar ratio in the product can be controlled by altering the relative amounts of gas reagents, the process is less endothermic due to the occurrence of the partial oxidation reaction and, finally, coke formation can be reduced by the presence of oxidants (H₂O and O₂; Eqs. (4)–(7)).



Synthesis gas produced by the tri-reforming of CH₄ can be used for the production of DME, Fischer–Tropsch synthesis fuels and high-valued chemicals [12,13] as well as applied to the fuel processor of solid oxide fuel cells (SOFC) and molten carbonate fuel cells (MCFC) systems.

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