



Steam-methane reforming at low temperature on nickel-based catalysts



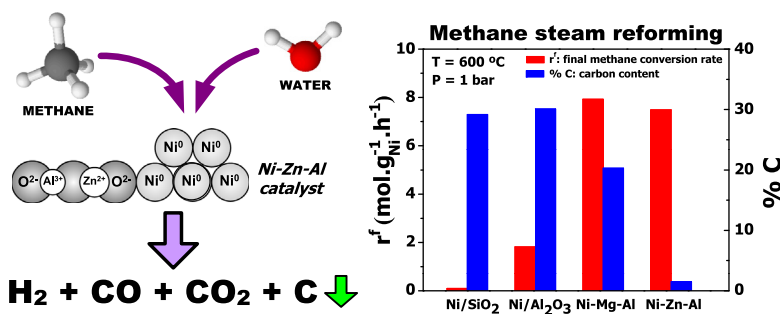
María A. Nieva, María M. Villaverde, Antonio Monzón, Teresita F. Garetto, Alberto J. Marchi*

Catalysis Science and Engineering Research Group (GICIC), Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE), FIQ-UNL-CONICET, Santiago del Estero 2654 (3000) Santa Fe, Argentina

HIGHLIGHTS

- A Ni–Zn–Al catalyst is active and stable for steam-methane reforming at low temperatures.
- Ni–Zn–Al catalyst is resistant to sintering and inhibits formation of carbonaceous deposits.
- Ni–Mg–Al catalyst is active for steam-methane reforming but produces carbon nanofibers.
- Intimate contact between Ni and spinel-like matrix is crucial for metal phase activity and stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 June 2013

Received in revised form 22 August 2013

Accepted 4 September 2013

Available online 12 September 2013

Keywords:

Steam-methane reforming
Nickel catalysts
Metal-support interaction
Synthesis gas
Hydrogen

ABSTRACT

In this work, we report the activity results obtained in steam-methane reforming (SMR) at 500 and 600 °C using four nickel-based catalysts: (a) Ni/ α -Al₂O₃ and Ni/SiO₂, prepared by incipient wetness impregnation method and (b) Ni–Zn–Al and Ni–Mg–Al, prepared by coprecipitation method. In all of the samples, the nickel load ranged between 7% and 9%. The catalytic activity in SMR at steady state followed the pattern: Ni–Mg–Al \cong Ni–Zn–Al > Ni/ α -Al₂O₃ > Ni/SiO₂. According to characterization results, the interaction between Ni²⁺ species and support in precursor oxides was stronger in Ni–Mg–Al and Ni–Zn–Al than in Ni/ α -Al₂O₃ and Ni/SiO₂. After activation in H₂ flow, large metal nickel particles with low or none interaction with the support were obtained in the case of Ni/ α -Al₂O₃ and Ni/SiO₂. On the contrary, small metal particles, between 3 and 6 nm, in high interaction with support were obtained in Ni–Zn–Al and Ni–Mg–Al catalysts. The metal phase formed in Ni–Mg–Al and Ni–Zn–Al was the most active and resistant to sintering under reaction conditions at $T \leq 600$ °C. It was also found that carbon nanofibers were formed on Ni/ α -Al₂O₃, Ni/SiO₂ and Ni–Mg–Al catalysts during SMR at 600 °C. The amount and diameter of nanofibers formed on Ni–Mg–Al were lower than on catalysts prepared by impregnation method, which is in agreement with the relative sizes of metal nickel particles in each case. Amazingly, no filamentary carbon was detected on the used Ni–Zn–Al sample: only amorphous coke in low amounts was formed. This was attributed to the proper interaction of small metal nickel particles with the non-stoichiometric zinc aluminate-like phase formed after thermal treatments of catalyst precursor.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

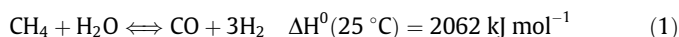
Steam-methane reforming (SMR) is the most common process at industrial scale for the production of hydrogen and synthesis

gas [1]. In particular, according to the US DOE, almost 95% of the hydrogen is produced in United States by SMR [2]. This process is employed in both petrochemical industry and energy production. For example, synthesis gas produced via steam reforming is employed in order to obtain the reducing gas for steel production and also as raw material in the ammonia, methanol and Fischer–Tropsch synthesis [1–4].

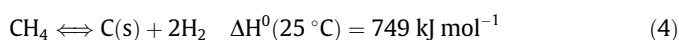
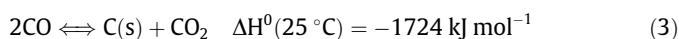
* Corresponding author. Tel.: +54 342 4533858; fax: +54 342 4531068.

E-mail address: amarchi@fiq.unl.edu.ar (A.J. Marchi).

The principal products in SMR are CO, CO₂ and H₂, which are produced according to reactions (1) and (2), being the first reaction highly endothermic and the second one slightly exothermic.



Simultaneously, CO disproportionation (3) and CH₄ decomposition (4) can take place, which are undesirable reactions because they produce carbon deposits and whiskers [5]. Both reactions can take place between 500 and 600 °C, but CO disproportionation is thermodynamically favored against CH₄ decomposition in this temperature range [3].



Since reaction (1) is highly endothermic, it is necessary to carry out the SMR process at high temperatures in order to reach complete methane conversion. Normally, the temperature at the reformer inlet is between 450 and 600 °C while at the outlet it is in the range of 850–950 °C [4]. Water–gas shift (WGS) reaction and CO disproportionation, Eqs. (2) and (3), respectively, are thermodynamically favored in the reformer low temperature region while CH₄ decomposition, equation (4), is favored in the high temperature zone.

There are many research papers in which the use of different type of metal-based catalysts and reactors were proposed with the aim of improving H₂ production and to minimize coke formation in methane reforming [4–29]. The most used catalysts were those based on noble and non-noble metals of group VIII. Among them, nickel is the preferred one in industrial applications due to its low cost and catalytic performance [4,6]. However, the C(s) produced by reactions (3) and (4) can be dissolved in the metal nickel particles and diffuse through it to form carbon whiskers [4]. If these whiskers are produced in large amounts, they can break-up the catalyst pellets and produce large amounts of powder. This will increase the pressure drop in the catalyst bed leading to operational problems in the reformer unit [7]. Formation of carbonaceous deposits is favored below a critical steam to carbon (S/C) ratio [4,6]. Therefore, S/C ratios used at industrial scale are higher than unity. Normally, values between 2.5 and 4.5 are used at the inlet of industrial reformers in order to reduce carbon production [2]. An alternative to control carbon deposit formation is the use of a pre-reformer unit that normally works between 400 and 600 °C [2,3]. The idea is to carry out the methane conversion under conditions that insure the inhibition of reactions (3) and/or (4). One proposal to fulfill this objective is to use a catalyst formed by a stable phase of metal nanoparticles being active at 500–600 °C for reaction (1) but that inhibits reactions (3) and (4).

The support and metal–support interaction are also influencing the formation of carbonaceous deposits and carbon whiskers during SMR process. The most common supports used in the open literature for SMR are α -Al₂O₃, γ -Al₂O₃, SiO₂, MgO, MgAl₂O₄, CeO₂, TiO₂ and ZrO₂ [8–18]. In some cases, surface acid sites are present and they promote hydrocarbon cracking and subsequent polymerization leading to formation of carbonaceous deposits on the catalyst surface [19]. Then, a way to suppress carbon deposition on Ni-based catalysts is by adding an alkali metal. However, addition of alkali promoters can decrease catalyst activity [20]. Then, it would be better to design the catalyst having the right acid–basic properties and the proper metal–support interaction in order to inhibit the formation of carbonaceous deposits.

Another aspect that must be taken into account for the design of a SMR catalyst is the particle sintering, since this is also one possible cause for catalyst deactivation. It is well known that the rate and extent of sintering depend on many factors, as for example metal load, crystallite size, support nature and reaction conditions. The most accepted mechanism for particle sintering is migration and coalescence [21]. In order to avoid particle migration on support surface, the interaction between metal nanoparticles and support must be the proper one. In this sense, a stable metal phase highly dispersed in a Ni–Mg–Al oxide was obtained from a hydrotalcite-like precursor [17,22]. In other cases, a noble metal phase highly dispersed in a Mg–Al oxide matrix was obtained following similar procedures [23,24].

In summary, the challenge is to design and develop a catalyst active in SMR at low temperature, resistant to sintering and with low formation of carbon deposits. In a previous paper, we studied the hydrogenation of acetylene with Ni-based catalyst having a non stoichiometric spinel-like structure and the carbon formation was considerably reduced respect to other Ni-based catalysts [30]. In this work we study the SMR at 500–600 °C over Ni–Mg–Al and Ni–Zn–Al catalysts, prepared by coprecipitation method, and compared their catalytic performance with that of Ni supported on SiO₂ and α -Al₂O₃, prepared by incipient wetness impregnation. The objective in this work is to obtain a stable phase of metal nickel nanoparticles with high activity for SMR, able to inhibit carbon production at temperatures below 600 °C and simultaneously resistant to sintering under reaction conditions. This catalyst could be useful in the low temperature range of a steam reformer or in a pre-reformer unit.

2. Experimental

2.1. Catalyst preparation

Two catalysts, Ni/SiO₂ (NS) and Ni/ α -Al₂O₃ (NA), were prepared by incipient wetness impregnation using as supports SiO₂ (Aldrich, S_g = 250 m² g⁻¹) and α -Al₂O₃ (Aldrich, S_g = 8 m² g⁻¹). A 0.5 M solution of Ni(NO₃)₂·6H₂O (Merck, for analysis) was added dropwise to the supports, previously calcined in air during 4 h at 500 °C. These hydrated precursors were dried in an oven at 100 °C for 12 h and then calcined in air flow (60 cm³ min⁻¹) at 400 °C for 6 h. Other two Ni-based catalysts, Ni–Mg–Al (NMA) and Ni–Zn–Al (NZA), were prepared by the co-precipitation technique according to the procedure described elsewhere [30,31]. The atomic ratios in samples NMA and NZA were Zn(Mg)/Ni \cong 3 and Zn(Mg)/Al \cong 0.75. An aqueous solution containing a mixture of the corresponding nitrates and a basic aqueous solution of K₂CO₃ (for NZA) or K₂CO₃/KOH = 0.125 (for NMA) were simultaneously added dropwise to 400 ml of distilled water at 60 °C while the pH was kept at 7.2 \pm 0.2 for NZA and 10 \pm 0.2 for NMA. The resulting precipitates were aged for 1 h at 60 °C in the mother liquor and then filtered, washed with deionized water at 60 °C and dried at 80 °C overnight. The hydrated precursors were decomposed in N₂ flow (60 cm³ min⁻¹) at 500 °C for 5 h to obtain the corresponding mixed oxides.

2.2. Catalyst characterization

Specific surface area (S_g) were measured by N₂ physisorption at –196 °C in a Quantachrome Autosorb I sorptometer. Elemental composition of the samples was determined by atomic absorption spectrometry (AA) using a Perkin Elmer Spectrometer AAnalyst 800. Hydrogen chemisorption was measured via volumetric adsorption experiments at room temperature in a conventional vacuum apparatus using the method described elsewhere [31,32].

Download English Version:

<https://daneshyari.com/en/article/148341>

Download Persian Version:

<https://daneshyari.com/article/148341>

[Daneshyari.com](https://daneshyari.com)