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Study of nickel catalysts for hydrogen production in sorption enhanced reforming process

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HIGHLIGHTS

- Ni based catalysts were compared to be used in sorption enhanced reforming.
- NiO/Si_3N_4 showed low CH_4 conversion at sorption enhanced reforming temperature.
- 10% $NiO/NiAl_2O_4$ and 20% NiO/α-Al_2O_3 are suitable to be applied in SER.
- The observed trend of carbon formation over catalysts was $Si_3N_4 > Al_2O_3 > NiAl_2O_4$.

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ABSTRACT

The performance of Ni based catalysts to be used in Sorption Enhanced Reforming (SER) is assessed. For this aim, both their activity at low temperature and their behavior during multiple oxidation–reduction cycles in steam methane reforming are studied. Ni catalysts supported on α-Al_2O_3, Si_3N_4 and $NiAl_2O_4$, with different amounts of Ni (0–50% NiO), are compared by testing their activity in a fixed bed micro-reactor. While Ni/Si_3N_4 catalysts do not show an appropriate performance at low temperature, Ni/α-Al_2O_3 and $Ni/NiAl_2O_4$ present a significant activity, close to equilibrium data, at the typical SER conditions. The best experimental results are attained for 20% NiO/α-Al_2O_3 and 10% $NiO/NiAl_2O_4$ catalysts that show an activity close to the equilibrium for steam to methane ratio of 4.5. Higher amounts of NiO in both catalysts do not reveal an improvement in conversion results. In addition, both 20% NiO/α-Al_2O_3 and 10% $NiO/NiAl_2O_4$ catalysts show a good reforming activity after oxidation–reduction cycles at typical SER temperatures. The observed trend to carbon deposition on the catalyst surface for the studied supports is $Si_3N_4 > Al_2O_3 > NiAl_2O_4$, being negligible when $NiAl_2O_4$ support is used. These results suggested that 10% $NiO/NiAl_2O_4$ and 20% NiO/Al_2O_3 catalysts could be perfect candidates to be used in SER process.

1. Introduction

It is well known that hydrogen is an advantageous energy carrier due to its clean combustion products and easy conversion to generate heat or electricity [1]. In addition, hydrogen is used as a feedstock in many industrial processes such as petroleum refining, ammonia or methanol production [2]. Therefore an increasing demand of hydrogen is expected in the short term. Most of the hydrogen produced worldwide is obtained from natural gas conversion. However, the possible depletion of gas fields together with an increase in global warming, make necessary to develop new efficient processes with low CO_2 emissions. Nowadays, steam reforming of natural gas is the most economical and widely used technology for H_2 production in industrial applications [1,3–6]. This process includes several steps in pressure and temperature under severe conditions. The first step is the reforming of methane with steam at 800–900 °C and 15–30 bar in tubular reactors externally heated and filled with nickel based catalyst, mainly producing H_2 and CO according to Eq. (1):

$$CH_{4(g)} + H_2O_{(g)} \leftrightarrow 3H_{2(g)} + CO_{(g)} \quad \Delta H^0_{298} = 208 \text{ kJ mol}^{-1} \tag{1}$$

The next step in this process is the water gas shift reaction (WGS) (high and low temperature stages) where undesired CO is converted to CO_2 and hydrogen yield is increased according to Eq. (2):

$$CO_{(g)} + H_2O_{(g)} \leftrightarrow H_{2(g)} + CO_{2(g)} \quad \Delta H^0_{298} = -41 \text{ kJ mol}^{-1} \tag{2}$$

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At last, optional purification methods, like pressure swing adsorption, allow high H_2 concentrations in the final product [3,4,7]. Although steam reforming is the dominant process for commercial hydrogen production, it is very energy intensive and high CO_2 producer [3]. So, it is necessary to develop new commercial technologies in order to improve that process, such as Sorption Enhanced Reforming (SER). In this process, the reforming catalyst is combined with a CO_2 acceptor (a sorbent, usually based on CaO) in order to in situ remove the CO_2 as soon as it is formed (Eq. (3)):

$$CO_{2(g)} + CaO_{(s)} \leftrightarrow CaCO_{3(S)} \quad \Delta H^0_{298} = -179 \text{ kJ mol}^{-1} \tag{3}$$

Thus, all steps (reforming, WGS and CO_2 removal) take place in the same reactor [4] with the total reaction given in Eq. (4):

$$CH_{4(g)} + 2H_2O_{(g)} + CaO_{(s)} \leftrightarrow 4H_{2(g)} + CaCO_{3(S)} \quad \Delta H^0_{298} = -12 \text{ kJ mol}^{-1} \tag{4}$$

The sorbent addition makes the overall process slightly exothermic and shifts the equilibrium to favor the formation of higher hydrogen concentrations. Potential benefits from the SER process are extensively reported in the literature, such as lower operational temperatures (600 °C–700 °C), CO_2 capture, and the production of high purity H_2 [4], making this process attractive compared to the traditional steam reforming process that operates at industrial scale.

In a commercial process, the sorbent must be regenerated by calcination of $CaCO_3$ to CO_2 in an additional step to be reused, so a cyclic system consisting of two interconnected fluidized-bed reactors (reforming reactor and calcination reactor) has been proposed [7–10]. This technology allows to remove the spent sorbent and add fresh one during the process in order to get a continuously regenerated sorbent flow transferred to the reforming reactor. A conceptual scheme is shown in Fig. 1:

Reforming, WGS and carbonation reactions take place in the reforming reactor where a mixture of catalyst and sorbent is present. This reactor operates at low temperature ($\approx$600 °C–700 °C) and atmospheric pressure, resulting in a high purity H_2 stream, with steam and low quantities of CO, CO_2 and CH_4.

In the second reactor (calcination–oxidation) the used mixture of catalyst and spent sorbent is submitted to high temperature (depending on CO_2 partial pressure) to regenerate the sorbent. Additional fuel is required to provide the necessary heat to this step. O_2 is also added with this fuel to obtain a gas stream with concentrated CO_2.

The solid mixture of sorbent and catalyst is circulating continuously between the two beds, being repeatedly exposed to different reaction environments (oxidation–reduction) by short time intervals. The use of different sorbents in the SER process has been widely studied in the literature [4,11]. However, it is also necessary to find and to study appropriate reforming catalysts able to work at typical SER temperatures and in multiple cyclic operation (oxidation–reduction cycles). In addition, these catalysts must also be able to operate, if possible, at low steam/methane ratios in order to improve the energy efficiency of the process.

Ni has been generally used as the catalyst in steam methane reforming (SMR) because it presents a high activity and has a lower cost than other precious metals [3]. α-Al_2O_3 is frequently used as support due to its stability at high temperatures, lower trend to $NiAl_2O_4$ formation than γ-Al_2O_3, and its low price [3,12]. However, it is well known that this catalyst shows deactivation problems due to carbon formation during SMR [12–16]. Up to now, the catalytic activity of 15–20% NiO/α-Al_2O_3 has been studied in SER process at atmospheric pressure in a fixed bed reactor, showing satisfactory results with respect to methane conversion and hydrogen production [7,17–19].

Other promising catalysts could be NiO/Si_3N_4 and NiO/$NiAl_2O_4$ that have been used in other processes and, according to the literature, have good properties regarding to low catalyst coking and cyclic operation capacity [20,21].

Ni/Si_3N_4 has been used at high temperatures in the partial oxidation of methane to produce syngas. The results reported in the literature show that Si_3N_4 supported nickel catalyst have good catalytic activity and resistance to coke formation, mainly due to the interaction between the metal and the basic support [22].

Ni/$NiAl_2O_4$ catalyst has been used in several fields due to its resistance to high temperature and acidic or basic environments [23]. It has been applied in chemical looping showing good cyclic performance [20,24]. The good catalytic activity of this material has been also reported for SMR [6]. In addition, there are few studies applying this catalytic system in SER process but always at very high Ni contents [10,25].

In this scenario, the aim of the present work is to compare the catalytic activity in methane steam reforming of α-Al_2O_3, Si_3N_4 and $NiAl_2O_4$ supports with different NiO charges in order to select the most appropriate catalysts to be implemented in SER process. To achieve this objective, catalysts with diverse NiO loadings have

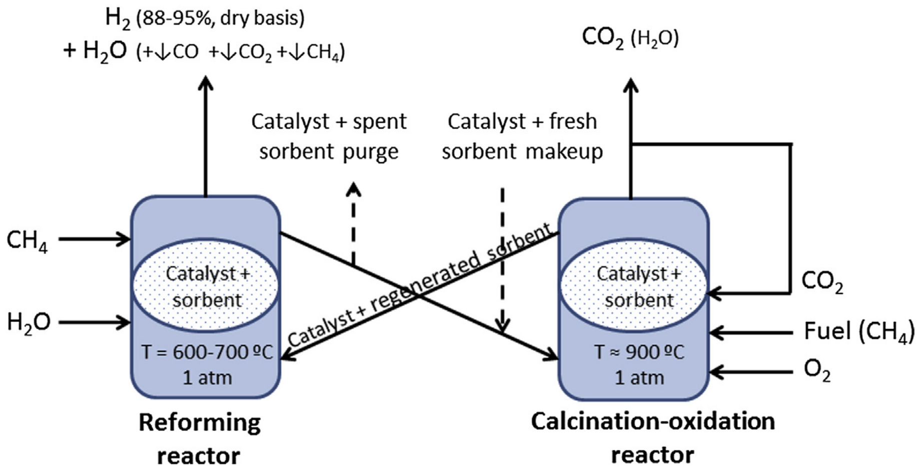

Fig. 1. Sorption enhanced process conceptual scheme.