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Hydrogen production from oxidative reforming of methane on Ni/γ-Al_2O_3 catalysts: Effect of support promotion with La, La–Ce and La–Zr

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ABSTRACT

Ni/Al_2O_3 catalysts promoted by adding La_2O_3, La_2O_3–CeO_2 and La_2O_3–ZrO_2 were investigated on oxidative and steam reforming aiming the hydrogen production. The samples were characterized by surface area estimation (BET), XRD, TPR, TPD-H_2 and XANES. Analysis of TEM and TPO was performed as complementary characterization for catalysts after reaction. The oxidative steam reforming of methane at temperatures above 500 °C reveals that all the promoted catalysts presented better activities than the unpromoted. Below 500 °C, the catalysts presented deactivation due to metallic nickel species oxidation and the TEM analysis of Ni/Al and Ni/La–Al catalysts revealed that the lanthanum addition led to a decrease in the Ni species particle size and also to a better active phase dispersion. The results suggest that below 500 °C the activity may be related to differences in the metallic area values, although the Ni/La_2O_3–Al_2O_3 catalysts have shown a different behavior.

1. Introduction

Methane steam reforming (MSR) (Eq. (1)) is the process used for industrial production of hydrogen and synthesis gas [1]. The water gas shift reaction (WGS, Eq. (2)) may occur as parallel reaction, increasing the H_2 yield and reducing the CO yield:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad \Delta H_{298K} = 206\ \text{kJ}\cdot\text{mol}^{-1} \tag{1}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \Delta H_{298K} = -41\ \text{kJ}\cdot\text{mol}^{-1}. \tag{2}$$

The overall process is endothermic, which results in the need for external heat and subsequent high cost [2]. One alternative to reduce the energy costs for H_2 production is by the reaction of partial oxidation of the methane (POM, Eq. (3)).

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{298K} = -38\ \text{kJ}\cdot\text{mol}^{-1} \tag{3}$$

POM is a more economic process for H_2 production when compared to MSR and has received considerable attention [3]. This reaction is mildly exothermic; however a small decrease for CO selectivity may lead to total oxidation of methane (Eq. (4)), a strong exothermic reaction, causing the formation of hot spots, which may lead to catalyst deactivation.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298K} = 803\ \text{kJ}\cdot\text{mol}^{-1} \tag{4}$$

The coupling of MSR and POM, known as auto-thermal reforming, was developed by Haldor Topsøe [4]. This reforming process may overcome the energy problems through better thermal control inside the reactor and also can avoid hot spot formation, preventing catalyst deactivation by sintering and reducing carbon deposition [5].

There is a huge interest in the development of active and stable catalysts for conversion of organic compounds in H_2. Nickel is an active and cheap component for MSR but, in oxygen presence, the Ni^0 active species may undergo oxidation and lose activity during the reaction run [6–9]. Considering the costs and availability of stable noble metal catalysts, the development of stable catalysts based on Ni is interesting from an industrial point of view. The catalyst must be stable under high temperature and pressure conditions and must have mechanical resistance without sintering [10].

Alumina is a support with high surface area and mechanical resistance. Rare earth is used to stabilize the γ-Al_2O_3 by avoiding phase transition. The addition of La_2O_3 can increase the thermal resistance of alumina [11], the dispersion of fine Ni particles over the support and hinder the sintering of Ni^0 particles during reforming reactions. CeO_2

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presents high oxygen storage and release capacity, which helps the carbon removal from metallic surfaces, stabilizes metal dispersion and promotes the catalytic activity for reforming reactions, due to a better adsorption and dissociation of water molecules associated to CeO_2 [12–17]. ZrO_2 has high ionic conductibility, thermal stability and low acidity. This oxide also has a low specific surface area and a higher cost than classic supports, however the literature indicates that the addition of small quantities of ZrO_2 improves Ni catalyst stability in the steam reforming of hydrocarbons [18].

In light of the above considerations, the goal of this work was the development of nickel catalysts deposited on a γ-alumina containing La_2O_3 and modified by CeO_2 and/or ZrO_2 for steam reforming and oxidative reforming of methane, in order to evaluate the effects of these additives on methane conversion and carbon deposition avoidance.

2. Experimental

2.1. Catalyst preparation

The catalyst containing 15 wt.% Ni was prepared by wet impregnation of commercial γ-Al_2O_3 (Alfa Aesar = 212 $m^2 \cdot g^{-1}$) with aqueous $Ni(NO_3)_2 \cdot 6H_2O$. After the impregnation, the sample was dried at 100 °C and calcined in air flow at 550 °C.

The La_2O_3–Al_2O_3, La_2O_3–ZrO_2–Al_2O_3 and La_2O_3–CeO_2–Al_2O_3 supports were prepared by wet impregnation of γ-Al_2O_3 with aqueous solutions of nitrate metal salts to obtain a final load of 10 wt.% La_2O_3, 5 wt.% La_2O_3–5 wt.% ZrO_2 and 5 wt.% La_2O_3–5wt.% CeO_2. After impregnation, the solids were dried at 120 °C for 24 h and calcined in air flow at 550 °C for 3 h. Catalysts containing 15 wt.% Ni were prepared by wet impregnation of supports with $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution. After the impregnation, the samples were dried at 120 °C for 24 h and calcined in an air flow at 550 °C for 2 h. The samples were labeled Ni/La–Al, Ni/La–Zr–Al and Ni/La–Ce–Al according to the support.

2.2. Characterization of catalysts

Surface areas of the oxides were measured by N_2 adsorption/desorption cycles, according to the BET method, using a Quantachrome NOVA 1200 surface area analyzer.

The crystal structures were investigated by X-ray diffraction (XRD), in a Rigaku Multiflex diffractometer, using a Cu-Kα radiation source with Ni filter and a scan rate of 2° min^{-1}, ranging from 3° to 80°. The diffraction patterns were identified by comparison with those of known structure in the JCPDS (Joint Committee on Powder Diffraction Standards) database. The NiO apparent crystallite size (D_{NiO}) was determined by the Scherrer's Equation, using the reflection (2 0 0) of NiO.

Temperature-programmed reduction with hydrogen (H_2-TPR) of the catalysts was performed in a Micrometrics Chemisorb 2705 equipment, using 30 mg of catalyst, a temperature ramp from 25 to 1000 °C at 10 $°C \cdot min^{-1}$ and a flow rate of 30 $mL \cdot min^{-1}$ of 5%H_2/N_2. The amount of hydrogen consumed during a H_2-TPR peak was determined by comparing the area under the curve with that of a standard CuO sample and used to estimate the degree of catalyst reduction.

The estimation of metallic surface area was carried out in the same equipment used for H_2-TPR. For this analysis, 100 mg of catalyst was previously reduced at 700 °C for 2 h in a stream of H_2. Afterwards, the sample was cooled in N_2, flowing at 30 $mL \cdot min^{-1}$ up to 25 °C. At 25 °C, H_2 flowing at 30 $mL \cdot min^{-1}$ was passed through the sample for 1 h to promote the adsorption on the metal sites of the catalyst surface. Subsequently, the gas flow was changed to N_2, which was passed through the sample for 20 h, to clean (purge) the H_2 accumulated in the pores and to guarantee the presence of only chemisorbed H_2. After the purge, the H_2 desorption process was started in N_2 flowing at 30 $mL \cdot min^{-1}$ in a heating rate of 10 $°C \cdot min^{-1}$ up to 700 °C, the analysis temperature. The quantity of H_2 adsorbed on the catalyst was estimated by the integration of TPD-H_2 curve and calibration similar to that described in H_2-TPR. For this analysis it was considered that two active Ni^0 sites adsorb one molecule of H_2 ($2Ni^0 + H_2 \rightarrow 2Ni\text{–}H$) and each site has an area of 6.5×10^{-20} m^2.

The reduction pattern also was investigated by X-ray absorption near-edge structure (XANES) spectra at the Ni K-edge measured in the D06A-XAS beamline at synchrotron facility at LNLS (National Laboratory of Synchrotron Light — Campinas, Brazil). A Si (1 1 1) polychromator was used to select the X-ray beam from the synchrotron light produced by the 1.37 GeV electron storage ring, at a maximum current of 200 mA. The Ni K-edge absorption spectra were recorded in the transmission mode, in a photon energy range from 8200 to 8800 eV, using a CCD camera. The calcined oxide samples were heated under H_2, from 25 to 700 °C at 10 $°C \cdot min^{-1}$, and held at 700 °C for 20 min (A), after which the temperature was decreased to 600 °C under N_2 (B) and the steam reforming reaction started with a feed molar ratio of CH_4:H_2O = 1.0:4.0, maintained for 30 min (C); after that, O_2 was added to the feed, to yield a molar mixture of CH_4:H_2O:O_2 in proportions1.0:4.0:0.5 (D).

After each catalytic test, the used sample was submitted to temperature programmed oxidation (TPO) in a thermogravimetric analyzer (SDT 2960 Simultaneous DSC–TGA, TA Instruments), with synthetic air flow and a temperature ramp of 10 $°C \cdot min^{-1}$ up to 1000 °C, in order to observe the burning of the carbon deposited on the catalyst during the catalytic runs.

The morphology and the crystal shape of the fresh catalyst particles were examined by transmission electron microscopy (TEM) in a Philips CM120 transmission electron microscope operated at 200 kV.

2.3. Catalytic studies

The catalytic tests were performed at atmospheric pressure, in a fixed-bed tubular quartz micro-reactor with an inner diameter of 13 mm, in a temperature range varying between 350 °C and 700 °C in intervals of 50 °C during 30 min. The unconverted reactants and all the reaction products were analyzed in-line by gas chromatography, with two thermal conductivity detectors (TCDs). Prior to the reaction, 150 mg of the catalyst was introduced into the reactor, forming a bed shorter than 1 mm, in order to minimize the axial thermal dispersion. A thermocouple was used in a well inserted in the bed. The catalysts were reduced in situ in H_2 flowing (30 $mL \cdot min^{-1}$) at 700 °C (ramp of 10 $°C \cdot min^{-1}$) for 2 h, to activate the catalyst. The catalytic bed temperature was monitored through a thermocouple introduced close to the bed. The reaction was conducted in a hydrogen-free feed. For the oxidative steam reforming (OSR), an H_2O:CH_4:O_2 feed in the molar ratio of 4:1:0.5 was used, with a methane flow of 20 $mL \cdot min^{-1}$, 47 $mL \cdot min^{-1}$ of synthetic air (considering 21.3% O_2) and a water flow of 3.9 $g \cdot h^{-1}$ at 25 °C and 1 atm. The gas flow was established by mass flow controllers (MKS Instruments, model 247 with four channels). Water was vaporized in a preheating chamber (180 °C) before reaching the reactor. On leaving the reactor, remaining water was condensed in a cold trap. The dry gaseous products were analyzed in-line by gas chromatography in a CG-3800 Varian chromatograph with two streams, passing respectively through two Molecular Sieve 13X columns to retain CO, H_2 and N_2 and through a Porapak N column to retain CO_2. At the end of the catalytic test, the feed was stopped and system cooled under a N_2 flow [19].

The methane conversion (X_{CH4}) and selectivities to H_2, CO and CO_2 were calculated by the following equations:

$$X_{CH_4} = \frac{(\text{mols of } CH_4)_{in} - (\text{mols of } CH_4)_{out}}{(\text{mols of } CH_4)_{out}} * 100 \tag{5}$$

$$S_i = \frac{\text{mols of i produced}}{\text{mols of } CH_4 \text{ converted}}, \text{ where } i = H_2, \text{ CO or } CO_2. \tag{6}$$