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CO_2 reforming of CH_4 over La–Ni based perovskite precursors

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Abstract

$LaNiO_3$ and La_2NiO_4 type perovskites were prepared by the ''self-combustion'' method and were used as catalyst precursors for the CO_2 reforming of CH_4 reaction at 700 °C. The catalysts were tested in reduced and non-reduced form. High CH_4 and CO_2 conversion were obtained without carbon deposition. This result was explained by the occurrence of the RWGS (reverse water gas shift) reaction. The La_2NiO_4 perovskite used as precursor presents the smallest nickel particles after the reduction treatment. Consequently the catalytic activity is higher than that obtained with Ni/La_2O_3 or $LaNiO_3$.

When La_2NiO_4 is used without treatment prior to the reaction high methane and carbon dioxide conversions are reached but a carbon deposition is observed. The perovskite structure is not completely transformed and the presence of metallic nickel particles at the surface of La_2NiO_4 would be responsible for the carbon deposition. It is assumed that the role of the support is to allow the activation of carbon dioxide, which is favoured over La_2O_3 whereas it is limited over La_2NiO_4. Consequently the reaction between the complex C–Ni species (resulting from methane activation at the surface of the nickel particle) and gaseous CO_2 is inhibited over Ni/La_2NiO_4 leading to a carbon accumulation at the surface of the catalyst.

As soon as the perovskite structure is completely transformed, after reductive treatment or during the reaction, a high activity is reached and no carbon deposition was further observed, the catalytic performances being optimal when the average nickel particles size is the smallest.

Keywords: Perovskite precursors; La_2NiO_4; $LaNiO_3$; CO_2/CH_4 reforming; Coke formation

1. Introduction

The process of carbon dioxide reforming of methane to produce synthesis gas ($CO + H_2$) has received considerable attention in recent years as it constitutes a very attractive route for the conversion of two low-cost products which can be used for the production of liquid hydrocarbons in the Fischer–Tropsch reaction [1] or in the production of methanol. The reaction has been investigated over both, noble metal [2–6] and Ni based [7–11] supported catalyst. Industrially the metal of choice is nickel due to its inherent availability, low cost and high activity in comparison to noble metals. However, the major problem encountered with the reaction of CO_2 reforming of methane is the coke formation leading to the catalyst deactivation especially when Ni is used. Nevertheless it has been shown that a high dispersion of the metal species over the support can limit the coke formation [12].

Shiozaki et al. [13] showed that a metal oxide with a well-defined structure can be a source of small metal particles. Hayakawa et al. used $CaTi_{1-x}Ni_xO_3$ as catalyst precursor for the partial oxidation of methane to syngas [14], highly dispersed Ni metals were formed in situ during the reaction resulting in a high activity and stability.

In previous papers we have shown that $LaNiO_3$ perovskite used as catalyst precursor, leads to a very active catalyst for the CO_2 reforming of CH_4 [15,16]. A reducing treatment under hydrogen is not necessary before reaction since the perovskite structure is completely destroyed under reactants and products during the reaction at 700 °C, the only species detected by XRD after 15 h of reaction being Ni^0 and $La_2O_2CO_3$. Moreover we showed that the average nickel

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particle size (measured after reaction) was smaller when the catalyst was used without pre-treatment (20 nm) than when it was reduced under hydrogen prior to the reaction (27 nm). It was expected that the better the dispersion of nickel, the higher is the catalytic activity [17]. In our case, the performance was as high as the thermodynamic equilibrium indicates.

The aim of the present work was to investigate the activity and stability of the perovskite La_2NiO_4 and to compare its performance with that of $LaNiO_3$ and Ni/La_2O_3. Ni/La_2O_3 was used as a reference catalyst as suggested by Zhang and Verykios [18]. Low nickel content in La_2NiO_4: 15 wt.% against 24 wt.% in $LaNiO_3$ would allow to obtain smaller nickel particle size.

For that purpose the reaction was conducted within the kinetic-controlling regime. The catalyst was characterized at the different steps of the reaction: before reaction, after reducing treatment and after reaction.

2. Experimental

2.1. Catalyst preparation

The perovskite type oxides $LaNiO_3$ and La_2NiO_4 were prepared by the self-combustion method [19]. Glycine ($H_2NCH_2CO_2H$) was used as ignition promoter was added to an aqueous solution of metal nitrates with appropriated stoichiometry, in order to get a $NO_3^-/NH_2 = 1$ ratio. The resulting solution was slowly evaporated until a vitreous green gel was obtained. The gel was heated up to 250 °C, temperature at which the ignition reaction occurs yielding to the formation of a powdered precursor which still contains carbon residues. Calcination at 700 °C for 6 h eliminates all of the remaining carbon and leads to the formation of the perovskite structure.

Catalysts containing 1, 5 and 17% Ni/La_2O_3 were prepared by the wet impregnation method using nitrate salt as metal precursor. Nickel nitrate was placed in a beaker with 60 mL of distilled water. After complete dissolution, the appropriated amount of La_2O_3 was added under continuous stirring. The slurry was then heated up to 90 °C until the water was evaporated. The residue was then dried at 120 °C for 12 h and subsequently calcinated at 700 °C for 6 h under N_2.

2.2. Characterization

2.2.1. X-ray diffraction

The catalysts were characterized by powder X-ray diffraction using a Siemens D-5000 diffractometer with Cu $K\alpha_1 = 1.5406$ and Cu $K\alpha_2 = 1.5439$ Å, operated at 40 kV and 30 mA. The diffraction patterns were recorded in the 2θ values range 10–90° with a step size of 0.01° and 1 s per step.

2.2.2. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was carried out on a Philips CM120 instrument, with LaB_6 filament and equipped with an energy dispersive X-ray analyzer (EDX).

2.2.3. Temperature programmed reduction (TPR) and H_2 pulses chemisorption

TPR and H_2 chemisorption experiments were carried out in a Micromeritics Autochem 2910 using about 160 mg of catalyst. TPR experiments were performed using 5% hydrogen in argon, 50 mL/min, with a heating rate of 5 °C/min, from room temperature to 900 °C. H_2 consumption was obtained from the integrated peak area of the reduction profiles relative to the calibration curve.

Before hydrogen chemisorption, the samples were reduced in a 5% H_2/Ar flow while the temperature was risen at 5 °C/min from ambient to 700 °C and maintained at this temperature for 6 h. Then the system was purged in Ar at 720 °C for 3 h and cooled to 50 °C. Hydrogen pulse chemisorption was started at 50 °C using 5% H_2/Ar and repeated at 5 min intervals until the hydrogen area picks became identical. The amount of hydrogen consumption was measured with a thermal conductivity detector. Metal dispersion on the surface was calculated assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom ($H/Ni_s = 1$).

2.2.4. BET

All samples were degassed with He for 30 min at 623 K before measurement, the adsorption–desorption isotherm of N_2 was measured using 30% N_2/Ar as the adsorbate on a Micromeritics Flowsorb II 2300 apparatus at −196 °C.

2.2.5. Catalytic reaction

The reaction was carried out by passing a continuous flow of $CH_4/CO_2/He = 10/10/80$ over the catalyst bed. The amount of catalyst was fixed at 20 mg with a total flow rate of 100 mL/min which corresponds to a space velocity of 3×10^5 mL h^{-1} g^{-1}, in order not to reach the thermodynamic equilibrium (at 700 °C, the equilibrium state is reached for: CH_4 conversion = 90% and CO_2 conversion = 93%).

All measurements were conducted using catalyst grain size of 180 μm in order to perform the experiments within the region of intrinsic kinetics.

The temperature was increased from room temperature to 700 °C at a rate of 5 °C/min, and maintained at this temperature for the desired reaction time. The temperature was measured with a thermocouple located inside the reactor but without direct contact with the catalyst.

In some experiments the perovskite catalyst was used without pre-treatment or after reduction under hydrogen at 700 °C for 1 h. The reaction products were analyzed by an online mass spectrometer. The detection limit was estimated to be around 0.04 μmol. According to the intensity of the signal measured by the MS, this value corresponds to about 1% of the total amount detected.

3. Results

3.1. X-ray diffraction characterization

The X-ray diffraction patterns obtained for $LaNiO_3$ and La_2NiO_4 are shown in Figs. 1 and 2, respectively. After