Plain and CeO_2 – Supported La_xNiO_y catalysts for partial oxidation of CH_4

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$LaNiO_3$ and La_2NiO_4, as such and in combination with CeO_2, were prepared by microwave assisted co-precipitation procedure and tested in the catalytic partial oxidation of methane (CPO). The materials were characterized by BET, TGA/DTG, XRD, TPR and TEM techniques. In the absence of CeO_2, the microwave processing allowed obtaining perovskite and spinel phases in high percentage at milder conditions as compared to traditional methods. In the presence of CeO_2, $Ce_{1-x}La_xO_{2-x/2}$ solid solutions and NiO formed. At high temperature (~ 800 °C) all the catalysts exhibited high methane conversion with near 100% CO selectivity and good stability. Activation of the catalysts occurred during temperature cycling. At the temperature corresponding to $\sim 60\%$ conversion, the CeO_2-free sample deactivated quickly, differently from the CeO_2 containing sample being very stable during the 18 h of reaction. The temperature surface reaction (TPSR) of CH_4 without O_2 confirmed the differences between the two systems, i.e. with and without CeO_2. The $LaNiO_3$-CeO_2 activated the decomposition of methane with simultaneous CO/CO_2 evolution in a large range of temperature contrary to $LaNiO_3$ activating methane decomposition only in a narrow range of temperature, without any CO/CO_2 evolution. As shown from TPR analyses, an intimate contact between nickel phases and ceria was required to promote CPO activity. According to TGA and as confirmed by TEM analyses, formation of carbon was inhibited over the CeO_2 containing catalysts, whereas different types of carbons were formed over the spinel and the perovskites formulation samples.

1. Introduction

As compared to endothermic methane reforming process, the exothermic partial oxidation of methane is a cost efficient way to produce synthesis gas with H_2/CO molar ratio equal to 2, suitable for methanol and also for Fisher Tropsch syntheses [1–3]. Among the elements being investigated as possible catalysts for the catalytic partial oxidation of methane (CPO), nickel is considered the most suitable one in terms of activity and cost. However, if not properly supported it tends to deactivate by metal sintering and/or coke poisoning. As recently shown, the use of lanthanide oxides as supports enhances the CPO activity of Ni catalysts consisting of a variety of La_xNiO_y oxide phases [3,4]. The good thermal conductivity of the La_2O_3, avoiding hot spot formation and its strong interaction with nickel inhibits metal sintering during the high temperature reaction [2]. CeO_2, in virtue of its peculiar redox properties is a suitable support for this type of reaction [5]. It was recently reported for differently supported Ni on CeO_2 that an intimate contact between Ni and the oxide increases the reducibility of the catalyst and favors the removal of the carbon arising from the

CH_4 decomposition [5]. Moreover, the use of a stable structure like $LaNiO_3$ perovskite as catalyst for the partial oxidation of methane was described to enhance nickel stability against sintering and carbon deposition [6,7]. Contradictory results for the use of perovskite were also reported stating the unsatisfactory performance of the perovskite–based catalysts due to the possible formation of undesired phases, such as $La(OH)_3$, $La_2O_2CO_3$, La_2NiO_4 and NiO depending on the reduction environment [8]. The spinel La_2NiO_4 and the perovskite $LaNiO_3$ prepared by citric acid complex method, were investigated as precursors of nickel catalysts for the partial oxidation of methane [9,10]. The use of either precursor produced only small differences in the catalytic behavior [10]. Since the stabilization of the nickel particles for this high temperature reaction is crucial, different types of preparation procedures were considered [11–14]. For the purpose of the present study as an alternative to the complex and expensive sol-gel synthesis for the attainment of pure ceramic phases, the use of microwave processing was explored. Indeed, the use of microwave energy for processing of materials, such as ceramics, metals and composites, offers some advantage over the conventional heating

methods. These advantages include unique microstructure and properties, energy and time savings and reduction in manufacturing costs [15].

Aiming to investigate the synergy between the redox properties of CeO_2 and the role of La_xNiO_y precursor structures, in the present study La_2NiO_4 and $LaNiO_3$ as bare and also in combination with CeO_2 were prepared by microwave assisted procedures. Their catalytic activity in the partial oxidation of methane were compared and discussed in terms of structural properties.

2. Experimental

2.1. Sample preparation

$LaNiO_3$ and La_2NiO_4 oxides were synthesised by microwave (mw) assisted co-precipitation. According to the procedure, required amount of the nickel (II) nitrate and lanthanum(III) nitrate were dissolved in ethanol with stirring. 10 M NaOH solution was added dropwise until the pH of the resulting solution was 9–10. The suspension with the precipitated hydroxides was placed in a conventional microwave oven set at 180 W power and operated in 30 s cycles (on for 10 s, off and stirring for 20 s) for a total timing of 30 min. After cooling, filtering and washing with distilled water, the precipitate was dried at 80° C and finally calcined for 2 h at 800 °C. The samples containing CeO_2 were prepared by similar procedure but with the addition of the cerium(III) nitrate and considering the proper amount of nickel as spinel and perovskite to give a nickel loading of 6 wt%. These samples were labelled as $LaNiO_3$-CeO_2 and La_2NiO_4-CeO_2. By the same procedure the pure CeO_2 oxide was also prepared and calcined at 800 °C. A sample $LaNiO_3$-CeO_2*mix_mw* was prepared by mixing together in ethanol solution the proper amount to yield 6 wt% of Ni, of preformed $LaNiO_3$ and CeO_2, followed by microwave treatment as above. Thereafter the solid was filtered, dried at 100 °C and then calcined at 550 °C for 4 h. For comparison reason the sample $LaNiO_3$-CeO_2*mix,* a simple mechanical mixture of pre-formed $LaNiO_3$ and CeO_2 was prepared and tested in CPO reaction.

2.2. Catalysts characterization

The specific surface area of the supports were determined from N_2 adsorption–desorption isotherms at -196 °C using the Sorptomatic 1900 (Carlo Erba) instrument through the Brunauer–Emmett–Teller (BET) calculation methods [16]. Before the measurements, samples were heated in vacuum at 250 °C for 2 h.

The phase composition of crystalline components of fresh and aged samples was investigated by X-ray diffraction (XRD) analyses. The XRD patterns were recorded in Bragg-Brentano para-focusing geometry using the Bruker D5000 diffractometer, equipped with Cu Kα anode and graphite monochromator. The XRD data were collected in the 2θ angular range 10°–80° with 0.05° step size and counting time of 5 s per step. The assignment of the various crystalline phases was based on the JCSD powder diffraction file cards [17]. The diffraction patterns were analysed by Rietveld refinement using the GSAS package [18] as previously described [3,5]. From fitting results, the structural parameters of the investigated compounds and, in particular, the cell edge lengths and the relative phase composition were obtained. An estimation of the mean crystal size values was obtained from the line broadening calculated by Rietveld analysis in agreement with the GSAS package procedure [18] and with the Scherrer equation [19].

Temperature programmed reduction (TPR) experiments were carried out with the Micromeritics Autochem 2950 HP apparatus equipped with thermal conductivity detector (TCD). The gas mixture with composition 5% H_2 in Ar (30 ml/min) was used to reduce the samples (50 mg) heating from room temperature to 1050 °C at the rate of 10 °C/min. Before starting the TPR analyses, the catalysts were pretreated with a flowing gas mixture of 5% O_2 in He (50 ml/min) at 350 °C for 30 min, then cooling down under He.

The thermogravimetric analyses (TGA) of the samples after the catalytic reactions were performed in air using the TGA 1 Star System of Mettler Toledo. About 10 mg of sample was heated from room temperature to 1100 °C at the rate of 10 °C/min. The evolution of the CO_2 was monitored by mass quadrupole analyser.

The morphology of the samples was determined by transmission electron microscope (TEM) using a Jeol JEM 2100.

2.3. Catalytic measurements

Methane oxidation catalytic tests were performed in a U shaped quartz reactor with an inner diameter of 12 mm using the already described apparatus [1]. Prior to the catalytic testing, 50 mg of catalyst powder (sieved fraction between 180 and 250 μm) were treated "in situ" under flowing O_2 (5 vol.% in He, 50 ml/min) at 350 °C for 1/2 h. After cooling down to room temperature, the samples were reduced under flowing H_2 (5 vol.% in Ar, 30 ml/min) increasing the temperature to 750 °C with a 10 °C/min ramp and a holding time of 1 h. In the case of the unsupported perovskite and spinel samples appropriate amount of diluting SiC was added in order to achieve the same loading of nickel in each catalytic test regardless the catalyst formulation. In particular 12 mg of $LaNiO_3$ and 20.4 mg of La_2NiO_4 were diluted with SiC up to 50 mg. In all cases, the absence of hot spots was checked and no addition of inert diluent was needed for thermal management. The feed gas, consisting of 2 vol.% of CH_4 + 1vol.% O_2 in He, was led over the catalyst at a flow rate of 50 ml/min (STP), equivalent to a weight hourly space velocity (WHSV) of 60,000 ml g^{-1} h^{-1}. Effluents were analysed from 400 °C to 800 °C with 50 °C temperature intervals waiting 30 min for each step. The inlet and outlet gas compositions were analysed by on line mass quadrupole analyser (Thermostar™, Balzers), in order to follow the evolution of all the species, CH_4, CO, CO_2, H_2, H_2O, O_2. Accurate concentrations of CO, CO_2 and CH_4 species were obtained by IR analysers (ABB Uras 14, Uras 26), calibrated in the range 0–30%vol for CO, for CO_2 and for CH_4. The methane conversion X_{CH4} and the CO selectivity S_{CO} were calculated as $X_{CH4} = (CH_4^{in} - CH_4^{out})/CH_4^{in} \times 100$ and $S_{CO} = CO/(CO + CO_2) \times 100$ respectively. Carbon balance was close to $\pm$ 5% in all the catalytic tests.

For two selected samples, the unsupported $LaNiO_3$ and the ceria supported $LaNiO_3$, the influence of temperature was studied during a temperature ascending and descending cycle in the range of 500–800 °C. Thereafter, long run stability tests were performed at two slightly different temperatures corresponding for both samples to about 60% initial methane conversion.

The activation of methane by the catalysts was investigated by temperature-programmed surface reactions (TPSR) performed using the same sample pretreatment and the same experimental conditions as used for the TPR reaction except for the reactant gas mixture being 2 vol% CH_4 in He without oxygen. The evolution of CH_4, CO, CO_2 and H_2 was recorded as function of temperature.

3. Results and discussion

3.1. Catalytic activity and carbon formation

The performance of the catalysts in terms of CH_4 conversion and CO selectivity as a function of temperature between 600 °C and 850 °C is shown in Fig. 1. At the lower temperatures 100% selectivity to the total oxidation of methane to CO_2 was observed, in accord with the recent results on Ni catalysts supported over CeO_2 and La_2O_3 [3,5]. The switch to the partial oxidation occurred rather abruptly in a temperature range from 750 °C to 850 °C. With all the catalysts, including the physical mixture and the microwave activated physical mixture, methane conversion and CO selectivity close to thermodynamic values were obtained [1,2].

The sudden increase of the CO selectivity could be attributed to a