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Synthesis and support composition effects on CH_4 partial oxidation over Ni–CeLa oxides

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ABSTRACT

Two series of Ni (6 wt%) catalysts supported over CeO_2, La_2O_3 and mixed CeO_2–La_2O_3 were prepared by co-precipitation and by wet-impregnation. The effect of the two Ni loading procedures on the catalyst structural properties was investigated by XRD, TPR and XPS. The catalytic behavior of the catalysts was tested in the methane partial oxidation reaction performed at 1 atm in a temperature range of 400–800 °C using dilute feed gas mixture with $CH_4/O_2 = 2$ and gas hourly space velocity of 60,000 ml g^{-1} h^{-1}. Total methane combustion was observed within the $450\,°C \leq T \leq 650\,°C$ temperature range. Above 650 °C partial oxidation of methane started to occur, reaching at 800 °C a CO selectivity close to 90%. The lanthanum containing catalysts prepared by wet impregnation exhibited higher CPO activity at lower temperature as compared to the co-precipitated ones. Opposite behavior was observed with the Ni–CeO_2 catalysts. During the stability test at high temperature, carbon formed only over the single oxide supported catalysts, Ni–CeO_2 and Ni–La_2O_3. According to the characterization results carbon was not responsible for catalyst deactivation but it prevented the sintering of the nickel particle. The interplay of the crystallite sizes and the formation of various nickel–lanthanum oxide species with different Ni oxidation states were responsible for the differences in the CPO performance.

1. Introduction

The production of synthesis gas from natural gas is an important step in the gas to liquid (GTL) technology, accounting for 50–75% of the capital cost. The syngas may be actually produced by different processes such as steam reforming (SR), dry reforming (DR), partial oxidation of methane (POM) and autothermal reforming (ATR) which is a combination of the endothermic reforming reaction (SR) and the exothermic oxidation reaction [1–3]. Dry reforming is an interesting and promising process since it contributes to the removal of the greenhouse CO_2 present in the natural gas in a 2% amount [4]. However the difficulty to activate the stable CO_2 molecule and to avoid catalyst poisoning by the large amount of carbon deposition still prevents its application at industrial level. In fact, each of the mentioned processes presents peculiarity in terms of the produced H_2/CO ratio, carbon poisoning and energy efficiency. However, steam reforming (SR) and catalytic partial oxidation of methane (POM) are currently the preferred reactions to produce synthesis gas. With respect to the endothermic steam reforming, which is highly energetic and capital intensive [5,6] the partial oxidation reaction (1)

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \Delta H^{\circ}_{298\,K} = -35.5\,\text{kJmol}^{-1} \tag{1}$$

offers the following advantages: (a) H_2/CO ratio of 2, suitable for methanol or Fischer–Tropsch synthesis; (b) being mildly exothermic the CPO process does not require large heat exchange reactors and needs a more compact plant technology [7]. Nevertheless, as for all the reactions involving conversion of methane the choice of a catalyst, able to activate the molecule, is crucial due to the high dissociation energy of the first CH_3—H(g) bond (440 kJ/mol) [8]. Noble metals are appropriate for this kind of reaction, exhibiting high activity/selectivity and long term stability. However, since noble metals are rather expensive their use is prohibitive for industrial application. A more convenient alternative is represented by nickel which is also active but less stable, suffering from carbon deposition and metal sintering [5,9]. Still, in terms of cost and availability, the nickel based catalysts are the most interesting systems and much research is being addressed to their stability improvement [9]. To this respect the choice of an appropriate support is very

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important as the supports affect the metal dispersion, inhibit particle sintering and in the case of basic character they may minimize carbon formation [10]. Different types of oxides like Al_2O_3, MgO, La_2O_3 and CeO_2 have been investigated as nickel supports for CPO applications [11–17]. These oxides differ for oxygen mobility and for their different degree of interaction with nickel, both properties affecting the catalyst reducibility and their final catalytic behavior. According to the literature no definite conclusion on the most suitable support can be drawn. Indeed, the use of a specific support has yielded different catalytic results related to various factors such as the precursor of the catalyst components, the preparation methods, the nickel loading and the CPO reaction conditions.

The objective of the present study was to analyze the effect of the synthesis procedure and the effect of the nature of the support on the catalytic behavior of Ni over CeO_2, La_2O_3 and mixed oxide CeO_2–La_2O_3. The two oxides were selected because of their peculiar properties. CeO_2 is characterized by large oxygen mobility, playing an important role in the oxidation type of reaction [18,19]. La_2O_3 is characterized by a strong chemical interaction with nickel, forming several La–Ni oxide phases and therefore stabilizing the metal and possibly avoiding carbon formation [20,21]. The catalytic results in terms of methane conversion and CO selectivity were related to the structural and chemical properties of the samples investigated by XRD, XPS and TPR techniques.

2. Experimental

2.1. Sample preparation

2.1.1. Support preparation

La_2O_3, CeO_2 and La_2O_3/CeO_2(Ce/La = 50/50 wt%) oxides were prepared by (co)-precipitation from the corresponding nitrate precursors using K_2CO_3 to precipitate the corresponding hydroxides. After washing several times to remove the potassium and drying at 100 °C, the obtained solids were calcined at 800 °C for 4 h.

2.1.2. Catalyst preparation

Two series of catalysts were prepared by following two procedures. One series was prepared by wet impregnation (WI) consisting of impregnating the supports with $Ni(NO_3)_2$ aqueous solution, of the appropriate concentration to obtain a final catalyst with 6 wt% Ni. The solid was dried overnight at 100 °C and then calcined at 800 °C for 4 h. The other series was prepared by co-precipitation (CP) with the procedure used for the supports alone except for adding $Ni(NO_3)_2$ to the rare earth nitrate solution. All the reagents were from Aldrich. The obtained samples were labeled as Ni–La and Ni–Ce and Ni–CeLa followed by the notation of (CP) or (WI).

2.2. Sample characterization

The specific surface area of the supports were determined from N_2 adsorption–desorption isotherms at −196 °C using a Sorptomatic 1900 (Carlo Erba) instrument through the Brunauer–Emmett–Teller (BET) calculation methods [22]. Before the measurements, samples were heated in vacuum at 250 °C for 2 h.

The phase composition of crystalline components of fresh and spent samples was investigated by X-ray diffraction (XRD) analyses and Rietveld refinement. XRD patterns were recorded in Bragg-Brentano para-focusing geometry using a Bruker D5000 diffractometer, equipped with Cu Kα anode and graphite monochromator. The XRD data were collected in the angular range 10–80° in 2θ using 0.05° step size and counting time of 5 s per step. The assignment of the various crystalline phases was based on the JPDS powder diffraction file cards [23]. The diffraction patterns were analyzed by Rietveld refinement using the GSAS package [24]. Chebyschev polynomials and Pearson VII functions were chosen for the background and for the peak profile fitting, respectively. In the structure refinement, lattice constants, zero offset, scale factors and full width half maximum (FWHM) were considered as variable parameters. 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 [24] and with the Scherrer equation [25].

Temperature programmed reduction (TPR) experiments were carried out with a Micromeritics Autochem 2910 apparatus equipped with a 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 800 °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 550 °C for 30 min, then cooling down under He.

The thermogravimetric analyses (TGA) were performed in O_2 using the TGA 1 Star System of Mettler Toledo. About 5 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.

The X-ray photoelectron spectroscopy (XPS) analyses of the calcined and spent catalysts were performed with a VG Microtech ESCA 3000 Multilab, equipped with a dual Mg/Al anode. The spectra were excited by the unmonochromatised Mg Kα source (1253.6 eV) run at 14 kV and 15 mA. The analyzer operated in the constant analyser energy (CAE) mode. Survey spectra were measured at 50 eV pass energy. For the individual peak energy regions, a pass energy of 20 eV set across the hemispheres was used. The sample powders were mounted on a double-sided adhesive tape. The pressure in the analysis chamber was in the range of 10^{-8} Torr during data collection. The constant charging of the samples was corrected by referencing all the energies to the C 1s peak energy set at 285.1 eV, arising from adventitious carbon. Analyses of the peaks were performed with the software provided by VG, based on non-linear least squares fitting program using a weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley and Sherwood [26,27]. Atomic concentrations were calculated from peak intensity using the sensitivity factors provided with the software. The binding energy values are quoted with a precision of ±0.15 eV and the atomic percentage with a precision of ±10%.

2.3. Catalytic measurements

Methane oxidation catalytic tests were performed using a U shaped quartz reactor with an inner diameter of 12 mm, electrically heated in a furnace. The catalyst powder (sieved fraction between 180 and 250 μm) was diluted 1:2 with inert SiC, in order to avoid thermal gradients. The reaction temperature was measured by a K-type thermocouple in contact with the catalytic bed long 12 mm. Prior to the catalytic testing, the samples were treated “in situ” under flowing O_2 (5 vol.% in Ar, 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 He, 50 ml/min) increasing the temperature to 750 °C with a 10 °C/min ramp and a holding time of 1 h. The feed gas consisting of 2 vol.% of CH_4 + 1 vol.% O_2 in He, was led over the catalyst (50 mg) 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}. The activities were measured as a function of temperature from 400 °C to 800 °C with a heating rate of 10 °C/min.

For detection signal stabilization, at the chosen interval of 50 °C the temperature was held for 30 min, thereafter the signals were