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CO₂ methanation on hard-templated NiO–CeO₂ mixed oxides

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ABSTRACT

Mesostructured NiO–CeO₂ mixed oxides, with Ni loadings in the range 5–35 wt% (g_{Ni}/g_{CeO_2}), were synthesized by the hard template procedure using SBA-15 as the template. A hard-templated CeO₂ was also prepared and used as the support for depositing Ni (5–35 wt%) by impregnation. Two NiO–Al₂O₃ catalysts were synthesized for comparison, by impregnating nickel on a commercial γ -alumina. All the samples were characterized by different techniques as to their chemical composition, structure, morphology, texture, and redox features. The catalytic performance was investigated in the CO₂ methanation reaction after mild reduction pretreatment (H₂ at 400 °C for 1 h). Catalytic testing was performed under atmospheric pressure, 300 °C, 72,000 cm³ h⁻¹ g_{cat}⁻¹, and stoichiometric H₂/CO₂ molar ratio. High catalytic activity, with CH₄ selectivity values ≥ 93 mol%, was obtained with the NiO–CeO₂ mixed oxides (CO₂ conversions up to 76 mol%). When γ -Al₂O₃ was used as the support, catalysts with low activity (CO₂ conversion ≤ 20 mol%) were obtained. On selected samples, additional catalytic runs were also performed for reaction times up to 30 h or with a higher space velocity value. The catalytic results were explained by taking into account the role of the nickel-ceria interactions both during the reduction of NiO and in the reactants activation.

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Introduction

CO₂ chemical recycling is attracting the increasing interest of academics and industry researchers as a means for reducing greenhouse gas emissions. Among the different options to convert carbon dioxide, hydrogenation to form hydrocarbons and/or oxygenates is the most investigated by using homogeneous and heterogeneous conventional catalysis [1] as well as

photocatalysis [2]. Methanation to synthetic natural gas (SNG) can be a valuable route for CO₂ conversion, especially if the required H₂ is produced from renewable sources. Since CO₂ methanation is strongly exothermic, a reaction temperature not exceeding 300 °C should be used in order to obtain high CH₄ yields at 1 atm; however, the presence of significant kinetic limitations makes the eight-electron reduction of CO₂ to CH₄ by hydrogen difficult, highly active catalysts being then

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required to achieve acceptable rates and selectivities [3]. CO₂ methanation has been extensively studied on catalytic systems based on noble (e.g. Ru, Rh) and non-noble (Ni) metals supported on different metal oxides [4,5]. Ni-based catalysts have been mainly investigated, due to their low cost, high activity, and high methane selectivity. The effect of different promoters, supports, and preparation methods on the catalytic activity and stability of Ni-based catalysts has been studied [5,6]. Due to its high oxygen storage capacity and redox properties, which can affect dispersion, morphology, and electronic properties of the supported metals, hence improving their catalytic activity, CeO₂ is widely used as a support in catalysis. However, to the best of the present authors' knowledge, only a few works report on NiO–CeO₂ systems for CO₂ hydrogenation to methane [7–10], almost all [7–9] dealing with catalysts with a fixed amount of Ni (10 wt%) deposited by impregnation on the previously prepared ceria support. Among the preparation procedures, the hard-template (HT) method has attracted increasing interest for the synthesis of ordered mesoporous metal oxides, often using a mesostructured silica as a template [11].

In this work, two different mesostructured NiO–CeO₂ systems were synthesized: (i) by the HT procedure using SBA-15 as the template or (ii) by impregnating NiO on a hard-templated CeO₂ support. Nickel content was increased from 5 to 35 wt% (g_{Ni}/g_{CeO_2}), with the aim of investigating the effect of metal loading on the catalytic behavior and the influence of the preparation procedure on the dispersion of increasing amounts of nickel oxide. Two NiO–Al₂O₃ catalysts (15 and 35 wt%) were also prepared for comparison, by depositing nickel on a commercial γ -alumina using incipient wetness impregnation. The obtained samples were characterized as to their composition, structure, texture, and redox features. CO₂ methanation was investigated in a fixed-bed continuous-flow quartz-glass microreactor, at atmospheric pressure, 300 °C, and stoichiometric H₂/CO₂ molar ratio (4 mol mol⁻¹). Stability tests were performed on the hard-templated and impregnated NiCe catalysts with 15 wt% of Ni, whose catalytic performance was also investigated at different space velocity values.

Experimental

Materials

Tetraethylorthosilicate (TEOS, 98%), Pluronic copolymer P123 (EO₂₀PO₇₀EO₂₀), Ni(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O, and NaOH (pellets) were supplied by Aldrich. Ethanol (absolute, $\geq 99.8\%$) was supplied by Sigma–Aldrich. HCl (37%) was provided by Merck. All the materials were reagent grade. Commercial γ -Al₂O₃ was provided by CONDEA. CuO for H₂-TPR calibration was provided by ThermoQuest.

Synthesis

SBA-15 mesostructured silica was prepared as previously reported by Zhao et al. [12] (see Section S1 in supplementary material for details) and used as the template in the synthesis of NiO–CeO₂ mixed oxides. In a typical synthesis, Ni and Ce

nitrates were dissolved in 25 cm³ of ethanol to obtain a total concentration of the metals equal to 0.7 M. The relative amounts of the oxides precursors were adjusted to have Ni contents in the range 5–35 wt% (g_{Ni}/g_{CeO_2}). 15 cm³ of the obtained solution were then added to 1 g of SBA-15 and the suspension was stirred at room temperature for 1 h. Next, the solvent was evaporated at 60 °C overnight and the resulting solid was transferred into a furnace and calcined at 500 °C for 3 h to decompose the nitrates into the corresponding oxides. The impregnation (with the remaining 10 cm³ of the ethanolic solution), drying, and calcination steps were then repeated with the aim of filling the SBA-15 pores completely. The SBA-15 template was then removed by leaching with a NaOH solution (2 M) at 50 °C. Lastly, the resulting material was washed to pH 7 with distilled water, dried at 60 °C for 12 h and then calcined at 500 °C under static conditions for 3 h, and the leaching-calcination cycle was then repeated. The obtained samples were named NiCe(x)_{HT}, where x is the nominal value of the Ni content (g_{Ni}/g_{CeO_2}). The HT procedure was also used to prepare a pure CeO₂ sample (named CeO₂_{HT}), on which Ni was deposited through the incipient wetness impregnation (IWI) technique. Appropriate volumes of aqueous solutions, containing suitable Ni(NO₃)₂ amounts, were added to 0.5 g of CeO₂_{HT}. The resulting paste was then dried at 60 °C overnight and the solid was subsequently calcined at 500 °C for 3 h. The obtained catalysts were named NiCe(x)_{IWI}, where x is the nominal Ni loading ranging between 5 and 35 wt%. For comparison, two Ni/alumina catalysts with a Ni nominal content of 15 and 35 wt% (NiAl(15)_{IWI} and NiAl(35)_{IWI}) were synthesized through the IWI procedure by supporting Ni on commercial γ -alumina.

Characterization

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses were performed with a Varian Liberty 200 spectrophotometer to determine the Ni and Si contents. In the case of Ni determination, samples (ca. 0.015 g) were first dissolved in concentrated hydrofluoric acid (40%); after evaporation, the residues were dissolved in a mixture of HCl (37%) and HNO₃ (70%) (3:1 by volume) and then diluted to 250 cm³ with Milli-Q water. For determining the Si content, about 0.1 g of sample were placed in a platinum crucible. After addition of 1.5 g of Na₂B₄O₇, alkaline fusion was performed in the furnace at 1000 °C for 30 min. Then the “pearl” was transferred into a beaker, 100 cm³ of HNO₃ (5 vol%) were added and the mixture was heated at 80 °C until complete dissolution of the sample (typically for 30 min). The solution was finally transferred into a volumetric flask and diluted to the final volume with Milli-Q water for ICP-AES analysis.

Structural characteristics of the samples were investigated by X-ray diffraction (XRD) on a Seifert X3000 diffractometer with θ - θ Bragg-Brentano geometry using Cu-K α wavelength and a graphite monochromator before the detector. The average crystallite sizes (D_c) were estimated by the Scherrer equation [13].

Electron micrographs were obtained with a transmission electron microscope (JEOL 200CX) operating at an accelerating voltage of 200 kV. Finely ground samples were dispersed in

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