CO$_2$-reforming of natural gas components over a highly stable and selective NiMg/Al$_2$O$_3$ nanocatalyst

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A B S T R A C T

A NiMg catalyst supported on a nanofibrous alumina and prepared by the reverse microemulsion method was studied and compared with other Ni-based catalysts for the dry reforming of the major components of natural gas (methane and propane). A NiMg catalyst supported on Al$_2$O$_3$ and prepared by impregnation was also synthesized for comparative purposes. The catalysts were characterized by conventional methods and tested under reactions conditions. Characterization results after reaction revealed that Mg stabilizes the Ni species on the surface by avoiding the Ni diffusion into the alumina lattice and inhibits the global carbon formation. The addition of alkali-earth metal, as Mg or Ba, accelerates the gasification rate of carbon deposits, enhancing the stability of Ni catalysts for the dry reforming of methane and larger alkanes. The microemulsion method improves these effects in the NiMg catalyst, leading to stronger interactions between Ni and Mg, and the formation of a NiO–MgO solid solution with metallic Ni on top. NiMg catalysts prepared by microemulsion allow a stable and carbon-free operation of the dry reforming of methane and propane reactions.

1. Introduction

Natural gas and specifically methane and propane could be chemically reassessed by the catalytic reforming with CO$_2$ to produce syngas with a low H$_2$/CO ratio. Dry reforming could be useful in the reduction of the emissions of harmful greenhouse gases, such as CO$_2$ and CH$_4$ [1]. Ni-based catalysts are widely used for reforming reactions [2], however, they tend to deactivate because of metal sintering and the high rate of carbon formation [3–5]. Noble metals such as Pt [6,7], Rh [8,9], Ru [9,10] and Ir [10] have shown to present stable operations for carbon dioxide reforming of methane with low carbon formation or deposition on the catalysts during the reaction [6–8]. The high cost and restricted availability of noble metals make the development or enhancement of non-noble metal catalysts attractive. Different strategies have been employed in the modification of Ni-based catalysts, such as the addition of promoters or a second metal, the modification of the support and the use of novel synthesis techniques. It is well known that the addition of alkali elements (K, Ca, Ba or Mg [11–14]) and rare earth metals (La, Ce or Zr [15–18]) to Ni-based catalysts can inhibit the net carbon formation, characteristic of Ni catalysts, because these elements facilitate the CO$_2$ activation and promote the removal of the carbon formed. In a previous work [13] we have reported the development of a NiBa/Al$_2$O$_3$ system prepared by mixture, in which

Ba and Ni are incorporated in a single step. This catalyst reached good activity levels and was rather stable for the DRM, allowing a low carbonation level, characterized by the formation of a highly stable Ba spinel (BaAl$_2$O$_4$) ensuring the accessibility of Ni stabilized particles.

Several Ni based catalysts modified with Mg have been also reported to be reactive and stable for the dry reforming of methane: Ni/MgAl$_2$O$_4$ [19], NiMg/Al [20,21] and NiO/MgO [22–24], which were either prepared by precipitation or co-precipitation methods. The high success of NiMg catalysts has been attributed in most of the cases to the formation of a MgO–NiO solid-solution, whose formation is favored by the isomorphic structure of Mg and Ni oxides. MgO–NiO solid-solutions possess a basic surface with small nickel particles on the surface of the solid solution [25,26], both characteristics are desirable for the inhibition of the carbon deposition. These materials could be effective catalysts for the dry reforming of higher hydrocarbons, for which the carbon formation rate is expected to be higher than for methane.

Here, we report the development of a NiMg nanocatalyst, supported on a nanofibrous gamma Al$_2$O$_3$ and synthesized by the reverse microemulsion method (water-in-oil microemulsion) for reforming reactions. This NiMg nanocatalyst has been tested for the CO$_2$-reforming reaction of the major Natural Gas components, methane and propane; its performance is compared with a conventional NiMg catalyst prepared by impregnation and reported in this study, and with Ni and NiBa catalysts previously synthesized and studied for the dry reforming of methane [6,7,13]. The aim of the present contribution is to combine the excellent

properties of reforming NiMg nanocatalysts with the high surface and stability of the nanofibrous alumina, which has shown to be an ideal support for Ni catalysts modified with noble metals [6–8], by using the reverse microemulsion method to enhance the Ni–Mg interactions and control their disposition and composition. The reverse microemulsion method is an attractive approach to prepare metallic nanocatalysts, as the metal species in the catalyst can be homogeneously dispersed [7]. Additionally, upon high temperature treatments ideal mixed oxide compositions can be easily obtained. The reverse microemulsion synthesis has proved to be a powerful method for the preparation of stable and highly reactive PtNi nanocatalysts for the dry reforming of methane [7]. The NiMg/Al$_2$O$_3$ catalyst here reported has shown to be very stable and selective towards syngas production during the dry reforming of methane (DRM) and propane (DRP), showing a better performance than impregnated Ni and NiMg catalysts supported on a nanofibrous alumina.

2. Experimental

2.1. Catalysts preparation

A synthesized nanofibrous γ-Al$_2$O$_3$ ($A_{BET} = 300\,m^2\,g^{-1}$, $V_P = 1\,cm^3\,g^{-1}$) was employed as support. The nanostructured alumina was prepared using NaAlO$_2$ as precursor, as is reported in [6]. In detail, an aqueous NaAlO$_2$ solution was added dropwise to 5 N acetic acid solution. The precipitate obtained was decanted, filtered and washed with water. The white powder was dried overnight at 373 K and subsequently mixed with a non-ionic surfactant (Tergitol 15-TS-5, Sigma) using a Tergitol/Al ratio of 0.5. The mixture was autoclaved for 72 h at 373 K and later treated in stagnant air at 773 K for 20 h. Before the catalysts preparation, the support was treated in stagnant air at 1073 K for two hours (10 K min^{-1}). This alumina exhibits a nanofibrous morphology, with fibers of less than 2 nm in diameter; characterization of the support has been already reported elsewhere [6].

A bimetallic NiMg supported catalyst (Ni 4 at nm^{-2}–10 wt.%; denoted as NiMg/Al$_2$O$_3$ ME) was synthesized by the reverse microemulsion method. The reverse microemulsion was prepared by mixing, under continuous stirring, two different reverse micelle solutions; one solution containing the reductant agent (N$_2$H$_4$, Fluka) and another one containing the Ni precursor (Ni(NO$_3$)$_2$·6H$_2$O). Triton X-100 (Merck) was employed as non-ionic surfactant, 1-propanol (Acros Organics) as co-surfactant and cyclohexane (Sigma–Aldrich) as the organic phase. The metal concentration in the aqueous phase was 1.5 M. The volumetric proportions employed for each solution were Triton X-100/1-Propanol/Cyclohexane/aqueous phase = 12/8/78/2.

The alumina and MgO (Mg/Al = 0.5 mol) was added to the resultant reverse microemulsion and stirred for 3 h. Afterwards, Tetrahydrofuran-THF (Sigma) was incorporated (50 ml g^{-1} of support, at a rate of 0.8 ml min^{-1}) to destabilize the reverse microemulsion. The solution was stirred for 24 h, decanted, filtered and finally washed with ethanol and water. The obtained solid was dried overnight at 373 K and treated in air at 1073 K for 2 h (10 K min^{-1}).

A bimetallic NiMg (denoted as NiMg/Al$_2$O$_3$ IM) was also prepared by incipient wetness impregnation of the support, for comparative purposes. The metal loading, the Ni and Mg precursors, and the pre-treatment procedures were the same that those employed for the catalyst prepared by the reverse microemulsion method. Before Ni impregnation the alumina was mixed with MgO and treated in air at 1073 K for 1 h (5 K min^{-1}).

2.2. Characterization

X-ray Powder Diffraction data have been recorded with an X'Pert MPD PRO diffractometer (PANalytical) using CuKα1 radiation ($\lambda = 1.54059\,\text{Å}$) and a Ge(1 1 1) primary monochromator. The X-ray tube worked at 45 kV and 35 mA. The measurements were done from 10° to 70° (2θ). X-ray Photoelectron Spectra were recorded on a Physical Electronic 5701 equipped with a multichannel detector and a hemispherical PHI 10-360 analyzer. MgK$_\alpha$ was used as X-ray source operating at a constant power of 300 W (15 kV, 20 mA). The data were acquired at a take-off angle of 45° and pass energy of 29.35 eV. The pressure in the analysis chamber was maintained at 8×10^{-7} Pa and the exposition time was 2.5 min. Binding Energy (BE) values were referred to the C1s peak (284.8 eV) from the adventitious carbon for the catalysts before reaction and to the Al2p peak for the catalysts after reaction. All deconvolutions of experimental curves were done with Gaussian and Lorenzian line fitting, minimizing the (χ^2) chi-square values.

X-ray photoelectron spectroscopy measurements were carried out on a Physical Electronics ESCA 5701 instrument, equipped with a multichannel detector and a hemispherical analyzer. Mg Kα radiation ($h\nu = 1253.6$ eV) was used as the exciting source, operated at a constant power of 300 W (15 kV, 20 mA). The data were acquired at a take-off angle of 45° and pass energy of 29.35 eV. The pressure in the analysis chamber was maintained at 8×10^{-7} Pa.

TEM images were taken with a Philips CM 200 of 200 kV. The carbon content of the catalysts after reaction was obtained via elemental analysis technique using an Elemental Analyzer Perkin–Elmer 2400CHN. Characterization of the catalysts before reaction was realized for the catalysts calcined.

2.3. Reactivity

Reactivity experiments were carried out in a Microactivity-Reference reaction system from PID Eng&Tech (Spain) at atmospheric pressure in a temperature range between 673 and 973 K for the DRM, and 673–1073 K for the DRP. A tubular fixed bed stainless steel reactor (i.d. 9 mm) with 100 mg of catalyst (250–420 μm) was employed. The total gas flow rate was kept constant at 50 N cm^3 min^{-1} with stoichiometric composition diluted in He (DRM: CH$_4$/CO$_2$/He = 20/20/60 and DRP: C$_3$H$_8$/CO$_2$/He = 10/30/60). The space velocity and the contact time were 6000 h^{-1} and 0.8 g h mol^{-1}, respectively; operating under plug flow conditions. Preliminary reactivity tests with different catalyst particle sizes and dilutions, measuring the radial and axial temperatures at different points, were performed to confirm the non-existence of heat or mass transfer limitations. Before reaction, catalysts were treated in situ with H$_2$ (3% in He, 30 Ncm^3 min^{-1}) at 973 K for 2 h. The reaction temperature was measured with a thermocouple placed in the reactor bed. The reactor effluent was analyzed by GC (Agilent 4890D) equipped with TCD and FID detectors. Stability runs were performed at 973 K at the same reaction conditions as in the activity tests. C, H and O balances were closed with deviations lower than 5%.

CO$_2$-temperature programmed reaction (CO$_2$-TPR) on the catalysts after the DRM reaction was performed in a TG/DTA thermal analyzer Q600-TA Instrument, at the temperature range of 433–1073 K with a heating rate of 10 K min^{-1} under 10%CO$_2$/He atmosphere. The gases at the outlet of the thermobalance were analyzed by mass spectrometry with a Pfeiffer PrismaTM QM200 Quadrupole Mass Spectrometer. The signals of H$_2$ ($m/z = 2$), CO ($m/z = 29$), and CO$_2$ ($m/z = 44$) were followed. Contribution of CO$_2$ to $m/z = 29$ was subtracted. The signals were normalized with respect to the maximum intensity of the signals during each experiment.