# Structure, reactivity and catalytic properties of nanoparticles of nickel ferrite in the dry reforming of methane

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## ABSTRACT

Nickel ferrite $NiFe_2O_4$ (spinel) was prepared and characterized by several physicochemical methods, and its catalytic properties were investigated in the reforming of methane with $CO_2$ to syngas. Nanoparticles were prepared by coprecipitation (CP), hydrothermal synthesis (HT) and sol–gel process (SG). The methods of preparation influenced strongly the textural and structural properties, as well as their reactivity. X-ray diffraction patterns showed that only HT and SG methods delivered pure $NiFe_2O_4$ nanoparticles (6–10 nm size). However the cell parameter $a$ calculated by Rietveld analysis being respectively larger (HT) or smaller (SG) than the standard value, a non stoichiometric defective mixed spinel could have been formed. The reducibility of samples was studied by two methods. $H_2$-temperature programmed reduction showed the formation of $Ni^0$ at increased temperature along SG $\approx$ HT < CP series, after which step $Ni_xFe_{2-x}O_4$ decomposed to iron suboxides and finally to $Fe^0$. In situ reduction by $H_2$ carried out by HT-XRD showed that the ultimate compound was $\gamma$-$Ni_xFe_{1-x}$ alloy, formed above 400 (SG, HT) or 450 °C (CP). The catalytic activity in the dry reforming of methane was higher with HT and SG than with CP, but values of conversion of $CH_4$ and $CO_2$ were low as compared with efficient catalysts in the literature. After being pre-reduced by hydrogen at 400 °C, a large improvement was observed with SG sample only, in which case the conversions of methane and $CO_2$ at 800 °C amounted to 80 and 93 mol%, respectively, with $H_2/CO = 1.2$.

## 1. Introduction

The reforming of methane using $CO_2$ instead of steam is an attractive route to syngas or hydrogen. This reaction is also interesting from the point of view of environmental sustainability because it uses two gases with high potential greenhouse effect. Like in the steam reforming of methane, whose mechanism is quite similar, a number of side reactions occur, among which the formation of carbon. Compared to expensive noble metals, the availability of which will soon be limited, nickel catalysts are cheap but they are very easily deactivated by coking [1–4]. For example, Rostrup-Nielsen and Bak Hansen [1] studied the decomposition of methane on Ni/MgO catalyst above 500 °C and showed that carbon whiskers encapsulated Ni particles of the same size (5–20 nm), because of the high solubility of carbon in nickel. The formation of carbon deposits that block the active sites and plug the pores of the support is facilitated when the particles of metallic nickel are large. Thus the stabilization of nanosized particles would be necessary, and it would also be a means to cope with sintering. A first way is to support the

nickel species on oxides, from acidic ($SiO_2$, $Al_2O_3$) to basic oxides like MgO [5,6]. Both high stability and resistance to carbon formation was found for Ni/MgO. These properties were attributed to the formation of a solid solution between NiO and MgO which was believed to suppress CO disproportionation. Later, Djaidja et al. [7] found that solid solutions $Ni_xMg_yO_z$ supported on alumina were active in the dry reforming of methane, with a good resistance to coke formation. Among oxidic supports, reducible oxides like $CeO_2$ could help to decrease the amount of carbon by means of the lattice oxygen of the support able to burn carbon deposits [8,9]. An in situ XAS analysis revealed that metallic nickel was not oxidized in the operating conditions [10].

Though the formation of $NiAl_2O_4$ spinel in $Ni/Al_2O_3$ was known to be detrimental to catalytic performance, the stability of Ni particles when deliberately supported on the Ni aluminate was found stronger than when other supports were used [11]. Using the stoichiometric $NiAl_2O_4$ spinel, Kiennemann et al. [12,13] showed that high selectivities to CO and $H_2$ and low carbon formation were obtained at high $CH_4$ conversion. The authors noted that for substoichiometry (Ni/Al < 0.5) the presence of nickel inside $NiAl_2O_4$ spinel structure was responsible for its high stability attributed to a good dispersion of the metallic particles. As they are structurally well-defined, the possibility of making solid solutions allows

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to vary the composition and thus the catalytic properties [1]. Another way could be to synthesize Ni-based mixed oxides and to control their reduction, in order to obtain nanoparticles of $Ni^0$ that would be "dispersed" on, or at least stabilized by, the oxidic matrix. Mixed oxides have recently been the matter of several papers. Spinels like $CaAl_2O_4$ and $MgAl_2O_4$ [14,15], perovskites like $BaTiO_3$, $Ca_{0.8}Sr_{0.2}TiO_3$ and $LaNi_xFe_{1-x}O_3$ [16–18], Ni-doped Ca-hydroxyapatite and Ca-fluoroapatite [19], Mg,Al hydrotalcite [20], $(Mg,Fe)_2SiO_4$ olivine [21], were used as precursors of active metallic nickel species. The interest is that, upon reduction of mixed oxides, the activity of the generated nickel particles is generally high and the stability is improved as compared with Ni supported on alumina. The importance of the method of preparation was highlighted, as the ultimate goal is to deliver nanoparticles of nickel well dispersed on a stable oxidic matrix. Finally, studies in literature show that one element of the structure or support may combine with Ni, which results in bimetallic species or alloy [22–24]. For example, Takanabe et al. [24] showed that the catalytic activity and stability of Ni were greatly enhanced by the formation of an alloy with cobalt, and they ascribed the enhanced performance to the improved catalyst resistance to metal oxidation. Recently we started to study the properties of nickel ferrite, $NiFe_2O_4$, prepared by coprecipitation and by hydrothermal synthesis [25,26]. As the activity of these catalysts in reforming of methane with $CO_2$ was not very high, we have prepared the spinel by using the sol–gel method. In this paper we report on the comparison of the textural and structural properties of these $NiFe_2O_4$ samples varying by preparation. The behavior in reducing atmosphere and the catalytic properties in DRM were also investigated.

## 2. Experimental

### 2.1. Catalyst preparation

The nickel ferrite catalysts were synthesized by three routes, coprecipitation, hydrothermal synthesis and sol–gel procedure, using stoichiometric amounts of Ni and Fe salts (Ni/Fe = 1:2). Coprecipitation (CP) was carried out by addition of sodium hydroxide 2 M (CP-Na) or ammonium hydroxide 2 M (CP-NH), up to pH 10, to an aqueous solution of hydrates of nickel and iron nitrates [25]. After washing by distilled water and drying at 80 °C, the CP precursors were calcined in air flow during 4 h at 650 °C (CP-Na-650 or CP-NH-650). For the hydrothermal (HT) synthesis of $NiFe_2O_4$, NaOH was added to an aqueous solution of Fe and Ni chlorides up to pH = 10 before loading in the hydrothermal cell. The cell was heated up to 140 °C for 1 or 12 h (HT-140-1 and -12). After reaction, the product was washed with distilled water and dried at 80 °C. In the third case (sol–gel), an aqueous solution containing nickel nitrate (0.4 M) and ferric nitrate (0.8 M) was prepared first, and then it was mixed with an aqueous solution of polyacrylic acid (polyacrylic acid/(Ni + Fe) = 0.5). A phase separation was observed. An appropriate amount of nitric acid was slowly added to finally obtain a green transparent solution, which was evaporated at ca. 50 °C until a transparent sol was formed. While heating at 50 °C for 10 h to remove water, the sol turned into a viscous brown gel. Finally, the gel was calcined at 5 °C/min heating rate in air up to 400 (SG-400) or 500 °C (SG-500) for 2 h.

### 2.2. Characterization methods

The surface area of samples was measured by $N_2$ physisorption after degassing at 200 °C for 30 min, using the B.E.T. method on a Micromeritics ASAP2010 apparatus. The crystalline phases were studied by X-ray powder diffraction (XRD) using Bruker AXS D8 Advance diffractometer equipped with an energy dispersive detector (Sol-X), with Cu Kα radiation ($\lambda$ = 0.15406 nm). The patterns were collected at room temperature, in the $2\theta$ = 10–90° range, with 0.02° step and 10 s counting time per step. EVA software was used for phase identification and determination of unit cell parameters and crystallite size. The unit cell parameters were refined by Rietveld method with the Fullprof program (Winplotr interface) [27]. Laser Raman Spectroscopy (LRS) was performed with Spectra Physics krypton ion laser at room temperature using the 647.1 nm excitation line. The beam was focused onto the samples using the macroscopic configuration, and samples were examined at low laser power (3 mW) to avoid damage due to laser heating. Four accumulated spectra were obtained in each spectral range. The scattered light was analyzed with an XY Raman Dilor spectrometer equipped with an optical multichannel charge coupled device liquid nitrogen-cooled detector. The spectral resolution was 0.5 cm$^{-1}$ in the 200–1500 cm$^{-1}$ range. The data processing was performed with the LABSPEC software. The composition and morphology of particles was examined by scanning electron microscopy (SEM) and X-ray energy dispersive microanalysis (EDX) using HITACHI 4100S apparatus at 6 kV. The finely ground catalyst samples were mechanically dispersed on an electrically conductive carbon tape which was placed on an aluminum disc. X-ray photoelectron spectroscopy (XPS) was carried out on Escalab 220 XL spectrometer (Vacuum Generators). The monochromatic Al Kα X-ray source was used and electron energies were measured in the constant analyzer energy mode. The pass energy was 100 eV for the survey of spectra and 40 eV for the single element spectra. All XPS binding energies were referred to C1s core level at 285 eV. The angle between the incident X-rays and the analyzer was 58°, photoelectrons being collected perpendicularly to the sample surface. Spectra were analyzed with CasaXPS software.

The reducibility of samples was studied by temperature-programmed reduction (TPR) and XRD at variable temperatures in diluted hydrogen. TPR experiments were carried out on Micromeritics-Autochem II 2920 with a gas chromatograph equipped with a thermal conductivity detector (TCD) to monitor the $H_2$ consumption. After calibration of $H_2$ on the TCD, 50 mg of sample were loaded in a U-shaped fixed-bed quartz reactor and heated (5 °C/min) from 25 to 1000 °C in 5 vol% $H_2$/Ar. X-ray diffraction at variable temperature ($H_2$-HTXRD) was performed on Bruker AXS D8 Advance diffractometer equipped with XRK 900 chamber and a Vantec detector. Diagrams were collected every 25 °C at 0.1 °C/s heating rate up to 800 °C, the counting time being chosen to collect a diagram in 15 min in the 10–90° $2\theta$ range. The sample was displayed on a platinum sheet and 3% vol% $H_2$/$N_2$ mixture was flowed in the chamber (5 L/h). After measurement, all samples were cooled down to room temperature (R.T.) at 0.3 °C/s cooling rate and the final pattern was acquired at R.T.

### 2.3. Catalytic experiments

The catalytic experiments were performed at atmospheric pressure in a conventional test rig. Methane and carbon dioxide were mixed with argon (all gas flow-rates measured by flow-mass controllers) and passed through the quartz U-shaped fixed bed reactor (10 mm inner diameter, 20 mm length) containing the catalyst. The effluents were analyzed before and after reaction using a Prisma 200 Pfeiffer mass spectrometer. Before loading in the reactor, 100 mg of powder sample were mixed with silicon carbide granules (total mass equal to 1000 mg). A mixture of $CH_4$, $CO_2$ and inert gases ($CH_4$:$CO_2$:He:Ar = 20:10:10:50, total flow 90 mL/min STP, contact time $\tau$ = 0.6 s, GHSV = 54 L h$^{-1}$ g$_{cat}$$^{-1}$) was introduced into the reactor. The calcined samples were heated at 5 °C/min heating rate up to 800 °C, and their catalytic performance was measured every 50 °C by decreasing the temperature down to 650 °C. After a series of experiments, the catalyst was reoxidized under