



## In situ XAS study of an improved natural phosphate catalyst for hydrogen production by reforming of methane



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### ABSTRACT

Some nickel catalysts supported on natural phosphate (NP) have been tested for the dry methane reforming reaction. Although the original impregnated 15%Ni/NP catalyst has no activity at all, the modification of the support by mechano-chemical and/or acid treatment strongly improved the catalytic performance, yielding a series of very active and stable catalysts. The chemical and physical characterization by X-ray diffraction (XRD), temperature programmed reduction (TPR), in situ X-ray absorption spectroscopy (XAS) and other techniques have shown that these treatments mainly modify the interaction between the nickel phase and the support surface. The nickel ions occupy calcium position in the surface of the phosphate phase, which stabilizes and improves the dispersion of nickel species. The final reduced catalysts present a much better dispersed metallic phase interacting with the NP surface, which has been identified as responsible for the observed outstanding catalytic performances.

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### 1. Introduction

The production of hydrogen and synthesis gas from natural gas is a first order priority in the international energy policies. Nowadays, the main industrial reaction for obtaining hydrogen is the steam reforming reaction of methane, the main component of natural gas. As during the last decade the number of natural gas fields has hugely increased, the reserves and price of this chemical has decreased and it is expected to be severely reduced in the next decades [1,2]. Although it is well known that various transition and noble metals have high catalytic performances for reforming of methane, nickel containing catalytic systems are widely used for this hydrocarbon reforming reaction, mainly due to the low price and acceptable catalytic performance for the production of hydrogen [3–6]. Beside this reaction, the dry reforming of methane (DRM), using carbon dioxide as oxidant, has attracted very much attention as an alternative reaction. Although some authors have pointed out that it is impractical for commercial hydrogen generation [7], the DRM has additional environmental and industrial interest, as it can be used to valorize and/or eliminate the CO<sub>2</sub> from natural gas deposits. Even more,

the use of two greenhouse gases (methane and CO<sub>2</sub>) for obtaining hydrogen and synthesis gas (CO/H<sub>2</sub>), which is one of the main chemicals currently used in major industrial processes as methanol synthesis, hydrogenations or Fischer–Tropsch reactions [8–10], has an unquestionable environmental interest.

The main issue related with the use of these Ni-based materials as catalysts is their low resistance to the coke deposition during reaction, which requires introducing regeneration steps during the catalytic process, hindering their use as a long term catalyst in industrial applications. It is well known that factors as the dispersion of the metallic phase onto the support, the morphology of the metallic particles or the interaction of these nickel metallic particles with the surface of the support are important factors determining the catalytic activity and stability of these catalysts [11–16]. In general, the preparation of well-dispersed Ni-based catalysts is not an easy task. Therefore, the choice of the support is one of the main factors affecting the stability of the Ni-based catalysts, and a great number of them have been studied by different authors [9,15,17–19]. Natural phosphate (NP), mainly obtained from an ore in Morocco (more than 75% of world reserves) has been used as catalysts in a wide range of catalytic reactions involving different types of organic reactions [20–22]. In this work, we have explored the application of NP as a support for nickel catalysts in the aforementioned reforming reactions as much as obtained from the ore

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as modified by different chemical and mechanical treatment. The use of different characterization techniques, as XRD, SEM or in situ XAS, has allowed us to determine and chemical and physical state of the nickel particles achieved under different preparation conditions and nickel content, namely 15 wt% and 3 wt% Ni/NP catalytic systems. As the former systems have a rather high nickel content, the 3 wt% Ni systems have allow us to study in details the interaction between the nickel phase and the support surface, mainly by XAS techniques.

## 2. Experimental

### 2.1. Catalysts preparation

Natural phosphate (NP) came from an extracted ore in the region of Khouribga (Morocco). The fraction of 100–400  $\mu\text{m}$  grain size was washed with water, calcined at 900 °C for 2 h, washed again, calcined again at 900 °C for 0.5 h and ground (63–125  $\mu\text{m}$  fraction). As in other previous works on the same support [21,22], the structure of NP is similar to that of carbonate hydroxyfluorapatite as shown by X-ray diffraction pattern and chemical analysis. Details about these treatment and elemental analysis can be found in the aforementioned works [21,22].

This NP phosphate support was then modified by two different treatments. So, a fraction of NP was submitted to a treatment with nitric acid 1 M. After contacting the powder during 2 h, the so prepared NP–H sample was water washed and dried at 120 °C. Alternatively, the NP was submitted to a ball milling mechanochemical treatment during 20 and 60 min, respectively. This kind of ball milling treatment was initially developed for diminishing its particle size. However, it has become during the last decade in a green chemistry method for synthesizing a large number of nanosized materials avoiding the use of solvents [23]. Even more, some previous works have shown it can improve the performance of different catalytic systems [24]. The samples have been ground by means of a high grinding energy ball mill SPEX, model Mixer mill 8000 M. Both grinding jars and balls made of hardened steel have been used. The volume of the jar was 50 cc with an internal diameter of 38 mm. Sample amounts of 3 g were ground using 5 balls with 12 mm in diameter in the whole set of grinding experiments. The powder to ball mass ratio was always closed to 1:12. The clamp speed of the shaker mill was 875 cycles/min. The supports obtained by this treatment were denoted as NP–B20, NP–B60, NP–H–B20 and NP–H–B60, indicating that the original or the acid treated phosphates were ball milled during 20 or 60 min. In both cases, no changes in the elemental composition of the NP were observed after the treatments.

As indicated in Section 1, two different nickel loadings were used, namely a 3 wt% and a 15 wt% Ni on NP, NP–H, NP–H–B20 and/or NP–H–B60. These nickel catalysts were prepared by aqueous slurry impregnation using a nickel acetate solution  $\text{Ni}(\text{CH}_3\text{COO})_2$ . The mixture was stirred at room temperature for 1 h, the slurry was dried at 120 °C in a sand bath, kept overnight at 120 °C in an oven, heated to 400 °C with a 1 °C/min ramp rate, and calcined in air at 400 °C for 2 h.

### 2.2. Catalytic activity tests

Dry reforming of methane reaction (DRM) was carried out in a fixed-bed tubular reactor described elsewhere [25], using 40 mg of catalysts between two pompons of quartz wool. Before reaction, samples were reduced with  $\text{H}_2$  at 500 °C during 1 h. The  $\text{CH}_4$  and  $\text{CO}_2$  reactants were mixed at a ratio of 1 diluted in He (10:10:80 in volume). The samples were heated from room temperature up to 750 °C at 1 °C/min rate, held at 750 °C during 12 h, and finally cooled

down to room temperature in the same reaction mixture. All reactives and products were analyzed by means of a gas chromatograph (Varian, CP-3800) equipped with a thermal conductivity detector (TCD) and a Porapak Q packed column.

### 2.3. Temperature programmed reduction (TPR)

TPR experiments were done from room temperature up to 750 °C, with a heating rate of 10 °C/min. A thermal conductivity detector (TCD), previously calibrated using CuO, and a mass spectrometer in line with the TCD, calibrated with reference mixtures, were used to detect variations of reducing agent concentration, and possible sub-products formation. A  $\text{H}_2/\text{Ar}$  mixture (5%  $\text{H}_2$ , 50 ml/min flow) was used for  $\text{H}_2$ -reduction. All the experimental conditions were chosen to assure that no peak coalescence occurs, according to the conditions indicated in Ref. [26].

### 2.4. X-ray diffraction (XRD), textural properties and scanning electron microscopy (SEM)

X-ray diffractograms were recorded in a Panalytical XPert PRO device, equipped with an X'Celerator Detector (active range of  $2\theta = 2.18^\circ$ ), with a Bragg–Brentano configuration, using Cu  $K\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ). General diagrams were collected in the range  $2\theta = 20^\circ$ – $80^\circ$ , with a step of  $0.05^\circ$  and an acquisition time of 80 s for each point. The mean size of the crystalline particles of nickel and support phases was calculated by the Scherrer formula. X-ray diffractograms were also collected in the range of  $2\theta = 35^\circ$ – $55^\circ$ , with a step of  $0.03^\circ$  during 100 s each point. The textural properties of solids (specific surface area) were determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature by using a Micromeritics ASAP-2010 instrument. Surface areas were calculated by the BET method. Prior to measurements, all samples were degassed at 110 °C to 0.1 Pa. SEM images were obtained in a Hitachi S-5200 microscopy equipped with a field emission filament, using an accelerating voltage of 5 kV.

### 2.5. X-ray absorption spectroscopy

X-ray absorption spectra (XAS) were recorded at the BM25 beam line (SPLINE) of the ESRF synchrotron (Grenoble, France). The spectra were acquired in transmission mode, using self-supported wafers of the Ni supported samples, in a modified commercial infrared cell (Specac) able to work up to 800 °C under controlled atmosphere [27]. XAS spectra were collected at different temperatures during treatments of the samples.

In all cases the self-supported pellets were prepared using the optimum weight to maximize the signal-to-noise ratio in the ionization chambers ( $\log I_0/I_1 \approx 1$ ). Mass flow controllers were used for dosing the gases to the cell. The composition of the gas mixtures was similar to that previously used in the TPR experiment during the hydrogen treatments. The energy calibration was accomplished using a standard Ni foil introduced after the second ionization chamber ( $I_1$ ). Typical XAS spectra of Ni  $K$ -edge were recorded from 8200 to 9100 eV, with a variable step energy value, with a minimum 0.5 eV step across the XANES region. Once extracted from the XAS spectra, the EXAFS oscillations were Fourier transformed in the range  $2$ – $11.0 \text{ \AA}^{-1}$ . Spectra were analyzed using the software package IFEFFIT [28]. The theoretical paths for Ni–Ni and Ni–O species used for fitting the first coordination shell of the experimental data were generated using the ARTEMIS program and the FEFF 7.0 program [29]. The coordination number, interatomic distance, Debye–Waller factor and inner potential correction were used as variable parameters for the fitting procedures. Reference spectra

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