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NiCo as catalyst for magnetically induced dry reforming of methane

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Abstract. In this paper we report the activation of the dry reforming reaction by induction heating of a NiCo alloy. The catalyst plays a double role, serving both as a promoter for the reforming reaction and producing the heat induced by dissipation of the electromagnetic energy. The elevated temperatures imposed by the reforming reaction suggest the choice of an alloy with a Curie temperature $>800^{\circ}\text{C}$. In this respect Ni:Co ratio 60:40 was chosen. Alloy active sites for CH_4 and CO_2 activation are created by a mechanochemical treatment of the alloy that increases solid-state defects.

The catalyst has been successfully tested in a continuous-flow reactor working under atmospheric pressure. Methane conversion and hydrogen production yields have been measured as a function of the applied magnetic field, reactant flow rate and time on stream.

1. Introduction

The possibility of utilizing magnetic materials in catalytic processes has been recently accomplished in the field of magnetically assisted fluidized bed reactors [1] and magnetic separations [2]. Recently, the opportunity of converting electromagnetic energy into heat by means of magnetic materials has been proposed in the field of catalysis [3]. In this respect, energy is supplied by induction under radiofrequency field in a fast and efficient way to a properly responding catalytic system generally containing both a magnetic and catalytic component. In such a way, heat is provided directly by the catalytic bed itself that selectively absorbs electromagnetic energy. Heat is promptly generated on the chemically active site and in principle, by a precise design of the magnetic material, it should be possible to supply exclusively the energy required to drive the chemical process, avoiding unnecessary heating (and dissipation) of the whole reactor and increasing the overall efficiency of the process.

The catalytic activity is usually performed by a different non magnetic component that it is either supported on the magnetic material or in close proximity.

So far, such approach has been successfully applied to “low temperature” chemical processes such as the direct synthesis of amide from amine and carboxylic acid [4] at 170°C , the Claisen rearrangement (200°C) and many areas of organic synthesis ($90\text{--}140^{\circ}\text{C}$) [5, 6]. Specific catalysts with optimized magnetic properties have been synthesized in order to adjust the reachable temperature and heating efficiency. Meffre et al. [7] reported the synthesis of complex nano-materials (Fe@FeCo , Fe@Ru) displaying high specific absorption rate (SAR) under external magnetic field. The nano-particles heated by induction were able to catalyze CO hydrogenation leading to Fischer-Tropsch



syntheses ($T > 200^\circ\text{C}$). Magnetic zeolites (TiO_2 -coated nickel ferrite particles coated with a layer of ZSM-5 zeolite crystals) were successfully tested for the isomerization of citronellal at 350°C [8]. Bordet et al. designed iron carbide nanoparticle with remarkable heating properties that when associated with catalytic metals (Ni, Ru) were able to efficiently catalyze CO_2 hydrogenation in a continuous-flow reactor ($\sim 350^\circ\text{C}$) [9].

This field of investigation is new and large improvement is expected in the design of specific catalysts with enhanced magnetic properties. Presently the achievement of high temperatures by means of magnetic nanoparticles seems challenging. To overcome this problem NiCo alloy has been synthesized by arc melting and successively grinded to the micrometer range by a mechanochemical process. Here we report on the catalytic properties of the material heated by induction under r.f. field toward a high temperature endothermic reaction, the dry methane reforming. The reaction is highly endothermic ($\Delta H_{298\text{K}} = 247 \text{ kJ mol}^{-1}$) and requires operating temperature in the range $800\text{--}1000^\circ\text{C}$ to accomplish high conversion of CH_4 and CO_2 to H_2 and CO . The most commonly used catalysts, apart from noble metal, are nickel based.

2. Material properties and applied methodologies

A NiCo alloy with atomic ratio (60:40) has been synthesized by arc melting (Edmund Buler GmbH). The alloy has been fragmented into powder by a mechanochemical treatment (20min) using a vibrating cup mill inside a tempered steel grinding set. The material has been characterized by X Ray Diffraction (XRD) in the angular range $4^\circ < 2\theta < 40^\circ$, using a Seifert Pad VI apparatus equipped with $\text{Mo K}\alpha$ radiation and a LiF monochromator on the diffracted beam. The resulting spectrum is reported in figure 1. It shows a single phase of NiCo alloy with an average crystallite dimension of $\sim 15\text{nm}$ (Debye-Scherrer). Scanning electron microscopy (SEM) images were acquired by using a high-resolution microscope (HRSEM LEO 130). In figure 2 a SEM picture of NiCo powder is reported showing particles with dimensions in the micrometer range.

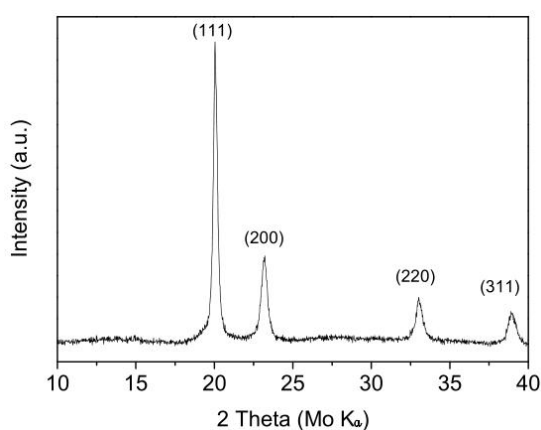


Figure 1. XRD spectrum of NiCo alloy.

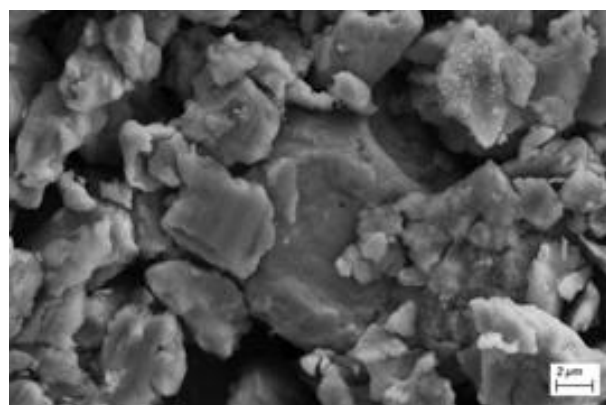


Figure 2. SEM image of NiCo powder as prepared.

Magnetic measurements have been carried out on tightly packed, randomly oriented powder using a SQUID magnetometer (Quantum Design MPMS). Static magnetic properties of the as-prepared powder have been investigated by recording the hysteresis loop at room and low temperature (5 K), shown in figure 3. As expected, the sample displays very low coercive field (H_c), 70 Oe and 115 Oe for 300 K and 5 K, respectively. Saturation of the magnetization is already obtained at 10 kOe, and the saturation values slightly decrease on increasing temperature from 52 emu/g at 5 K to 50 emu/g at room temperature. Both the low coercivity and easiness of saturation agree with the soft magnetic properties expected for a NiCo alloy.

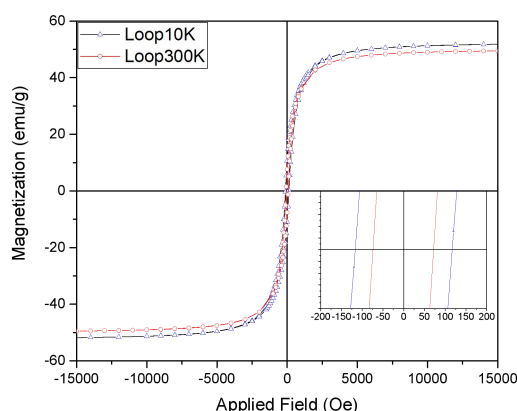


Figure 3. Hysteresis loops of NiCo alloy powder at room temperature (red curve) and 5K (blue curve). In the inset a magnification of the low field region is shown.

The capability of the NiCo alloy powder to act as a heat mediator has been evaluated by recording the temperature kinetics upon application of an alternating magnetic field with frequency $f = 183$ kHz and variable amplitude, H_0 from 3.0 to 17.0 kA/m. The sample was prepared pressing the powder into a pellet (8 mm diameter, 1mm thick) and the temperature was monitored using an optical fibre thermometer in contact with the surface of the pellet. The resulting temperature curve as a function of time (s) is shown in figure 4. Extrapolating the initial slope of this curve from a linear fit we estimated a temperature increment per second normalized to the sample mass of 66 °C/s•g, which, considering the heat capacity of the bulk alloy (0.468 J/g°C⁻¹ for Ni_{0.6}Co_{0.4}) corresponds to a dissipated power of 9.3 W/g. It is worth to note that the dissipated power scales linearly with the applied field.

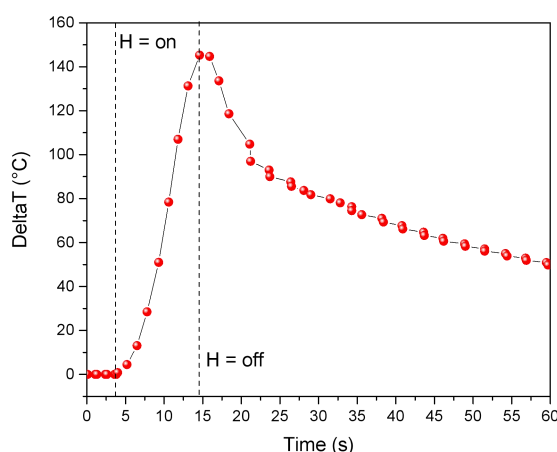


Figure 4. Temperature kinetics of the powder under the application of an alternating field of $H_0 = 17$ kA/m and $f = 183$ kHz. The starting temperature was 22 °C.

Functional tests have been performed utilizing the quartz reactor and gas distribution lines of a Temperature Programmed Desorption Analyzer-TPD (Micromeritics Autochem 2920). Catalyst powders were compacted (5 ton/cm²) into a disc (8mm diameter, 1mm thick) and placed inside a U quartz tube (figure 5). Before its utilization in the process conditions, the sample was reduced in He-H₂ (3%vol), 50ml/min flow, to clean the oxidized surface through a thermal treatment in TPD at

350°C (10 minutes). An Ambrell EasyHeat 2.4 apparatus has been utilized to heat the catalyst. The inductor is placed around the quartz tube as shown in figure 6. In figure 7 the power supplied to the coil to generate the magnetic field is displayed.



Figure 5. NiCo powders are compacted into a pellet (d=8mm, h=1mm) and placed in the quartz reactor. Reactive gases flow through the disc.

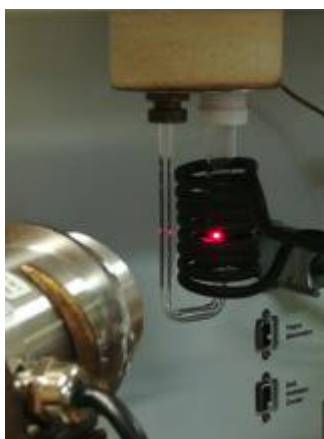


Figure 6. Inductor coil (d= 2.5cm, h=4.5cm) surrounding the reactor tube. A pyrometer provides an estimation of the catalyst surface temperature.

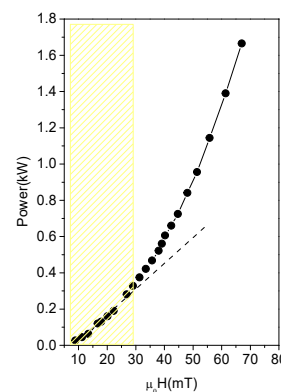


Figure 7. Power consumption vs. generated magnetic field for the coil utilized in this work. (f=190KHz). The linear response of the coil is highlighted.

The experimental set-up includes an optic pyrometer (IRTech Radiamatic IR20CF2150) to estimate the catalyst surface temperature. Such value is only an approximation of the real temperature since the emissivity of the catalyst is not known. GC analysis (Agilent GC490 equipped with two independent columns MS5A and PoraplotU) is utilized to determine the composition of the gas leaving the reactor.

Samples are heated by induction at 190kHz under argon flow until the temperature reaches a stable temperature (few minutes), then the gas is switched to a reactive mixture composed of 50ml/min Ar-CH₄ (10%) and 5ml/min CO₂.

3. Catalytic activity

The NiCo catalyst activity toward the dry reforming reaction was firstly investigated in the TPD reactor by conventional heating and results are reported in figure 8. Methane conversion and hydrogen production yield exceeding 70% were observed at 850°C. The measured conversion values are considered a reference to which results obtained by induction heating are compared.

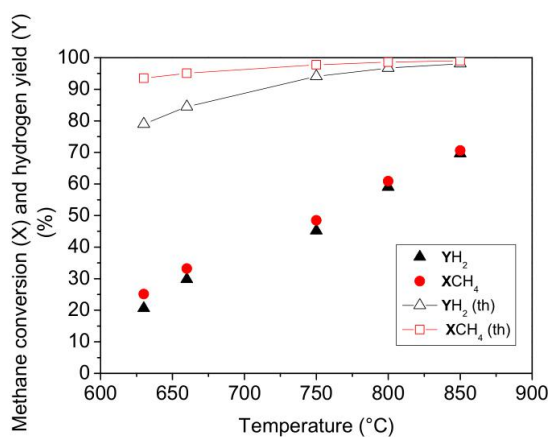


Figure 8. Methane conversion

$$X_{CH_4} = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \cdot 100 \quad \text{and}$$

$$\text{hydrogen yield } Y_{H_2} = \frac{[H_2]_{out}}{2[CH_4]_{in}} \cdot 100$$

measured when NiCo catalyst is conventionally heated at different temperatures. Theoretical expected values, calculated on the basis of thermodynamic equilibrium data (HSC Chemistry 6.1 software) taking into consideration multiple equilibria, are reported.

The NiCo activity was measured heating the catalyst by induction for magnetic field amplitudes ranging from 26 to 32mT (limited to the coil linear response range in figure 7). In figure 9 the methane conversion (X_{CH_4}) and hydrogen yield (Y_{H_2}) are reported as a function of the applied magnetic field. When compared to measurements performed by conventional heating, the catalyst shows a better performance suggesting that NiCo surface is higher than 850°C. In figure 10 the effect of the gas feed on the catalyst activity is reported, keeping $CH_4:CO_2$ ratio 1:1. Conversion data versus time on stream are reported in figure 11. These data, a preliminary investigation on catalyst stability, are very promising considering that the metallic catalyst is not dispersed or supported on an inert substrate and that annealing phenomena could easily deactivate it.

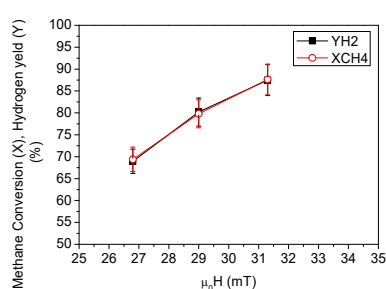


Figure 9. Methane conversion (X_{CH_4}) and hydrogen yield (Y_{H_2}) as a function of magnetic field amplitude. $GHSV=9330h^{-1}$.

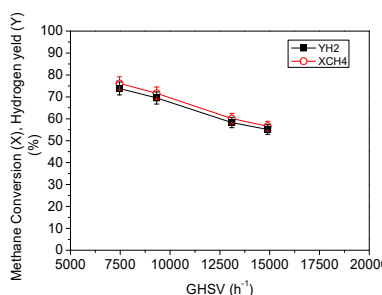


Figure 10. Effect of the gas feed on methane conversion (X_{CH_4}) and hydrogen yield (Y_{H_2}). Magnetic field amplitude 27mT, 0.32kW.

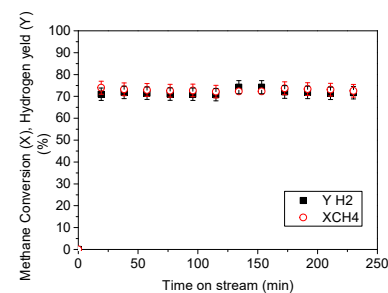


Figure 11. Catalytic results as a function of time on stream. Preliminary test of the stability of the catalyst. Magnetic field amplitude 27mT, 0.32kW, $GHSV=9330h^{-1}$.

The mass balance between gases feed and outlet shows a carbon deficit (0.5-3%). Preliminary SEM observation does not evidence carbon deposits on the powder and a longer time on stream operation is needed to clarify this indication.

4. Conclusion

A NiCo alloy catalyst is proposed to carry out the dry reforming of methane supplying the required energy by a radiofrequency alternating electromagnetic field. Catalyst powders are heated by induction to very high temperatures ($>850^\circ C$). The developed material has been utilized at the same time as a catalyst and heating agent to perform dry-methane reforming with conversion values up to 90%. Preliminary tests have been performed to evaluate the effect of gas feed and the stability of the developed catalyst. Reported evidences open new opportunities in the research of magnetic materials for industrial chemical processes.

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