Magnetic nanoparticles to drive reforming of methane by induction heating

Canio Scarfiello*, Mariangela Bellusci#, Aurelio La Barbera#, Francesca Varsano#

#ENEA C.R. Casaccia, Roma, Italy. francesca.varsano@enea.it, ° Chemistry Dep. University of Roma "La Sapienza", Italy

*Current Affiliations: a) Université de Toulouse, IMT Mines Albi ,UMR CNRS 5302, Centre RAPSODEE, Campus Jarlard, 81013 Albi, cedex 09 (France); b) LPCNO, Université de Toulouse, CNRS, INSA, UPS 135 avenue de Rangueil, 31077 Toulouse (France); c) LCC, CNRS-UPR 8241, ENSIACET Université de Toulouse (France)

Magnetic nanoparticles immersed in an alternating electromagnetic field dissipate energy, generating heat. Major advantages are an **increased energy efficiency** of chemical processes due to a rapid, remote and contactless transfer of energy to the catalytic bed, very quick start up of reactions that account for the possibility of coupling endothermic processes to discontinuous energy inputs and immediate shut down that improves security of exothermic processes. At the centre of such innovation is the **catalyst** material which implement the **dual function** of catalyzing the chemical reaction and acting as a dissipating agent when immersed in an alternating electromagnetic field.

Aim of this work is the synthesis of supported magnetic catalysts ($Ni_{60}Co_{40}$ on γ-Al_2O_3), the structural and morphological characterization of the prepared materials and the testing of their activity for the steam reforming of methane reaction powered by induction heating.

Synthesis and induction heating setup

Catalysts have been prepared dipping cylindrical (1/8'') alumina pellets (Alfa Aesar) in a $Ni(NO_3)_2$*$6H_2O$ and $Co(NO_3)_2$*$6H_2O$ (Merck-EMSURE) solution. Support specific surface area is 250 $m^2 g^{-1}$. Two solutions having 4 M and 8 M total concentration, with the same Ni:Co (60:40) ratio were prepared. The dried samples were calcined to remove the nitrates in air flow (50 mLmin^{-1}) for 1hour. Three different calcination temperatures (T_{calc}), i.e. 450°C, 600°C and 750°C were used. Finally the pellets were reduced at 900°C by Temperature Programmed Reduction technique (TPR) in Ar-H_2 (3%vol) flow (50 mL min^{-1}) for 5h. Samples are labeled as NiCoxY, were x stands for the metal total loading and Y for the calcination temperature.

Table1. List of prepared samples. Effect of synthesis conditions on particle size

	Me(wt%)	T calc (°C)	Cristallite size[1] (nm)	Particle size[2] (nm)
$NiCo_{17}450$	17	450	7±1	9±2
$NiCo_{17}600$	17	600	9±2	10±2
$NiCo_{17}600$*	17	600	20±2	23±5
$NiCo_{17}750$	17	750	24±3	29±5
$NiCo_{17}750$*	17	750	28±2	29±5
$NiCo_{30}450$*	30	450	32±1	38±9
$NiCo_{30}600$	30	600	25±2	23±5
$NiCo_{30}600$*	30	600	19±2	18±5
$NiCo_{30}600$**	30	600	80±2	52±15
$NiCo_{30}750$	30	750	45±2	35±12

1. by XRD Analysis applying the Debye-Scherrer equation, 2. by SEM Analysis, applying the Lognormal size distribution curve to size distribution histograms.*Sample aged in glass desiccator before calcination (6 months), ** Static calcination.

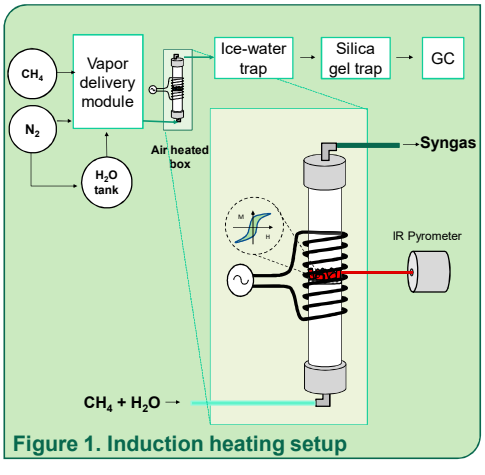


Figure 1. Induction heating setup

Results

Catalyst characterization: XRD patterns for the low metal content catalysts calcined at different temperature are reported in figure 2 after reduction (900 °C, Ar-H_2, 5 hours). Together with the substrate, only the peaks belonging to a single fcc metallic phase are visible.

The BET surface area is 180m^2g^{-1} for $NiCo_{17}$ samples and 110 m^2g^{-1} on $NiCo_{30}$ ones.

The SEM images of all samples show that the metal nanoparticles are evenly distributed within the porous alumina structure. Particles size distribution histogram yielded the particle average diameter (Table 1) that is in line with crystallite size calculated form XRD data, an indication that metallic particles are mostly **single crystalline domain.**

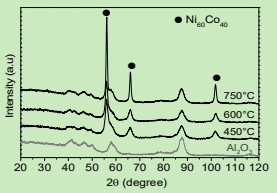
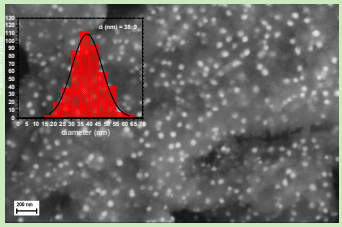


Figure 2. XRD of γ-Al_2O_3 supported $Ni_{60}Co_{40}$ catalysts. The cell parameter for the metallic phase is the same (3.532(1) Å) for all the samples.

Figure 3. SEM image of $NiCo_{30}450$*. Metal nanoparticles (light grey) are well dispersed on the substrate



Heating performances and catalytic activity: The temperature reached in the catalytic bed under nitrogen flow (90 mL min^{-1}) for different values of applied magnetic field is presented in figure 4 for $NiCo_{30}600$. Such trend is typical for all the samples, whereas the maximum temperature reached by each sample (TN_2 in table 2) is different and depends on nanoparticles features. In the figure inset the variation of temperature as a function of time is recorded for a fixed input power. The measured methane conversions reported for all samples in table 2 is the one expected at the temperature reached on the pellets.

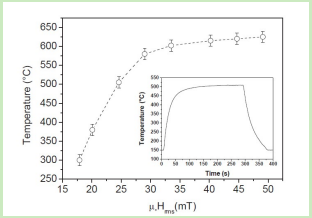


Figure 4. Temperature reached on the catalyst surface (18 pellets,) as a function of the applied field amplitude. The catalytic bed consists in 18 pellets of $NiCo_{30}600$ forming a catalyst monolayer inside the reactor. Heating is performed under nitrogen flow (90 mL min^{-1}).

Table 2. Temperature on samples surface when heated by induction T_{N2}, and during the reforming reaction, T_{reac}; methane conversion, X_{CH4}, and catalyst reaction rate.

	T_{N2}(°C)[1]	T_{reac}(°C)[1,2]	X_{CH4}(%)	Reaction rate (Mol$_{CH4}$ g$_{Me}^{-1}$h^{-1})
$NiCo_{17}450$	520	490	**19**	0.40
$NiCo_{17}600$	560	525	**36**	0.74
$NiCo_{17}600$*	575	550	**44**	0.93
$NiCo_{17}750$	570	535	**38**	0.80
$NiCo_{17}750$*	536	510	**33**	0.69
$NiCo_{30}450$*	665	618	**60**	0.58
$NiCo_{30}600$	630	600	**56**	0.55
$NiCo_{30}600$*	570	530	**45**	0.45
$NiCo_{30}600$**	415	400	**15**	0.15
$NiCo_{30}750$	625	605	**48**	0.50

The methane conversion (X_{CH4}) and the temperature reached on the sample surface in nitrogen flow (T_{N2}) resulted to be a function of the metal particle diameter. It is evident (fig 5) a strong dependence of T_{N2} (and thus of the methane conversion which directly depends on it) on the size of the nanoparticles. These profiles follow the dependence of the Specific Power Loss on particles size which has been modeled by Hergt et al. [*J. Phys: Condens. Matter*, 2008, **20**, 385214] and are the result of different magnetic loss mechanisms intervening in the heat dissipation. In figure 6 the composition of the mixture exiting the catalytic reactor (180 pellets) depicted in the picture below.

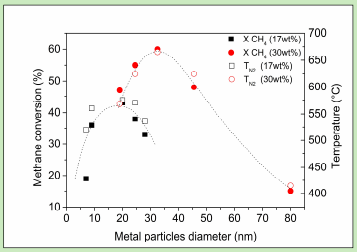


Fig.5. Methane conversion and Temperature developed on the catalyst as a function of particles diameter. All measurements were carried out keeping constant the number of catalyst pellets in the reactor, the gas flow and the applied magnetic field (frequency and amplitude).

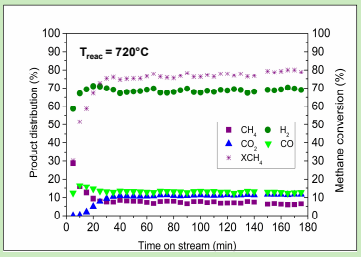


Fig. 6. Experimental product distribution and methane conversion values for sample $NiCo_{30}600$. Volumetric inlet flow: N_2 = 90 mL min^{-1}, CH_4 = 50 mL min^{-1}, H_2O = 100 mL min^{-1}. GHSV = 2800 h^{-1}.

Image of the magnetic catalytic bed during steam methane reforming process powered by induction heating

Conclusions

The progress in the design and development of **materials for magnetic catalysis** has the potential to allow the implementation of highly **energy-intensive processes** on a low scale thank to the rapid and targeted response of ferromagnetic nanoparticles to an applied magnetic field. Ferromagnetic $Ni_{60}Co_{40}$ nanoparticles supported on commercial γ-Al_2O_3 pellets are found to be active for the steam methane reforming reaction, when inductively heated by a radiofrequency alternating magnetic field, demonstrating their dual function as heat dissipating agent and active catalyst for the chemical process. Despite the high metal loading of the synthesized catalysts (17% and 30%), $Ni_{60}Co_{40}$ nanoparticles are well dispersed on the support. The measured **methane conversion values** give indication of an important and peculiar dependence on **the metal particle size distribution** that reflects the ability of the nanoparticles to dissipate energy into heat upon the application of the magnetic field. In fact, **the particle size is a critical key factor to obtain a high heating rate and an efficient conversion of magnetic energy into heat, essential to maximize the catalyst performance**. Optimization of synthesis parameters is therefore of utmost importance to obtain nanoparticles with fine-tuned features in terms of dissipating agents and active surface. Some of the materials designed and produced achieve methane conversions close the target value.

Nano Innovation 2021 Rome, 21-24 September Conference & Exhibition

Acknowledgements

This work has been conducted within the framework of the "PTR2019-2021" Ministero dello Sviluppo Economico-ENEA", Project 1.6 Efficienza energetica dei prodotti e dei processi industriali

C. Scarfiello et al. "Supported catalysts for induction-heated steam reforming of methane", Int. J. Hydrogen Energy. 46 (2021) 134.