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# Low temperature ethanol steam reforming for process intensification: New Ni/M<sub>x</sub>O–ZrO<sub>2</sub> active and stable catalysts prepared by flame spray pyrolysis

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## ABSTRACT

Steam reforming of hydrocarbons is a mature technology and its implementation on other substrates such as bio-ethanol appears as a ready opportunity to produce H<sub>2</sub> from renewable sources. The Low Temperature Ethanol Steam Reforming (LT-ESR, 300–500 °C) could be a really efficient technology from the energetic point of view. However, deactivation by coke deposition remains the biggest issue, due to inefficient carbon gasification by steam in such low temperature range. We demonstrated the feasibility of the process at low temperature taking into account both activity and deactivation issues. The attention was focused on the addition of basic promoters and on the development of an unconventional preparation procedure, in comparison with a traditional precipitation/impregnation route, to improve stability and activity.

Therefore, in this work several catalysts were studied, differently promoted by alkali and alkali earth oxides (CaO, MgO, K<sub>2</sub>O) using a non conventional doping method. H<sub>2</sub> yield and selectivity to CO demonstrated tightly related to the promoter adopted. Flame Spray Pyrolysis synthesis of nickel nanoparticles stabilized in a zirconia matrix (Ni/M<sub>x</sub>O–ZrO<sub>2</sub>) was performed, obtaining more stable catalysts toward deactivation by coking with respect to the analogous prepared by traditional precipitation/impregnation. The effect of the doping using a scalable one-pot technique was investigated by means of characterization of fresh catalysts and activity testing. Catalyst resistance toward deactivation was studied by SEM-EDX, TEM, Raman spectroscopy and temperature programmed analysis. Among the promoters, CaO and K<sub>2</sub>O showed the best performance, producing a reformat with low CO/CO<sub>2</sub> ratio and, thus, leading to higher H<sub>2</sub> yield with consequent lower impact on H<sub>2</sub> purification in an integrated process. K<sub>2</sub>O deeply modified the chemical behaviour of the catalyst allowing to achieve a significant H<sub>2</sub> production also at very low temperature (300 °C).

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## Introduction

There is a pressing need to underpin the sustainable and economic growth of a biofuel-based industry that can put together the rising fuel demand with urgent environmental issues [1]. Hydrogen is the ideal energy carrier to solve distributed emissions problems and there is increasing interest for effective alternatives to produce it safely and cleanly from renewable sources [2]. However, efficient processes should be developed for its production and process intensification is a pivotal step for the economic sustainability of the proposed technologies. Among the various achievable and renewable feedstocks, bioethanol is considered at least since 10–15 years a promising raw material, because it can be produced by biomass fermentation and it is expected to be available industrially on a large scale in the near future from second generation biomass [2,3]. Hence, Ethanol Steam Reforming (ESR) represents a promising way to produce hydrogen thermo-catalytically, though the process needs heat input due to the endothermicity of the reaction. The possibility to work at Low Temperature (LT) is very interesting for this process, due to the much lower thermal energy need, which leads to lower operational costs (thus process intensification), and to avoid catalyst de-activation through sintering, easily occurring at the commonly used high temperatures ( $T > 650\text{ }^{\circ}\text{C}$ ) [4]. Moreover, the CO concentration in the outlet gas is strongly reduced at low temperature due the contribution of the exothermal Water Gas Shift (WGS) reaction. Therefore, the research of catalysts which promote as much as possible the Steam Reforming of Ethanol at Low Temperature (LT-ESR) is very challenging. The application of the process in demonstrative stage is already accomplished [5,6], so that the optimisation of catalyst formulation and process intensification are now required.

The reaction network is usually affected by the formation of several by-products, thus reducing the selectivity to hydrogen and possibly leading to the formation of coke, especially at low temperature where C gasification is not favoured [7]. Besides tuning the operating conditions, the use of highly active and stable catalysts plays a crucial role, overcoming the activity and selectivity aspects, due to the much easier reformation of ethanol with respect to other substrates such as methane or heavier hydrocarbons [4].

Carbon deposition can occur through three different pathways: i) decomposition of hydrocarbons; ii) CO disproportion (Boudouard reaction); iii) olefins polymerization. During the LT-ESR, coking occurs mainly by the last two routes, because the former is a strongly endothermal process, prevailing at higher temperature (650–800  $^{\circ}\text{C}$ ), only [8]. Ethylene is the main olefin generated during the process, as result of the ethanol dehydration, favoured over acid sites, while CO disproportion strongly depends on the selectivity of the catalysts and on the presence of  $\text{CO}_2$  [9]. In addition, not only the source, but also the nature of the carbon formed is fundamental. Carbon can either be found as ordered (filamentous or graphitic) or amorphous structures [4].

*In primis*, the support plays a crucial role towards coking resistance, thanks to its own acid-base character and to

metal-support interactions [10]. The modification of the support properties can be done choosing carriers with basic/amphoteric features such as  $\text{La}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MgO}$  [11–14], or combining different properties by doping [15–17].  $\text{ZrO}_2$  has been proposed as valuable support for the catalytic reforming of methane [18,19] and oxygenated compounds [20,21]. Its beneficial features are attributed to the steam adsorption ability, which promotes water activation and coke gasification. Strong metal-support interaction can be also achieved when nickel is used as active phase [22]. In addition, the high thermal stability of this material allows its use in thermocatalytic processes [12].

A criticism is represented by its intrinsic acidity, usually of Lewis type, possibly leading to ethanol dehydration and polymerization to form coke. Doping with alkali and alkali-earth metal oxides can be a suitable way to improve the catalyst stability toward deactivation phenomena. Basic doping has been previously investigated in the case of catalysts prepared by traditional wet-methods, such as incipient wetness impregnation, co-precipitation and sol-gel methods [23–29]. This strategy has been selected here to prepare  $\text{MO}_x$ -modified zirconia ( $M = \text{Ca}, \text{Mg}, \text{K}$ ) as a support for LT-ESR, in order to couple its water activation properties with a limited acidity, to prevent extensive coking.

Nickel was added as active phase, because of its very high activity and selectivity among non-noble metals, coupled with much lower cost and availability for industrial and commercial purposes [3,16,30]. However, poor resistance to carbon formation with respect to noble metals, forced to find alternative preparation strategies because of the tight correlation between the coking phenomena and support properties or metal dispersion [12,31–33].

The Flame Spray Pyrolysis (FSP) technique is a powerful method for the scalable synthesis of nanostructured materials [34], since it allows the simultaneous synthesis and calcination of oxide nanomaterials. The transfer from the laboratory level to the plant scale concerning flame aerosol process is nowadays a very intriguing point due to the easy scalability of this one-pot synthesis if the key parameters are properly controlled. Pilot scale reactor and economic analysis carried out by Wegner and co-workers [34,35] for zirconium oxide further enhanced the interest toward this non-conventional synthesis. This may allow overcoming major drawbacks of traditional preparation processes, such as the long processing time, batch-to-batch synthesis and uneasy control over active phase dispersion. By contrast, flame- and aerosol-based processes offer the advantages of simple and often lower cost synthesis, with a continuous production process combined with a short processing time [36].

The main goal of this work was to demonstrate the feasibility of low temperature ethanol steam reforming addressing both the activity and deactivation issues. To do this, we focused on a specifically developed preparation procedure and on catalyst doping with alkali and alkali-earth ions. FSP was therefore employed in this work for the synthesis of the materials as a key to impart strong metal-support interaction and high metal dispersion [37]. These have been proved key points to ensure sufficient resistance to coking for this application.

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