

# Ni/ZrO<sub>2</sub> catalysts for ethanol steam reforming: effect of Ca-doping

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## 1 Introduction

One of the main challenges for scientists today is to reduce the dependence from fossil fuels. But how can we meet the ever growing world energy demand in a clean and sustainable way? Renewables can be the answer. Hydrogen (and renewables-derived hydrogen in particular) is the ideal candidate for both energy and transport sectors. It is a high-density energy vector; it is clean and carbon-free, so its sole combustion product is water. Ethanol emerged as a good candidate for hydrogen production because it is renewable, easy to store, handle and transport because of its low volatility and atoxicity and has a high hydrogen content. Ethanol steam reforming is promising to produce hydrogen in a sustainable way. Ni is widely used in reforming reactions because of its high activity, comparable to noble metals, although it can be quickly deactivated by coking and sintering [1]. Also the support plays a key role, affecting the stability of the catalyst in reaction conditions that can favor carbon deposition [2]. ZrO<sub>2</sub> is widely used as support because of its properties, such as thermal stability and oxygen storage capacity, though Lewis acid sites on its surface may play an important role in coke formation. We recently studied the activity of Ni/ZrO<sub>2</sub> catalysts in steam reforming reactions [3-5]. These catalysts proved to be highly active and selective even though, in certain reaction conditions, a slight deactivation due to coke deposition was detected. The addition of basic oxides to ZrO<sub>2</sub> can improve the properties of both the support (oxygen transport, acidic/basic and redox properties) [6] and the catalyst (dispersion of the active phase, interactions between metal and support) [7]. The aim of this work is to properly modify the zirconia support in order to improve the catalytic performance of the catalyst, in particular with regard to carbon balance. Ni/ZrO<sub>2</sub> catalysts doped with various percentage of CaO were then synthesized and characterized. The effect of Ca-doping was evaluated in terms of both physico-chemical properties and catalytic performance of the samples.

## 2 Experimental/methodology

Zr(OH)<sub>4</sub> was prepared by a precipitation method [3] at a constant pH of 10. Ni (8 wt%) and CaO (0, 3, 6, 9 wt%) were introduced on the support by means of co-impregnation with an aqueous solution of the corresponding precursors. Samples were finally calcined at 500 °C. Samples are denoted as ZCa<sub>x</sub>Ni, where Ca<sub>x</sub> denotes the percentage of CaO. The catalysts were characterized by temperature programmed reduction (TPR), X-ray diffraction (XRD), N<sub>2</sub> physisorption, O<sub>2</sub> chemisorption, FT-IR spectroscopy of adsorbed CO and high-resolution transmission electron microscopy (HR-TEM). Activity tests were performed after reduction of the catalysts in H<sub>2</sub> flow for 1 h at 500 °C. The activity tests were carried out at atmospheric pressure by feeding a 3:1 (mol/mol) H<sub>2</sub>O:CH<sub>3</sub>CH<sub>2</sub>OH mixture at 500 °C.

## 3 Results and discussion

The experimental results evidenced that the addition of CaO to Ni/ZrO<sub>2</sub> catalysts affects neither the morphology of the support, nor the dimension of Ni nanoparticles. All the samples exhibit a IV-type isotherm containing a H3-type hysteresis, typical of materials that don't possess a well-defined mesoporous structure. Surface area is about 140 m<sup>2</sup>/g, independently of the CaO content. Ni particles size is about 4 nm, as revealed by O<sub>2</sub> chemisorption analyses, also in this case irrespective of the percentage of CaO.

On the contrary, Ca-doping deeply influenced the interaction between the active phase and the support. The TPR profiles of the catalysts present various reduction peaks, indicating NiO species differently interacting with the support. In particular, it was observed that the intensity of the Ni-support interaction lowered with the increasing of the CaO percentage. This phenomenon is usually ascribed to the presence of oxygen vacancies generated by the replacement of the Zr<sup>4+</sup> cation in the ZrO<sub>2</sub> lattice with cations with lower positive charge, as Ca<sup>2+</sup>. These oxygen

vacancies weaken the Ni-O bond, thus facilitating NiO reduction. The substitution of Zr<sup>4+</sup> with Ca<sup>2+</sup> was confirmed by XRD analyses: the continuous shift of the peak at 30° (characteristic of the tetragonal phase of zirconia) to smaller angles, as well as the regular and incremental variation of the lattice parameters (Fig. 1), with increasing the CaO content, is a clear evidence of the doping effect of calcium.

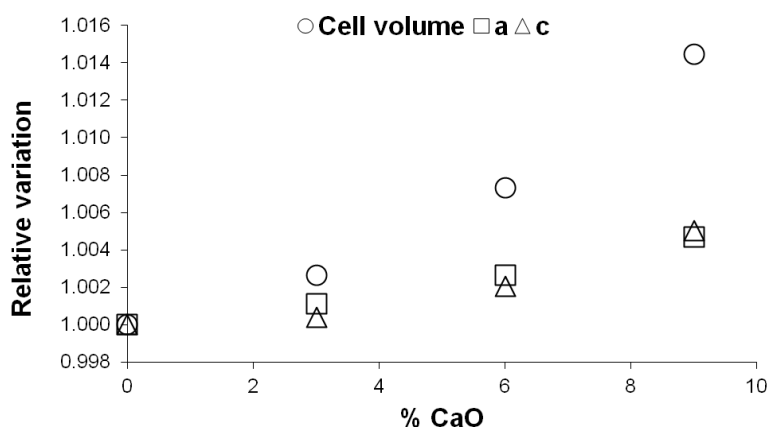


Fig. 1. Relative variation of the lattice parameters as a function of the CaO percentage.

FTIR spectra of adsorbed CO at RT revealed that the Zr<sup>4+</sup>-CO spectral component ( $\nu_{\text{CO}} \sim 2175\text{-}2178 \text{ cm}^{-1}$ ), that forms on all samples upon the adsorption of the same amount of CO, exhibits a decreasing intensity as a function of the increasing of the CaO content, thus indicating that Lewis acidity is still present, but the amount of the Lewis acid sites is decreasing with continuity.

The decrease of the Lewis acidity of the support seems to positively influence the catalytic performance of the catalyst. The activity tests revealed a clear improvement of the carbon balance as the CaO content of the catalyst increased: sample ZCa<sub>9</sub>Ni showed the best performance. These results can be ascribed: i) to the decrease of the Lewis acidity of the support, which contributes to the side reactions which lead to coke deposition; ii) to the presence of oxygen vacancies, which can activate CO<sub>2</sub>, thus favoring the gasification of coke.

#### 4 Conclusions

This study evidences the key role of the support in the performance of Ni/ZrO<sub>2</sub> catalysts in steam reforming reactions. The addition of CaO to the support modifies the Lewis acidity of ZrO<sub>2</sub>, involved in coke deposition that contributes to the deactivation of the catalyst itself. Ca-doping also produces oxygen vacancies, which affect both the activity of the catalyst and the interaction between the support and the active phase. The sample doped with the maximum percentage of CaO presents an optimum carbon balance, which can favour the catalyst durability.

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