

This is an Open Access document downloaded from ORCA, Cardiff University's institutional repository: <https://orca.cardiff.ac.uk/id/eprint/118438/>

This is the author's version of a work that was submitted to / accepted for publication.

Citation for final published version:

Di Michele, Alessandro, Dell'Angelo, Anna, Tripodi, Antonio, Bahadori, Elnaz, Sanchez Trujillo, Felipe Juan, Motta, Davide, Dimitratos, Nikolaos, Rossetti, Ilenia and Ramis, Gianguido 2019. Steam reforming of ethanol over Ni/MgAl₂O₄ catalysts. *International Journal of Hydrogen Energy* 44 (2), pp. 952-964. 10.1016/j.ijhydene.2018.11.048

Publishers page: <http://dx.doi.org/10.1016/j.ijhydene.2018.11.048>

Please note:

Changes made as a result of publishing processes such as copy-editing, formatting and page numbers may not be reflected in this version. For the definitive version of this publication, please refer to the published source. You are advised to consult the publisher's version if you wish to cite this paper.

This version is being made available in accordance with publisher policies. See <http://orca.cf.ac.uk/policies.html> for usage policies. Copyright and moral rights for publications made available in ORCA are retained by the copyright holders.



Steam reforming of ethanol over Ni/MgAl₂O₄ catalysts

Alessandro Di Michele ^a, Anna Dell'Angelo ^b, Antonio Tripodi ^b,
Elnaz Bahadori ^b, Felipe Sanchez ^c, Davide Motta ^c, Nikolaos Dimitratos ^c, Ilenia
Rossetti ^b, Gianguido Ramis ^{d,*}

^a Dip. Fisica e Geologia, Università degli Studi di Perugia, Via Pascoli, 06123, Perugia, Italy

^b Chemical Plants and Industrial Chemistry Group, Dip. Chimica, Università degli Studi di Milano, INSTM Unit Milano-Università and CNR-ISTM, via C. Golgi, 19, I-20133, Milano, Italy

^c Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF103AT, UK

^d Dip. di Ingegneria Civile, Chimica e Ambientale, Università degli Studi di Genova and INSTM Unit Genova, via all'opera Pia 15A, Genoa, Italy

article info

Article history:

Keywords:

Hydrogen

Ethylene

Ni catalysts

Bioethanol conversion to chemicals Steam reforming

abstract

Hydrogen is considered one of the most promising energy vectors in order to match the current energy and environmental issues. Bioethanol steam reforming is a sound opportunity and close to the industrialization considering an integrated biorefinery concept. MgAl₂O₄ was selected as a stable support, with improved activity, selectivity and stability due to negligible acidity. Increasing the Ni loading from 1.5 to 10 wt% over MgAl₂O₄ improved the conversion of ethanol as well as the yield of hydrogen, while the carbon deposition and yield of byproducts decreased.

Small acidity characterised the samples, attributed exclusively to the Ni active phase. This prevented extensive catalyst coking due to ethylene formation and subsequent polymerisation. Consequently, small coke amount was found on the spent catalysts, mainly amorphous, allowing rather easy regeneration.

DRIFT analysis of adsorbed ethanol at variable temperature evidenced the in-intermediates of reaction and their evolution with temperature, allowing to suggest the main reaction paths. Acetaldehyde was found as intermediate, rapidly evolving to reformate. Among the possible evolution paths of acetaldehyde, the oxidation to acetate and car-bonate species (likely stabilised by the support) was preferred with respect to decomposition to methane and CO. This is reflected in the products distribution evidenced through activity testing.

* Corresponding author.

E-mail address: gianguidoramis@unige.it (G. Ramis).

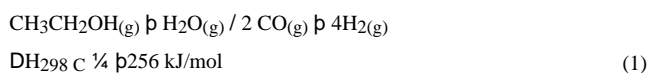
Introduction

Increasing attention is focused on hydrogen as a clean energy vector, because its oxidation is highly exothermal and the only product is water [1]. Despite the huge potential benefits, the use of hydrogen is currently limited by the insufficient capacity of hydrogen storage technologies and by the safety issues related with its storage and transportation under mild conditions [2]. Furthermore, nowadays 47% of global hydrogen is produced from natural gas, 30% from oil, 19% from coal and the remaining fraction via water electrolysis [3]; therefore, ca. 96% of hydrogen derives from the conversion of fossil re-sources, which means a net co-production of CO₂. New sources and new processes are needed to produce hydrogen in a sustainable way.

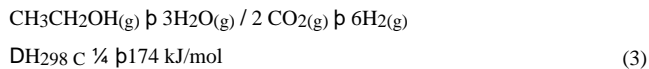
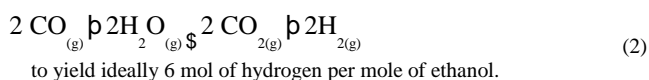
Ethanol steam reforming (ESR) has received considerable attention, because ethanol is mainly obtained by renewable sources [4], it is simple to store, handle and transport because of its low volatility and toxicity [5]. This process could be industrially advantageous, ideally yielding 6 mol of H₂ per mole of ethanol reacted. A major drawback is the endo-thermicity of the reaction, so for process intensification the lowest admissible temperature should be searched. In addition, at low temperature (below 500 C), side reactions that yield alternative products such as acetic acid, acetaldehyde and ethylene are favored. These byproducts compete for hydrogen atoms, thus lowering the overall H₂ yield [6,7] and can also be related to catalyst deactivation.

It is well known that both the active phase and the support play a key role in determining the productivity and selectivity of the reaction, because different catalysts induce different pathways for H₂ production [5,8,9]. Several metal-based catalysts [4,10e17] have been proposed for the steam reforming of alcohols. Nickel is particularly attractive because of its high activity and selectivity in breaking C-C bonds and its lower cost if compared with noble metals. It also catalyzes the water-gas shift reaction [18,19], improving H₂ yield and its subsequent purification from CO. However, other challenges related to metal sintering and coke deposition are still open. From these points of view, the choice of the support is crucial. Indeed, the cooperation between the support and the metal is fundamental to stabilize the active phase, increase its dispersion and decrease the rate of coke formation [20e22].

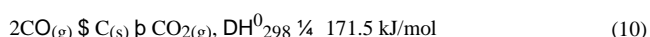
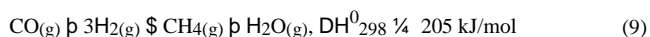
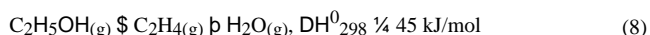
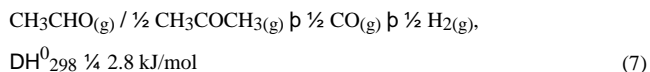
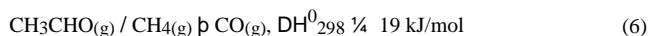
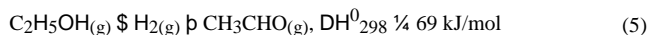
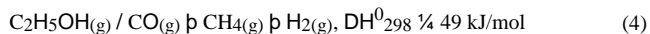
The general reaction scheme is the following:



which couples with the water gas shift (WGS) reaction, which is slightly exothermic



However, these reactions are not particularly descriptive of the real steam reforming process, which actually occurs through various intermediates. The possible reactions through which ethanol reforming can occur, individually or concurrently, are very numerous and depend on catalyst formulation [22e24]. The main ones are the following:



In this study, MgAl₂O₄ was employed as support for Ni-based catalysts. Mg-Al mixed oxide supported Ni catalysts showed high activity in terms of H₂ productivity and catalyst stability compared to nickel catalysts supported on pure oxides [25]. MgAl₂O₄ was chosen due to the following factors: (i) it is a slightly basic material, (ii) it exhibits moderate acidic and basic site strength and density, (iii) it limits the promotion of reactions (8) and (11), thus, minimises coke formation and therefore enhances catalyst stability [26]. For example, Katheria et al. investigated this spinel as support for nickel during methane steam reforming, revealing a strong dependence of catalyst activity on the synthetic conditions. In particular, an increase of methane conversion was attributed to a higher metal dispersion and lower active metal particle size of the catalyst obtained by the reported washcoating synthesis technique on FeCr-alloy [27].

Therefore, in this manuscript we investigated a series of Ni/MgAl₂O₄ catalysts with different Ni loading and prepared with an ultrasound assisted technique to achieve high surface area and, thus, metal dispersion. Ethanol Steam Reforming (ESR) tests were carried out in a continuous bench scale reactor operated at 625 C, 500 C and 400 C, especially focusing on low temperatures for this application, for process intensification. A critical value of ethanol/water molar feed ratio was used (1:3 mol/mol) as stressing condition to monitor catalyst deactivation. Rival data in the literature (vide infra) are indeed collected at higher water/ethanol ratio. The effect of metal loading on activity and hydrogen selectivity was investigated, together with possible deactivating phenomena. Finally, DRIFTS analysis allowed to evidence the intermediates and their evolution with reaction temperature as a support to discriminate between different reaction paths.

Experimental section

Catalysts preparation

MgAl₂O₄ was prepared as follows. 150 ml of a solution of 1.9 M HCl and 16 g of CTABr (Trimethylcetylammmonium bromide) were mixed under magnetic stirring at 40 C to a solution of 300 ml of ethanol in which 123 g of aluminium isopropoxide and 13 g of Mg(OCH₂CH₃)₂ were dissolved. Part of the MgAl₂O₄ was dried at 110 C and calcined at 650 C for 3 h under static air. The active phase was added to the support through the co-precipitation method under high power ultrasound irradiation using an Ultrasonic processors VC750 Sonics and Materials, 20 KHz with a diameter tip of 13 mm. For the synthesis 100 mL of a NH₄HCO₃ 1 M solution were dropped, under ultrasound irradiation for 1 h at 50% of Amplitude, to a diluted solution of nickel acetate-MgAl₂O₄, in the desired concentration in order to obtain 1.5 wt% Ni/MgAl₂O₄ (M1), 5 wt% Ni/MgAl₂O₄ (M2) and 10 wt% Ni/MgAl₂O₄ (M3) loading. The pre-precipitates were dried and calcined at 500 C for 3 h under static air.

Catalysts characterization

XRD data were collected at ambient temperature with a PANalytical X'PertPRO X-ray diffractometer using Cu K α radiation and operated at 40 kV and 30 mA. X-ray diffraction patterns were recorded between 2 θ ¼ 10e80 at a step size of 0.017 . The crystallite size was calculated by the Scherrer equation:

$$D = \frac{Kl}{\Delta 2\theta \cos \theta}$$

where D is the mean size of the crystalline domains, K is a dimensionless shape factor, with a typical value of about 0.9, l is the X-ray wavelength, Cu K α radiation ¼ 0.154059 nm; L is the line broadening at half the maximum intensity (FWHM), θ is the Bragg angle (in degrees).

X-ray photoelectron spectra (XPS) were recorded through a K-Alpha™ X-ray Photoelectron Spectrometer (XPS) System using a monochromatic Al K α X-ray source. X-ray source (75e150W) and analyser pass energies were 160 eV (for survey scans) or 40 eV (for detailed scans).

The morphology was examined by Field Emission Gun Electron Scanning Microscopy (FE-SEM) through a LEO 1525 ZEISS instrument. Elemental composition was determined using a combined Bruker Quantax EDS. Transmission Electron Micrographs (TEM) were collected on the fresh and spent samples using a Philips 208 Transmission Electron Microscope. The samples were prepared by putting one drop of an ethanol dispersion of the catalysts on a copper grid, pre-coated with a Formvar film and dried in air.

Adsorption/desorption isotherms were collected at liquid nitrogen temperature (196 C) using a Micromeritics ASAP 2020 instrument. Surface area was calculated on the basis of the Brunauer, Emmet and Teller equation (BET), while the pores size distribution was determined by the BJH method, applied to the N₂ desorption branch of the isotherm. Prior to the analysis the samples were outgassed at 300 C for 24 h.

NH₃-TPD was carried out using a Quantachrome ChemBET TPR/TPD chemisorption analyser with a TCD, following a method including four main steps. During the pre-treatment, 50 mg of sample were heated at 15 C/min up to 130 C during 1 h in a flow of He (80 ml/min), followed by adsorption of ammonia at room temperature for 20 min to ensure saturation. Then, the physisorbed ammonia was removed at 100 C (1 h, 15 C/min) in He flow. The last step was the desorption of chemisorbed ammonia by heating up to 800 C (at 10 C/min) in He monitoring the desorption with a TCD at attenuation 1 and current 180 mV.

Temperature Programmed Reduction (TPR) measurements were performed by placing the catalyst in a quartz reactor and heating by 10 C/min from r.t. to 800 C in a 10 vol% H₂/N₂ gas stream flowing at 40 ml/min. TPO (Temperature Programmed Oxidation) measurements were performed placing the spent catalysts in a quartz reactor. The temperature was increased at a rate of 10 C/min from r.t. to 800 C in a 10 vol% O₂/He gas stream (40 ml/min) and the data obtained were elaborated by the Origin Pro 8.5 software.

DRIFTS analysis was performed with a Bruker Tensor 27 spectrometer fitted with a HgCdTe (MCT) detector, a Harrick Praying Mantis HVC-DRP-4 cell equipped with two ZnSe windows and operated with OPUS software. The DRIFTS cell included gas inlet and outlet ports that have the capability to heat and cool the sample. This technique was applied to study the interaction of ethanol with the catalysts. The sample was heated to 120 C under 20 ml/min of N₂ for 30 min, in order to eliminate any physisorbed molecule on the material, after that time an IR background spectra was collected. Afterwards, ethanol was supplied until saturation (around 20 min). Then N₂ flow was continued until adsorbed ethanol was evacuated. When the DRIFT spectra were not changing, the temperature was increased to 200 C for 30 min and the resulting spectra recorded. This last step was repeated for other temperatures (i.e. 300, 400 and 500 C). The data are reported as absorbance. Each spectrum represents an average of 64 scans collected with a spectral resolution of 2 cm⁻¹. In the reported spectra, a positive peak intensity indicates an increase of population of a given species, whereas a negative deflection shows a loss of the same.

Micro-Raman sampling was made by an OLYMPUS microscope (model BX40) connected to an ISA Jobin-Yvon model TRIAX320 single monochromator, with a resolution of 1 cm⁻¹. The source of excitation was a Melles Griot 25LHP925 He-Ne laser that was used in single line excitation mode at ¼ 632.8 nm. The power focused on the samples was always less than 2 mW. The scattered Raman photons were detected by a liquid-nitrogen cooled charge coupled device (CCD, Jobin-Yvon mod. Spectrum One).

Activity testing

Activity tests were run through a continuous micropilot plant constituted by an Incoloy 800 downflow reactor (internal diameter 0.9 cm and length 40 cm), heated by an electric oven. The reactor temperature was controlled by an Eurotherm 3204 TIC. The catalysts were pressed, ground and sieved into 0.15e0.25 mm particles and 0.5 g of catalyst were loaded into the reactor after dilution 1:3 (vol/vol) with SiC of the same

particle size. Catalyst activation was accomplished by feeding 50 ml/min of a 20 vol% H₂/N₂ gas mixture at 625 C for 1 h. During activity testing 0.017 ml/min of a 3:1 (mol/mol) water/ ethanol liquid mixture were fed to the reactor by means of a Hitachi, mod. L7100, HPLC pump, added with 50 ml/min of N₂, used as internal standard, and 174 ml/min of He. The liquid mixture was vaporized in the hot inlet of the reactor before reaching the catalyst bed. Such dilution of the feed stream allowed to keep the reactants mixture in the vapour phase even at zero conversion at the reactor outlet. The activity tests were carried out at atmospheric pressure, with a Gas Hourly Space Velocity (GHSV) of 2700 h⁻¹ (referred to the water/ ethanol gaseous mixture), corresponding to ca. 1000 g min⁻¹/mol, at 625, 500 and 400 C. The testing sequence was pro-grammed from the highest temperature to the lowest, in order to avoid possible deactivation by coking of the samples and structural changes of the catalyst. The test duration does not allow to fully assess stability, however, as for an internal comparison, the monitoring of coke accumulation for a fixed reaction time is still a valid measure of catalyst stability. Therefore, the testing sequence was on purpose from the highest temperature to the lowest in order to progressively accumulate coke (when relevant), accumulation that is favored at low temperature since the carbon gasification ac-tivity is poor.

Analysis of out-flowing gas was performed by a gas chro-matograph (Agilent, mod. 7980A) equipped with two columns connected in series (Poraplot Q and Molecular Sieves) with a thermal conductivity detector (TCD), properly calibrated for the detection of ethanol, acetaldehyde, acetone, acetic acid, water, ethylene, CO, CO₂ and H₂. Repeated analyses of the effluent gas were carried out every hour and the duration of every test at each temperature was 8 h-on-stream to reach steady-state conditions. The raw data, expressed as mol/min of each species outflowing from the reactor, have been elab-orated as detailed elsewhere [26,28]. Material balance on C-containing products was used as first hand indicator to eval-uate coke deposition.

Results and discussion

Catalyst characterization

X-ray diffraction patterns of the fresh catalysts are shown in Fig. 1. In all the cases, broad diffraction peaks corresponding to MgAl₂O₄ (2θ ¼ 19.03, 31.3, 36.8, 44.8, 55.6, 59.4 and 65.2 de-grees), NiO (2θ ¼ 43.3, 37.3, 62.9 degrees) and metallic Ni (2θ ¼ 77 degrees) were detected [28]. The Figure shows well-defined and large peaks, which demonstrate well-dispersed particles with uniform size and good crystallinity. Peak broadening testifies the presence of very small crystal size, which is important for the present application to ensure Ni resistance towards the accumulation of subsurface carbides, which are precursors of C nanotubes [29e35].

Table 1 shows the crystallite size (D), calculated using the Scherrer equation.

The specific surface area of the samples is also shown in Table 1. The impregnation leads to a very slight decrease of surface area while increasing Ni loading (238e228 m²/g). Small

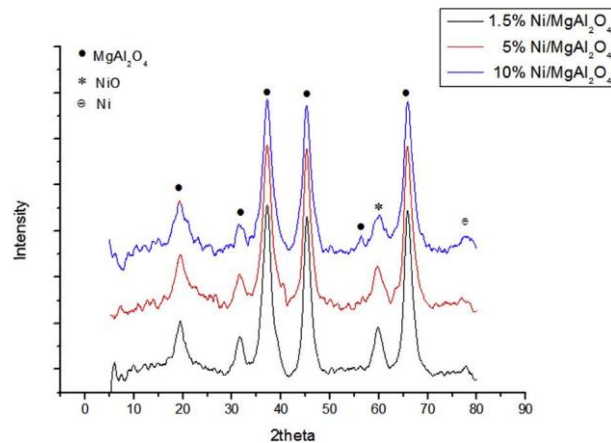


Fig. 1 e Diffraction patterns of fresh catalysts.

Table 1 e Crystal size calculated through the Scherrer equation and specific surface area (SSA) from BET analysis.

Sample	Particles	2q	FWHM	D (nm)	SSA (m ² /g)
1.5% Ni fresh	Ni	76	0.4	24.9	238
	NiO	63	1.6	5.8	
5% Ni fresh	Ni	76	0.4	24.9	228
	NiO	63	1.5	6.1	
10% Ni fresh	Ni	76	0.3	33.2	228
	NiO	63	1.4	6.6	

crystal size and high surface area are formed thanks to the optimized preparation procedure, assisted by ultrasounds. The Ni particle size does not vary very much with increasing Ni loading. It remains almost unchanged when passing from 1.5 to 5 wt%, whereas it increases from ca. 25 to ca. 33 nm when further doubling the Ni loading. The residual NiO particles are even smaller with slightly increasing size with increasing metal amount. This supports the ability of the support and the preparation method in keeping sufficiently dispersed the active phase, which does not coalesce in bigger particles event at highly increasing loading.

The X-ray photoelectron spectroscopy (XPS) results are summarized in Table 2 as relative atomic percentage. The results on the fresh samples show a linear decrease of NiO with a decrease of nominal Ni wt% and at the same time an increase of Ni(OH)₂ on the surface. Fig. 2 shows the deconvolution of Ni2p_{3/2} for all the samples. Ni2p peak has significantly split spin-orbit components and Ni metal spectrum has a complex shape. In the spectra are visible the specific energy binding ascribable to Ni metal (852.6 eV), NiO (853.7 eV) and Ni(OH)₂ (855.6 eV) [36,37].

Different oxidation states of Ni were also visible in the XRD patterns (Fig. 1), in agreement with XPS data. In the 10 wt% Ni/ MgAl₂O₄ spent sample a low amount of metallic Ni was also present. We observed that the surface composition of the spinel changed for 10 wt% Ni/MgAl₂O₄. This could be explained by the substitution of Ni for Mg in the spinel structure. NiAl₂O₄ could form predominantly at the surface, so both Ni and Al exposure increases with respect to the sample

Table 2 e XPS of the fresh catalysts.

Catalyst	Name	Pos	FWHM	Atom %
1.5% Ni	O 1s	530.86	3.32	48.67
	C 1s	284.86	3.01	2.4
	Ni 2p	855.86	3.5	0.66
	Mg 2s	88.86	4.14	13.55
	Al 2p	74.86	2.89	34.71
5% Ni	O 1s	532.08	3.32	47.27
	C 1s	285.08	3.37	2.84
	Ni 2p	856.08	4.11	1.14
	Mg 2s	89.08	4.08	13.61
	Al 2p	75.08	2.93	35.18
10% Ni	O 1s	531.86	3.42	43.29
	C 1s	284.86	2.85	2.66
	Ni 2p	855.86	4.32	3.05
	Mg 2s	88.86	4.13	9.22
	Al 2p	74.86	3.09	41.78

5 wt% Ni/MgAl₂O₄. The incorporation of Ni in the support surface increases its dispersion even for high metal loading. This is typically desirable to improve resistance to the formation of C nanotubes over Ni particles, as already mentioned above.

The fresh catalysts were constituted by rather uniform oxide particles, ca. 25e45 nm, with a homogeneous distribution of the active phase over it (Figs. 3 and 4).

Activity tests

The results of catalytic testing at 625 °C are summarized in Table 3 and Fig. 5. Ethanol conversion was 86% for sample 1.5 wt% Ni, while increased with increasing Ni content.

Indeed, samples 5 wt% Ni and 10 wt% Ni led to full ethanol conversion with the highest H₂ productivity. Increasing Ni loading also improved the productivity of H₂ due to higher activity for the water gas shift reaction (lower CO/CO₂ ratio) and decreased selectivity to CH₄ (Fig. 6). Ethylene was observed at the lowest Ni content, only, due to insufficient activity for the further reforming of this intermediate. Low Ni loading is characterised by insufficient activity for C-C bond cleavage, leaving indeed unreacted ethanol and unconverted ethylene.

Sample 1.5 wt% Ni proved also insufficiently stable, since ethanol conversion started decreasing after 450 min-on-stream and the selectivity to acetaldehyde increased simultaneously (Fig. 5). On the contrary, samples 5 wt% Ni and 10 wt% Ni were stable for the whole duration of the test, with

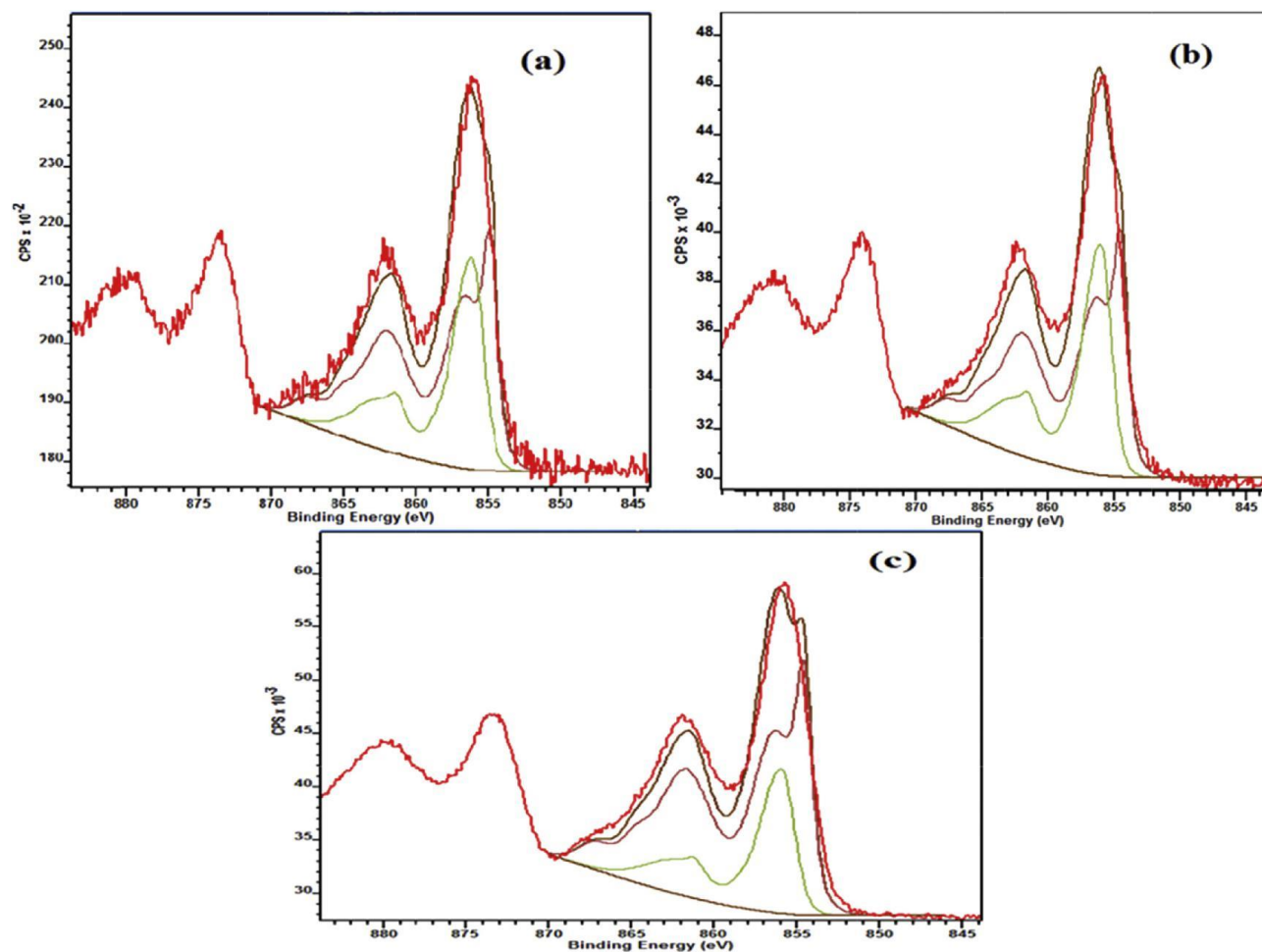


Fig. 2 e XPS spectra deconvolution of Ni_{2p3/2} for catalysts 1.5 wt% (a), 5 wt% (b) and 10 wt% (c) Ni/MgAl₂O₄.

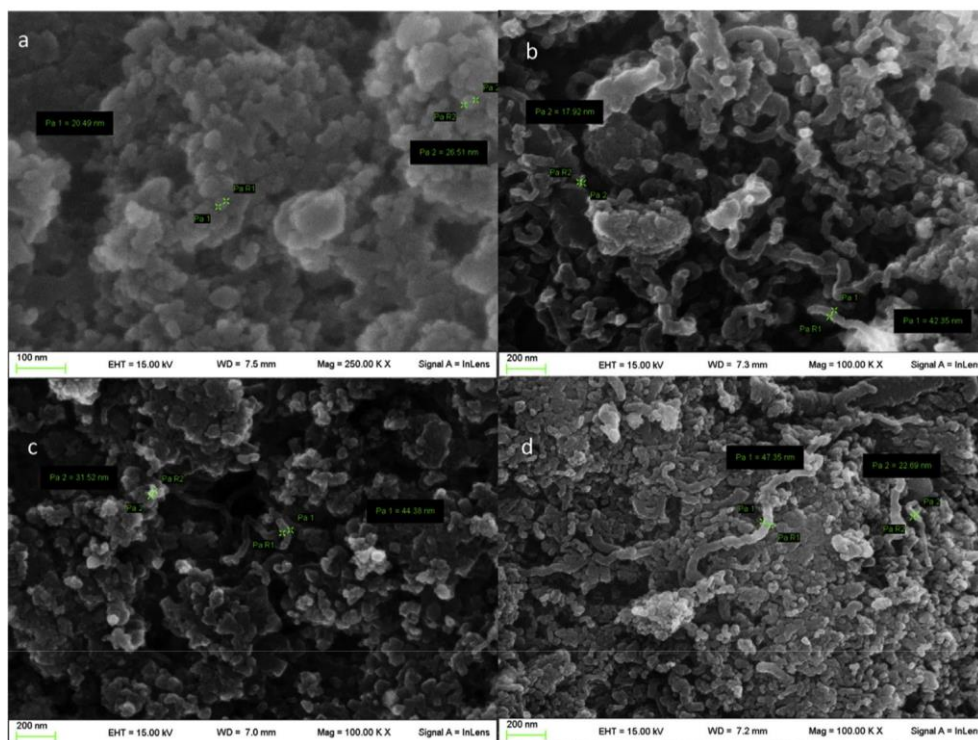


Fig. 3 e FE-SEM images for catalysts Ni/MgAl₂O₄ 1.5 wt%, fresh (a), 1.5 wt%, after reaction (b), 5 wt% after reaction (c) and 10 wt% after reaction (d).

negligible selectivity to acetaldehyde, confirming the better stability of these samples.

When the catalytic performance of the samples was evaluated at 500 C the same trend of activity versus Ni loading was confirmed, but the catalysts were generally much less active than at higher temperature (Table 4). A lower CO/CO₂ ratio was obtained irrespectively of the sample due to the thermodynamically favored equilibrium of the water gas shift reaction at lower temperature. Catalyst activity at this temperature was insufficient to fully convert byproducts, e.g. acetone and acetaldehyde, and, as a matter of fact, ethylene was the main product of the reaction.

A further decrease of the operating temperature, the only sample maintaining a (limited) activity for ESR was 10 wt% Ni (Table 5). The main products were ethylene and acetaldehyde, with a non negligible fraction of acetone, especially at low Ni loading.

TPD of preadsorbed NH₃

In previous studies we have shown the essential role of acidic sites for facilitating the formation of ethylene and affecting hydrogen productivity. The acidity of the catalysts was evaluated and compared by temperature programmed desorption of ammonia (NH₃-TPD). The strength of the acid sites was estimated according to the intensity and temperature of the NH₃ desorption peak. The acid strength can be classified as weak (150-250 C), medium (250-420 C) and strong (420-750 C) according to the temperature range of ammonia release. Fig. 7 shows the results of the analysis. Negligible ammonia adsorption was achieved for the bare support and

for sample Ni 1.5 wt%. By contrast, for Ni 5 wt% three desorption peaks were evident at 370, 504 and 660 C, while for Ni 10 wt% three at 416, 630 and 756 C indicating the presence of both medium and strong acid sites, with increasing amount and strength with increasing Ni loading (increasing ammonia desorption temperature and peak intensity). Hence, acidity was mainly ascribed to Ni and not to the basic support. This acidity is the responsible factor of promoting ethanol dehydration to ethylene and the somehow stronger acidity observed at the highest Ni loading can explain the deactivation of the 10 wt% Ni catalyst even at the highest temperature; if C accumulates over Ni particles their activity for ESR and in general for C-C bond cleavage decreases. The increase of acid sites influenced the deposition of carbon which increased proportionally with nickel loading, as shown in the TPO chart (vide infra).

DRIFTS analysis of ethanol adsorption/desorption

To get insight on the possible surface species responsible for the activity and selectivity adsorption/desorption studies of ethanol were carried out in the temperature range 110-400 C. Fig. 8 shows the resulting DRIFTS spectra of the samples, which were interpreted on the basis of the relevant literature as for bands assignment [38-40]. The spectra correspond to the adsorption of ethanol at 400 C. The observed small band at 1249 cm⁻¹ corresponds to the OH bending (δ) mode of un-dissociated adsorbed ethanol. The negative band near 3740 cm⁻¹ is due to the interaction of the free surface OH groups with the adsorbed molecules. The sharpness of the latter band and the absence of broad absorption between 3000

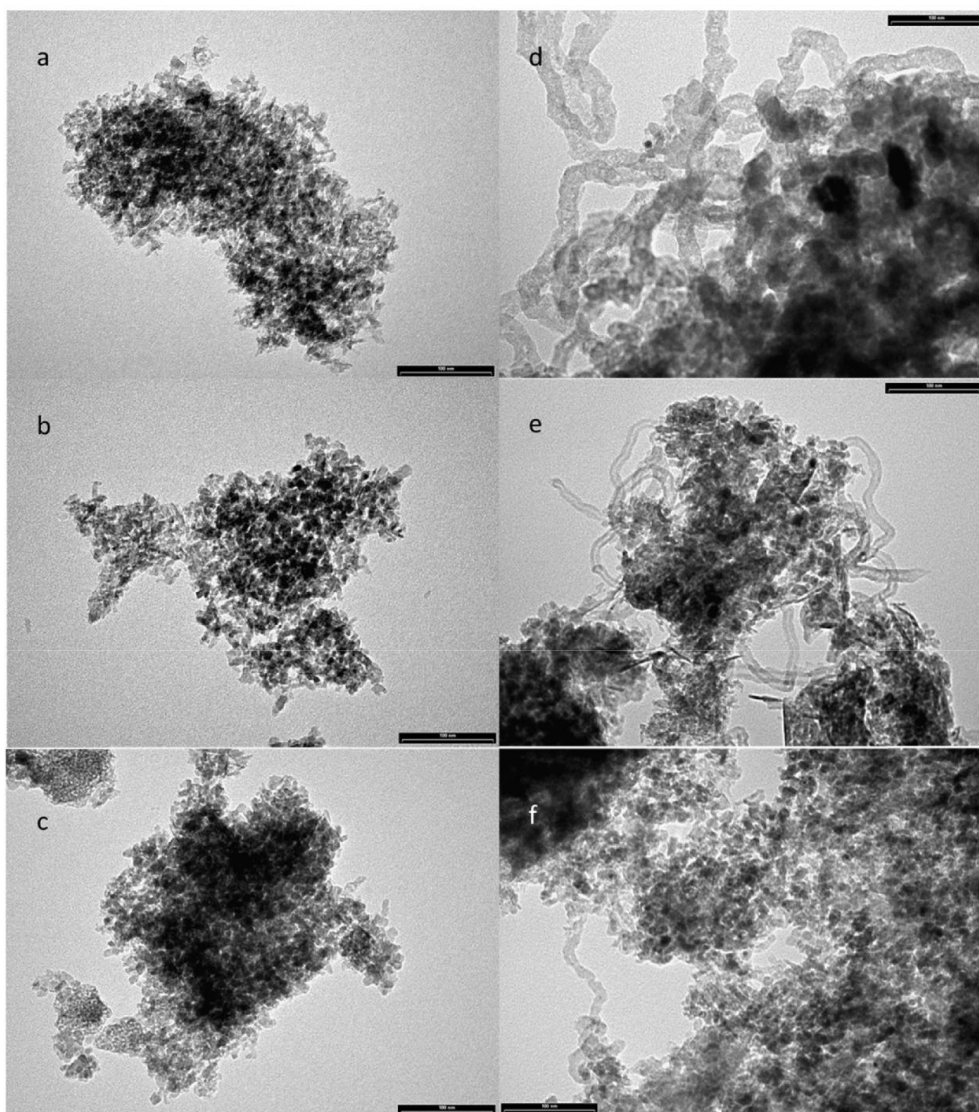


Fig. 4 e TEM images of the catalysts Ni/MgAl₂O₄ 1.5 wt%, (a ¼ fresh, d ¼ spent), 5 wt% (b ¼ fresh, e ¼ spent) and 10 wt% (c ¼ fresh, f ¼ spent).

and 3500 cm⁻¹ indicate that this species should be chemisorbed through the oxygen lone pair, rather than being H bonded. The complex absorption found in the region 2800-2400 cm⁻¹ (unusually strong) is associated with this

species and is likely due to a Fermi resonance of the overtone of the OH d vibration mode with the CH stretching (n), sym-metric (s) and asymmetric (as) modes, found at 2967, 2924, and 2879 cm⁻¹ (CH₃ n_{as}, CH₂ n_{as} and CH₃ n_s). At high temperature (Fig. 9), some new bands appeared at 1332, 1415, and 1476 cm⁻¹ (the last two being very broad). These bands may be assigned to the vibrational modes of acetate species (CH₃ d, OCO n_s, and OCO n_{as}, respectively) [41,42], confirming the acetaldehyde formation upon ethanol dehydrogenation as first step of the reforming path.

Table 3 e Results of ESR activity testing at 625 C.

	1.5 wt% Ni	5 wt% Ni	10 wt% Ni
C ₂ H ₅ OH conversion (%)	86 ± 3	100	100
C balance (%)	107 ± 3	93 ± 3	98.4 ± 0.7
H ₂ productivity (mol/min kgcat)	0.57 ± 0.05	1.18 ± 0.06	1.23 ± 0.04
CO/CO ₂	7.0 ± 0.3	1.05 ± 0.12	1.18 ± 0.13
Sel. CH ₄ (%)	6.9 ± 0.4	1.40 ± 0.09	0.79 ± 0.02
Sel. CH ₃ CHO (%)	2.8 ± 0.8	0 ± 0	1.7 ± 0.4
Sel. CH ₃ COCH ₃ (%)	2.4 ± 0.6	0 ± 0	0 ± 0
Sel. CH ₂ CH ₂ (%)	40.8 ± 1.1	0 ± 0	0 ± 0
Yield H ₂ (mol H ₂ out/mol C ₂ H ₅ OH in)	1.8 ± 0.2	3.8 ± 0.2	3.87 ± 0.13

The broadening of the band at 1476 cm⁻¹ and the apparent complexity of both main components suggest that carbonate species, responsible for bands in the same region, should also form. Their appearance is caused by the formation of CO₂ derived by the ethanol reforming, which remains adsorbed as carbonate on the basic support used. The shoulder around 1631 cm⁻¹ may be assigned to the CeO stretching of acetaldehyde, which may be rapidly oxidized to acetate species. These results are in agreement with the catalytic data

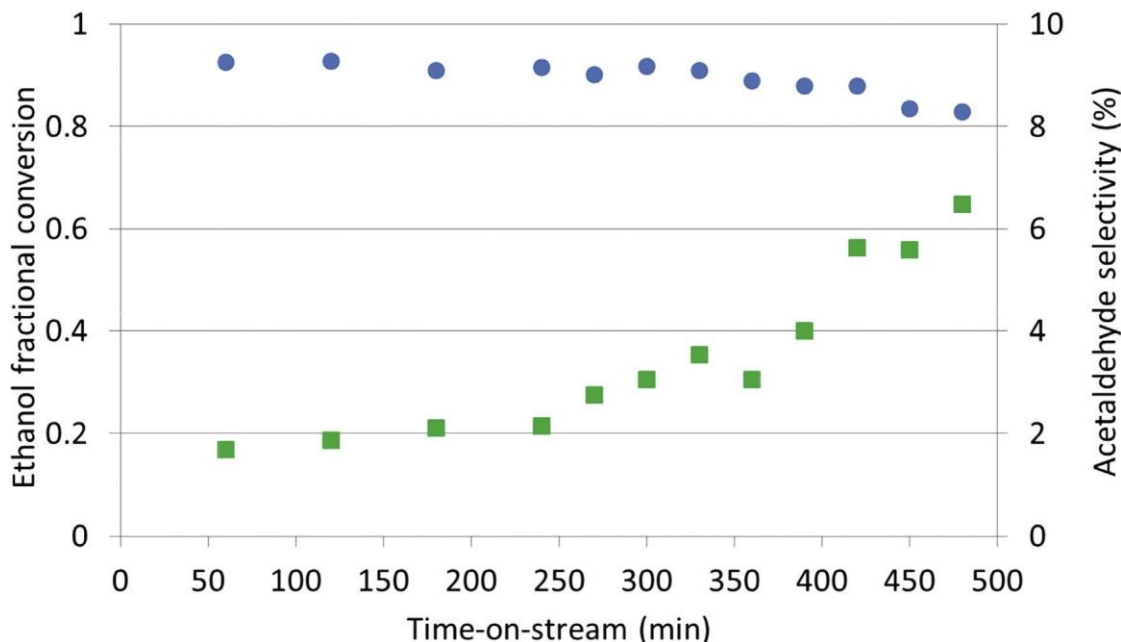


Fig. 5 e Ethanol conversion (blue circles) and acetaldehyde selectivity (green squares) of 1.5% Ni/MgAl₂O₄ at 625 C. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

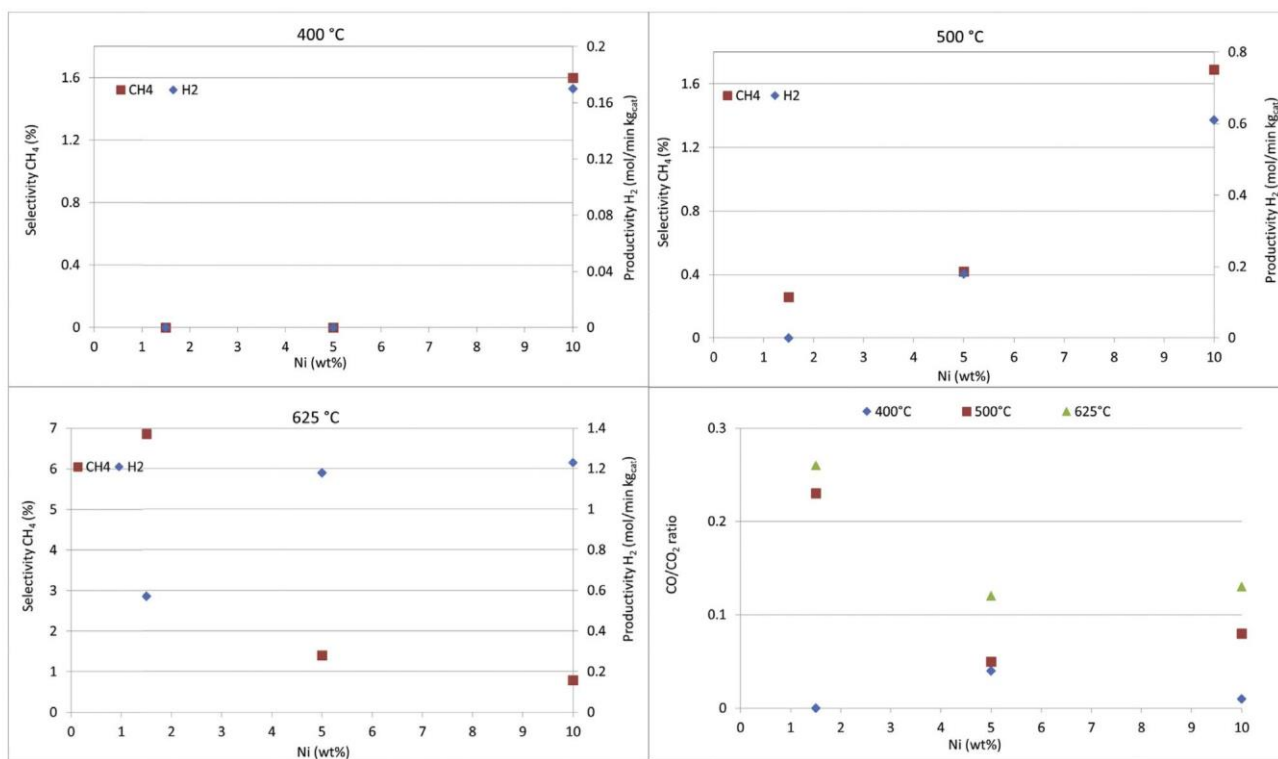


Fig. 6 e Trends of hydrogen productivity, methane selectivity and CO/CO₂ ratio at different Ni loading and temperature.

obtained at lower temperature where one of the intermediates detected was acetaldehyde. Often, acetaldehyde is not detected in the products distribution due to its rapid evolution by further oxidation or decomposition to CO and CH₄.

DRIFTS experiments also highlighted the formation of acetates, based on the bands at 1332 and 1415 cm⁻¹ [43]. The

spectral profile of sample 10 wt% Ni (Fig. 9) shows a reduction of bands intensity of CH_x during the temperature increase, with a corresponding increase of the carbonate ones. Also, the formation of a shoulder at ca. 1700 cm⁻¹, appearing at 300 C and increasing at higher temperature is related to oxidized C species, such as carbonyls and carboxylic groups. This

Table 4 e Results of ESR activity testing at 500 C.

	1.5 wt% Ni	5 wt% Ni	10 wt% Ni
C ₂ H ₅ OH conversion (%)	100	100	100
C balance (%)	90 ± 2	85.4 ± 0.2	92 ± 2
H ₂ productivity (mol/min kgcat)	0 ± 0	0.181 ± 0.014	0.61 ± 0.02
CO/CO ₂	1.0 ± 0.2	1.0 ± 0.2	1.0 ± 0.2
Sel. CH ₄ (%)	0.26 ± 0.02	0.42 ± 0.04	1.69 ± 0.12
Sel. CH ₃ CHO (%)	8.9 ± 0.5	2.37 ± 0.07	0 ± 0
Sel. CH ₃ COCH ₃ (%)	1.41 ± 0.07	2.48 ± 0.07	3.2 ± 0.3
Sel. CH ₂ CH ₂ (%)	77 ± 3	66.03 ± 0.18	41.2 ± 0.9
Yield H ₂ (mol H ₂ out/mol C ₂ H ₅ OH in)	0 ± 0	0.58 ± 0.05	1.91 ± 0.06

Table 5 e Results of ESR activity testing at 400 C.

	1.5 wt% Ni	5 wt% Ni	10 wt% Ni
C ₂ H ₅ OH conversion (%)	57 ± 4	87.67 ± 0.14	100
C balance (%)	95.5 ± 0.8	89 ± 6	89 ± 3
H ₂ productivity (mol/min kgcat)	0 ± 0	0 ± 0	0.169 ± 0.010
CO/CO ₂	0 ± 0	1.0 ± 0.5	0 ± 0
Sel. CH ₄ (%)	0 ± 0	0 ± 0	1.6 ± 0.3
Sel. CH ₃ CHO (%)	4.8 ± 1.0	4.8 ± 0.3	8.2 ± 0.4
Sel. CH ₃ COCH ₃ (%)	19.3 ± 1.2	10.5 ± 1.0	2.9 ± 0.9
Sel. CH ₂ CH ₂ (%)	68.0 ± 1.0	74 ± 3	63.6 ± 1.3
Yield H ₂ (mol H ₂ out/mol C ₂ H ₅ OH in)	0 ± 0	0 ± 0	0.53 ± 0.03

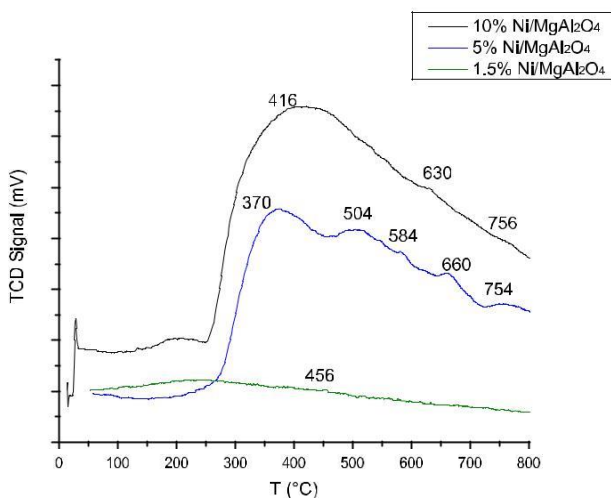


Fig. 7 e NH₃-TPD of the different samples. Ni loading increasing from bottom to upper curve.

supports the oxidative evolution of acetaldehyde over the present catalysts, rather than its decomposition. It should be underlined that acetaldehyde formation by dehydrogenation of ethanol is catalyzed by Ni active sites, which remain active for this reaction even when possible coke accumulation occurs over it. The C-C bond cleavage, mediated by the same active sites, becomes inactive after encapsulating coking occurs, thus leading to increasing presence of unconverted acetaldehyde in the products distribution. This latter is indeed a fingerprint of the formation of encapsulating coke.

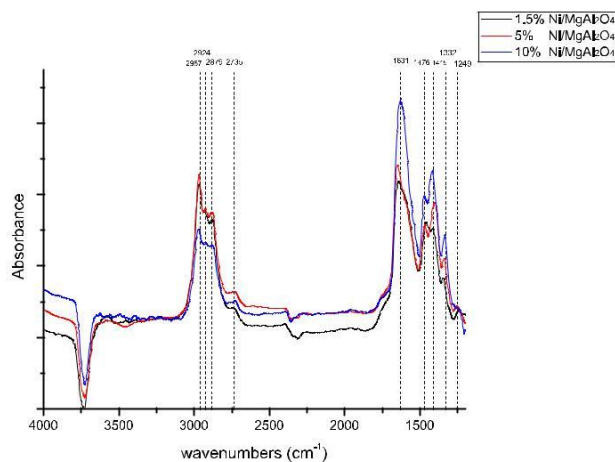


Fig. 8 e DRIFT spectra after adsorption of ethanol at 400 C.

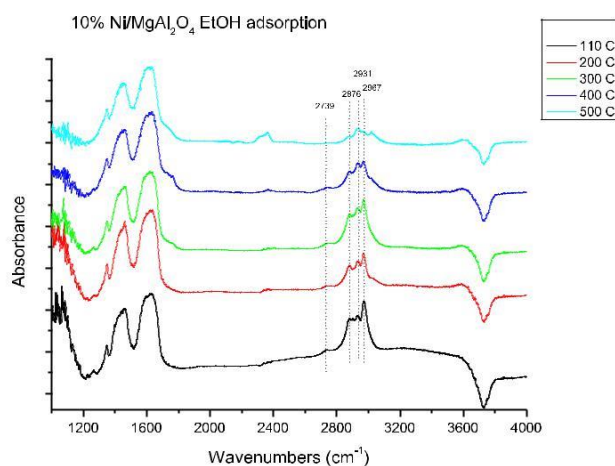


Fig. 9 e DRIFTS spectra of ethanol adsorption on 10 wt% Ni/ MgAl₂O₄ at different temperature.

The higher activity of the 10 wt% Ni sample is here testified by the increased intensity of the bands of the more oxidized species (acetates, carbonates) with respect to the CH_x bands.

Temperature programmed reduction (TPR)

Temperature programmed reduction profiles are presented in Fig. 10. Each positive peak represents the consumption of H₂. The highest is the reduction temperature, the hardest the reducibility of that species. The TPR for 10 wt% Ni/MgAl₂O₄ shows a main, broad reduction feature between 300 and 400 C, representing the reduction of NiO. A small shoulder at higher temperature can represent a fraction of Ni^{2p} as aluminate. The TPR profile of sample 5 wt% Ni presents a peak around 250 C which suggests the presence of Ni^{2p} species very similar in nature, but in lower amount than 10 wt% Ni, in agreement with XPS data. Additionally, a low temperature peak appeared, due to NiO poorly interacting with the support (for instance bigger particles) and is present also at the lowest Ni loading.

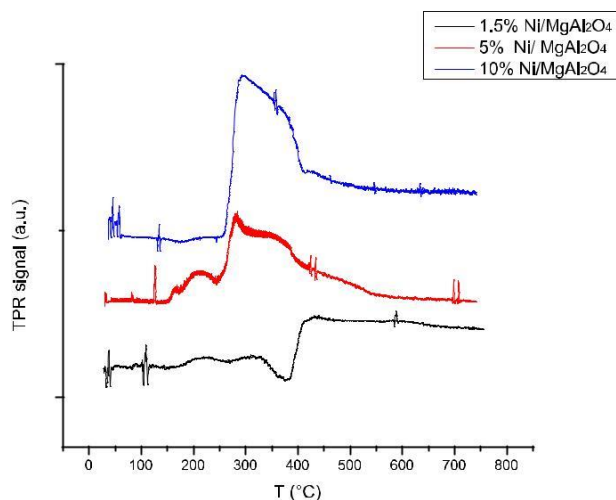


Fig. 10 e TPR profiles of the three catalysts.

From these data, one can conclude that at the selected activation temperature NiO species are fully reduced to metallic Ni. Very similar NiO species are present in all samples, when the chosen reduction temperature was between 300 and 400 C. These are accompanied by low temperature reduction features in the case of 1.5 wt% Ni and 5 wt% Ni, almost undetectable for the highest Ni loading, which showed the most uniform NiO particles.

Characterization of the spent samples

The TPO analyses were carried out on the spent catalysts, to quantify both the nature (amorphous or ordered C, depending on the oxidation temperature) and their amount. The profiles show that C oxidation occurred at ca. 370 C for sample 1.5% Ni/MgAl₂O₄ and 10% Ni/MgAl₂O₄ likely corresponding to amorphous carbon on Ni particles, while at ca. 538 C for catalyst 5% Ni/MgAl₂O₄ (Fig. 11). This higher oxidation temperature and lower intensity can be ascribed to more structured C, such as the presence of graphitic layers. The quantification of C deposition is also reported in Table 6. The presence of structured C deposits is also confirmed by TEM and FE-SEM analysis, which evidence the presence of C

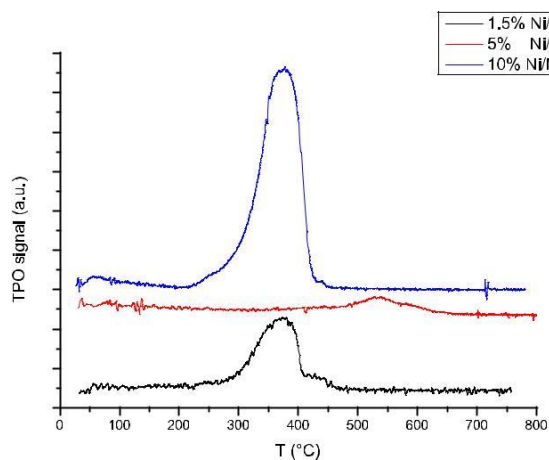


Fig. 11 e TPO profile of Ni catalysts.

Table 6 e Mass of carbon per mass of spent catalyst expressed as %.

Sample	C wt%
1.5% Ni/MgAl ₂ O ₄	6.58
5% Ni/MgAl ₂ O ₄	5.29
10% Ni/MgAl ₂ O ₄	14.86

nanotubes (Figs. 3 and 4) and by micro-RAMAN spectroscopy (Fig. 12). The latter presents for each sample the typical D and G bands usually found in the presence of multiwalled C nanotubes, with higher intensity for the highest Ni content.

General discussion

Based on the negligible acidity of the support, the ethanol dehydration features are attributed only to Ni Lewis acidity. However, under the present conditions, limited effect of Ni coking was observed in the case of the lowest and highest Ni loading for different reasons. The amorphous coke characterizing both catalysts likely formed due to ethanol dehydration to ethylene during low temperature testing (400 C). Reactivity for dehydration was quite limited due to small acidity (TPD of ammonia) in the case of 1.5 wt% Ni, whereas it was higher for 10 wt% Ni in virtue of its higher acidity, due to Ni particles. This form of coking is much more limited at higher reaction temperature due to consecutive reforming of the ethylene formed (if any), as testified by the products distribution. Furthermore, it can be tuned by increasing the water amount in the feed and is reversible by periodic regeneration of the catalyst. Even if higher acidity of 10 wt% Ni could lead to higher ethylene formation, its higher CeC bond cleavage activity improved its further conversion to reformat.

On the other hand, the higher coke oxidation temperature observed in the case of 5 wt% Ni suggests a more structured carbon, usually in form of nanotubes. This implies a more critical failure of the catalyst, which brings to reactor fouling and to the physical detachment of the active phase from the support surface. This (limited) coke formation can be favored by NiO species poorly interacting with the support, likely being bigger particles, represented by the low temperature

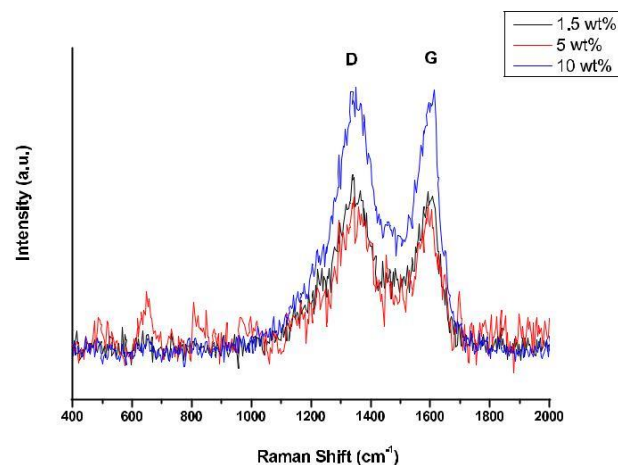


Fig. 12 e Micro-RAMAN spectra of used catalysts (last testing temperature ¼ 400 C).

reduction feature in TPR analysis. The incorporation of part of Ni in the spinel phase for 10 wt% Ni observed by XPS and XRD analysis may improve its overall dispersion (even at such a high loading), thus preventing the formation of bigger Ni particles as in the case of 5 wt% Ni. The latter are involved in the formation of C nanotubes as previously discussed. These results confirm the effect of Ni dispersion, of its particle size and the interaction with the support in limiting the coking activity. This point has been already discussed in the literature [12e17,29,30,44e46].

On the basis of all the considerations above reported, 10 wt% Ni/MgAl₂O₄ represents an active and stable catalyst when tested at 625 C. This operating temperature is lower than that usually applied to this reaction, in light of process intensification. The absence of intrinsic acidity of the support limits the deactivation phenomena by coking due to ethanol dehydration paths. However, a limited contribution to acidity is also attributed to Ni itself, increasing with Ni loading. Unfortunately, the catalyst with low Ni loading, favorable from the point of view of low Ni acidity and low coking rate, was insufficiently active for steam reforming, due to insufficient C-C bond cleavage activity.

On the other hand, the support plays a significant role in this reaction by contributing to steam activation, forming activated OH species and ensuring their mobility towards the active Ni particles to provide oxidizing moieties.

DRIFT analysis allowed to investigate and get insight into possible reaction mechanisms. The first reaction step seems the formation of acetaldehyde through ethanol dehydrogenation. This intermediate may decompose to methane and CO or further oxidise to carbonate, acetate and in general carboxylic species. The latter path seems favored over the present catalysts based on DRIFT analysis and on the very limited concentration of methane in the products distribution. This evolution mechanism of acetaldehyde may be favored by the

basic character of the support, which stabilizes acidic functions such as carboxylic acids and CO₂.

As a general comparison with similar catalysts, Aupetre et al. [47] reported a RhNi/MgAl₂O₄ catalyst leading to 100% ethanol conversion with 4.41 mol H₂/mol of ethanol, at 700 C, GHSV ¼ 13,400 h⁻¹, with a more favorable water/ethanol ratio of 4 mol/mol than the stoichiometric ratio here used.

Similarly, Olivares et al. [48] reported almost full ethanol conversion and ca. 4.7 mol H₂/mol of ethanol, over a Ni/MgAl₂O₄/CeO₂ catalyst at 650 C, W/F ¼ 49 g min/mol, with a water/ethanol ratio of 5 mol/mol.

Szjijarto et al. [49] reported a kinetic study on Ni(Co,Ce)/MgAl₂O₄ with almost full ethanol conversion and ca. 55% H₂ yield, at 400 C, W/F ¼ 1333 g min/mol, with a water/ethanol ratio of 9 mol/mol. Accordingly, the present samples showed competitive with what reported in the literature. Indeed, comparable activity and hydrogen productivity was achieved without the addition of a noble/rare metals, by using a lower water/ethanol ratio and at relatively low temperature.

Conclusions

A series of Ni-based catalysts supported over MgAl₂O₄ have been prepared with small Ni crystallite size and high surface

area thanks to an ultrasound assisted synthesis. Sufficiently dispersed Ni particles were obtained even at high Ni loading. The catalysts showed limited acidity, essentially due to the presence of Ni, acidity increasing with its loading, responsible of the ethanol dehydration to ethylene at low temperature. Ethylene can be further reformed provided that sufficiently active Ni species are present, such as in the case of 10 wt% Ni.

Acetaldehyde was found as intermediate by DRIFT analysis, formed by ethanol dehydrogenation and further reformed. Its evolution follows an oxidative path rather than decomposition.

Coking of these samples was in general very limited, due to small acidity, which limits one of the possible coking modes, i.e. ethylene polymerisation. Some amorphous coke was found on the catalysts with the lowest and highest Ni loading, whereas the 5 wt% Ni sample was characterised by more structured carbon, which can be more critical as for regeneration.

Overall, 10 wt% Ni/MgAl₂O₄ proved active and sufficiently stable catalyst at 625 C and even at 500 C to represent a promising candidate for further optimisation of the process parameters.

Acknowledgements

The valuable help of Dr. Matteo Compagnoni (Universita degli Studi di Milano), Dr. James Carter (Cardiff University), Dr. Simon Kondrat (formerly Cardiff University, now Loughborough University) is gratefully acknowledged.

references

- [1] Park S, Vohs JM, Gorte RJ. Direct oxidation of hydrocarbons in a solid-oxide fuel cell. *Nature* 2000;404:265e7. <https://doi.org/10.1038/35005040>.
- [2] Baykara SZ. Hydrogen as fuel: a critical technology? *Int J Hydrogen Energy* 2005;30:545e53. <https://doi.org/10.1016/j.ijhydene.2004.06.010>.
- [3] Stiegel GJ, Ramezan M. Hydrogen from coal gasification: an economical pathway to a sustainable energy future. *Int J Coal Geol* 2006;65:173e90. <https://doi.org/10.1016/j.coal.2005.05.002>.
- [4] Le Valant A, Can F, Bion N, Duprez D, Epron F. Hydrogen production from raw bioethanol steam reforming: optimization of catalyst composition with improved stability against various impurities. *Int J Hydrogen Energy* 2010;35:5015e20. <https://doi.org/10.1016/j.ijhydene.2009.09.008>.
- [5] Calles JA, Carrero A, Vizcaíno AJ. Ce and La modification of mesoporous CuNi/SBA-15 catalysts for hydrogen production through ethanol steam reforming. *Microporous Mesoporous Mater* 2009;119:200e7. <https://doi.org/10.1016/j.micromeso.2008.10.028>.
- [6] Carrero A, Calles JA, Vizcaíno AJ. Hydrogen production by ethanol steam reforming over Cu-Ni/SBA-15 supported catalysts prepared by direct synthesis and impregnation. *Appl Catal Gen* 2007;327:82e94. <https://doi.org/10.1016/j.apcata.2007.04.030>.
- [7] Lindo M, Vizcaíno AJ, Calles JA, Carrero A. Ethanol steam reforming on Ni/Al-SBA-15 catalysts: effect of the aluminium

- content. *Int J Hydrogen Energy* 2010;35:5895e901. <https://doi.org/10.1016/j.ijhydene.2009.12.120>.
- [8] Haryanto A, Fernando S, Murali N, Adhikari S. Current status of hydrogen production techniques by steam reforming of Ethanol: a review. *Energy Fuel* 2005;19:2098e106. <https://doi.org/10.1021/ef0500538>.
- [9] De Lima SM, Da Cruz IO, Jacobs G, Davis BH, Mattos LV, Noronha FB. Steam reforming, partial oxidation, and oxidative steam reforming of ethanol over Pt/CeZrO₂ catalyst. *J Catal* 2008;257:356e68. <https://doi.org/10.1016/j.jcat.2008.05.017>.
- [10] Pompeo F, Santori GF, Nichio NN. Hydrogen production by glycerol steam reforming with Pt/SiO₂ and Ni/SiO₂ catalysts. *Catal Today* 2011;172:183e8. <https://doi.org/10.1016/j.cattod.2011.05.001>.
- [11] Wang F, Cai W, Provendier H, Schuurman Y, Descorme C, Mirodatos C, et al. Hydrogen production from ethanol steam reforming over Ir/CeO₂ catalysts: enhanced stability by PrO_x promotion. *Int J Hydrogen Energy* 2011;36:13566e74. <https://doi.org/10.1016/j.ijhydene.2011.07.091>.
- [12] Nichele V, Signoretto M, Menegazzo F, Rossetti I, Cruciani G. Hydrogen production by ethanol steam reforming: effect of the synthesis parameters on the activity of Ni/TiO₂ catalysts. *Int J Hydrogen Energy* 2014;39:4252e8. <https://doi.org/10.1016/j.ijhydene.2013.12.178>.
- [13] Rossetti I, Lasso J, Finocchio E, Ramis G, Nichele V, Signoretto M, et al. TiO₂-supported catalysts for the steam reforming of ethanol. *Appl Catal A* 2014;477:42e53. <https://doi.org/10.1016/j.apcata.2014.03.004>.
- [14] Finocchio E, Rossetti I, Ramis G. Redox properties of Co- and Cu-based catalysts for the steam reforming of ethanol. *Int J Hydrogen Energy* 2013;38:3213e25. <https://doi.org/10.1016/j.ijhydene.2012.12.137>.
- [15] Rossetti I, Lasso J, Finocchio E, Ramis G, Nichele V, Signoretto M, et al. Silica and zirconia supported catalysts for the low-temperature ethanol steam reforming. *Appl Catal B* 2014;150e151:257e67. <https://doi.org/10.1016/j.apcatb.2013.12.012>.
- [16] Compagnoni M, Lasso J, Di Michele A, Rossetti I. Flame-pyrolysis-prepared catalysts for the steam reforming of ethanol. *Catal Sci Technol* 2016;6:6247e56. <https://doi.org/10.1039/C5CY01958C>.
- [17] Rossetti I, Lasso J, Compagnoni M, Finocchio E, Ramis G, Di Michele A, et al. Syngas production via steam reforming of bioethanol over Ni-BEA catalysts: a BTL strategy. *Int J Hydrogen Energy* 2016;41:16878e89. <https://doi.org/10.1016/j.ijhydene.2016.07.149>.
- [18] Vizcaino AJ, Carrero A, Calles JA. Hydrogen production by ethanol steam reforming over CuNi supported catalysts. *Int J Hydrogen Energy* 2007;32:1450e61. <https://doi.org/10.1016/j.ijhydene.2006.10.024>.
- [19] Dave CD, Pant KK. Renewable hydrogen generation by steam reforming of glycerol over zirconia promoted ceria supported catalyst. *Renew Energy* 2011;36:3195e202. <https://doi.org/10.1016/j.renene.2011.03.013>.
- [20] Denis A, Grzegorzczak W, Gac W, Machocki A. Steam reforming of ethanol over Ni/support catalysts for generation of hydrogen for fuel cell applications. *Catal Today* 2008;137:453e9. <https://doi.org/10.1016/j.cattod.2008.03.006>.
- [21] Wen G, Xu Y, Ma H, Xu Z, Tian Z. Production of hydrogen by aqueous-phase reforming of glycerol. *Int J Hydrogen Energy* 2008;33:6657e66. <https://doi.org/10.1016/j.ijhydene.2008.07.072>.
- [22] Konsolakis M, Ioakimidis Z, Kraia T, Marmellos GE. Hydrogen production by Ethanol Steam Reforming (ESR) over CeO₂ supported transition metal (Fe, Co, Ni, Cu) catalysts: insight into the structure-activity relationship. *Catalysts* 2016;6(39):1e27. <https://doi.org/10.3390/catal6030039>.
- [23] Compagnoni M, Tripodi A, Rossetti I. Parametric study and kinetic testing for ethanol steam reforming. *Appl Catal B* 2017;203:899e909. <https://doi.org/10.1016/j.apcatb.2016.11.002>.
- [24] Tripodi A, Compagnoni M, Rossetti I. Kinetic modeling and reactor simulation for ethanol steam reforming. *ChemCatChem* 2016;8:3804e13. <https://doi.org/10.1002/cctc.201601075>.
- [25] Coleman LJI, Epling W, Hudgins RR, Croiset E. Ni/MgAl mixed oxide catalyst for the steam reforming of ethanol. *Appl Catal A* 2009;363:52e63. <https://doi.org/10.1016/j.apcata.2009.04.032>.
- [26] Trane-Restrupa R, Dahlb S, Jensen AD. Steam reforming of ethanol over Ni-based catalysts: effect of feed composition on catalyst stability. *Int J Hydrogen Energy* 2014;39:7735e46. <https://doi.org/10.1016/j.ijhydene.2014.03.107>.
- [27] Katheria S, Deo G, Kunzru D. Washcoating of Ni/MgAl₂O₄ catalyst on FeCrAlloy monoliths for steam reforming of methane. *Energy Fuel* 2017;31(3):3143e53. <https://doi.org/10.1021/acs.energyfuels.6b03423>.
- [28] Barroso MN, Galetti AE, Abello C. Ni catalysts supported over MgAl₂O₄ modified with Pr for hydrogen production from ethanol steam reforming. *Appl Catal A* 2011;394:124e31. <https://doi.org/10.1016/j.apcata.2010.12.038>.
- [29] Rossetti I, Gallo A, Dal Santo V, Bianchi CL, Nichele V, Signoretto M, et al. Nickel catalysts supported over TiO₂, SiO₂ and ZrO₂ for the steam reforming of glycerol. *ChemCatChem* 2013;5:294e306. <https://doi.org/10.1002/cctc.201200481>.
- [30] Rossetti I, Biffi C, Bianchi CL, Nichele V, Signoretto M, Menegazzo F, et al. Ni/SiO₂ and Ni/ZrO₂ catalysts for the steam reforming of ethanol. *Appl Catal B* 2012;117e118:384e96. <https://doi.org/10.1016/j.apcatb.2012.02.006>.
- [31] Mattos LV, Jacobs G, Davis BH, Noronha FB. Production of hydrogen from ethanol: review of reaction mechanism and catalyst deactivation. *Chem Rev* 2012;112:4094e123. <https://doi.org/10.1021/cr2000114>.
- [32] Centi G, Perathoner S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal Today* 2009;48:191e205. <https://doi.org/10.1016/j.cattod.2009.07.075>.
- [33] Chen D, Christensen KO, Ochoa-Fernandez E, Yu Z, Tøtdal B, Latorre N, et al. Synthesis of carbon nanofibers: effects of Ni crystal size during methane decomposition. *J Catal* 2005;229:82e96. <https://doi.org/10.1016/j.jcat.2004.10.017>.
- [34] Christensen KO, Chen D, Lødeng R, Holmen A. Effect of supports and Ni crystal size on carbon formation and sintering during steam methane reforming. *Appl Catal A* 2006;314:9e22. <https://doi.org/10.1016/j.apcata.2006.07.028>.
- [35] Gonzalez De La Cruz VM, Holgado JP, Pereni' guez~ R, Caballero A. Morphology changes induced by strong metal-support interaction on a Ni/ceria catalytic system. *J Catal* 2008;257:307e14. <https://doi.org/10.1016/j.jcat.2008.05.009>.
- [36] Grosvenor AP, Biesinger M, Smart R, McIntyre S. New interpretations of XPS spectra of nickel metal and oxides. *Surf Sci* 2006;600:1771e9. <https://doi.org/10.1016/j.susc.2006.01.041>.
- [37] Biesinger MC, Payne BP, Grosvenor P, Lau WM, Gerson AG, Smart RSTG. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl Surf Sci* 2011;257:2717e30. <https://doi.org/10.1016/j.apsusc.2010.10.051>.
- [38] Velasquez Ochoa J, Trevisan C, Millet JMM, Busca G, Cavani F. In situ DRIFTS-MS study of the anaerobic oxidation of ethanol over spinel mixed oxides. *J Phys Chem C* 2013;117:23908e18. <https://doi.org/10.1021/jp409831t>.

-
- [39] Song H, Ozkan US. Ethanol steam reforming over Co-based catalysts: role of oxygen mobility. *J Catal* 2009;261:66e74. <https://doi.org/10.1016/j.jcat.2008.11.006>.
- [40] Song H, Zhang L, Watson RB, Braden D, Ozkan US. Investigation of bio-ethanol steam reforming over cobalt-based catalysts. *Catal Today* 2007;129:346e54. <https://doi.org/10.1016/j.cattod.2006.11.028>.
- [41] Llorca J, Homs N, Ramirez de la Piscina P. In situ DRIFT-mass spectrometry study of the ethanol steam-reforming reaction over carbonyl-derived Co/ZnO catalysts. *J Catal* 2004;227:556e60. <https://doi.org/10.1016/j.jcat.2004.08.024>.
- [42] de Lima SM, da Silva AM, da Costa LOO, Assaf JM, Jacobs G, Davis BH, et al. Evaluation of the performance of Ni/La₂O₃ catalyst prepared from LaNiO₃ perovskite-type oxides for the production of hydrogen through steam reforming and oxidative steam reforming of ethanol. *Appl Catal A* 2010;377:181e90. <https://doi.org/10.1016/j.apcata.2010.01.036>.
- [43] Rintramee K, Fottinger K, Rupprechter G, Wittayakun J. Ethanol adsorption and oxidation on bimetallic catalysts containing platinum and base metal oxide supported on MCM-41. *Appl Catal B* 2012;115e116:225e35. <https://doi.org/10.1016/j.apcatb.2011.11.050>.
- [44] Palma V, Ruocco C, Meloni E, Ricca A. Highly active and stable Pt-Ni/CeO₂-SiO₂ catalysts for ethanol reforming. *J Clean Prod* 2017;166:263e72. <https://doi.org/10.1016/j.jclepro.2017.08.036>.
- [45] Vizcaíno AJ, Lindo M, Carrero A, Calles JA. Hydrogen production by steam reforming of ethanol using Ni catalysts based on ternary mixed oxides prepared by coprecipitation. *Int J Hydrogen Energy* 2012;37:1985e92. <https://doi.org/10.1016/j.ijhydene.2011.04.179>.
- [46] Palma V, Ruocco C, Meloni E, Ricca A. Influence of catalytic formulation and operative conditions on coke deposition over CeO₂-SiO₂ based catalysts for ethanol reforming. *Energies* 2017;10:1030e42. <https://doi.org/10.3390/en10071030>.
- [47] Aupretre F, Descorme C, Duprez D, Casanave D, Uzio D. Ethanol steam reforming over Mg_xNi_{1-x}Al₂O₃ spinel oxide-supported Rh catalysts. *J Catal* 2005;233:464e77. <https://doi.org/10.1016/j.jcat.2005.05.007>.
- [48] Villagran Olivares AC, Gomez MF, Barroso MN, Abello MC. Ni-supported catalysts for ethanol steam reforming: effect of the solvent and metallic precursor in catalyst preparation. *I.J.I.C.* 2018;9:61e73. <https://doi.org/10.1007/s40090-018-0135-6>.
- [49] Szijjarto GP, Paszti Z, Sajo I, Erdohelyi A, Radnoczi G, Tompos A. Nature of the active sites in Ni/MgAl₂O₄-based catalysts designed for steam reforming of ethanol. *J Catal* 2013;305:290e306. <https://doi.org/10.1016/j.jcat.2013.05.036>.