Short communication

Potassium improved stability of Ni/MgO in the steam reforming of ethanol for the production of hydrogen for MCFC

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Abstract

The catalytic behavior of the bare and K-promoted 21% Ni/MgO catalyst in the ethanol steam reforming at MCFC operative conditions has been investigated. The effect of K loading (1–3 wt.%) on the catalytic activity, stability and coking rate have been addressed. K addition stabilizes Ni catalyst mainly by depressing the metal sintering, while coke formation does not seem to be influenced by alkali addition. Endurance test ($500\,h^{-1}$) performed at $20,000\,h^{-1}$ allows foresee a very long catalyst life in the case of practical application. High H_2 productivity (>5 mol H_2/mol fed ethanol) was obtained. A change in the electronic properties of the active phase accounts for the effect of K addition on the catalytic behavior of the Ni/MgO catalyst.
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Keywords: Alkali doped Ni/MgO; Ethanol; H_2 production; MCFC

1. Introduction

It is a common opinion to consider hydrogen as the most accredited clean fuel for the near future. Several efforts are actually focused towards the development of innovative catalytic processes for the production of hydrogen.

Hydrogen can be produced from hydrocarbons [1], from water by electrolysis or splitting [2–4], from bio-mass [5,6] and from all organic materials characterized by an adequate hydrogen content. Among these source, due to the necessity to lower the emission of carbon dioxide, bio-mass has recently attracted a particular attention since they are considered a zero CO_2 emission energy source.

We have recently focused our efforts on the possibility to produce hydrogen from bio-ethanol by steam reforming process. In particular the possibility to use the "as produced" bio-ethanol, namely without a previous distillation, was evaluated. Reaction was performed at high temperature (650 °C) to exploit the possibility to perform the endothermic steam reforming of ethanol using the heat produced at cathode and anode in a molten carbonate fuel cell (MCFC) system.

We have already investigated different catalytic systems mainly based on the use of Rh, Co, and Ni as active metals [7,8]. Results obtained have clearly indicated that metal sintering and coke formation are the main problems to overcome. Among different catalysts investigated, Ni-based catalysts have shown the best performance in terms of hydrogen productivity even though the prevention of coke formation on Ni is of course a challenge. However, it has been seen that using basic carriers like MgO the coke formation rate could be taken under control.

In this paper, the effect of K doping on Ni/MgO catalyst behavior in the ethanol steam reforming reaction at MCFC operative conditions was investigated. The influence of K loading on catalyst activity, stability and H_2 productivity of Ni/MgO catalyst has been evaluated.

2. Experimental

2.1. Catalysts

21 wt.% Ni/MgO catalyst (A sample) was prepared by impregnation (incipient wetness method) of MgO Martin Marietta ($120\,m^2\,g^{-1}$) with a toluene solution of Ni acetate used as precursor. Before impregnation MgO was stabilized in steam atmosphere at 700 °C for 12 h. After impregnation, catalyst was dried at 80 °C for 12 h and calcined at 400 °C in air for 24 h. Potassium was added by incipient wetness impregnation using an *i*-propanol solution of CH_3COOK. After

impregnation K-doped catalysts (K1-A and K3-A samples) were dried at 80 °C and then calcined at 400 °C for 12 h. All the catalyst samples were pressed at 400 bar, crushed and sieved, and the 40–70 mesh fraction was used for the catalytic measurements.

2.2. Temperature-programmed reduction (TPR) measurements

Temperature-programmed reduction measurements in the range 25–800 °C have been performed in a flow apparatus using a 6% H_2/Ar mixture flowing at 60 STP cm^3 min^{-1}, a heating rate of 20 °C min^{-1} and a mass sample of 0.05 g.

H_2 uptake and the metal dispersion (D) of the "fresh" catalysts were evaluated by H_2-TPD measurements in the range −80 to 620 °C after reduction of the catalyst at 725 °C for 1 h.

2.3. Particle size distribution (PSD)

The particle size distribution of "fresh" and "used" catalysts was obtained by transmission electron microscopy (TEM) analysis made by a PHILIPS CM12 instrument equipped with a high resolution (HR) camera which allow acquisition and elaboration of TEM images.

2.4. Carbon

Carbon deposited during reaction was evaluated by using a CHSN—Carlo Erba elementary analysis instrument. Few mg of used catalyst were encapsulated and treated at high temperature in air. CO_2 produced during oxidation process was analyzed by a high sensitivity TC detector.

The list of catalyst samples along with the relative K loading and BET surface area values is reported in Table 1.

2.5. Catalytic measurements

Experiments were performed at atmospheric pressure in a fixed-bed tubular quartz micro reactor (i.d. = 4 mm; H_{bed} = 1.0–2.0 cm). 0.010–0.060 g of catalyst (grain size: 40–70 mesh) diluted with 150–300 mg of same sized carborundum (SiC) were used for the catalytic tests. Prior to each run, catalysts were reduced "in situ" at $T = 725$ °C for 1 h under flowing hydrogen and then cooled down to reaction temperature. Water/ethanol mixture was fed by an isocratic HP 1100 pump and vaporized at 120 °C in a current of N_2. Experiments were performed at 650 °C, gas hourly space velocities
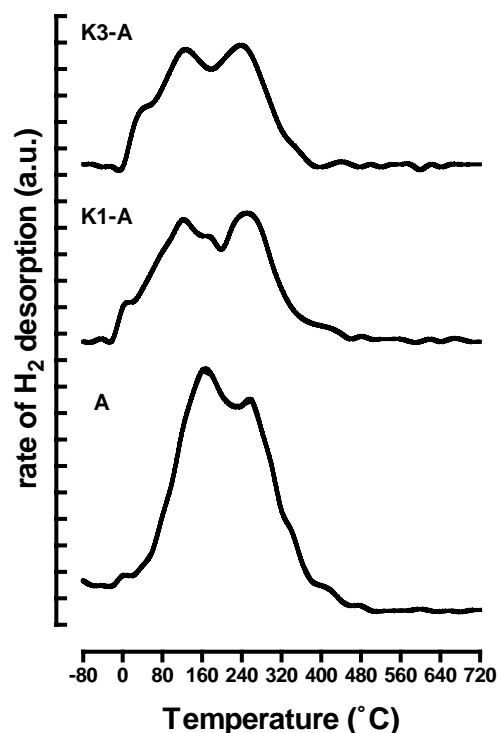
Table 1
List of bare and K-doped Ni/MgO catalysts

Sample	K loading (wt.%)	BET$_{SA}$ (m^2/g)
A	–	45.0
K1-A	1	14.5
K3-A	3	10.7

Fig. 1. TPR profile of bare and K-doped Ni/MgO catalysts.

(GHSV) ranging from 20,000 to 300,000 ml$_{EtOh}$ h^{-1} ml$_{cat}^{-1}$ and steam to carbon ratio (mol/mol) 4.2. The total flow corresponding to GHSV of 40,000 h^{-1} was 124 ml/min (24 vol% N_2; 68 vol% H_2O; 8 vol% EtOH).

Reaction stream was analyzed "on line" by a Hewlett Packard gas-chromatograph model 6890 Plus, equipped with a three columns (Molecular Sieve 5 Å, Porapack Q and Hysep) system and a thermal conductivity detector (TCD). Nitrogen was used as internal standard to carefully evaluate the carbon balance. GC data were acquired and elaborated by HP-IB interfaced computer system (HP Chemstation).

3. Results and discussion

TPR spectra of the A, K1-A and K3-A catalysts are shown in Fig. 1. The TPR pattern of the bare A catalyst consists of two main reduction peaks with maximum at 248 and 728 °C, respectively, accounting for an extent of reduction (reduced NiO/bulk NiO) equal to 0.80. Potassium addition does not significantly affect the reduction pattern of the Ni/MgO system, the main features of the bare system being still observable. At the lowest loading, K causes a slight broadening and shift of the T_{M1} peak to higher T (307 °C) along with a negative shift of the T_{M2} component by ca. 50 °C. A rise in the K loading to 3 wt.% (K3-A) further shifts the T_{M1} value to higher T, while the T_{M2} component appears considerably enhanced in intensity with the maximum centered at 695 °C. In spite of such minor changes in the qualitative features, however, the extent of
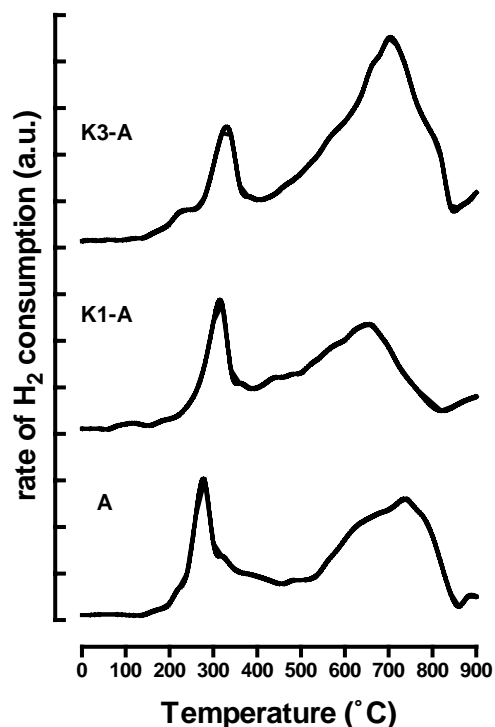
Fig. 2. H_2-TPD spectra of bare and K-doped Ni/MgO catalysts.

H_2 consumption keeps virtually constant accounting for a reduction degree ranging from 0.75 (K1-A) to 0.81(K3-A).

H_2-TPD profiles of bare and K-doped A catalysts are shown in Fig. 2, while the H_2 and O_2 uptake calculated from TPD peaks area, the percentage of reduced NiO (α) and the metal dispersion (D, %) values are listed in Table 2.

The TPD profile of the bare A catalyst features a main broad peak centered at 164 °C, strictly convoluted with a shoulder of H_2 desorption at higher T, and spanning the range 40–440 °C. Considering a reduction degree of ca. 33%, the H_2 uptake (ca. 136 µmol g^{-1}) accounts for a metal dispersion of 24.6% ($d_s = 6.0$ nm) and an average Ni particle size of ca. 4 nm.

K addition induces some slight differences in the desorption pattern, almost independently on the K loading. Namely, a decrease of the desorption kinetics at lower T, which leads to a more resolved T_{d2} peak indicates a change in the rel-

Table 2

Temperature-programmed desorption and H_2 chemisorption measurements of fresh Ni/MgO (sample A) and K-doped Ni/MgO catalysts (K1-A and K3-A samples)

	A	K1-A	K3-A
H_2 uptake (X_{H_2}) (Nµmol/g$_{cat}$)	136	63	77
O_2 uptake (X_{O_2}) (Nµmol/g$_{cat}$)	554	422	610
D (%)	24.6	15.0	12.6
d_s (Å)	41.0	67.3	80.2
MSA (m$^2_{Ni}$/g$_{cat}$)	10.6	4.9	6.0
α (%)	33.2	25.3	36.6

D, metal dispersion (Ni$^0_{surf}$/Ni^0); d_s, average crystallite size; α, NiO reducibility (Ni^0/Ni$_{tot}$).

ative site heterogeneity distribution. Further, a drop in the uptakes (63–77 µmol g^{-1}) coupled to minor changes in the extent of reduced NiO implies a drop in metal dispersion to ca. 15 and 13% on the K1-A and K3-A samples, which signal a rise in the average Ni particle size from 4 to 7 and 8 nm, respectively.

The catalytic behavior of bare and K-promoted Ni/MgO catalysts in the ethanol steam reforming is compared in Fig. 3 in terms of ethanol conversion versus reaction time. All catalysts show a comparable initial activity but a different deactivation pattern.

In particular on bare Ni/MgO catalyst the EtOH conversion lowers from 82 to 55% during 5 h of time on stream (t.o.s.), while on both K1-A- and K3-A-doped catalysts the loss of activity was less evident (EtOH conversion lowers from 94 to 78%).

Product distribution (see Table 3) seems not to be influenced by the presence of potassium. Only a slight difference of methane selectivity was observed, which was found to be slightly higher on K-doped catalysts (8.8% instead of 5.7%). The lower selectivity to CO (13–16.5%) respect to CO_2 (52.9–58.0%) signals that the high water content on the feed contributes to the shift of WGS reaction toward formation of H_2 and CO_2 ($CO + H_2O \rightarrow CO_2 + H_2$). However, we have seen that by operating at low GHSV (<5000 h^{-1}) even on bare Ni/MgO catalyst the only products detected were CO_2, CO and H_2.

To shed light on the benefits induced by K, used samples were analyzed by TEM and CHNS elementary analysis. Particle size distribution of fresh and used catalysts, obtained by TEM measurements, is shown in Fig. 4. It can be drown conclusion, that K adding depresses Ni sintering. Specially on K1-A only a slightly increasing of particle diameter (from 85 to 119 Å) was observed.

Results summarized in Table 2 reveal that K doping caused a consistent decrease of Ni surface area of bare catalyst, but in spite of that, the initial activity (as shown in Fig. 3) seems to be similar for all catalyst investigated. This allows foresee that a difference of Ni specific activity could exist. To shed light on this hypothesis, experiments in differential reaction conditions have been carried out
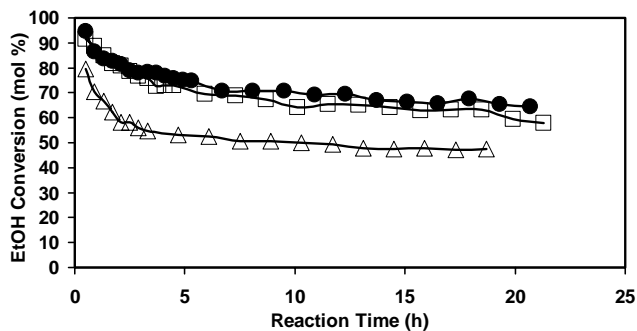

Fig. 3. Ethanol conversion as a function of time on stream: GHSV $= 40,000$ h^{-1}; $T_R = 650$ °C. (●) K1-NiMgO; (□) K3-Ni/MgO; (△) bare Ni/MgO.

Table 3
Steam reforming of ethanol at high space velocity (300,000 h^{-1}): a comparison in terms of product distribution, H$_2$ yield and turnover frequency

Sample	EtOH$_{conv.}$ (mol%)	Product distribution (%)				H$_2$ yield (mol$_{H_2}$/mol$_{EtOH_{in}}$)	TOF (s^{-1})
		CO$_2$	CH$_3$CHO	CH$_4$	CO		
A	10.36	58.21	19.60	5.67	16.52	0.42	0.47
K1-A	10.42	52.9	24.52	8.78	13.77	0.46	1.03
K3-A	9.29	56.63	24.34	7.21	12.09	0.39	0.75

at high space velocity (300,000 h^{-1}). Results summarized in Table 3 clearly demonstrate existing of a difference of specific activity between bare and doped Ni/MgO catalysts. In particular higher TOF values were found on K-doped catalysts, respect to the bare Ni/MgO catalyst. This result is probably ascribable to the change in the electronic properties of promoted Ni/MgO catalysts as a consequence of the electron transfer from alkali-oxide moieties to Ni particles, which strengthens the C–Ni bond and weakness the C–O bond enabling thus an easy dissociation of CO before desorption [9].

To evaluate the coke formation phenomena, which appears to be one of the main problem to take under control for the development of an efficient catalyst to perform EtOH steam reforming at MCFC operative conditions, CHNS elementary analysis and TEM measurements have been carried out on used catalysts.

In terms of coke formation rate no consistent difference was observed on different catalytic system investigated.

Coke formed on bare and K-doped catalysts with similar rate, however in any case such rate was almost one order of magnitude lower than that observed using Ni supported on acidic carrier [8].

Concerning the morphology of coke formed during reaction, TEM overview of used K1-A catalyst (see Fig. 5) revealed the formation of both filamentous and condensed carbon (A and B zones, respectively). In particular, carbon filament seems to be different than that observed in the past in the steam reforming of methane on Ni/MgO catalyst [10]. From ethanol carbon was not formed by a mechanism, which foresees the growth of filament with Ni at a tip, as in the methane reforming. In fact (see C zone of Fig. 5), Ni well remain anchored on MgO surface and no detached of Ni particles was observed.

To evaluate if the proposed catalytic systems could be useful for practical application, endurance tests at GHSV = 20,000 h^{-1} have been performed. Results reported in Fig. 6 clearly demonstrate that K-doped catalyst was much more
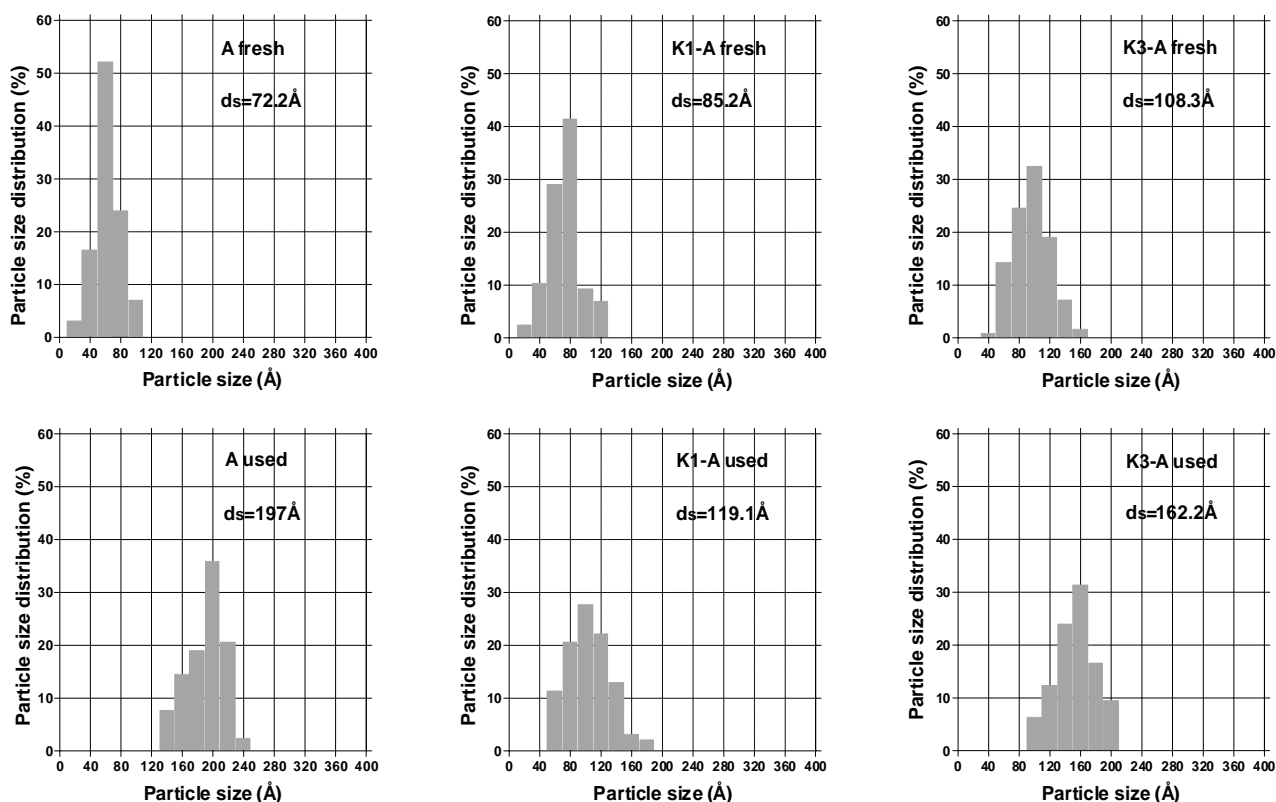

Fig. 4. Ni particle size distribution from TEM analysis of fresh and used bare and K-doped Ni/MgO catalysts.
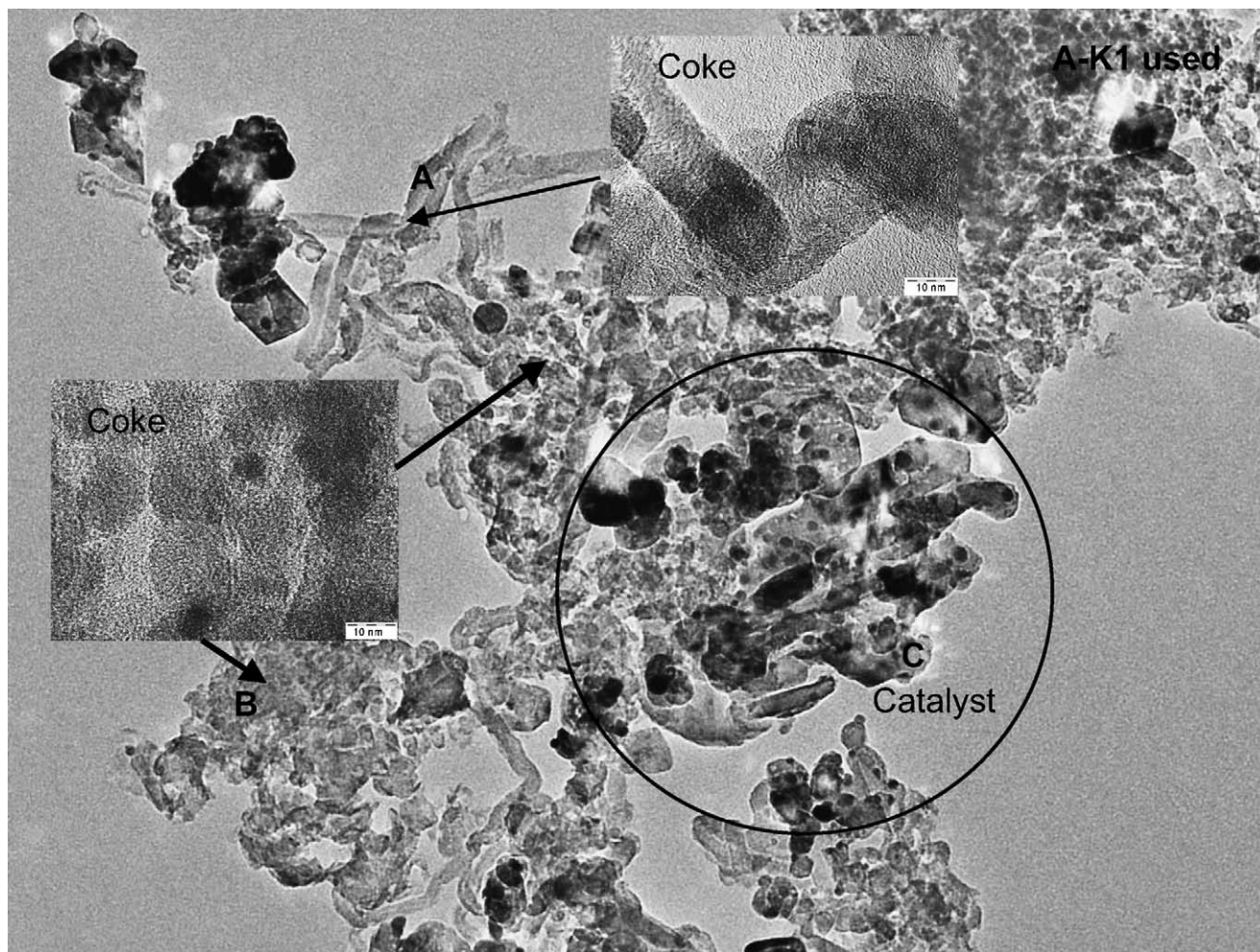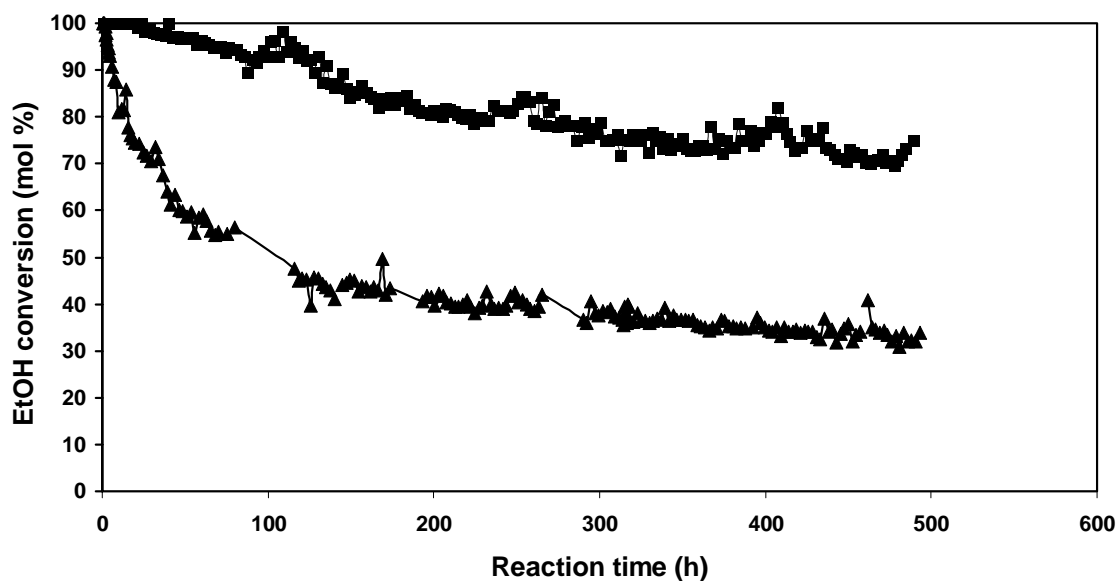
Fig. 5. TEM image of used K1-Ni/MgO catalyst.

Fig. 6. Endurance tests: a comparison between bare Ni/MgO and K1-Ni/MgO catalysts. $GHSV = 20,000\,h^{-1}$; $T_R = 650\,°C$.

active and stable than bare Ni/MgO catalyst. In fact, on bare Ni/MgO catalyst the EtOH conversion lowers from 100 to 40% along 500 h of time on stream, while on K1-A K-doped catalyst the lost of activity was much less evident (EtOH conversion lowers from 100 to 78%). On both bare and K-doped Ni/MgO catalysts, the H_2 productivity was found to be very close to 5 mol H_2/mol fed ethanol at total ethanol conversion. Such value can be considered very good taking into account that endurance tests were not performed at GHSV so low to allow all reactions responsible for the H_2 production to be at equilibrium (for example, CH_4 steam reforming).

4. Conclusions

K-doped Ni/MgO catalytic system appear to be suitable for MCFC hydrogen production by steam reforming of bio-ethanol. It seems, the large excess of water in the feed does not affect substantially the catalyst stability rather contribute to promote WGS reaction with a consequent improving of H_2 production. K addition stabilizes Ni catalyst mainly by depressing the metal sintering, while coke formation seems not to be influenced by alkali addition. Endurance test ($500\,h^{-1}$) performed at $20,000\,h^{-1}$ allows fore-see a very long catalyst life in case of practical application, where GHSV used are lower than $5000\,h^{-1}$. Further, the Ni/MgO catalytic system appears to be very selective toward H_2 formation. By operating at low GHSV H_2 productivity close to the stoichiometric value (6 mol H_2/mol ethanol) can be obtained.

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