

Steam reforming of ethanol on Ni/MgO catalysts: H₂ production for MCFC

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Abstract

H₂ production by ethanol steam reforming in simulating molten carbonate fuel cell (MCFC) conditions was explored. Ni/MgO catalysts exhibit very high selectivity to H₂ and CO₂ as a consequence of their low tendency to promote carbon monoxide methanation and ethanol decomposition reactions. Coke formation is strongly depressed due to the benefits induced by the use of basic carrier which positively modify the electronic properties of supported Ni. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of molten carbonate fuel cells for electrical power plants applications now approaches the size of sub-MW demonstrative facilities and this makes more important to have easily storable and processable fuels [1]. In particular, the use of liquid fuels as alternative sources for hydrogen production for molten carbonate fuel cell is desired [2,3]. Among different oxygenated products proposed, ethanol obtained from bio-mass looks as an interesting fuel because its use well fit with the requirements of safety handling, cheap and easy transport, low toxicity and bio-degradability. Unfortunately, bio-ethanol is a diluted aqueous solution (ethanol concentration less than 15%) and distillation, which as well known is a very expensive process, is required to separate ethanol. On this account, a cost effective process adequate to use directly the bio-ethanol to obtain useful products, for example hydrogen, is desired.

Abbreviations: MCFC, molten carbonate fuel cell; MR, ethanol/water molar ratio (mol/mol); i.d., internal diameter (mm); STP, measured at standard temperature and pressure conditions ($T = 273.16$ K and $P = 1$ atm); H-TPD, hydrogen-temperature programmed desorption; GHSV, gas hourly space velocity; TCD, thermal conductivity detector; GC, gas-chromatograph; TEM, transmission electron microscopy; PSD, particle size distribution; CHNS, carbon, hydrogen, nitrogen and sulphur elemental analysis; BET, Brunauer, Emmet and Teller method (equation); N2-A, N2-B, N-K1, G90-B, nickel based catalysts

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One of the methods suggested to process bio-ethanol to produce H₂ to be used in fuel cell system is the catalytic steam reforming reaction. Catalysts based on transition metals especially Co [4] and Rh [5] have already been proposed as efficient catalytic systems to perform such reaction. However, even though such catalysts seem to operate with high reaction rate some difficulties were met to reduce the contribution of the CO methanation and ethanol decomposition reaction which lower the H₂ yield.

This paper is concerned with the investigation of Ni based catalysts suitable to process bio-ethanol at simulated MCFC operative conditions. Attention was mainly devoted to the study of Ni sintering and coke formation phenomena which negatively affect the catalyst stability.

2. Experimental

2.1. Catalyst preparation

Ni/MgO catalyst (N2 sample) was prepared by the incipient wetness method using a 10% (v/v) C₂H₅OH–cyclohexane solution of nickel acetylacetonate (Ni(C₅H₇O₂)₂) and MgO “smoke powder” according to the procedure elsewhere described [6]. Two aliquots of such catalyst were treated by steam (sample N2-A) and air (sample N2-B) for 24 h at 923 K.

K-doped Ni/MgO (sample N-K1) catalyst was obtained by a “wet impregnation” of the calcined Ni/MgO catalyst sample with isopropanolic solutions of the K-acetate salt.

After impregnation catalyst was dried at 373 K and subsequently calcined at 673 K for 12 h. For comparison G90-B Sud-Chemie industrial catalyst was also used.

2.2. Catalyst characterisation

H-TPD measurements in the range 193–793 K were performed using Ar as carrier gas flowing at 30 STP $\text{cm}^3 \text{min}^{-1}$ and $\beta = 20^\circ \text{C min}^{-1}$. Before measurements, catalyst samples (50 mg) were reduced for half-an hour in flowing H_2 at 1000 K. Thereafter, the sample was cooled in flowing H_2 to room temperature, equilibrated for 15 min, and then further cooled to 193 K in H_2 for 5 min. Then, H_2 was shut off and the sample was purged by the carrier stream until to stabilisation of the baseline. The H-TPD was monitored and quantified by a TCD connected to a DP 700 data processor (Carlo Erba instruments). Before and after every H-TPD run, a calibration test of the peaks area was made by injecting in the carrier gas a known amount of H_2 , the reproducibility being better than $\pm 3\%$. Assuming the chemisorption stoichiometry $\text{H}_2:\text{Ni}_{\text{surf}} = 1:2$, metal dispersion (D) was calculated from the following experimental ratio:

$$D (\%) = \frac{V_{\text{H}_2}}{V_{\text{O}_2}} \times 100$$

where V_{H_2} ($\mu \text{mol g}_{\text{cat}}^{-1}$) is the amount of desorbed hydrogen and V_{O_2} ($\mu \text{mol g}_{\text{cat}}^{-1}$) is the amount of oxygen uptake at 773 K, corresponding to the fraction (α) of Ni^{++} reduced to Ni^0 .

The Ni PSD of “fresh” and “used” catalysts was obtained by TEM (PHILIPS CM12) analyses. Suitable transmission specimens were prepared by ultrasonic dispersion of fresh and used catalysts in isopropyl alcohol from a drop of suspension deposited on carbon supported films.

The amount of carbon deposited was evaluated by carbon hydrogen sulphur nitrogen/oxygen analysis (CHSN—Carlo Erba instrument) while surface area was measured by BET method using a Sorptomatic Carlo Erba instrument. In Table 1 are summarised the results of physico-chemical characterisation of the Ni supported catalysts prepared according to the aforementioned procedures.

2.3. Catalyst testing

Runs were performed using a fixed linear quartz micro-reactor (i.d. = 4 mm) and a catalyst sample of 0.015 g

Table 1
Physico-chemical properties of Ni supported catalysts

Sample	Composition	Ni loading (wt.%)	S.A. ($\text{m}^2 \text{g}^{-1}$)	Dispersion (%)	MSA ($\text{m}_{\text{Ni}}^2 \text{g}_{\text{cat}}^{-1}$)
N2	Ni/MgO	19.0	105	27.1	17.8
N2-B	Ni/MgO	19.0	—	14.0	4.54
N-K1	1%K-Ni/MgO	18.7	24	13.2	12.1
G90-B	Ni/CaAl _x O _y	11	6.8	2.0	1.0

diluted (1/10) with same sized carborundum (SiC). Before reaction, the catalysts were reduced “in situ” at 1000 K for 1 h under flowing hydrogen and then cooled down to 923 K. The ethanol/water mixture ($\text{MR} = 8.4 \text{ mol/mol}$) was fed by an isocratic HP 1100 pump. Experiments were performed at 923 K and GHSV ranging from 5000 to 300,000 h^{-1} . Both temperature and GHSV values have been prefixed to simulate a typical MCFC operating at indirect internal reforming conditions. In this kind of configuration catalyst is located closeness to the anode side but in a separate chamber. This assembling allows to use the heat generated at anode side and at same time avoid the poisoning of catalyst by the vapour of carbonates which could permeate through the anode itself.

Reaction stream was analysed “on line” by a Hewlett Packard GC model 6890 Plus equipped with three columns (Molecular Sieve 5 Å, Porapack Q and Hysep) system and a 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

The comparison of catalytic behaviour of different Ni based catalysts used in the steam reforming of ethanol at GHSV of 80,000 h^{-1} is reported in Fig. 1 in terms of ethanol conversion versus time on stream. It can be seen that Ni/MgO catalysts feature a high initial activity, ranging from 80 and 95%, which lower monotonically to ca. 55% after 5 h of reaction. After the initial loss of activity catalysts N2 and N-K1 slowly deactivate in the time while N2-B stabilises at a conversion of 55%. Industrial G90-B catalyst, further to drastically deactivate, also promotes a large amount of coke formation with consequent plugging of the reactor.

The performances of these catalysts were also compared in terms of acetaldehyde selectivity versus reaction time. As

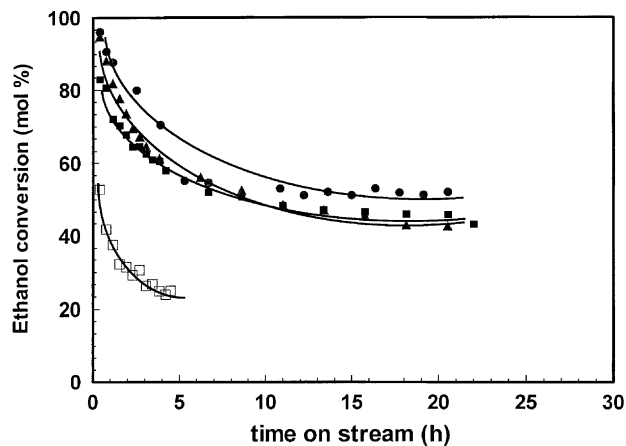


Fig. 1. Ethanol conversion as a function of time on stream: GHSV = 80,000 h^{-1} , $T_{\text{R}} = 923 \text{ K}$; (\blacktriangle) N2; (\blacksquare) N2-K1; (\square) G90-B; (\bullet) N2-B.

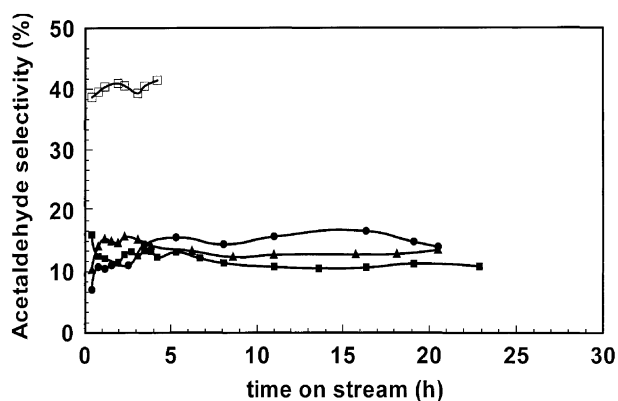


Fig. 2. Acetaldehyde selectivity vs. time on stream: GHSV = 80,000 h⁻¹, T_R = 923 K; (▲) N2; (■) N2-K1; (□) G90-B; (●) N2-B.

it can be seen from results shown in Fig. 2 acetaldehyde was formed in all experiments. This result clearly indicates that reaction could occur with a pathway which involves as first step the dehydrogenation of ethanol to acetaldehyde. The marked difference on acetaldehyde selectivities between commercial G90-B catalyst and Ni/MgO catalyst can be explained on the basis of their initial activity. It is generally accepted that, for consecutive (oxidation) reactions, the higher is the conversion the lower is the selectivity to the primary reaction product. However, for the Ni/MgO series catalysts, the difference in selectivity seems not to be justified on the basis of such criterion because of the slight difference in the initial conversion. It is also important to underline that during the incipient initial deactivation of Ni/MgO catalysts, selectivity to acetaldehyde does not change so much, and it is evident that, further to the conversion level, other factors should be taken into account. In order to shed light on the reasons of the initial deactivation, TEM characterisation of fresh and used N2-B catalyst was performed.

The marked broad in PSD of N2-B sample evidenced after reaction (see Fig. 3) is diagnostic of a high sintering rate which leads to the formation of larger Ni particles with the consequent lost of catalytic activity. This effect could be attributed to the leaching effect promoted by the presence of large amount of H₂O in the inlet stream. In fact, the water promotes the migration of small Ni particles on MgO surface and the consequent coalescence and formation of big particles. However, considering that after 5 h on stream catalytic activity stabilises, it is evident that sintering is not progressive and large particles are stabilised on MgO surface.

On the basis of the screening results reported in Fig. 1 we have focused our attention on N2-B sample which is the most active and stable catalyst among the Ni/MgO catalysts investigated. With regard the influence of space velocity on activity and selectivity of N2-B sample, results shown in Fig. 4 clearly indicate that even by operating at high space velocity (300,000 h⁻¹) catalyst retains a good activity and stability. Naturally, as the GHSV decreases the ethanol

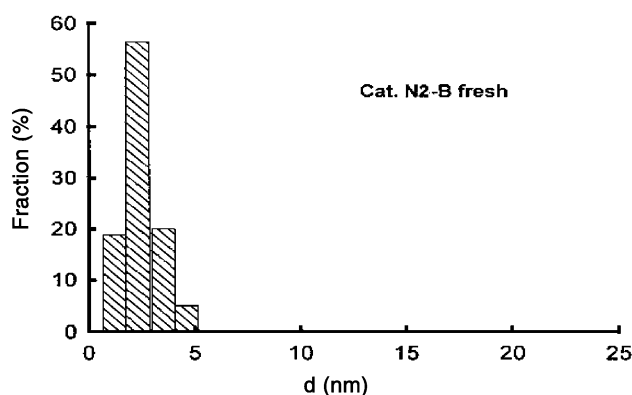
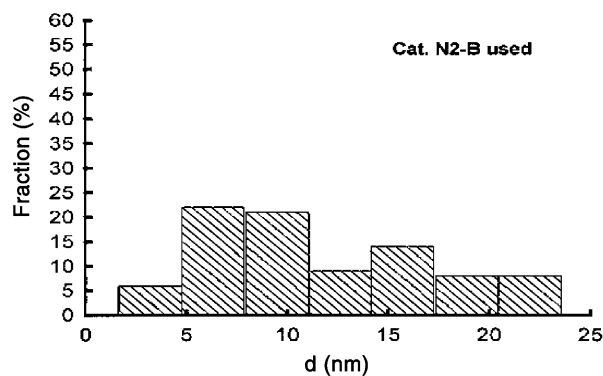


Fig. 3. PSD of fresh and used N2-B catalyst.

conversion increases till to reach the equilibrium conversion value (100%) at GHSV lower than 20,000 h⁻¹.

Table 2 summarises the selectivity data after 5 h on stream as a function of space velocity. As the space velocity increases acetaldehyde and methane selectivity increases while selectivity to CO and CO₂ decreases. At GHSV lower than 20,000 h⁻¹ acetaldehyde disappears and the methane approaches to a very low value (1%). In any case, in all experiments the main reaction products are CO, CO₂ and H₂. CO does not represent a poison in the MCFC due to the use

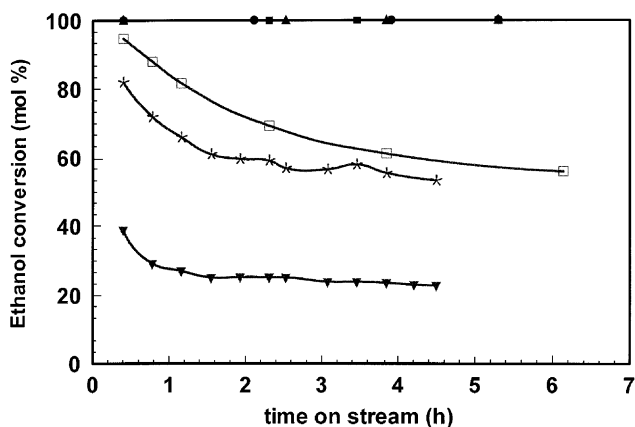


Fig. 4. Influence of GHSV on ethanol conversion as function of time on stream: (▲) 5000; (●) 10,000; (■) 20,000; (□) 80,000; (✱) 150,000; (▼) 300,000.

Table 2
EtOH conversion and product selectivity as a function of space velocity

GHSV (h ⁻¹)	EtOH _{conv} (mol%)	Selectivity (%)			
		CO	CO ₂	CH ₄	CH ₃ CHO
5000	100	29	70	1	0
10000	100	29	68	3	0
20000	100	27	70	3	0
80000	60	22	65	5	8
150000	40	21	60	6	12
300000	20	13	50	7	30

of high reaction temperature (650 °C) which prevent its absorption on Ni anode. Then CO can be processed as fuel together with hydrogen.

Data reported earlier allow to draw some consideration on the reaction mechanism. As generally accepted [7,8], even in our case the reaction proceeds via the formation of acetaldehyde ($\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2$) which consecutively decomposes to CH_4 and CO. The CH_4 and CO are then equilibrated by the steam reforming and the water gas shift reactions. Considering that we operate with a very high $\text{H}_2\text{O}/\text{C}$ ratio, the water–gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) strongly moves towards the CO_2 formation with the consequent increase of H_2 and the decrease of the CO concentration in the outlet stream. Further to such consideration, it is important to remark that on Ni/MgO catalytic system methane formation is strongly limited if compared with catalytic systems, recently proposed and based on Rh and Co as active metals [9,10]. As well known, both Rh and Co are particularly active in the CO methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) and ethanol decomposition ($\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2$) reactions, respectively. According to our opinion, the low activity in CO methanation and ethanol decomposition observed on Ni/MgO system could probably be attributed to the electronic properties of Ni modified by the interaction with MgO characterised by strong basic properties [11].

In order to shed light on the stability of Ni/MgO system an endurance test of 700 h by using N2-B sample has been performed at GHSV equal to 10,000 h⁻¹ and $T_R = 923$ K. As it can be seen from Fig. 5, Ni/MgO catalyst has worked at 100% of ethanol conversion for 700 h of time on stream. Any changing on the product distribution was evidenced. The CO_2 (67%) and CO (30%) were the main reaction products and very low amount of methane has been detected (3%).

Another important factor to be taken into account in reforming reactions is the coke formation. As it is well known the hydrocarbon reforming reactions are normally affected by coke formation which usually depends upon reaction conditions and physico-chemical properties of the catalyst. In our case, the high reaction temperature (923 K) of the reaction involving organic molecules easily subjected to the thermal decomposition, would represent a serious problem to be taken under control to avoid incipient coke

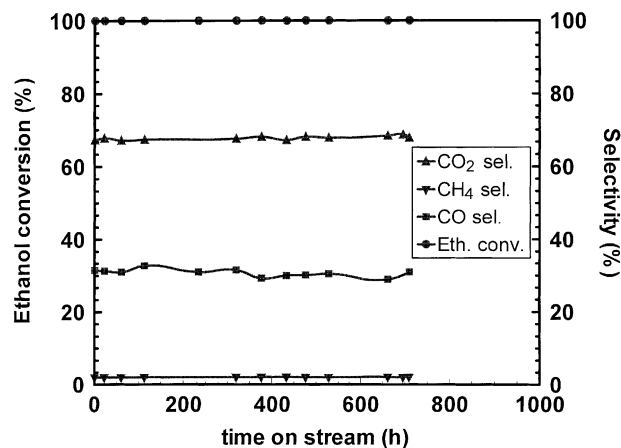


Fig. 5. Endurance test of N2-B sample: GHSV = 10,000 h⁻¹, $T_R = 923$ K.

formation and consequent catalyst deactivation and plugging of the reactor. This problem has been experimentally evaluated by a set of tests performed at GHSV of 80,000 h⁻¹ for 20 h, and CHNS analysis on spent catalysts was used to measure the amount of deposited coke.

Results shown in Fig. 6 clearly indicate that coke formation occurs on industrial G90-B catalyst with a rate much higher than that of Ni/MgO catalysts. The large amount of coke formed on G90-B catalyst is probably produced by the presence of very large Ni particles which promote both the Boudouard reaction [12] and the ethanol decomposition [13]. On the contrary, on Ni/MgO catalysts, a change in the electronic properties of the active phase likely accounts for dropping in the rate of carbon deposition. Notably, we have also previously documented that the *electronic enrichment* induced by alkalis on the active phase of the Ni/MgO system results in a lower activity for Boudouard reactions [14] while it is likely that this modified reactivity could also reflect in a lower affinity for hydrocarbon dehydrogenation reaction.

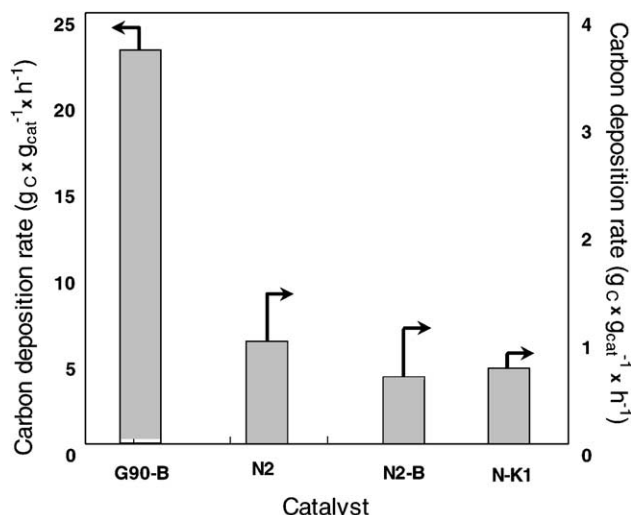


Fig. 6. Coke formation (two scales) on Ni supported catalysts.

4. Conclusions

Results here reported clearly indicated that Ni-MgO catalytic systems possess adequate properties to be proposed as an efficient catalyst for hydrogen production by ethanol steam reforming at operative MCFC conditions. Catalyst exhibits very high selectivity to H₂ and CO₂ as a consequence of the low tendency to promote carbon monoxide methanation and ethanol decomposition reactions. In addition, coke formation is strongly depressed because of the benefits induced by the use of the basic carrier which positively modifies the electronic properties of Ni.

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