Rh based catalysts for indirect internal reforming ethanol applications in molten carbonate fuel cells

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Abstract

The feasibility of coupling a processor for internal indirect reforming of ethanol/water with molten carbonate fuel cells has been verified by several experiments. Two different Rh/Al_2O_3 catalysts have been prepared and characterised. Several tests to measure the catalytic activity on ethanol steam reforming process have been performed both on alumina and supported catalysts. The tests evidenced that ethanol can be decomposed and steam reforming process can be obtained at well determined conditions of temperature and catalyst load. The 5% Rh/Al_2O_3 catalyst produced, at 923 K, hydrogen rich gas mixture, that can be considered of high interest for molten carbonate fuel cell applications because it is free from any production of ethylene or other undesirable products. Further, this interest has been confirmed by the good results obtained in the long-term tests carried out on the 5% Rh/Al_2O_3 catalyst. © 2001 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 make more important to have easily storable and processable fuels [1]. To this purpose, extensive researches have been conducted on the utilisation of the reformed methane as raw fuel for such typology of fuel cells [2–5]. Nevertheless, this way shows promising aspects, it is a fact that some basic problems, correlated to the storage and handling of the methane, remain due to the gaseous state of this fuel. Today, researches are investigating the use of liquid fuels as alternative sources of hydrogen for molten carbonate fuel cells, because of simplicity to transport and storage these products [6,7]. Between oxygenated products, the ethanol looks as interesting product because its properties well fit with the requirements of safety handling, cheap and easy transport, low toxicity and biodegradability. Further, the ethanol reduces the carbon dioxide emission because it can be produced by fermentation of sugar cane or other vegetables. The use of ethanol for the production of hydrogen rich gas mixture instead of its direct combustion into an engine, offers the meaningful advantage to avoid any undesirable aldehyde formation as produced by uncontrolled combustion [8]. The ethanol produced from bio-masses appears like an aqueous solution (water/ethanol molar ratio about 10) that requires to be concentrated before commercial use [9–10]. At contrary, it can be used, without any preliminary treatment, for hydrogen production if steam reformed on appropriate catalysts. The thermodynamic feasibility of this process has been, already, established [8,11,12], even if it has been very little explored under an experimental point of view [13–14]. For the above reasons, we explored experimentally the feasibility to develop a process of ethanol/water reforming with characteristics to be usable as internal indirect one for molten carbonate fuel cells (MCFC). Rh based catalysts have been produced and tested in simulating operative MCFC conditions. The ethanol decomposition mechanisms have been studied and very encouraging results have been obtained in terms of H_2 rich gas mixture production, with stable compositions in the time on stream and without any production of undesirable products.

2. Experimental

2.1. Catalysts

The 5% Rh/Al_2O_3 catalysts have been prepared by the incipient wetness method.

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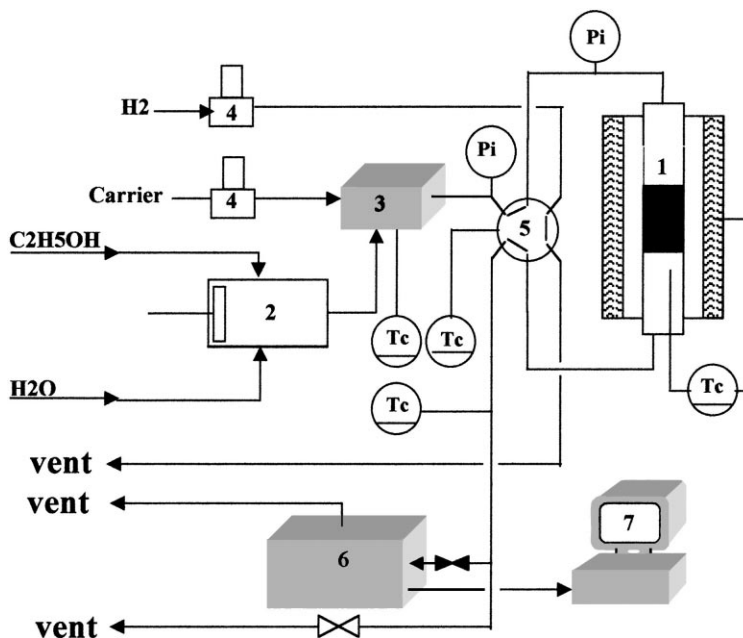*E-mail address*: itae@itae.me.cnr.it (S. Freni).

Fig. 1. Experimental apparatus for ethanol steam reforming tests. Main components: continuous flow microreactor (1); isocratic HP 1100 pump (2); thermo-regulated vaporiser (3); mass flow regulator system (4); six-ways valve (5); gas-chromatograph device (6); interfaced computer (7).

In fact, samples of γ-Al_2O_3 (AKZO 0.001-3P) with a BET surface of $250 \, m^2 \, g^{-1}$ were impregnated by $RhCl_3 \cdot 3H_2O$ and the obtained samples were treated at 923 K for 16 h. At end of preparation procedure, the catalysts have been characterised by SEM, EDX, XRD and atomic adsorption spectroscopy techniques.

2.2. Apparatus and tests conditions

Fig. 1 shows a simplified scheme of the experimental plant. The continuous flow microreactor (1) was made by a quartz tube ($\phi_{int} = 4$ mm) packed with a 20 mm catalytic bed. The bed contained about 0.016 g of active catalyst pellets (40–70 mesh) dispersed with a large mass of inert material to minimise thermal spots effects. SiC pellets have been selected as inert after testing to verify the absence of catalytic effects on the studied reactions. A fine regulation of the reagents inlet flow was controlled by an isocratic HP 1100 pump (2), in order to operate at gas hourly space velocity (GHSV) carefully prefixed (i.e. GHSV = 150,000 h^{-1}). The ethanol/water reaction mixture, with an inlet steam/carbon (S/C) molar ratio of 4.2 mol mol^{-1}, was vaporised into a thermo-regulated ($T_v \geq 473$ K) vaporiser (3) packed with SiC, where the reagents flow was also simultaneously mixed with a small amount of nitrogen ($F_{N_2} = 20 \, cm^3 \, min^{-1}$). Before any test, the catalysts were reduced "in situ" at $T = 575$ K, for 1 h, under hydrogen flow $F_{H_2} = 100 \, cm^3 \, min^{-1}$. Both nitrogen and hydrogen flows were carefully regulated by means of a mass flow regulator system (4) ASM 2500 and the flow selected by a six-ways valve (5). Endurance tests have been carried out at constant temperature ($T_r \leq 923$ K), while catalytic performances were screened by using the temperature programmed reaction mode (TPR), where T_r was increased with a slope $dT/dt = 1.5$ K min^{-1}. Reagent and reacted gases were analysed "on line" by means of a Hewlett Packard gas-chromatograph model 6890 Plus (6) using the TCD detector and equipped with a three columns (Molecular Sieve 5 Å, Porapack Q and Hysep) interchangeable system. A temperature-time program ensured the right correspondence among the temperature, the opening/closing valves action time and the overall analysis time. The nitrogen was, also, used as internal standard and it permits precise evaluation of the outlet composition by the HP-IB interfaced computer (7) system (HP Chemstation). In all (T_c) points reported in Fig. 1, the temperature was regulated by means of chromo-alumel thermocouples and electrical resistances, both connected with Yokogawa UP 25S thermo-regulators.

3. Results and discussion

In literature, it is known that alumina shows catalytic activity in the dehydration of ethanol and produces ethylene that acts as very strong promoter of carbon formation. This is considered a very dangerous event that can plug gas channels and lead the system to a rapid collapse. For this reason and in consideration to the fact that our catalysts are supported on alumina, the experimental evaluation of the support catalytic properties on the decomposition of ethanol/water mixture has been considered as primary target. Further, few published data are related to the decomposition of pure ethanol on alumina and indicate that this proceeds
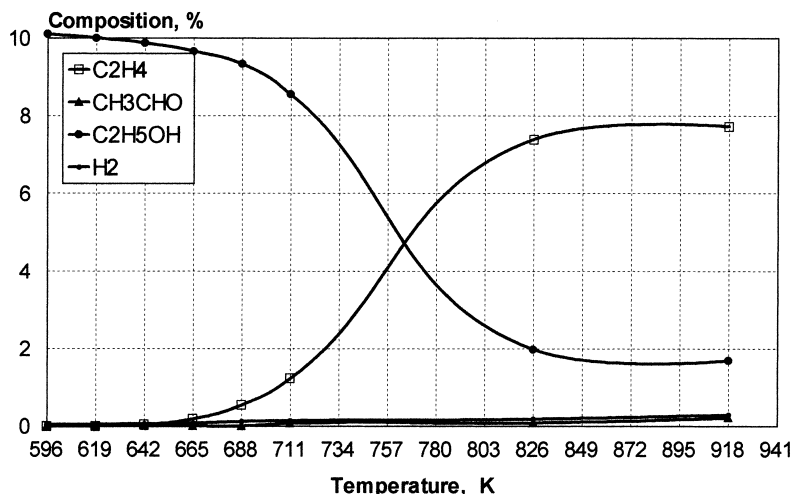
Fig. 2. Test to detect catalytic activity of alumina support. Composition of outlet gas as a function of T_r, carried out at $P = 0.14$ MP, GHSV = 72,700 h^{-1}, $H_2O/C_2H_5OH = 8.4$.

by the reaction:

$$CH_5COH \rightarrow C_2H_4 + H_2O \qquad (1)$$

Now, in our experiments we used a mixture with about 90% mol of water that in principle should act to hinder the formation of ethylene. Thus, the study of catalytic properties of alumina was considered of strategic interest for the understanding of ethanol steam reforming process.

The results obtained in these tests are reported in Fig. 2, as percentage composition in function of reaction temperature. They indicate the catalytic activity of alumina is not negligible starting from 620 K and production of C_2H_4 and H_2O starts. The production rate of ethylene increases with the temperature and reaches the equilibrium at about 873 K. The presence of CH_3CHO has been, also, detected from 673 K, but there is a small variation of its content with the temperature, and the same trend has been found for the hydrogen.

The analysis of the results indicate that water content does not influence the ethylene formation. This one seems to confirm that the ethylene is formed by the abstraction of a methyl hydrogen with the simultaneous rupture of a C–O bond, like proposed by Arai et al. [15]. The presence of CH_3CHO between the decomposition products has been observed by others researchers [16] and can be attributed to a loss of α-hydrogen from C_2H_5O species. This mechanism is in agreement with the behaviours of CH_3CHO and H_2 detected during the test.

The concrete utilisation of ethanol/water mixture to supply molten carbonate fuel cells, under indirect internal reforming mode, requires that hydrogen should be produced by ethanol steam reforming reaction without any potential dangerous species, like ethylene that can cause serious damages to the cell components. Thus, to hinder the catalytic effect of alumina, we loaded the support by 5% of Rh that has good catalytic properties. The tests of ethanol steam reforming have been conducted at reaction temperature ranging from 665 to 923 K.

The results of this investigation are reported in terms of selectivity for C_2H_4, CO_2, CO, CH_4 and CH_3CHO and contents of H_2O and H_2, in the outlet gas, as a function of reaction temperature and they are shown in Fig. 3.

In the range of temperature until 734 K, the production of hydrogen is very limited (below 2% in concentration) as well as ethylene and acetaldehyde selectivities, while the selectivity towards CO and methane is high (57.4 and 42.6%, respectively, at 665 K). In these conditions, it appears evident that ethanol steam reforming reaction is almost absent; in fact, there is not any consumption of water and the hydrogen production misses. Further, the formation of CO and methane suggest that a first step could be the dehydrogenation of ethanol into ethoxide, that decomposes at low temperature to form CO and methane [17]. This mechanism well fits with the trend of the outlet gas compositions, where very little decomposition of ethanol has been found, together a small formation of hydrogen, CO and CH_4 and lack of CH_3CHO.

From 734 to 923 K of temperature, the prevailing process seems to be the ethanol steam reforming. In fact, several factors indicate this change in the mechanism, between them meaningful are the drops of CO and CH_4 selectivity, the increase of CO_2 selectivity as well as hydrogen content and a consistent rate of water consumption.

The ethanol steam reforming seems to prevail up to highest limit of temperature tested in the experiments (923 K), even if, other reactions overlap to this process. In the range of temperature from 780 to 850 K, the CH_3CHO production of this specie reaches 0.24% in the outlet gas composition. In the meantime, we detected a lowering in the rate of water consumption and a flattening in the CO_2 selectivity. These factors can indicate that a minor part of ethanol can be decomposed by dehydrogenation with formation of acetaldehyde. The influence of this mechanism becomes quite negligible over 850 K, where the methane steam reforming reaction could join the ethanol steam
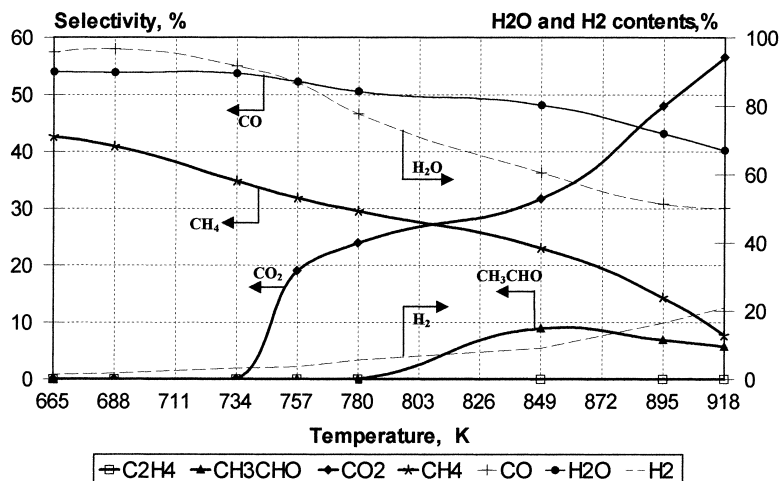
Fig. 3. Catalytic activity test of 5% Rh/Al$_2$O$_3$ catalyst. C$_2$H$_4$, CH$_3$CHO, CO$_2$, CH$_4$ and CO selectivities and contents (H$_2$O and H$_2$) as a function of T_r, carried out at $P = 0.14$ MP, GHSV = 75,000 h^{-1}, H$_2$O/C$_2$H$_5$OH = 8.4.

Table 1
Conditions and outlet data for ethanol steam reforming on 5% Rh based catalyst[a]

	H$_2$	CO$_2$	C$_2$H$_4$	H$_2$O	CH$_3$COH	C$_2$H$_5$OH	CH$_4$	CO
Outlet composition (%)	30.10	7.50	0	56.52	0	0	1.69	4.19
Selectivity (%)	–	56.07	0	–	0	–	12.66	31.27
Conversion (%)	–	–	–	–	–	100	–	–

[a] Catalyst: 5% Rh/Al$_2$O$_3$; load cat. = 0.016 g; GHSV = 37,500 h^{-1}; reaction temperature = 923 K; reaction pressure = 0.16 MP; inlet H$_2$O/C$_2$H$_5$OH = 8.4 mol vol^{-1}; H$_2$O flow = 168 ccm min^{-1}.

reforming in the production of CO$_2$ and hydrogen, and the following reactions can be considered:

$$C_2H_5OH + H_2O \rightarrow 4H_2 + 2CO \qquad (2)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (3)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (4)$$

From these experiments, the indication of a possible utilisation of a 5% Rh/Al$_2$O$_3$ catalyst for indirect internal reforming of ethanol in molten carbonate fuel cells appeared quite promising. This preliminary indication has been confirmed by the analysis of outlet gas composition and selectivities as determined by testing the 5% Rh/Al$_2$O$_3$ in conditions of full thermodynamic equilibrium as reported in Table 1. It is evident that the 5% Rh based catalyst is active toward steam reforming of ethanol, and no selectivity to C$_2$H$_4$ or CH$_3$CHO has been found. The outlet composition presents a production of hydrogen (30.10%) and smaller percentage of methane (1.69%) and carbon monoxide (4.19%). The final conversion of ethanol reaches 100% and no ethylene or acetaldehyde have been detected in the outlet gas.
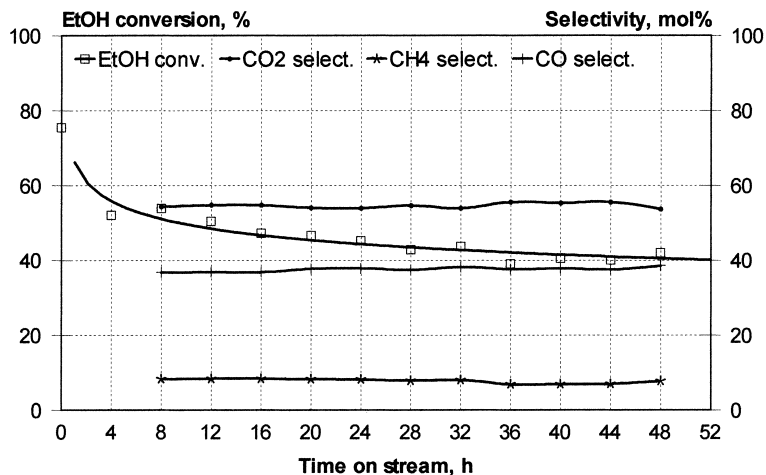

Fig. 4. Endurance test of 5% Rh/Al$_2$O$_3$ catalyst, carried out at $P = 0.14$ MP, GHSV = 142,800 h^{-1}, H$_2$O/C$_2$H$_5$OH = 8.4; ethanol conversion, CO$_2$, CH$_4$ and CO selectivities as a function of the time on stream.

The commercial development of a fuel cell device requires, also, a good stability. For this reason, we considered very important to explore the effect of the time on the 5% Rh/Al_2O_3 catalyst, mainly under work conditions similar to those of molten carbonate fuel cells. Thus, a further test has been planned and critical conditions (temperature = 923 K, pressure = 0.14 MP, H_2O/C_2H_5OH = 8.4 and GHSV = 142,800 h^{-1}) have been selected. The behaviour of ethanol conversion and products selectivity are reported in Fig. 4. As expected, in the initial phase of the test (4 h) the conversion lost 23.45% (from 75.5 to 52.05%), then the catalyst approached a conversion value of 40%. In effect, the loss of activity, detected during the initial step of the test, is an event that can be considered almost a rule because it is a consequence of the catalyst particles size modification under the thermal effect of the reaction temperature. For example, in the case of our endurance test, the effect of the temperature is expressed as a loss of the catalyst dispersion degree and a growing of the catalyst grains. It is well evidenced from the TEM analyses carried out, by Philips CM12 TEM Instrument, on fresh and spent samples of catalyst and reported in Fig. 5. In terms of selectivity, the CO_2 averaged values was about 53% with negligible variations during the time on stream, while methane and CO are almost constant with an averaged values of 7.7 and 36.5%, respectively.

4. Application in MCFC

The results of the long term experiment have been considered very promising for fuel cell utilisation because of the following considerations: (i) the typical working temperature of a MCFC (923 K) allows the catalyst can reach full thermodynamic equilibrium and full conversion of the ethanol; (ii) the catalyst looks enough stable and assures a constant hydrogen rate production; (iii) the absence of dangerous products, as ethylene, reduces the risk that carbon deposition can occur.

It remains some preliminary consideration about the performance that MCFCs can reach with this quality of fuel. In fact, as reported in Table 1, the gas mixture obtained by ethanol steam reforming process contains about one third of hydrogen, but there are, also, 56.52% of steam that represents, in the meantime, the reaction product of the anode half-reaction. In other words, it seemed the hydrogen could be too diluted to have an appreciable value for the cell potential. Thus, by easy calculations, we determined the Nernst potential for a MCFC supplied in the anode with gas composition as reported in Table 1 and in the cathode with a gas composition of 80% air and 20% CO_2. The Nernst potential calculated by the expression:

$$V = V_0 + \frac{RT}{2F} \ln \left[\frac{P_{H_2} \cdot P_{O_2}^{1/2} \cdot P_{CO_2(c)}}{P_{H_2O} \cdot P_{CO_2(a)}} \right]$$
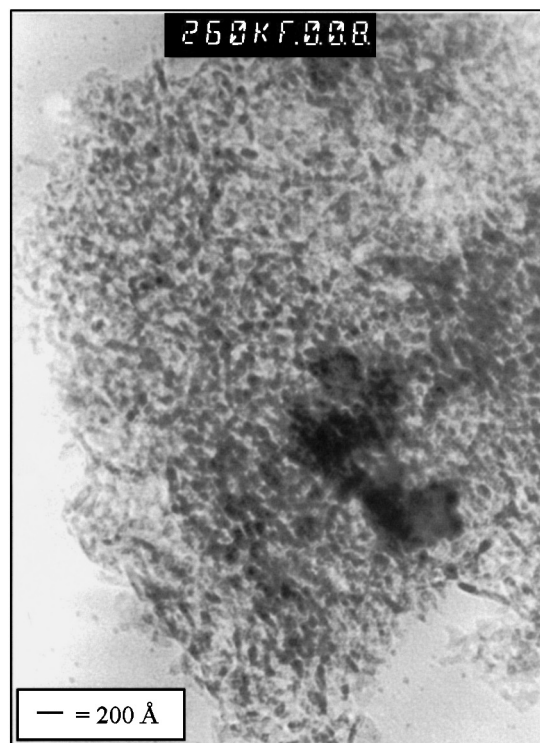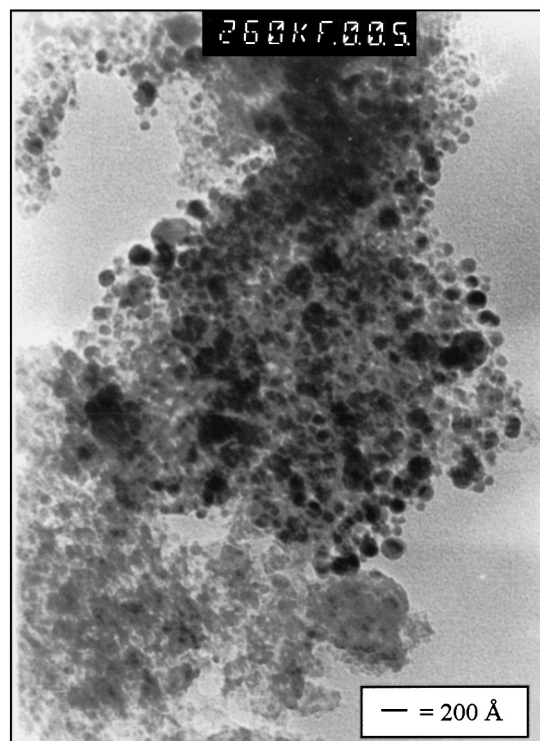
Fig. 5. Transmission electronic microscope images of 5% Rh/Al_2O_3 catalyst, (a) before endurance test, and (b) after endurance test.

gives V = 1.151 V, where V_0 results equal to 1.021 V. This value of Nernst potential, that can be expected if MCFC is supplied with gas of composition of Table 1, appears quite acceptable if compared to that other kinds of fuels yield.

5. Conclusions

The investigation on the possibility of application of Rh based catalyst for indirect internal ethanol steam reforming in molten carbonate fuel cells demonstrated that problems will arise if alumina will be used as support. The Al_2O_3 shows catalytic activity with prevailing production of C_2H_4 and H_2O. Concrete utilisation of ethanol/water mixture has been considered by loading the support with 5% of Rh. The results of this investigation showed that at moderate temperature, the ethanol steam reforming reaction is almost absent, while a process of ethanol dehydrogenation into ethoxide, that forms CO and methane could prevails. From 734 K, the ethanol steam reforming could be the prevailing process as several factors seem to indicate.

The 5% Rh/Al_2O_3 catalyst, in conditions of full thermo-dynamic equilibrium, was active toward steam reforming of ethanol, with a conversion of 100%, and no yield of C_2H_4 or CH_3CHO was detected.

The stability of this catalyst has been fully demonstrated by an endurance test and the results of these experiments seemed to be very promising for molten carbonate fuel cell applications, even if a loss of activity, due to a particles growing, has been found in the initial step.

A simple calculations of the Nernst potential of MCFC supplied by processed gas composition gave further indication of the applicability of this process to MCFC.

References

[1] R. Figueroa, J. Otahal, R. Rivera, J. Scroppo, E.R. Laurence, in: Proceedings of the Fuel Cell Seminar, 17–20th November, Orlando, USA, 1996, p. 8.
[2] S. Freni, S. Cavallaro, M. Aquino, N. Giordano, J. Power Sources 39 (2) (1992) 203.
[3] A.L. Dicks, J. Power Sources 61 (1996) 113.
[4] J.R. Nostrup-Nielsen, L.J. Christiansen, Appl. Catal. A: Gen. 126 (1995) 381.
[5] S. Freni, P. Staiti, G. Calogero, M. Minutoli, Natural Gas Conversion V-studies in surface and catalysis, Elsevier ed., 119 (1998) 53.
[6] J.C. Amphlett, J.C. Forsyth, R.M. Holland, R.F. Mann, B.A. Peppley, in: T.O. Saetre (Ed.), Hydrogen Power: Theoretical and Engineering Solutions, Kluwer Academic Publishers, Dordrecht, 1997, p. 575.
[7] G. Maggio, S. Freni, S. Cavallaro, J. Power Sources 74 (1998) 17–23.
[8] E.Y. Garcìa, M.A. Laborde, Int. J. Hydrogen Energy 16 (1991) 307.
[9] F. Haga, T. Nakajima, H. Miya, S. Miskima, Cat. Lett. 48 (1997) 223.
[10] D. Wang, S. Czernik, D. Montanè, M. Mann, E. Chornet, Ind. Eng. Chem. Res. 36 (1997) 1507.
[11] K. Vasudeva, N. Mitra, P. Umasankar, S.C. Dhingram, Int. J. Hydrogen Energy 21 (1996) 13.
[12] S. Freni, G. Maggio, S. Cavallaro, J. Power Sources 62 (1996) 67.
[13] N. Iwasa, N. Takezawa, Bull. Chem. Soc. Jpn. 64 (1991) 2619.
[14] F.J. Marino, E.G. Cerella, S. Duhalde, M. Jobbagy, M.A. Laborde, Int. J. Hydrogen Energy 23 (12) (1998) 1095.
[15] H. Arai, T. Take, Y. Saito, Y. Yoneda, J. Catal. 9 (1967) 146.
[16] B. Chen, J.L. Falconer, J. Catal. 144 (1993) 214.
[17] C.J. Houtman, M.A. Barteau, J. Catal. 130 (1991) 528.