Catal Lett (2009) 128:443–448
DOI 10.1007/s10562-008-9771-3

Hydrogen Formation via Steam Reforming of Ethanol Over Cu/ZnO Catalyst Modified with Nickel, Cobalt and Manganese

W. Grzegorczyk · A. Denis · W. Gac ·
T. Ioannides · A. Machocki

Received: 17 July 2008 / Accepted: 9 November 2008 / Published online: 26 November 2008

Abstract The greatest influence of nickel, cobalt and manganese modifiers of CuZn-based catalyst is observed at low temperatures of the ethanol steam reforming. Below 480 °C the most advantageous effects are: a decrease in the methane formation and an increase in the hydrogen selectivity, yield and its productivity. At 480 °C the formation of organic by-products (methane excluding) is almost completely depressed. However, significant lowering in the methane selectivity and a high production of hydrogen require higher temperatures of the process.

Keywords Hydrogen · Bio-ethanol · Steam reforming · Copper–zinc oxide based catalysts

1 Introduction

Hydrogen is considered to be the energy carrier of the future. In the frame of sustainable development, the hydrogen production should be based on renewable sources, such as biomass and renewable electricity. The use of liquid bioethanol as hydrogen carrier is an attractive option. It offers the advantages of production from diverse biomass sources and ease of transportation through existing networks. Production of hydrogen from ethanol takes place via catalytic steam reforming $C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$. The final hydrogen productivity will also depend on the intensity and the state of the equilibrium of the water gas shift reaction ($H_2O + CO = H_2 + CO_2$), as well as successful inhibition of non-selective transformations of ethanol to acetaldehyde, ethylene, methane and other by-products which may be formed in successive side reactions [1–8].

There is no commercial catalysts for that process. There has been no need for them since we only witness intense preparations for an expansion of hydrogen power industry. As an active phase researchers consider first of all: noble metals, nickel and cobalt, but there were also reported copper-containing catalysts [1–8].

From the formal point of view, the generation of hydrogen through the steam reforming of ethanol seems to be a process analogous to the steam reforming of methanol. Therefore it would seem that the catalysts employed in the latter process also met the requirements of ethanol steam reforming. However, the significant differences in the course of the steam reforming of ethanol and that of methanol are caused by a more complicated structure of a molecule of ethanol due to the presence of a C–C bond. It induces more complex pathways of its transformations and the number of potential by-products formed from ethanol is therefore greater than those formed from methanol.

One of the objectives of current research efforts (e.g. one of the energy topics within the Seventh Framework Programme of the European Community) is to develop an efficient and low cost catalyst for advanced multi-fuel processors for distributed small scale production of hydrogen with minimal environmental impact. The aim of our studies was to use a copper–zinc oxide catalyst for the production of hydrogen-containing reformate gas from

---

W. Grzegorczyk · A. Denis · W. Gac · A. Machocki (✉)
Faculty of Chemistry, Department of Chemical Technology,
University of Maria Curie-Sklodowska,
3 Maria Curie-Sklodowska Square, 20-031 Lublin, Poland
e-mail: machocki@umcs.lublin.pl

T. Ioannides
Foundation for Research & Technology-Hellas,
Institute of Chemical Engineering and High Temperature
Chemical Processes (FORTH/ICE-HT), P.O. Box 1414,
26500 Patras, Greece
e-mail: theo@iceht.forth.gr

ethanol at low temperatures. It would seem advantageous to employ a modified copper–zinc oxide based catalyst. The copper–zinc oxide catalyst is active and selective in the steam reforming of methanol [6, 9–13] and nickel or cobalt catalysts modified with copper were considered as a good active phase for the ethanol steam reforming [1–8, 14–23]. The presence of manganese oxide also favourably influenced the properties of catalysts in the ethanol [1–7, 24] and methanol steam reforming [25].

The present paper reports experimental results on the use of a commercial copper–zinc oxide catalyst in the steam reforming of ethanol and on the influence of those modifiers on the catalyst activity, selectivity and hydrogen yield and its productivity.

2 Experimental

The commercial copper–zinc oxide stabilised with 10 wt% of gamma-alumina (INS Pulawy, Poland, 50% of CuO) was used as a catalyst. It was modified with nickel, cobalt and manganese by the method of incipient wetness impregnation with appropriate metal nitrate solutions. The catalyst precursors were dried at 110 °C, calcined at 400 °C for 2 h and finally, prior to their use, all catalysts were reduced with hydrogen at 350 °C for 1 h. The wt% content of the modifiers are indicated in the catalyst symbol: CuZn, 5Ni/CuZn, 5Co/CuZn and 5Co5Mn/CuZn.

The bulk contents of nickel, cobalt and manganese in modified catalysts were determined by the X-ray fluorescence spectroscopy technique, by means of an energy-dispersive XRF spectrometer (Canberra 1510) equipped with a liquid nitrogen-cooled Si(Li) detector. The AXIL software package was used for spectral deconvolution and for the calculation of the modifier component contents.

The temperature-programmed reduction of the catalysts was carried out in the apparatus AMI-1 (Altamira Instruments Inc.) using 0.05 g of catalyst (0.1–0.2 mm) placed in a quartz flow reactor with an internal diameter 7 mm. A 6% H_2–Ar mixture was used as carrier gas at a flow rate of 30 cm^3/min; the linear temperature increase was 10 °C/min. Water vapour formed during reduction was removed in a cold trap (immersed in liquid nitrogen–methanol slush, at −98 °C) placed before the thermal conductivity detector (TCD). The TCD signal was calibrated by injecting 55 μL of argon to the carrier gas.

The steam reforming of ethanol was carried out under atmospheric pressure in a fixed-bed continuous-flow quartz reactor over catalysts (0.1 g, grain size of 0.2–0.5 mm) reduced in situ with hydrogen at 350 °C for 1 h, prior to the reaction. The catalyst was diluted (at the weight ratio of 1:10) with 0.2–0.5 mm grains of quartz in order to ensure the constant temperature in the catalytic layer. In a preliminary experiment it was found that the conversion of ethanol over quartz starts, to a small extent, at higher temperatures (>700 °C) than those at which the steam reforming of ethanol in the presence of catalysts was investigated. The aqueous solution of ethanol (with a molar EtOH/water ratio equal to 1/4) was supplied by a peristaltic pump (Masterflex LS with 7013-20 head) to a liquid preheater/evaporator (150 °C) and the reactant vapours without diluting with any inert gas were fed to the reactor at a flow rate of 0.27 mol/h. The reaction temperature, measured in the centre of the catalyst + quartz bed, was changed from 350 to 600 °C. The temperature was increased step-by-step and analyses of the reaction products were conducted several times during about 2 h of the reaction at each of the temperatures, and then results were averaged.

The analysis of the reaction mixture and the reaction products (all in gas phase) were carried out on-line by means of two gas chromatographs. One of them, Varian CP-3800 was equipped with two capillary columns, the first one contained a porous polymer Porapak Q (for all organics, carbon dioxide and water vapour) and the second of them—an activated molecular sieve 5A (for methane and carbon monoxide analysis). Helium was used as a carrier gas and a TCD detector was employed. The hydrogen concentration was analysed by the second gas chromatograph, Chromatron GCHF 18.3, using a column packed with an activated charcoal, nitrogen as a carrier gas and a TCD detector. The sensitivity of the detectors to the analysed compounds (response factors) was determined, before and after each catalytic test, by their calibration against external standards of single compounds or their certified (Praxair) mixtures composed of carbon oxides and hydrocarbons in helium. The concentrations of the external standards were comparable with those of analysed products. The reproducibility of the analysis of the components of the certified mixtures was about ±2%. Because of some tailing of chromatographic peaks of water, the reproducibility of its analysis was lower than other compounds, about ±5 relative percent.

The total conversion of ethanol X_{EtOH}, conversion of water $X_{\mathrm{H_2O}}$ and conversions of ethanol into particular carbon-containing products, X_{CP}, were calculated on the basis of their concentrations before and after the reaction, with a correction introduced for the volume change during the reaction, from equations:

$$X_{\mathrm{EtOH}} = \frac{c^{\mathrm{in}}_{\mathrm{EtOH}} - c^{\mathrm{out}}_{\mathrm{EtOH}} \cdot K}{c^{\mathrm{in}}_{\mathrm{EtOH}}} \times 100$$

$$X_{\mathrm{H_2O}} = \frac{c^{\mathrm{in}}_{\mathrm{H_2O}} - c^{\mathrm{out}}_{\mathrm{H_2O}} \cdot K}{c^{in}_{\mathrm{H_2O}}} \times 100$$

$$X_{\mathrm{CP}} = \frac{c^{\mathrm{out}}_{\mathrm{CP}} \cdot K}{n/2 \cdot c^{\mathrm{in}}_{\mathrm{EtOH}}} \times 100\,(\%)$$

where $c^{\mathrm{in}}_{\mathrm{EtOH}}$ and $c^{\mathrm{in}}_{\mathrm{H_2O}}$—are the molar concentrations of ethanol and water in the reaction mixture, mol%, $c^{\mathrm{out}}_{\mathrm{EtOH}}$ and $c^{\mathrm{out}}_{\mathrm{H_2O}}$—are the molar concentrations of ethanol and water in the post-reaction mixture, mol%, $c^{\mathrm{out}}_{\mathrm{CP}}$—is the molar concentration of carbon-containing products in the post-reaction mixture, mol%, n—is the number of carbon atoms in the carbon-containing molecule of the reaction product, K—is the volume contraction factor ($K = c^{\mathrm{in}}_{\mathrm{C}}/c^{\mathrm{out}}_{\mathrm{C}}$ where $c^{\mathrm{in}}_{\mathrm{C}}$ and $c^{\mathrm{out}}_{\mathrm{C}}$ are the molar concentrations of carbon in ethanol fed to the reaction and in all carbon-containing compounds which were present in post-reaction gases, respectively).

The selectivity of ethanol conversion into individual carbon-containing products was expressed as $(X_{\mathrm{CP}}/X_{\mathrm{EtOH}}) \times 100$. The carbon mass balances, based on the carbon selectivities at each of the reaction temperatures, were close to 100 ± 3%.

The hydrogen and oxygen balances were not recorded. The selectivity of hydrogen formation was determined from the equation:

$$\mathrm{H_2 selectivity} = \frac{c^{\mathrm{out}}_{\mathrm{H_2}} \cdot 100}{c^{\mathrm{out}}_{\mathrm{H_2}} + 2 \cdot c^{\mathrm{out}}_{\mathrm{CH_4}} + 2 \cdot c^{\mathrm{out}}_{\mathrm{C_2H_4}} + 2 \cdot c^{\mathrm{out}}_{\mathrm{CH_3CHO}} + 3 \cdot c^{\mathrm{out}}_{\mathrm{C_2H_6}} + 3 \cdot c^{\mathrm{out}}_{\mathrm{C_3H_6}} + 3 \cdot c^{\mathrm{out}}_{\mathrm{CH_3COCH_3}} + 4 \cdot c^{\mathrm{out}}_{\mathrm{C_3H_8}}} \ (\%)$$

where c^{out}—are the molar concentrations of the hydrogen-containing reaction products, mol%.

3 Results and Discussion

Experiments of the reducibility of the CuZn catalyst have shown (Fig. 1) that its reduction occurs in two regions: a low-temperature region, up to about 420 °C, and a high-temperature region—up to above 800 °C. The reduction peaks are complex and their interpretation is complicated. The reduction begins at about 220 °C and the maximum rate of the low-temperature stage of the reduction occurs at about 320 °C. That stage of reduction may be interpreted as a reaction of copper oxide phase with a weak strength of the metal–oxygen bonds in the main oxide being reduced, i.e. with a weak interaction with the remaining oxides: zinc oxide and alumina. The hydrogen consumption peaks in the second stage of CuZn catalyst reduction, at higher temperatures, are associated with the reduction of copper ions strongly interacted with the support oxides, with their very intimate contact or even incorporated in the zinc oxide and alumina structure. The modification of CuZn catalyst with nickel, cobalt and manganese considerably increased the temperature of the reduction. It is well known that the reducibility of oxides of those metals is more difficult than that of copper oxide. In the case of modified catalysts interactions of a copper oxide phase not only with the support but also with modifier oxides are very strong, the reducibility of copper oxide in the range of lower temperatures is therefore very hard. The copper oxide phase in the 5Ni/CuZn, 5Co/CuZn and 5Co$_5$Mn/CuZn catalysts underwent reduction only to some extend at 350 °C, which was the temperature of pre-reduction (activation) of all catalysts before steam reforming of ethanol experiments.

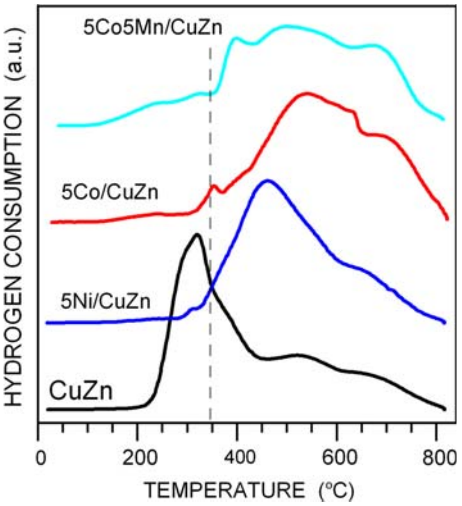

Fig. 1 H$_2$-TPR profiles of modified CuZn catalysts

The lower reducibility of modified catalysts has not significantly influenced their activity in the steam reforming of ethanol process (Fig. 2). The overall conversion of ethanol is very high, in most cases the conversions were equal to 100%. Only in the case of 5Co$_5$Mn/CuZn catalyst the conversion of ethanol at 350 °C is about 80%. However, above 480 °C conversions slightly decrease, most probably due to sintering of catalysts, but they still exceeded 90%.

The conversion of water is much lower than those of ethanol (Fig. 2). It is caused, on the one hand, by the excess of water in relation to the stoichiometry of the reforming reaction, and, on the other hand, by nonselective ethanol transformations (Fig. 3) occurring without participation of water. Except of the 5Co$_5$Mn/CuZn catalyst water conversions are very similar and only to a small extent dependent on the modifier introduced into CuZn catalyst.

Methane—from ethanol decomposition as well as small amounts of acetaldehyde from ethanol dehydrogenation

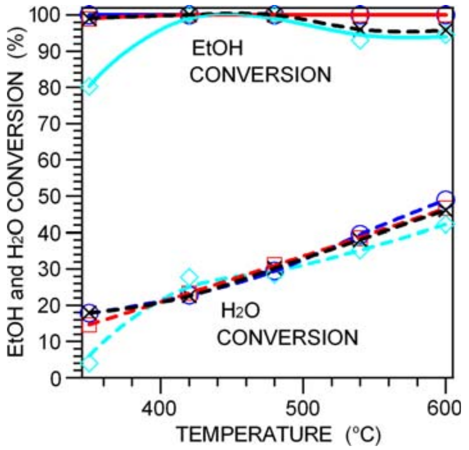

Fig. 2 Effect of modification of CuZn catalyst with nickel, cobalt and manganese on the conversion of ethanol and water in steam reforming of ethanol (×—CuZn, ◯—5Ni/CuZn, ☐—5Co/CuZn, ◇—$5Co_5Mn/CuZn$)

and other organic by-products are formed in side reactions (Fig. 3). Particularly, the selectivity towards methane is high in the range of lower temperatures, at which methane is a the dominant organic by-product. Over CuZn catalyst up to 450 °C about 50% of ethanol transforms into methane, directly ($C_2H_5OH \rightarrow CH_4 + CO + H_2$) or in a sequence of two steps ($C_2H_5OH \rightarrow CH_3CHO + H_2$ and $CH_3CHO \rightarrow CO + CH_4$). Higher temperatures of the steam reforming of ethanol cause lowering in methane formation and at 600 °C its selectivity drops to 10%. Moreover, modified catalysts show variations in methane selectivity at temperatures below 480 °C. Addition of nickel, cobalt and manganese modifiers decreases its formation.

The selectivity of the whole process of the conversion of ethanol to methane is in agreement with the selectivity of the carbon monoxide formation (Fig. 3). The formation of large amounts of methane as a by-product of the ethanol conversion is disadvantageous because its subsequent reaction with water require high temperatures, typically in the process of steam reforming of natural gas.

The dehydrogenation of ethanol to acetaldehyde is a minor direction of the ethanol transformation in the whole range of temperatures almost on all catalysts (Fig. 3). An exception is the $5Co_5Mn/CuZn$ catalyst, over which, at 350 °C, acetaldehyde is formed with a selectivity higher than 20%. At the temperature of 420–480 °C the formation of acetaldehyde is completely depressed over all catalysts. The selectivity of ethanol conversion into other organics (ethylene, ethane, propylene, propane, acetone) is also very low and at 420–480 °C they are not formed at all (Fig. 3).

The selectivity of hydrogen formation at temperatures below 420 °C is about 40–50% (Fig. 3). Modification of the CuZn catalyst, particularly with cobalt and manganese, slightly increases this selectivity. At temperatures higher than 420 °C the hydrogen selectivity increases with the temperature of the steam reforming of ethanol. Modifiers does not influence the hydrogen selectivity above 480 °C.

The course of the reaction of the ethanol reforming in the most desirable direction—the formation of hydrogen and carbon dioxide—is ensured by higher temperatures (Fig. 3). However, the significant increase of hydrogen formation in the range of higher temperatures, which seems to be very advantageous for its production, is accompanied by an equal increase in the carbon monoxide formation (Fig. 3). At low temperature, 350 °C, modified catalysts produce higher amounts of carbon monoxide, the highest selectivity towards carbon monoxide was obtained over $5Co_5Mn/CuZn$ catalyst. Carbon monoxide is one of the undesirable products of the process of reforming because it

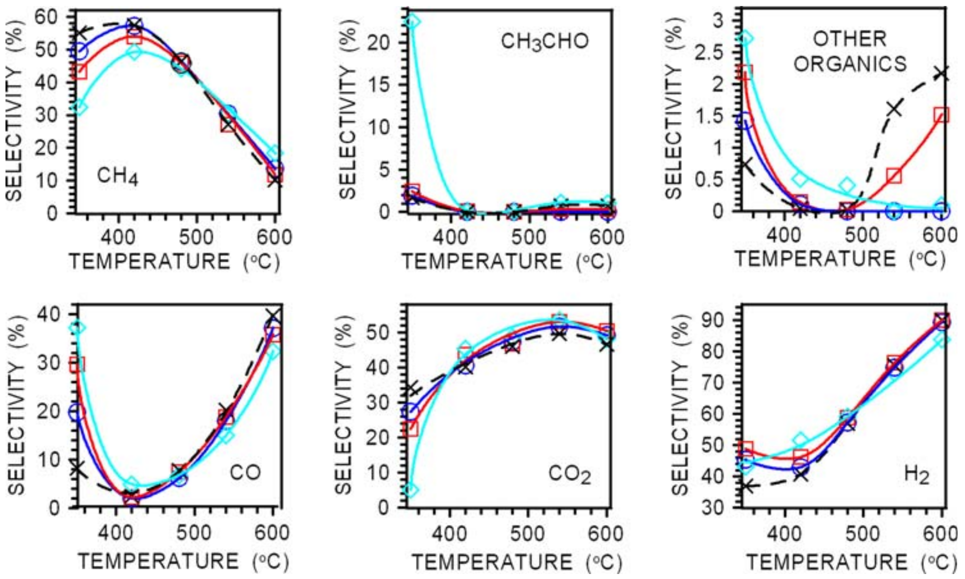

Fig. 3 Effect of modification of CuZn catalyst with nickel, cobalt and manganese on the selectivity in steam reforming of ethanol (×—CuZn, ◯—5Ni/CuZn, ☐—5Co/CuZn, ◇—$5Co_5Mn/CuZn$)

poisons the platinum anodes of low-temperature fuel cells, e.g. SPEFCs, PEMFCs (solid polymer electrolyte fuel cells, proton-exchange membrane electrolyte fuel cells), which are regarded to be most suitable for the application in small stationary power plants. Therefore, the temperature for the ethanol steam reforming over CuZn-based catalysts may be about 420–480 °C. At those temperatures the selectivity of the reforming process towards carbon monoxide is very low, below 5%, carbon dioxide is also formed with the high selectivity, close to the values characteristic for much higher temperatures.

It should be noticed that the greatest differences in the selectivity of the steam reforming of ethanol over all catalysts appear at the lowest temperature of the process, i.e. at 350 °C. At that temperature there were also the greatest differences in the extend of reduction of catalysts (Fig. 1). When the reducing agents (mainly hydrogen) are formed at higher temperatures of the steam reforming of ethanol the catalysts begin to be reduced to a higher extent and the differences in the catalyst selectivities are also diminished.

At the temperatures below 480 °C, the yield of hydrogen (expressed as moles of hydrogen formed from one mole of reacted ethanol) in the ethanol steam reforming over CuZn-based catalysts is equal to 1.5–2.5 (Fig. 4). It is not a very high value. The hydrogen productivity in the range of those temperatures is also lower than at higher temperatures (Fig. 4). Therefore, such catalysts would be not recommended for hydrogen generation in a processor dedicated only to ethanol as a fuel. However, CuZn-based catalysts may be applied in low-temperature multi-fuel (methanol and/or ethanol) processors designed for distributed small scale production of hydrogen. In such a case the application of the ethanol-derived reformate gas to a fuel cell for on-site electricity and heat (by utilisation of methane leaving stack of fuel cells [26]) generation is possible. Advantageous effects of the modification of the CuZn catalyst with cobalt and manganese for such applications are: a decrease in the methane formation and an increase in the hydrogen selectivity, yield and its productivity. However, taking into account the high selectivity towards hydrogen and its high yield and productivity, it would be more interesting to operate at higher temperatures and add a water-gas shift reactor and probably also a preferential carbon monoxide oxidizer.

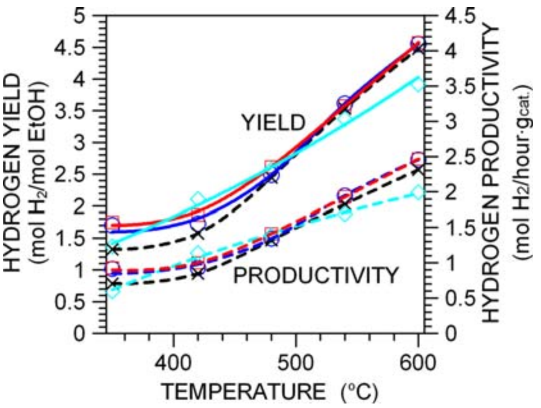

Fig. 4 Effect of modification of CuZn catalyst with nickel, cobalt and manganese on the yield and productivity of hydrogen formation in steam reforming of ethanol (×—CuZn, ◯—5Ni/CuZn, □—5Co/CuZn, ◇—5Co$_5$Mn/CuZn)

4 Conclusions

The greatest influence of nickel, cobalt and manganese modifiers of CuZn-based catalyst is observed at low temperatures of the ethanol steam reforming. Below 480 °C the most advantageous effects are: a decrease in the methane formation and an increase in the hydrogen selectivity, yield and its productivity. At 480 °C the formation of organic by-products (methane excluding) is almost completely depressed. Significant lowering in the methane selectivity and a high production of hydrogen require higher temperatures of the process.

The application of the ethanol-derived reformate gas produced over CuZn-based catalysts in low-temperature multi-fuel (methanol and/or ethanol) processors designed for distributed small scale fuel cell for on-site electricity and heat (by utilisation of methane leaving stack of fuel cells) generation is possible. However, taking into account the selectivity towards hydrogen and its yield and productivity, it would be more interesting to operate at higher temperatures and add a water-gas shift reactor and probably also a preferential carbon monoxide oxidizer.

Acknowledgments The authors acknowledge financial support from the Ministry of Science and Higher Education of Poland and the General Secretariat for Research and Technology of Greece in the frame of the Polish-Greek Scientific and Technological Programme. We also acknowledge financial support from the Ministry of Science and Higher Education of Poland, in the frame of the Research Project No. N N204 228534.

References

1. Subramani V, Song C (2007) Catalysis 20:65 and references cited therein
2. Ni M, Leung DYC, Leung MKH (2007) Int J Hydrog Energy 32:3238 and references cited therein
3. Frusteri F, Freni S (2007) J Power Sources 173:200 and references cited therein
4. Piscina PR, Homs N (2006) In: Minteer S (ed) Alcoholic fuels. Taylor & Francis, Boca Raton, pp 233–248 and references cited therein
5. Machocki A (2006) Przem Chem 85:1045 and references cited therein

6. Cheekatamarla PK, Finnerty CM (2006) J Power Sources 160:490 and references cited therein
7. Vaidya PD, Rodrigues AE (2006) Chem Eng J 117:39 and references cited therein
8. Joensen F, Rostrup-Nielsen JR (2002) J Power Sources 105:195 and references cited therein
9. Wang JB, Li C-H, Huang T-J (2005) Catal Lett 103:239
10. Zhang X-R, Wang L-C, Yao C-Z, Cao Y, Dai W-L, He H-Y, Fan K-N (2005) Catal Lett 102:183
11. Lee JK, Ko JB, Kim DH (2004) Appl Catal A 278:25
12. Shen J-P, Song CH (2002) Catal Today 77:89
13. Peppley BA, Amphlett JC, Kearns LM, Mann RF (1999) Appl Catal A 179:21
14. Youn MH, Seo JG, Kim P, Kim JJ, Lee H-I, Song IK (2006) J Power Sources 162:1270
15. Homs N, Llorca J, Piscina PR (2006) Catal Today 116:361
16. Velu S, Suzuki K, Vijayaraj M, Barman S, Gopinath CHS (2005) Appl Catal B 55:287
17. Marino F, Boveri M, Baronetti G, Laborde M (2004) Int J Hydrog Energy 29:67
18. Marino F, Baronetti G, Jobbagy M, Laborde M (2003) Appl Catal A 238:41
19. Velu S, Satoh N, Gopinath ChS, Suzuki K (2002) Catal Lett 82:145
20. Klouz V, Fierro V, Denton P, Katz H, Lisse JP, Bouvot-Mauduit S, Mirodatos C (2002) J Power Sources 105:26
21. Marino F, Boveri M, Baronetti G, Laborde M (2001) Int J Hydrog Energy 26:665
22. Llorca J, Homs N, Rossell O, Seco M, Fierro J-LG, Piscina PR (1999) J Mol Catal A 149:225
23. Marino FJ, Cerrella EG, Duhalde S, Jobbagy M, Laborde MA (1998) Int J Hydrog Energy 23:1095
24. Torres JA, Llorca J, Casanovas A, Dominguez M, Salvado J, Montane D (2007) J Power Sources 169:158
25. Papavasiliou J, Avgouropoulos G, Ioannides T (2005) Catal Commun 6:497
26. Qi A, Peppley B, Karan K (2007) Fuel Process Technol 88:3 and references cited therein