

Biodiesel reforming with a $\text{NiAl}_2\text{O}_4/\text{Al}_2\text{O}_3$ -YSZ catalyst for the production of renewable SOFC fuel

N. Abatzoglou, C. Fauteux-Lefebvre & N. Braidy

*Department of Chemical & Biotechnological Engineering,
Université de Sherbrooke, Canada*

Abstract

Biodiesel's contribution as a renewable energy carrier is increasing continuously. Fuel cell market penetration, although slow, is now an irreversible reality. The combination of solid oxide fuel cells (SOFC) with biodiesel offers considerable advantages because it entails both high energy conversion efficiency and near-zero atmospheric carbon emissions.

This work is aimed at proving the efficiency of a newly-developed (patent pending), $\text{Al}_2\text{O}_3/\text{YSZ}$ -supported NiAl_2O_4 spinel catalyst to steam reform biodiesel. Reforming converts biodiesel into a gaseous mixture, mainly composed of H_2 and CO , used directly as SOFC fuel.

The work is performed in a test rig comprising a lab-scale, fixed-bed isothermal reactor and a product-conditioning train. The biodiesel/water mixtures are emulsified prior to their spray injection in the reactor preheating zone, where they are instantaneously vaporized and rapidly brought to the desired reaction temperature to avoid thermal cracking. Reforming takes place at gas hourly space velocities equal to or higher than those in industrial reforming units. The products are analysed by at-line gas chromatography.

The results show that biodiesel conversion is complete at steady state. Thermodynamic calculations reveal that the fast reforming reaction reaches chemical equilibrium. The catalyst's performance is very efficient and prevents carbon formation and deactivation.

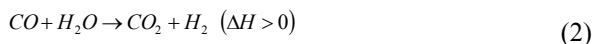
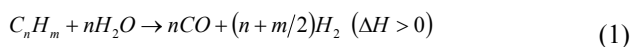
Keywords: biodiesel, steam reforming, SOFC, nickel, spinel.



1 Introduction

Fuel cell efficiency in converting chemical energy into electricity is significantly higher than internal combustion engines. With the world need for sustainable development, via substantial cuts to greenhouse gas emissions and energy costs, the combination of fuel cells with renewable fuels, such as biodiesel, is promising.

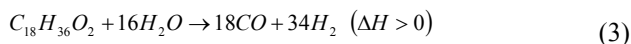
Hydrogen (H_2) is the ideal fuel, but solid oxide fuel cells (SOFC) can also be fed by carbon monoxide. Therefore, biodiesel catalytic reforming can serve as a SOFC liquid fuel conversion technology. The main products of biodiesel catalytic reforming are H_2 , carbon monoxide (CO) and carbon dioxide (CO_2). Equation (1) is the core reaction of hydrocarbon steam reforming and (2) is the water gas shift (WGS), a secondary reaction.



The purpose of this work is to test a new nickel-alumina spinel (Al_2O_3 /YSZ-supported $NiAl_2O_4$) material [1] as catalyst of biodiesel steam reforming.

1.1 Biodiesel reforming

Biodiesel reforming can be represented by the following global reaction (3):



Even though biodiesel is well known as a renewable source of fuel for the future, biodiesel steam reforming has not been investigated extensively.

In [2], the authors reported a thermodynamic simulation study of autothermal (ATR) and steam (SR) reforming of various liquid hydrocarbon fuels. They found the highest theoretical conversion efficiency in gasoline, but biodiesel was in the same range (1% lower on average), depicting its feasibility for in-line reforming with fuel cells.

In [3], biodiesel reforming has been simulated and tested in a heat-integrated fuel processor. A commercial precious metal-based catalyst was tested in the fuel processor. These authors obtained 99% conversion in the ATR processor with a steam to carbon molar ratio of 2.5, added oxygen, pressure of 2.1 bar, and gas hourly space velocities (GHSV) of $30,000 \text{ h}^{-1}$.

In [4], an experimental study of ATR was performed with platinum (Pt) and rhodium (Rh)-based catalysts synthesized. Hydrogen was produced at temperatures higher than 510°C with a steam to carbon molar ratio of 2 and an oxygen to carbon molar ratio of 0.4. Coke formed on the catalyst and reactor vessel walls.

Only ATR was investigated in all biodiesel conversion studies reported, both theoretical and experimental. In the experimental studies, only noble metal

catalysts were tested. Transition metals (noble and non-noble) are the most catalytically active in hydrocarbon reforming, and noble metals are known to be more resistant but also more expensive [5, 6].

1.2 Liquid hydrocarbon reforming

There are 3 main routes for catalyst deactivation in hydrocarbon reforming: sintering, sulphur poisoning, and coking. Sintering is a typical deactivation mechanism for every high temperature catalytic reaction. Sulphur poisoning is expected when fossil fuels are used; this is not the case with biodiesel, which does not contain sulphur moieties. Two main reaction pathways are responsible for coking: the Boudouard reaction (CO disproportionation to C and CO_2), and hydrocarbon cracking. Coke formation mechanisms are different in non-noble and noble metals. Nickel catalysts are prone to coking, because nickel allows carbon diffusion and dissolution which results in whisker carbon formation [7]. Noble metals do not dissolve carbon significantly, but considerable amounts of carbon-rich structures (i.e. graphite layers along the metallic surface) are produced via other carbon deposition mechanisms [7] which lead to coking.

Catalysts used for liquid hydrocarbons reforming reactions are usually deactivated within 100 hours of use [8–10]. In some cases, concentrations closed to theoretical thermodynamic equilibrium can be reached, depending on the catalyst and reaction severity (mainly sufficiently low space velocities).

Noble metal catalysts are deactivated at a slower rate than non-noble metal catalysts. Strohm et al. [10] investigated the SR of simulated jet fuel without sulphur and reported constant hydrogen concentrations of 60%vol for 80 hours with a Ceria- Al_2O_3 -supported Rh catalyst. The reactions occurred at temperatures below 520°C and water to carbon molar ratio of 3. With sulphur added in the feed (35 ppm), the catalyst was deactivated within 21 hours. Ming et al. [11] obtained constant H_2 concentrations of 70% over a 73-hour steady state operation for hexadecane steam reforming with an Al_2O_3 -supported bimetallic noble metal catalyst and metal-loading $<1.5\%$. The operating conditions were water to carbon molar ratio was 2.7 and an operating temperature of 800°C .

In most of the cases, deactivation occurs within 8 hours when non-noble metal catalysts (mainly nickel) are employed under most reaction severities, with less H_2 in the products [7, 12, 13]. However, Kim et al. [14] reported activity of a catalyst over a 53-hour steady state operation, but under favourable conditions. The H_2 concentrations decreased from 72% to 65% with a magnesia-alumina-supported Ni catalyst ($\text{Ni/MgO-Al}_2\text{O}_3$) at a temperature of 900°C , GHSV of $10,000 \text{ h}^{-1}$, and a water to carbon molar ratio of 3. They reported lower deactivation rates for bi-metallic catalyst using noble metal, with addition of Rhodium to the catalyst.

1.3 Spinel catalyst

Spinel NiAl_2O_4 has been studied with fuel cells for internal methane reforming [15]. The catalyst was prepared by solid surface reaction with stoichiometric

quantities of Al_2O_3 and nickel oxide (NiO) to form spinel. It was reduced prior to its use; the so-reduced final fresh catalyst was in the form of $\text{Ni}_x/\text{Ni}_{1-x}\text{Al}_2\text{O}_{4-x}$. It was reported to be active and relatively stable at a temperature of 800°C in a 250-hour test.

The formation and the stability of spinel and its capacity to be reduced seem to vary according to the reaction undertaken to form spinel, the stoichiometry and Al_2O_3 -type. In [16], spinel was produced by solid state reaction with nanometric gamma phase alumina ($\gamma\text{-Al}_2\text{O}_3$) impregnated with nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), at temperatures ranging between $1,000^\circ\text{C}$ and $1,300^\circ\text{C}$. The authors observed that the catalyst was totally reduced at temperatures higher than 950°C , with a mixture of CO and CO_2 as reducing atmosphere (and oxygen partial pressure of 1×10^{-15} atm). In [17], the authors noted that spinel formed of NiO and $\alpha\text{-Al}_2\text{O}_3$ could be reduced at 650°C , in severe reducing conditions with pure H_2 (oxygen partial pressure of 1.9×10^{-18} to 1.0×10^{-20} atm).

2 Experimental

2.1 Catalyst preparation

The NiAl_2O_4 -based catalyst tested in this work was produced by the wet impregnation method. Al_2O_3 (mixture of amorphous and $\gamma\text{-Al}_2\text{O}_3$) and YSZ ($\text{Y}_2\text{O}_3\text{-ZrO}_2$) (50%–50%) support was prepared by mixing the 2 powders mechanically. Al_2O_3 powder size was $40\text{ }\mu\text{m}$, and YSZ powder size distribution had an upper limit at $20\text{ }\mu\text{m}$. The Al_2O_3 and YSZ powders were impregnated with an $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution (targeting a 5% w/w nickel (Ni) load in the final formulation). Water was evaporated, and the resulting impregnated powder was dried overnight at 105°C . The so-dried mixture was calcined at 900°C for 6 hours to form spinel, by a solid state reaction.

2.2 Catalyst characterization

The composition and morphology were analysed by scanning electron microscopy (SEM). SEM was performed using Hitachi field emission gun and energy dispersive X-ray spectroscopy (EDXS) Oxford detector with an ultra-thin ATW2 window.

2.3 Reforming experimentation

A schematic of the reactor is presented in Figure 1. Reactor inner diameter was 46 mm, and catalytic bed length was 60 mm. The catalyst in powder form was dispersed in quartz wool, which was then compacted in the reactor to form a catalytic bed of quartz fibre containing catalyst particulates. This configuration prevented channelling issues and helped obtain a uniform catalytic bed with a small amount of catalyst.

An emulsion-in-water technique was adopted for biodiesel injection. This method was chosen to enhance hydrocarbon/water mixing. The 2 immiscible

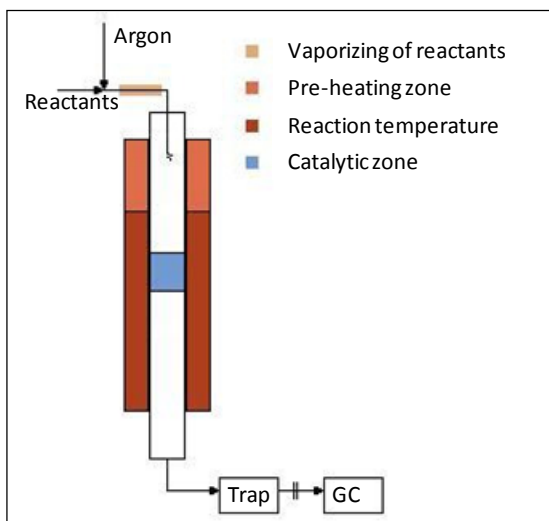


Figure 1: Schematic of the reforming set-up.

reactants were emulsified according to a surfactant-aided protocol. The reactants entered at room temperature and were rapidly heated and vaporized in the pre-heating zone maintained at 550°C. The temperature just before the catalyst bed was between 30°C and 45°C below the reaction temperature, depending on operating parameters. Argon served as inert diluent and internal standard for liquid hydrocarbon steam reforming.

The water to steam molar ratio was varied between 1.9 and 2.4. Operating temperatures were 700°C and 725°C with GHSV ranging from 5,500 and 13,500 cm³_{reac} g_{cat}⁻¹ h⁻¹ at barometric pressure. Reforming products were analysed by Varian CP-3800 gas chromatography (GC). The exit gaseous flow rate was measured by a flow rate mass meter (Omega FMA-700A). Biodiesel, from used vegetable oil, was produced by a transesterification process developed by Biocarburant PL (Sherbrooke, Qc, Canada; www.biocarburantpl.ca).

Experimental conversion was calculated (4):

$$X = \frac{N_{CO_{out}} + N_{CO_2_{out}} + N_{CH_4_{out}}}{N_{C_{in}} \times m + N_{Surfactant} \times Y} \quad (4)$$

with N_i being the total number of moles of component i at the reactor exit or inlet, and Y being the number of carbon atoms in the surfactant. Overall conversion was calculated for liquid hydrocarbon reforming based on the total amount of carbon fed in the reactor. Hydrocarbons were considered to be converted when they were transformed into gaseous products (CO, CO₂ or CH₄). Carbon found in the reactor after the experiment was therefore not considered as converted hydrocarbon.

In the reported tests, the reactor exit concentrations of H_2 , CO , CO_2 and CH_4 were compared to theoretical thermodynamic equilibrium concentrations, to determine if equilibrium was reached. Thermodynamic equilibrium concentrations were calculated with FactSage software on the basis of Gibbs energy minimization.

3 Results and discussion

The catalyst presented here for biodiesel reforming has already proved to be efficient for liquid hydrocarbon steam reforming at high GHSV and relatively low temperatures and water to carbon ratio [1].

3.1 Catalyst characterization

The catalyst formulation was analyzed using SEM analysis. The targeted catalyst form is $NiAl_2O_4$ spinel on the surface of an alumina support without any metallic nickel or nickel oxide.

Surface SEM and SEM-EDXS analyses of the fresh catalyst are reported in [1]. Figure 2 is a SEM analysis of the fresh catalyst surface and more particularly of the Al_2O_3 surface which is known to be the main support of the spinel phase.

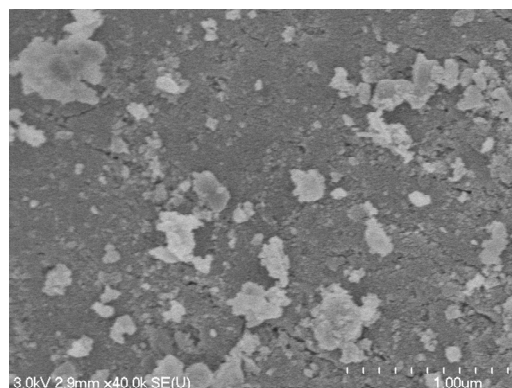


Figure 2: SEM micrograph of the Al_2O_3 surface.

3.2 Steam reforming results

3.2.1 Measurement errors

The errors associated with concentration data obtained by GC appear in Table 1. They were calculated with an external standard.

Table 1: Gas concentration measurement errors.

Gas	Standard gaseous concentration (%)	Absolute error (on % concentration of the standard)	Relative error (%)
H ₂	55.16	0.46	0.83
CO	19.70	0.21	1.05
CO ₂	6.96	0.38	5.45
CH ₄	2.08	0.04	1.87
Ar	16.10	0.22	1.37

In addition to GC concentration measurement errors, the mass flow meter for quantifying exit gas flow introduced a second error in the conversion calculations. The accuracy of the mass flow meter was 1%. Maximum and minimum values were therefore calculated for each conversion, with extreme values for concentrations and flow rates based on known error and accuracy.

3.2.2 Biodiesel steam reforming

Table 2 lists the conditions of 3 different biodiesel reforming test runs with the associated overall conversion calculated.

Table 2: Biodiesel reforming test run description.

Run	1	2	3
Temperature (°C)	700	725	725
Catalyst weight (g)	5.0	3.0	3.0
Run time (h)	3	4	2
GHSV (cm ³ g ⁻¹ h ⁻¹)	8,700	5,500	13,500
H ₂ O/C ^a (mol/mol)	1.9	1.9	2.4
Conversion (± 3%)	88	100	85

^aWater to carbon (H₂O/C) ratio calculated including surfactant.

Dry gaseous concentrations at the reactor exit are presented in Figure 3. Concentrations were stable for the entire reaction time with no catalyst deactivation observed.

Temperature increase and flow rate decrease would obviously lead to 100% conversion. It can also be observed that an increase of GHSV decreases conversion, even at a higher H₂O/C ratio. This reduction of conversion is associated with reaction kinetics. Figure 3 compares the theoretical equilibrium and experimental concentrations of the dry gas at the reactor exit.

These preliminary data are indicative of the ability of this catalytic formulation to efficiently steam reform commercial biodiesel. The catalyst is not poisoned by sulphur (not present in biodiesel in detectable quantities), and since carbon formation is insignificant, the only remaining catalyst deactivation mechanism is sintering. Although the extent of the performed tests is not

sufficient to allow us to evaluate such a mechanism, NiAl_2O_4 thermal mobility is much lower (insignificant at reaction conditions) than that of metallic Ni. Thus, the expected life cycle of the proposed catalyst is considerably longer than any other metallic Ni-based formulation.

High GHSV, which give complete biodiesel conversion, are indicative of a rather surface reaction kinetics-controlled process. However, additional experiments are needed, in conditions under which the reaction does not reach chemical equilibrium, in order to evaluate the kinetic parameters (mainly activation energy) as well as the mass transfer and chemical reaction resistances.

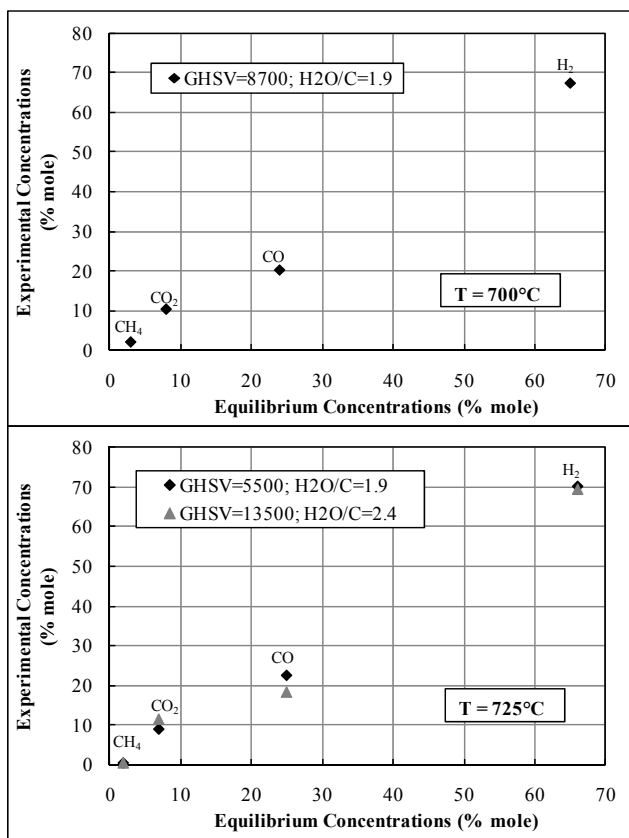


Figure 3: Experimental vs theoretical concentrations in biodiesel reforming product (Errors in values are less than 1% in all cases).

The concentrations for run 2 were equal to those at chemical thermodynamic equilibrium. In run 1, even if conversion was not complete, the concentrations were near equilibrium. It should be noted that for biodiesel reforming below 700°C, theoretical equilibrium concentrations predict the presence of significant

amounts of methane and coke formation if the water to carbon ratio in reactants is not higher than stoichiometric ratio.

3.3 Used catalyst characterization

Figure 4 is a SEM micrograph of an Al_2O_3 particulate of the NiAl_2O_4 catalyst used in run 2 of the biodiesel reforming test and comparison with Figure 2, which is the same for the fresh catalyst, proves that there was no significant carbon deposition on the surface. Some carbon whiskers were found on an extent lower than 5% of the surface; this is, however, expected because of local surface nanoheterogeneities and the possibility that some NiO on the surface was not transformed into NiAl_2O_4 which could form Ni during SR reactions.

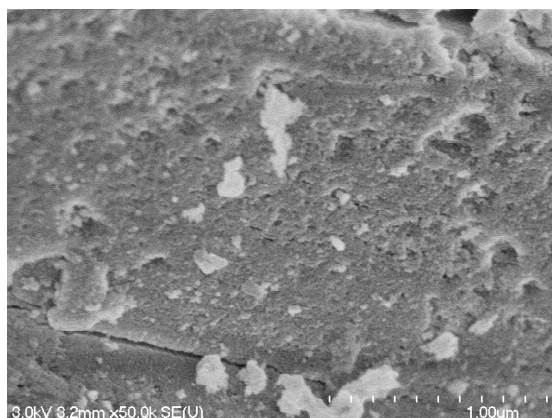


Figure 4: SEM picture of the catalyst after run 2.

4 Conclusion

An $\text{Al}_2\text{O}_3/\text{YSZ}$ -supported NiAl_2O_4 catalyst has been tested efficiently in biodiesel SR. 100% conversion was obtained at relatively low severity conditions. Increasing GHSV above $10,000\text{cm}^3\text{g}^{-1}\text{h}^{-1}$ decreased conversion, but dry concentrations of the exit gas were still near equilibrium. No catalyst deactivation was encountered. There was no observable carbon on the surface of the catalyst used in these conditions, even with a water to carbon ratio lower than 2.

Acknowledgements

The authors are indebted to SOFC Network Canada and the Agricultural Biomass Innovation Network (ABIN) for funding related to this project. The financial contribution of the National Science & Engineering Research Council (NSERC) of Canada through Discovery Funding and Students Awards is also



acknowledged along with the Le Fonds québécois de la recherche sur la nature et les technologies (FQRNT) for Students Awards. Biodiesel was kindly provided by Biocarburant PL. Many thanks are due to Carmina Reyes Plascencia and Henri Gauvin for their technical support and to Sonia Blais and Stéphane Gutierrez for their help in catalyst characterization. Finally, special thanks to Ovid Da Silva for reviewing the manuscript.

References

- [1] Fauteux-Lefebvre, C., Abatzoglou, N., Blanchard, J. & Gitzhofer, F., Steam reforming of liquid hydrocarbons over a nickel-alumina spinel catalyst, *Journal of Power Sources*, **195(10)** pp. 3275-3283, 2010.
- [2] Specchia, S., Cutillo, A., Saracco, G. & Specchia, V., Concept study on ATR and SR fuel processors for liquid hydrocarbons, *Industrial and Engineering Chemistry Research*, **45(15)** pp. 5298-5307, 2006.
- [3] Kraaij, G.J., Specchia, S., Bollito, G., Mutri, L. & Wails, D., Biodiesel fuel processor for APU applications, *International Journal of Hydrogen Energy*, **34(10)** pp. 4495-4499, 2009.
- [4] Ospinal-Jiménez, M., Hydrogen production study using autothermal reforming of biodiesel and other hydrocarbons for fuel cell applications, 2006, Master of Science degree thesis, University of Puerto Rico.
- [5] Ibarreta, A.F., Sung, C., Optimization of Jet-A fuel reforming for aerospace applications, *International Journal of Hydrogen Energy*, **31(8)** pp. 1066-1078, 2006.
- [6] Lucka, K., Kohne, H., Challenges in diesel reforming: Comparison of different reforming technologies, *Clean Air*, **7(4)** pp. 381-390, 2006.
- [7] Alvarez-Galvan, M.C., Navarro, R.M., Rosa, F., Briceno, Y., Gordillo Alvarez, F. & Fierro, J.L.G., Performance of La,Ce-modified alumina-supported Pt and Ni catalysts for the oxidative reforming of diesel hydrocarbons, *International Journal of Hydrogen Energy*, **33(2)** pp. 652-663, 2008.
- [8] Cheekatamarla, P.K., Lane, A.M., Catalytic autothermal reforming of diesel fuel for hydrogen generation in fuel cells: I. Activity tests and sulfur poisoning, *Journal of Power Sources*, **152(1-2)** pp. 256-263, 2005.
- [9] Rosa, F., Lopez, E., Briceno, Y., Sopena, D., Navarro, R.M., Alvarez-Galvan, M.C., Fierro, J.L.G. & Bordons, C., Design of a diesel reformer coupled to a PEMFC, *Catalysis Today*, **116(3)** pp. 324-333, 2006.
- [10] Strohm, J.J., Zheng, J. & Song, C., Low-temperature steam reforming of jet fuel in the absence and presence of sulfur over Rh and Rh-Ni catalysts for fuel cells, *Journal of Catalysis*, **238(2)** pp. 309-320, 2006.
- [11] Ming, Q., Healey, T., Allen, L. & Irving, P., Steam reforming of hydrocarbon fuels, *Catalysis Today*, **77(1-2)** pp. 51-64, 2002.
- [12] Gardner, T.H., Shekhawat, D., Berry, D.A., Smith, M.W., Salazar, M. & Kugler, E.L., Effect of nickel hexaaluminate mirror cation on structure-sensitive reactions during n-tetradecane partial oxidation, *Applied Catalysis A: General*, **323** pp. 1-8, 2007.



- [13] Gould, B.D., Tadd, A.R. & Schwank, J.W., Nickel-catalyzed autothermal reforming of jet fuel surrogates: n-Dodecane, tetralin, and their mixture, *Journal of Power Sources*, **164(1)** pp. 344-50, 2007.
- [14] Kim, D.H., Kang, J.S., Lee, Y.J., Park, N.K., Kim, Y.C., Hong, S.I. & Moon, D.J., Steam reforming of n-hexadecane over noble metal-modified Ni-based catalysts, *Catalysis Today*, **136(3-4)** pp. 228-234, 2008.
- [15] Kou, L., Selman, J., Activity of NiAl₂O₄ catalyst for steam reforming of methane under internal reforming fuel cell conditions, *Electrochemical Society Proceedings*, **99(19)** pp. 640-646, 1999.
- [16] Huang, Z.R., Jiang, D.L., Michel, D., Mazerolles, L., Ferrand, A., di Costanzo, T. & Vignes, J.L., Nickel-alumina nanocomposite powders prepared by novel in situ chemical reduction, *Journal of Materials Research*, **17(12)** pp. 3177-3181, 2002.
- [17] Jiong, Y.S., Kou, L., Nash, P. & Selman, J.R., Behavior of nickel aluminate spinel under reducing conditions, pp. 456-68, 1997.

