GLYCEROL STEAM REFORMING ON NICKEL LOADED APATITE-TYPE LANTHANUM SILICATES

MARIA A. GOULA[1]*, NIKOLAOS D. CHARISIOU[1], PAVLOS PANDIS[2], VASSILIS STATHOPOULOS[2]

[1]*Laboratory of Alternative Fuels and Environmental Catalysis (LAFEC), Department of Environmental and Pollution Control Engineering, School of Technological Applications, Technological Educational Institute of Western Macedonia (TEIWM), GR – 50100, Koila, Kozani, Greece*
[2]*Laboratory of Chemistry and Materials Technology, Department of Electrical Engineering, School of Technological Applications, Technological Educational Institute of Sterea Ellada (TEISTE),GR – 34400 Psahna, Chalkida, Greece*

Being a biomass derivative, glycerol is currently produced in large quantities in the process of trans-esterification of fatty acids into biodiesel. The steam reforming of glycerol appears as a potential alternative for producing hydrogen in the near future with significant impact in the viability of numerous bio-refining processes [1,2]. Lanthanum silicates of the apatite structure have attracted considerable attention as oxygen ion conductors because of their high ionic conductivity at intermediate temperatures and low activation energy. Recently an increased interest is observed for the apatite-type lanthanum silicates in the field of catalysis, as it has been proven that substitution of Si in the apatite structure increase apatite-type lanthanum silicate activity, mainly due to oxygen excess [3,4].
In the present paper for the first time it is reported the application of apatite-type lanthanum silicates in the steam reforming of glycerol reaction. The $La_{9.83}Si_5Fe_{0.75}Al_{0.25}O_{26\pm d}$, apatite oxide prepared by solid state synthesis was applied as a supporting material for a 8wt% Ni catalyst. Apatite oxide and catalyst (fresh, reduced and used) samples were characterized by means of the XRD, SEM, TEM techniques. Catalytic testing experiments were performed using a fixed bed reactor at temperatures ranging from 400 to 700 ^oC with a feed consisting of $C_3H_8O_3$ (20% v/v.) and H_2O in the liquid phase.
Comparing with a 8%Ni/alumina the Ni/apatite catalyst exhibited a superior performance, with a glycerol conversion close to 100% for the whole range of temperatures and a higher H_2 concentration at the gaseous products even for low temperatures, ranging between 25 and 40 % v/v for 500-750 ^oC. Moreover, CO_2 and CO concentrations were rather constant having the values of 10 and 5% v/v for the aforementioned temperature range, respectively. Liquid products as acetol, acetone, allyl alcohol, acetic acid and acetaldehyde were detected only for T<700 ^oC and at rather low concentrations.

[1] Charisiou N.D., Bereketidou O.A., Goula M.A.(2012), ‘Environmental assessment of glycerol utilisation for hydrogen production’, 4th International Symposium on Energy from Biomass and Waste, Venice, Italy, November 12-15, 2012.
[2] Charisiou N.D., Papageridis K.N., Goula M.A.(2014), ‘Study of the glycerol steam reforming reaction using nickel supported on alumina catalysts’, 13th Panhellenic Symposium on Catalysis, Agios Athanasios Pellas, Greece, October 16-19, 2014
[3] Gasparyan H., Neophytides S., Niakolas D., Stathopoulos V, Kharlamova T., Sadykov V., Van der Biest O., Jothinathan E., Louradour E., Joulin J.-P, Bebelis S. (2011), ‘Synthesis and characterization of doped apatite-type lanthanum silicates for SOFC applications’, Solid State Ionics 192 (1), 158-162
[4] Kharlamova T., Sadykov V., Stathopoulos V. (2014), ‘Lanthanum silicates as catalysts for oxidative condensation of methane’, 13th Panhellenic Symposium on Catalysis, Agios Athanasios Pellas, Greece, October 16-19, 2014

ACKNOWLEDGEMENTS
Financial support by the programs THALIS and Archimedes III implemented within the framework of Education and Lifelong Learning Operational Programme, co-financed by the Hellenic Ministry of Education, Lifelong Learning and Religious Affairs and the European Social Fund, Projects: ‘Production of Energy Carriers from Biomass by Products. Glycerol Reforming for the Production of Hydrogen, Hydrocarbons and Superior Alcohols’ and ‘Synthesis, Characterization and study of properties of solid electrolytes of the apatite structure for fuel cell applications - APACELL’, is gratefully acknowledged.