THE MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION
NATIONAL RESEARCH TOMSK STATE UNIVERSITY

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
V International scientific school-conference for young scientists

September 25-29, 2018

Tomsk 2018

Ni/La$_2$O$_3$ catalysts for dry reforming of methane: effect of synthesis conditions on the structural properties and catalytic performances

F. Puleo[1], M. V. Grabchenko[2], G. Pantaleo[1], O. Vodyankina[2], L.F. Liotta[1]

[1]Institute for the Study of Nanostructured Materials, Palermo, Italy
[2]Tomsk State University, Tomsk, Russia

marygra@mail.ru

Dry reforming of methane (DRM) is highly endothermic ($\Delta H°_{25°C}$ = 247 kJ/mol) and normally requires temperatures above 700°C to attain good conversion levels [1]. Nickel is the most frequently reported metal in DRM because of its good catalytic activity and its cost-effectiveness as compared with Rh, Ru, Pt, and Pd-based catalysts [2]. However, the main drawback of Ni based catalysts is represented by the production of significant amount of carbon and by the sintering at the high temperatures of the reaction. Carbon deposits are formed when the rate of methane dissociation is faster than the oxidation of carbon by the surface oxygen species arising from CO$_2$ dissociation on the metal component or from carbonates formed at the metal support interface [3, 4]. Until now, many studies have demonstrated that metal oxides such as CeO$_2$, MgO, ZrO$_2$ have positive effects on catalytic activity, stability and carbon suppression of nickel catalysts for DRM [5, 6].

In the present work the physical chemical properties, the related catalytic activity and the long-run stability of Ni-La$_2$O$_3$ catalysts have been evaluated in DRM reaction. The aim was to investigate the effect of ammonia addition during the synthesis of La$_2$O$_3$ oxide carried out by sol-gel method in presence of citric acid. Ni(10%wt) was deposited by wetness impregnation over two La$_2$O$_3$ oxides prepared with and without adding NH$_3$ solution during the synthesis, the corresponding catalysts were labelled as *Ni-La CA* and *Ni-La CA-NH$_3$,* respectively. The so far prepared catalysts were characterized by BET, XRD and TPR techniques. The XRD patterns of the supports calcined at 800 °C showed that ammonia addition favors the formation of La$_2$O$_3$ phase with respect to La(OH)$_3$. La$_2$O$_3$ was the only lanthanum phase detected in the XRD pattern of *Ni-La CA-NH$_3$*, after calcination at 600 °C and reduction treatment at 700 °C, moreover, weak features attributed to dispersed metallic Ni particles were found. While in the case of *Ni-La CA*, both phases, La$_2$O$_3$ and La(OH)$_3$ were present along with well visible peaks of metallic Ni suggesting the presence of big clusters. DRM gradient catalytic test performed between 400°C to 800°C revealed higher catalytic activity of *Ni-La CA*, nevertheless long run test showed a better stability of *Ni-La CA-NH$_3$* catalyst. The spent catalysts were characterized by XRD, TGA, Raman and TEM analyses. In both samples La$_2$O$_2$CO$_3$ phase was formed together with C graphite peak of higher intensity in the case of *Ni-La CA* in agreement with greater weight loss revealed by TGA and stronger deactivation during long run with respect to *Ni-La CA-NH$_3$*. The effect of the nature of the catalyst on the amount of carbon coke formed during DRM was also confirmed by Raman and TEM results.

References
1. Lavoie, J.M. *Front Chem.* **2014**, *11*, 2-81.
2. Pakhare, D.; Spivey, J. *Chem. Soc. Rev., 2014, 43,* 7813-7837.
3. Jia, Z.; Kou, K.; Qin, M. et al. *Catalysts* **2017**, *7*, 256-276.
4. Horváth, A.; Guczi, L.; Kocsonya, A. et al. *Appl. Catal. A: General* **2013**, 468 250– 259.
5. Mesrar, F.; Kacimi, M.; Liotta, L.F. et al. *Int. J. Hydrogen Energy* **2017**, 42, 19458-19466.
6. Fan, M.S.; Abdullah, A.Z.; Bhatia, S.; *ChemSusChem* **2011**, *4*, 1643-1653.