



4th International Conference on Process Engineering and Advanced Materials

## Improvement on Coke Formation of CaO-Ni/Al<sub>2</sub>O<sub>3</sub> Catalysts in Ethylene Production via Dehydration of Ethanol

Nurliyana Masiran<sup>a</sup>, Dai-Viet N. Vo<sup>b</sup>, Md. Abdus Salam<sup>a</sup>, Bawadi Abdullah<sup>a,\*</sup>

<sup>a</sup>Centre for Biofuel and Biochemical, Green Technology, Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia.

<sup>b</sup>Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Malaysia

### Abstract

Carbon deposition during ethanol dehydration remains an issue that needs a conceivable solution as ethylene is coke-precursor for acidic-type catalysts. This research is focused on bimetallic CaO-Ni/Al<sub>2</sub>O<sub>3</sub> catalyst to increase the resistance of coke formation on catalyst which mainly due to decomposition of carbon. Using wet impregnation procedure, various metal loadings of CaO and Ni (2-10wt%) were introduced onto  $\gamma$ -alumina support. The prepared catalysts then were subjected to in-situ activation in a fixed-bed reactor using H<sub>2</sub>/N<sub>2</sub> gas mixture before underwent the ethanol dehydration process in the same reactor. Catalysts were characterized using TEM, FTIR and FESEM. While CHNS Elemental Analyzer was used to observe coke formation before and after reaction. Based on the results obtained, the catalyst composition 6wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> shows the best conversion of ethylene (87.89 %) at 450°C of reaction temperature. It also suppressed the carbon formation only 13.28 % carbon content after the reaction.

© 2016 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of ICPEAM 2016

**Keywords:** Ethanol dehydration; ethylene production; coke formation; bimetallic catalyst; Al<sub>2</sub>O<sub>3</sub> support; CaO-Ni/Al<sub>2</sub>O<sub>3</sub>

\* Corresponding author. Tel.: +6-05-368-7633.

E-mail address: [bawadi\\_abdullah@petronas.com.my](mailto:bawadi_abdullah@petronas.com.my)

## 1. Introduction

The global demand of ethylene is estimated to rise up to the average of five percent annually between 2012 and 2017[1]. The increased of ethylene consumption leads to a high producing rate by various manufacturers which typically produce by thermal cracking using petroleum and natural gas. However, this will also lead to the increased of production cost due to the shortage of natural resources and the exponential increased in crude oil prices altogether with the forecast that petroleum resources will inevitably depleted. All these factors are indeed, limit the production rate and tend to increase the price. Therefore, alternative resources for the ethylene production are essential and thereby could serve as new sustainable ways for this production.

In dehydration of ethanol to produce ethylene, catalyst is used to increase the rate of selectivity of the chemical reaction and reduce the activation energy of the process without being consumed at the end of the reaction. Among noble and transition metals, Ni is the most promising choice as it is cheap, comparatively more active and high selective [2, 3]. Bimetallic catalyst is an advance type of catalyst which produced by combining two types of metal. It is evident the bimetallic catalysts can further improve the ethylene selectivity as compared to monometallic catalysts [4-9]. Thus, bimetallic catalysts were used in this research for bioethanol dehydration to form ethylene. Traditionally, Ni-based catalysts undergo catalyst deactivation mainly due to coking process as a result of decomposition of ethylene. Therefore, improving the resistance of catalyst toward coke formation is essential in order to extend the lifespan of catalyst and simultaneously reducing the cost of regenerating the catalyst. It was reported that addition of basic metal oxide into the catalyst can help to reduce the formation of coke on the surface of catalyst [10]. In this research, series of metal loadings of CaO-Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were tested for its effectiveness in reducing the formation of coke on catalyst's surface in ethanol dehydration.

## 2. Experimental

### 2.1. Catalyst Preparation

Catalysts were prepared using wet impregnation method according to a procedure available in the literature [11]. Accurately weighed of calcined aluminium oxide (Merck) were loaded dropwise with Ca(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous solution followed by Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O aqueous solution using pipette. After magnetically stirred for 1h on Thermo Scientific Super-nuova Hot Plate, the slurry mixture was oven-dried for 12h at 100 °C and calcined in WiseTherm Chamber Furnace at 500 °C for 6h. The cooled catalyst were crushed and sieved using Retsch AS 200 digit Sieve Shaker to obtain the final particle range of 45-125 µm for characterization and reaction studies. In this work, six types of CaO modified catalysts were synthesized, viz. 2 wt%, 4 wt% and 5 wt% Ca-loadings and 5 wt% and 10 wt% Ni-loadings, respectively.

### 2.2. Physicochemical Characterization

CO - FTIR technique method according to a procedure available in the literature [12] was used. The samples spectra were recorded in 450 – 4000 cm<sup>-1</sup> range using Perkin Elmer Spectrum One/BX FTIR spectrometer with high-vacuum purge system (HVPS). Catalyst surface morphology was observed using field emission scanning electron microscopy (FESEM) technique at magnifications of 1000X to 50,000X and transmission electron microscopy (TEM) with electron energy loss (EELs).

### 2.3. Catalytic Ethanol Dehydration

Hydrocracker Reactor was used for catalytic ethanol dehydration using 450 and 500 °C temperatures under atmospheric pressure. The reactor was charged with 2.0 g of the prepared catalyst. Prior to the reaction, the prepared catalysts then were subjected to in-situ activation in a fixed-bed reactor using H<sub>2</sub>/N<sub>2</sub> gas mixture before undergoes the ethanol dehydration process in the same reactor at 450-500 °C range of reaction temperature for 1 h with 1 mLmin<sup>-1</sup> flow rate of ethanol. Gaseous product was collected and analyzed using GC-TCD model Shimadzu GC-

8A. Column used was 3m Molecular Sieve 5A at 101 kPa. Perkin Elmer CHNS elemental analyzer was used to analyze total carbon content of spent catalyst.

### 3. Results & Discussion

#### 3.1. Characterizations

The dark zones in Fig. 1 corresponded to a wide variety of metallic particle. The EELs spectrum in Fig. 1 (b) showed two visible peak around 355 – 365 eV confirmed the presence of Ca element. According to David Muller et al.[13], Ni element peak typically visible at 870 eV which based on Fig. 1 (c), there was no visible peak. While in another spot (Fig. 1 (d)), there were visible peaks at both Ca and Ni EELS spectrum (Fig. 1 (e & f)) which indicates the presence of both elements on that spot.

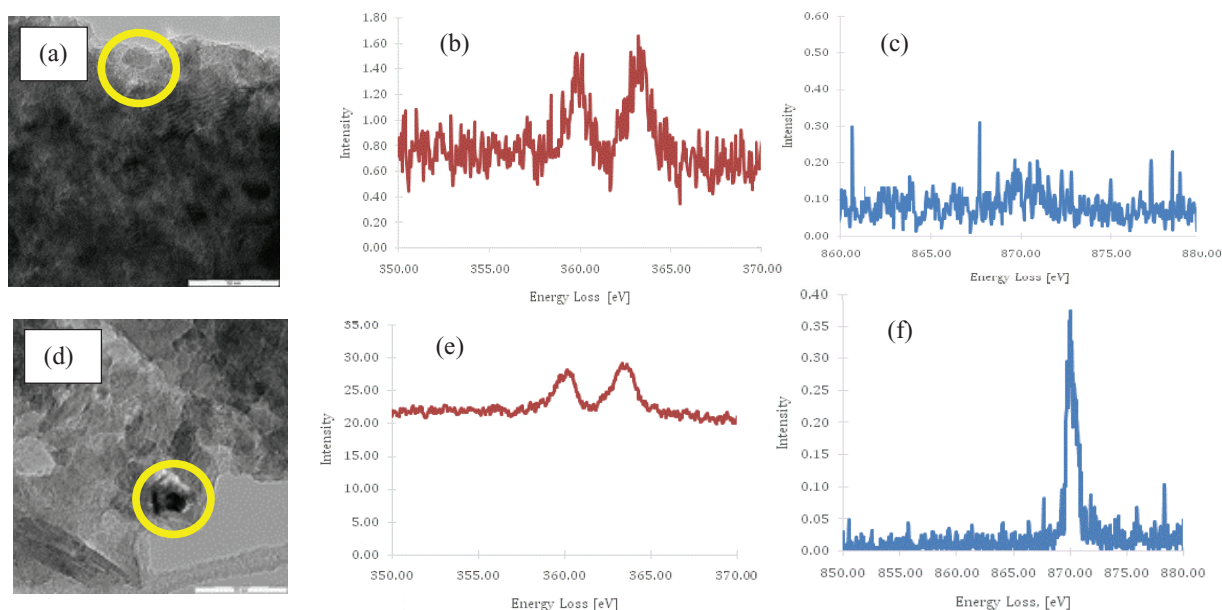


Fig. 1 TEM images of 6wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> at two different places (a & d) and EELS spectrum of Ca (b & e) and Ni (c & f) at two different spots.

Within each type of Lewis acid site, which were determined with pyridine as a probe molecule, there were distinctions in acidity that cannot be revealed with the use of strong bases. In this connection, it was very advantageous to employ the adsorption of weak bases like CO. The application of such probe molecules makes it possible to estimate both the concentration and the acid strength of OH groups and Lewis acid sites in zeolites, oxide and other systems [14]. Broad absorbance band around 3400 cm<sup>-1</sup> in Fig. 2 (a) and (b) were assigned to hydrogen bond OH groups. In Fig. 2 (a), FTIR spectra of adsorbed CO shown by low frequency a. b. around 2100 cm<sup>-1</sup> (purple box) corresponded with stretching vibrations of CO molecules of weak Lewis acid sites. However, there is a slight shift of adsorb CO a. b. in Fig. 2 (b) around 2300 cm<sup>-1</sup> compare to Fig. 2 (a) that corresponded with stretching vibrations of CO molecules of strong Lewis acid sites. This may caused by calcination process. By increasing CaO loading concentration, Lewis acid sites on Ni/Al<sub>2</sub>O<sub>3</sub> surface are decreased. This may caused by CaO acting as a poison on the acid sites of the catalyst surface [15].

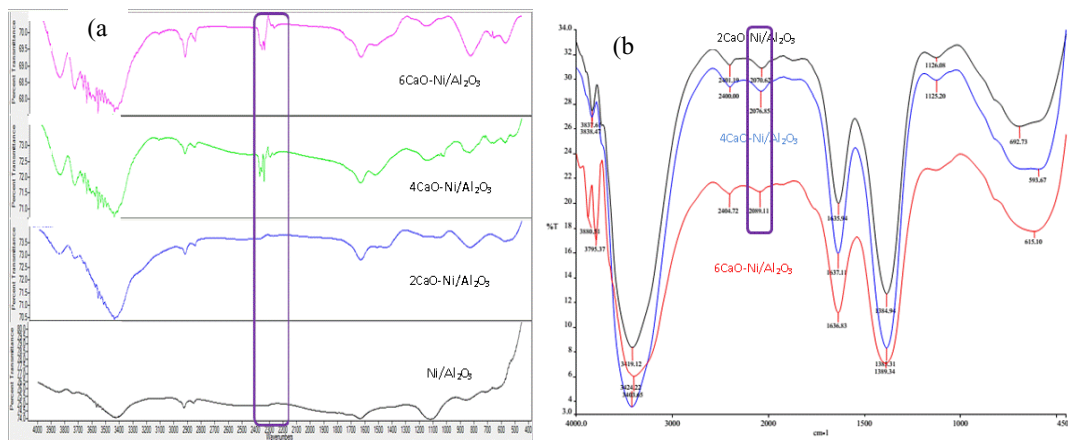


Fig. 2 CO-FTIR spectrum of Ni/Al<sub>2</sub>O<sub>3</sub> and CaO-Ni/Al<sub>2</sub>O<sub>3</sub> (a) before and (b) after calcination

### 3.2. Analysis of Ethylene & Coke Formation

Based on Fig. 3 (a), 6wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts produced the highest ethylene (87.89 %). This may be caused by good doping dispersion of Ni particle on catalyst surface. Though, 6wt%CaO-5wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (c.f. Fig. 3 (b)) formed the lowest carbon formation (9.66 %). The presence of high Ca concentration causes catalyst surface to become more basic which inhibited coke from forming at rapid rate [16-20]. Comparing between reaction temperatures, CaO-Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at 450 °C reaction temperature yield more ethylene and less coke form than 500 °C. High reaction temperature caused ethylene decomposition rate to accelerate thus increased coke formation rate.

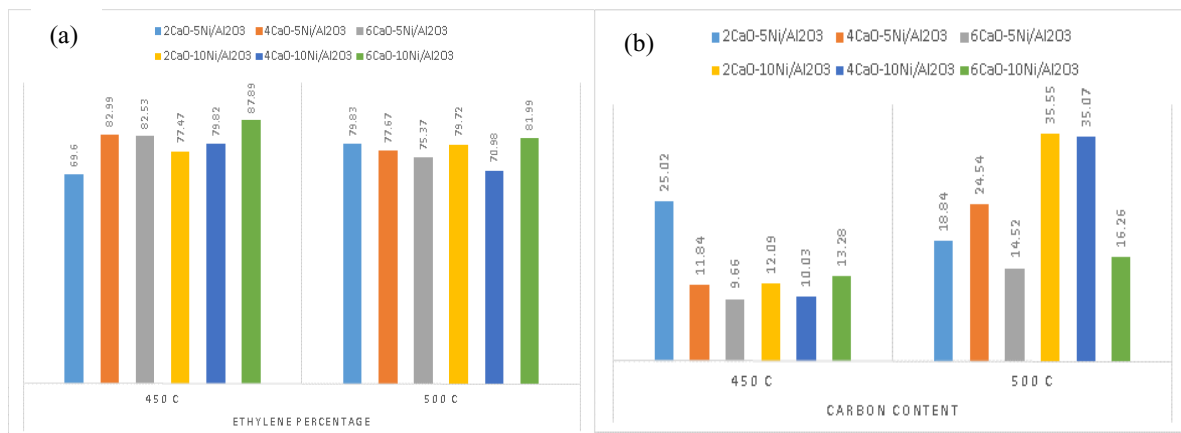


Fig. 3 CaO-Ni/Al<sub>2</sub>O<sub>3</sub> catalysts result of (a) ethylene percentage and (b) carbon content of catalytic ethanol dehydration reaction at 450 °C and 500°C reaction temperature and various metal loading concentrations.

At reaction temperature of 500 °C, Fig. 4 showed significant difference of coke formations on CaO modified catalyst surfaces. Visible nano-flakes formed on the surface of 6wt%CaO-5wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts (cf. Fig. 4 (a. ii)) which consistent with results (cf. Fig. 3 (a),(b)) where ethylene production were relatively high causing coke to form at faster rate compare to 450°C reaction temperature. Figs. 4 (b. ii) and (c. ii) display thick coke layer on catalyst surface. These results are in agreement with results obtained in Fig. 3 for 2wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> and 4wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. This implied to high concentration of Ni which favorable in producing ethylene but not conducive to prevent coke formation at high reaction temperature. Even though a 6wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst able to produce high ethylene, however carbon formation is relatively high compared to the same catalyst at 450 °C reaction temperature.

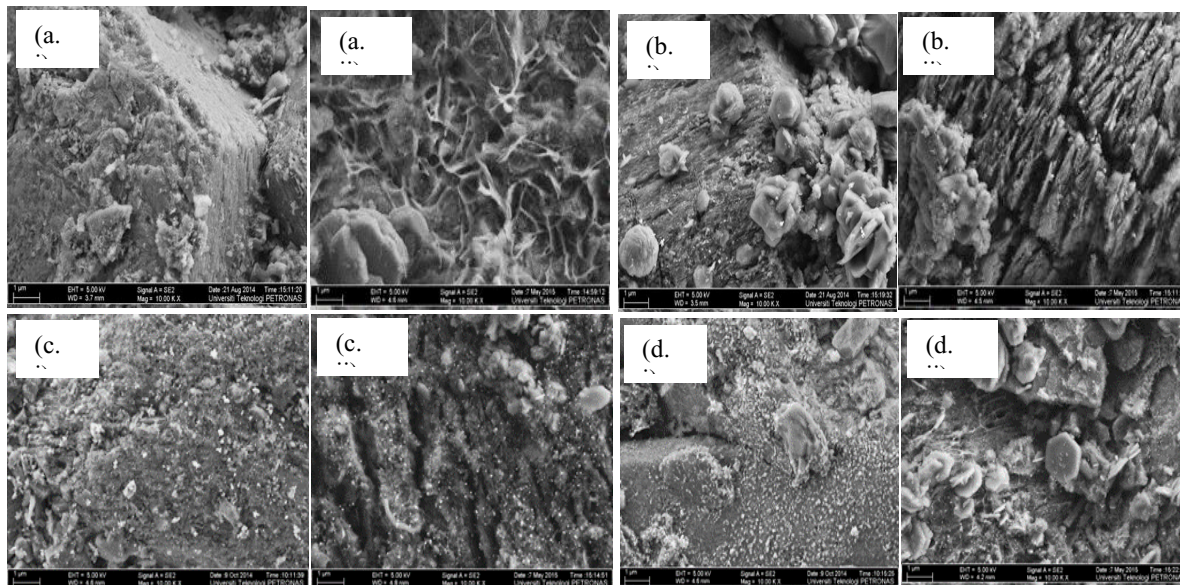


Fig. 4 FESEM photographs of (a) 6wt%CaO-5wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, (b) 2wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, (c) 4wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, and (d) 6wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalysts, (i) before and (ii) after reaction at 10000X magnification for 500 °C reaction temperature.

#### 4. Conclusion

CaO has basic property to reduce the active site of catalysts, enough to reduce carbon formation but still able to produce high ethylene. CaO modified Ni/Al<sub>2</sub>O<sub>3</sub> catalyst able to produce more ethylene product at 450 °C reaction temperature with less coke formation. The catalyst deactivates faster at higher than 450°C reaction temperature. Reaction temperature at 450°C and 6wt%CaO-10wt%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is the optimal condition and catalyst for this research.

#### Acknowledgements

The authors gratefully acknowledged the financial support from Yayasan Universiti Teknologi PETRONAS (Y-UTP) (Grant No: 0153AA-89). We thank UTP for providing a congenial work environment and state-of-the-art research facilities.

#### References

- [1] Westervelt, R. (2013, October, 8). Ethylene outlook muted by weak demand, supply surge. Available: [http://www.chemweek.com/lab/Ethylene-outlook-muted-by-weak-demandsupply-surge\\_50823.html](http://www.chemweek.com/lab/Ethylene-outlook-muted-by-weak-demandsupply-surge_50823.html)



- [2] N. Yang, R. Wang, Sustainable technologies for the reclamation of greenhouse gas CO<sub>2</sub>, *Journal of Cleaner Production* 103 (2015) 784-792.
- [3] K. Selvarajah, N.H.H. Phuc, B. Abdullah, F. Alenazey, D.V.N. Vo, Syngas production from methane dry reforming over Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, *Research on Chemical Intermediates*, (2016) 1-20.
- [4] H. Idriss et al., in *Proceedings of 10th International Congress on Catalysis*, Budapest, 1992, p. 2119.
- [5] F. Epron, F. Gauthard, C. Pinéda, J. Barbier, Catalytic Reduction of Nitrate and Nitrite on Pt–Cu/Al<sub>2</sub>O<sub>3</sub> Catalysts in Aqueous Solution: Role of the Interaction between Copper and Platinum in the Reaction, *Journal of Catalysis*, 198 (2001) 309-318.
- [6] W. Gao, R. Jin, J. Chen, X. Guan, H. Zeng, F. Zhang, N. Guan, Titania-supported bimetallic catalysts for photocatalytic reduction of nitrate, *Catalysis Today* 90 (2004) 331-336.
- [7] F.B. Noronha, M. Schmal, C. Nicot, B. Moraweck, R. Frety, Characterization of Graphite-Supported Palladium–Cobalt Catalysts by Temperature-Programmed Reduction and Magnetic Measurements, *Journal of Catalysis* 168 (1997) 42-50.
- [8] R. Melendrez, G. Del Angel, V. Bertin, M. A. Valenzuela, J. Barbier, Selective hydrogenation of carvone and o-xylene on Pd–Cu catalysts prepared by surface redox reaction, *Journal of Molecular Catalysis A: Chemical* 157 (2000) 143-149.
- [9] M. B. Bahari, N.H.H. Phuc, B. Abdullah, F. Alenazey, D-V. N. Vo, Ethanol Dry Reforming for Syngas Production over Ce-promoted Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst, *Journal of Environmental Chemical Engineering* (2016).
- [10] K.Y. Koo, H.S. Roh, Y.T. Seo, D.J. Seo, W.L. Yoon, S.B. Park, Coke study on MgO-promoted Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in combined H<sub>2</sub>O and CO<sub>2</sub> reforming of methane for gas to liquid (GTL) process, *Applied Catalysis A: General*, 340 (2008) 183-190.
- [11] K.W. Siew, H.C. Lee, J. Gim bun, C.K. Cheng, Characterization of La-promoted Ni/Al<sub>2</sub>O<sub>3</sub> catalysts for hydrogen production from glycerol dry reforming, *Journal of Energy Chemistry* 23 (2014) 15-21.
- [12] X. Zhu, Y.P. Zhang, C.J. Liu, CO Adsorbed Infrared Spectroscopy Study of Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst for CO<sub>2</sub> Reforming of Methane, *Catalysis Letters* 118 (2007) 306-312.
- [13] D.A. Muller, D.J. Singh, J. Silcox, Connections between the electron-energy-loss spectra, the local electronic structure, and the physical properties of a material: A study of nickel aluminum alloys, *Physical Review B* 57 (1998) 8181-8202.
- [14] O.B. Belskaya, A.V. Lavrenov, I.G. Danilova, M.O. Kazakov, R.M. Mironenko, V.A. Likholobov, FTIR Spectroscopy of Adsorbed Probe Molecules for Analyzing the Surface Properties of Supported Pt (Pd) Catalysts, *Infrared Spectroscopy in Materials Science, Engineering and Technology*, P. T. Theophile, Ed., ed: InTech, 2012.
- [15] K.F. Elias, A.F. Lucredio, E.M. Assaf, Effect of CaO addition on acid properties of Ni–Ca/Al<sub>2</sub>O<sub>3</sub> catalysts applied to ethanol steam reforming, *International Journal of Hydrogen Energy* 38 (2013) 4407-4417.
- [16] S. Sengupta, G. Deo, Modifying alumina with CaO or MgO in supported Ni and Ni–Co catalysts and its effect on dry reforming of CH<sub>4</sub>, *Journal of CO<sub>2</sub> Utilization* 10 (2015) 67-77.
- [17] A.J. Vizcaino, A. Carrero, J.A. Calles, Comparison of ethanol steam reforming using Co and Ni catalysts supported on SBA-15 modified by Ca and Mg, *Fuel Processing Technology* 146 (2016) 99-109.
- [18] Z. Alipour, M. Rezaei, F. Meshkani, Effect of alkaline earth promoters (MgO, CaO, and BaO) on the activity and coke formation of Ni catalysts supported on nanocrystalline Al<sub>2</sub>O<sub>3</sub> in dry reforming of methane, *Journal of Industrial and Engineering Chemistry* 20 (2014) 2858-2863.
- [19] T. Baidya, R.J. Cattolica, Improved catalytic performance of CaO and CeO<sub>2</sub> promoted Ni catalyst on gasifier bed material for tar removal from producer gas, *Applied Catalysis A: General* 498 (2015) 150-158.
- [20] C.K. Choong, L. Huang, Z. Zhong, J. Lin, L. Hong, L. Chen, Effect of calcium addition on catalytic ethanol steam reforming of Ni/Al<sub>2</sub>O<sub>3</sub>: II. Acidity/basicity, water adsorption and catalytic activity, *Applied Catalysis A: General* 407 (2011) 155-162.