Activated Carbon Supported Ni Catalysts for Gas Phase Dehydrogenation of Decalin

Bukya Padma, Burri David Raju and Kamaraju Seetha Rama Rao*

Catalysis laboratory, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, **INDIA**
Email: ksramaraoiict@gmail.com

_____

ABSTRACT

The work is proposed to bring a continuous down flow reactor for the dehydrogenation processes of one of the hydrogen production platform molecule decalin over a non-noble metal Ni based catalysts. Various amount of Ni supported on carbon catalysts were prepared by wet impregnation method and catalysts were evaluated in continuous gas phase dehydrogenation of decalin at atmospheric pressure. Among the prepared catalysts, 15 wt. % Ni/C catalyst exhibited the best catalytic activity due to presence of a greater number of surface Ni species and higher surface area than other catalysts. Cis-decalin performed higher rate of conversion than trans-decalin due to flexible geometric structure of Cis-decalin molecule and it makes easier to be adsorbed on the catalyst surface.

Graphical Abstract
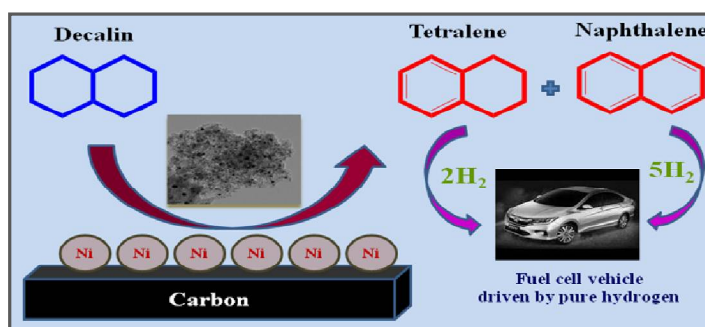
Keywords Activated Carbon, Ni, Decalin, Dehydrogenation.
_____

INTRODUCTION

The reversible dehydrogenation/hydrogenation liquid organic hydrides were proposed as potential hydrogen storage molecules due to their technical and electronic feasibility [1]. Cyclohexane/benzene, methyl cyclohexane/toluene; and decalin/naphthalene liquid pairs were most reviewed [2]. These liquids have a potential system to store and deliver hydrogen in a non-gaseous infrastructure concept and the hydrogen released is CO and CO_2 free with high purity [3-5]. The cycloalkanes

dehydrogenation produces useful aromatic products which made the cycloalkanes dehydrogenation as a cost-efficient method for hydrogen production and all cycloalkane liquids were stable. Most of the researchers studied the cycloalkanes dehydrogenation reactions over Pt based catalysts. Okada *et al.* studied the Pt/Al$_2$O$_3$ catalysts formethylcyclohexane dehydrogenation in a fixed bed reactor [6]. Saito et al. performed dehydrogenation of decalin at 210°C with carbon supported Pt catalysts in a batch reactor [7]. Huffman used stacked-cone carbon nanotubes (SC-CNT) as support medium to prepare Pt and Pd catalysts for the dehydrogenation of cyclohexane and methylcyclohexane to produce pure hydrogen [8]. Froment et al. studied the kinetics of the dehydrogenation of methylcyclohexane in a tubular reactor on commercial Pt/Al$_2$O$_3$ and Pt-Re/Al$_2$O$_3$ reforming catalysts [9]. Cooper et al. have also studied the possibility of using liquid phase cycloalkane hydrogen carriers (cyclohexane, methylcyclohexane, tetralin, decalin, etc.) to supply and store hydrogen [10]. Hodoshima *et al.* and Kariya et al., studied under reactive distillation and liquid film concept for decalin dehydrogenation over platinumbased catalysts [11-15]. Ichikawa et al. investigated the dehydrogenation of cyclohexane, methylcyclohexane and decalin over activated carbon supported Ni, Pt and Ni-Pt catalysts using a spray pulse mode reactor operating at 287-375°C [16, 17]. Anderson and co-workers investigated the dehydrogenation of cyclohexane on Pt/SiO$_2$ in a pure membrane reactor, a conventional packed bed reactor, and hybrid membrane reactors consisting of a packed bed reactor segment followed by a membrane reactor segment in the temperature range 190-220°C [18]. All these catalytic systems consist of noble metals and complex and tedious catalyst preparation methods. Hence there is a room for the development of non-noble metal based catalytic systems for the cycloalkanes dehydrogenation. Ni is one of the non-noble metal with excellent catalytic activity in both hydrogenation and dehydrogenation reactions. The preparation of supported Ni catalysts is a challenging one in terms of choosing support material and to disperse well distributed Ni particles. The catalytic activities of supported metal catalysts are strongly dependent on the shape, size and size distribution of the metal particles [19-21]. Activated carbon is a support with its high surface area and adequate porosity made it an efficient support in the catalytic reactions [22, 23]. In this work, activated carbon supported Ni catalysts were prepared and characterized by the XRD, BET-surface area analyzer, H$_2$ Pulse chemisorption, H$_2$-TPR and TEM techniques. The catalytic activity of these catalysts was investigated for the catalytic dehydrogenation of decalin under fixed-bed down flow reactor at atmospheric pressure conditions. The catalytic activity was correlated with the characterization results.

MATERIALS AND METHODS

Catalyst preparation: Activated carbon supported nickel catalysts were prepared by wet impregnation method. In a typical procedure, requisite amount of Ni (NO$_3$)$_2$ 6H$_2$O (M/s. LOBA Chemie, India) was dissolved in water to this solution calculated amount of activated carbon (M/s. Sud Chemi, India) was added. The mixture was heated on a hot plate with constant stirring at 60°C until to complete dryness. The solid was oven dried at 100°C for 12 h, later it was calcined at 450°C for 4 h. The resultant solid was labelled as xNC where x denotes the weight % of Ni.

Catalytic characterization: The structural characterization was acquired using a Ultima IV X-ray powder diffractometer, (M/s. Rigaku Corporation, Japan) with a scanning step of 0.02° using Ni filtered Cu Kα radiation (λ= 1.5406 Å) with a scan speed of 6° min^{-1} and a scan range for low angle 0.7-5° and for wide angle 10-80° at 40 kV and 20 mA. Textural features of supported Ni catalysts were measured by N$_2$physisorption at liquid nitrogen temperature on a Quadrasorb SI system (M/s. Quantachrome Instruments, USA). Scanning electron microscopy and Transmission electron microscopic (TEM) analysis was made using a S-3700, serial number 370701-14 and Philips Technai G2 FEI F12 at an accelerating voltage of 80-100 kV. Hydrogen pulse chemisorption experiments were performed on an automated gas sorption analyzer AUTOSORB-iQ (M/s. Quanta chrome Instruments, USA) to measure active metal surface area, metal particle size and metal dispersion.

Catalytic activity: A quartz fixed bed down flow reactor (10 mm i.d. and 30 cm length) was used for decalin dehydrogenation. In each experiment, 500 mg of catalyst along with 500 mg of silicon beads were sandwiched between the quartz wool at the centre of the reactor. Prior to the reaction, the catalyst was reduced at 600 °C for 3 h. Afterwards the temperature was cooled down to the reaction temperature The decalin was fed at a flow rate of 0.5 mL h^{-1} using microperfusor feed pump in N$_2$ stream (20 mL min^{-1}). The product analysis was performed by means of a gas chromatograph (GC-17A, M/s. Shimadzu Instruments, Japan) with an OV-1 capillary column (0.53 mm×30 m). The identification of products was done by performing a GC-MS (QP-5050 model, M/s. Shimadzu Instruments, Japan) analysis equipped with an EB-5MS capillary column (0.32 mmx25 m).

RESULTS AND DISCUSSION

The wide angle XRD patterns of reduced carbon supported Ni catalysts were presented in figure 1. A broad diffraction signal in all the supported Ni catalyst at around 2θ value of 23.3° designates the presence of carbon. The diffraction signals at 2θ values of 43.82, 51.33 and 76.99° indicates the existence of metallic Ni species with face centered cubic lattice. The crystallite sizes of reduced carbon supported Ni catalysts were calculated by using Scherrer's formula from their full width at half maximum (FWHM) values and presented in table1. BET-surface areas of xNC catalysts were presented in table 1. The surface area of activated carbon is decreased with the increase in Ni loading.
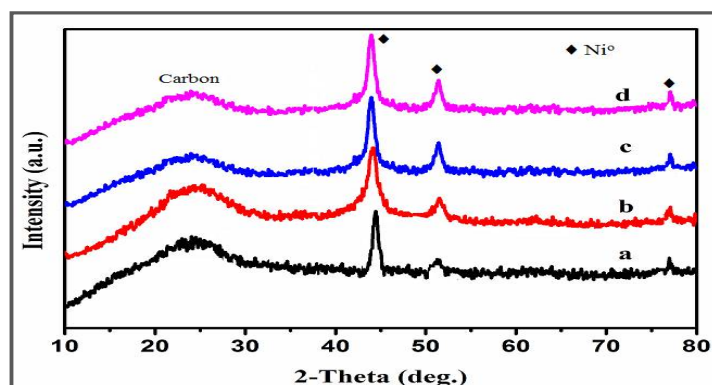

Figure 1. Wide angle XRD patterns of reduced catalysts
a) 5NC b) 10NC c) 15 NC andd) 20NC.

Table 1. Textural properties of xNC catalysts

Catalyst	XRD Crystalline size (nm)	BET Surface area (m^2 g^{-1})
Carbon	-	901
5 NC	7.4	848
10 NC	9.3	782
15 NC	11.3	736
20 NC	14.9	694

H$_2$-temperature programmed reduction: (H$_2$-TPR) experiments were carried out in order to investigate the reducibility of the nickel oxide species, metal-support interactions and the respective profiles were presented in figure 2. The reduction profiles of carbon supported Ni catalysts show two reduction patterns. The low temperature reduction peak at around T$_{max}$ of 400°C is observed which corresponds to reduction of bulk nickel oxide species to metallic Ni species. The high reduction temperature peak indicates the strong metal support interactions between the nickel oxide and activated carbon which decreases the susceptibility for nickel oxide to reduce into metallic nickel species. It can be observed that the increase in Ni loading the reduction temperature peak is shifted to

low reduction temperatures. It suggests that the increase in Ni loading, the bulky nature of the nickel oxide species increases which moves the reduction temperatures to low values.
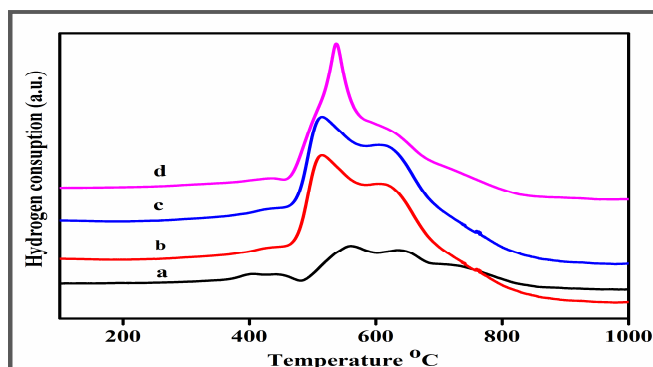

Figure 2. H_2-TPR profiles of xNC catalysts is a) 5NC
b) 10NC c) 15NC and d) 20NC.

Transmission Electron Microscopy: TEM images and particle size distribution of fresh and spent 15NC catalyst were depicted in figure 3. The nickel particles are well dispersed on the surface of the support in fresh and spent catalyst with the average particle size of ~8.5 nm and 22.5 nm respectively and these values are relatively close to particle sizes from H_2-Chemisorption (11.3 nm) studies.
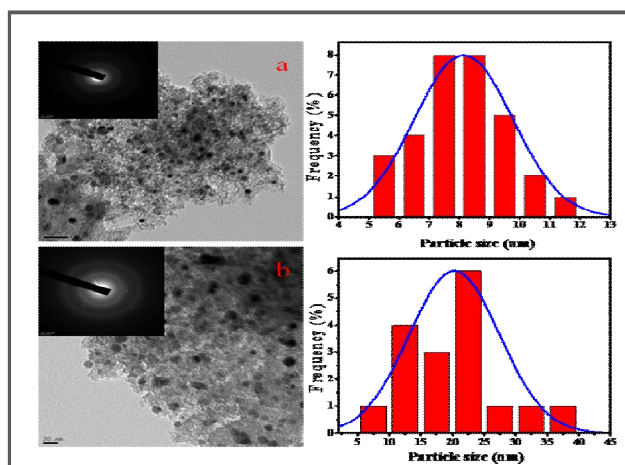

Figure 3. TEM images and particle size distribution of 15NC catalysts
a) Fresh and b) Spent.

SEM images and EDX spectrum of all the carbon supported nickel catalysts were depicted in figure 4 and 5. It can be seen that the all the images show sponge like materials with porous nature. The variation of the Ni loading in the catalysts can be clearly seen from the intensity observed in the EDX pattern.

The metal dispersion, average particle size and dispersion of the supported nickel catalysts was measured by H_2 pulse chemisorption and the results were presented in table 2. [24-26]. Based on the assumption that each Ni atom chemisorbs one H-atom, Ni dispersion, Ni-metal area and its particle size are determined. The amount of H_2 uptake is increases with Ni loading upto 15NC and then decreases. The particle size of metal increases with the increase in amount of metal loadings, consequently, the dispersion of active metal decreases. The number of surface Ni species increases with loading whereas the Ni dispersion decreases with loading. The Ni particle size increases with increase in Ni loading.
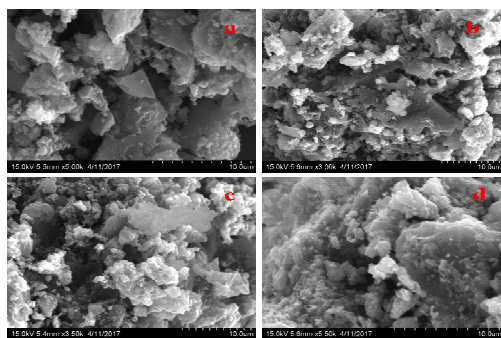
Figure 4. FE-SEM images of supported Ni catalysts
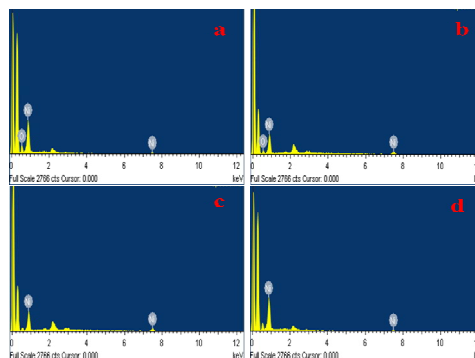a) 5NC b) 10NC c) 15NC and d) 20NC.

Figure 5. EDX spectra of supported Ni catalysts
a) 5NC b) 10NCc) 15NC and d) 20NC.

Table 2. H_2-chemisorption studies of nickel-based catalysts

Catalyst	H_2 Uptake (μ moles g^{-1})	Active surface area (m^2. g^{-1})	Average particle size (d) (nm)	Dispersion (%)
Carbon	-	-	-	-
5 NC	410.5	32.10	10.5	96.4
10 NC	736.6	57.6	11.7	86.5
15 NC	910.6	71.2	14.2	71.3
20 NC	763.5	59.7	22.6	44.8

Catalytic Performance: The catalytic dehydrogenation of decalin (DC) was performed over supported Ni catalysts in continuous process at atmospheric pressure and the results were presented in figure 6. The conversions of DC as well as selectivity to naphthalene (NP) are increased with nickel loading up to 15 wt. %. Further, increase in the nickel loading results gradual decrease in the both conversion of DC and selectivity of NP. The activity of Ni/C catalysts for the conversion of DC to NP and TT is influenced by active Ni metal surface area (Table 2). The conversions of DC as well as
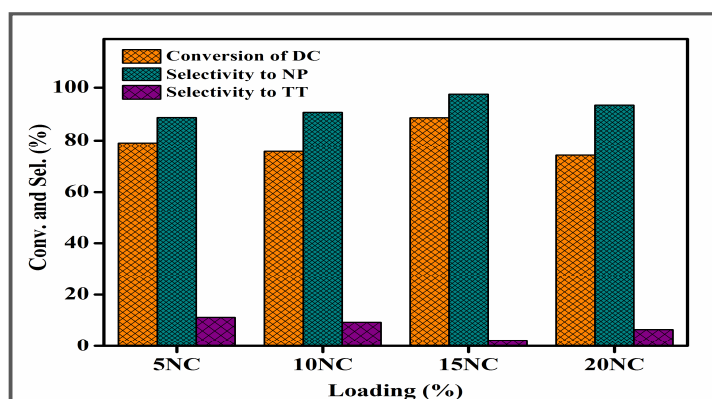

Figure 6. Influence of Ni loadings on the dehydrogenation of DC over supported Ni catalysts.
Reaction conditions: Weight of catalyst: 0.5g, Feed flow: 0.5 mLh^{-1}, N$_2$Flow: 20 mLmin^{-1},
Reaction temperature: 300 °C.

yield of NP are increased with nickel loading up to 15 wt. %. Further, increase in the nickel loading results gradual decreases in the both conversion of DC and selectivity to NP. The activity of supported Ni catalysts for the conversion of DC to NP and tetralin (TT) is influenced by active Ni metal surface area (Table 2). These results suggest that the catalytic dehydrogenation of DC to NP takes place over surface active metallic Ni sites. 15 wt % Ni/C catalysts with a greater number of surface- active metallic Ni sites show the best catalytic performance. While at higher loadings of Ni, the formation of bigger Ni particles decreases the active metal surface area and thereby diminishes the catalytic

performance in the dehydrogenation reaction. These results clearly indicate that the 15 wt. % Ni loading enough for getting good conversions and selectivity.

The influence of reaction temperature on the dehydrogenation of decalin (DC) was performed over 15NC catalyst and the results were presented in figure 7. The conversion of DC is increased with increase in reaction temperature up to 300°C and reaches a maximum of 88%. The selectivity to NP is also followed the same trend. Beyond this reaction temperature, both the conversion of DC and selectivity to NP is decreased. Hence, these results suggest that the optimum reaction temperature for this reaction under these reaction conditions is 300°C.
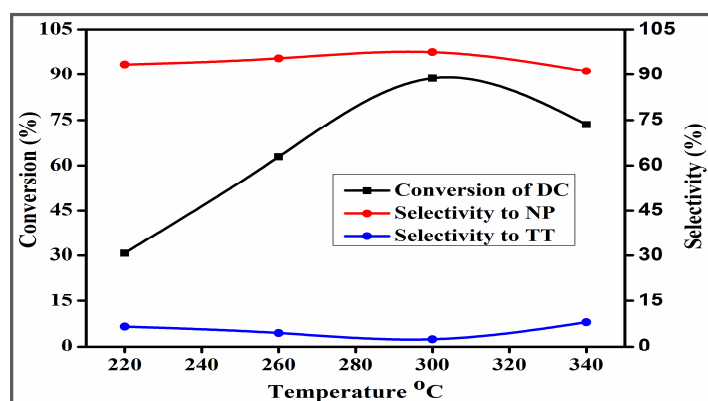

Figure 7. Effect of reaction temperature on dehydrogenation of DC over 15NC catalyst.
Reaction conditions: Weight of catalyst: 0.5g, Feed flow: 0.5 mLh^{-1}, N$_2$Flow: 20 mL min^{-1}.

The time on stream study was performed on 15NC catalyst and the results were presented in figure 8. The results indicate that, the rate of H$_2$ evolution is decreased during the 16 h time on stream study which means the dehydrogenation of DC is decreased during time on stream study. The reason for decrease in the rate of H$_2$ evolution can be assessed by the characterization of the spent catalyst. 15NC spent catalyst was characterized by Thermo Gravimetric Analysis (TGA), CHNS and TEM
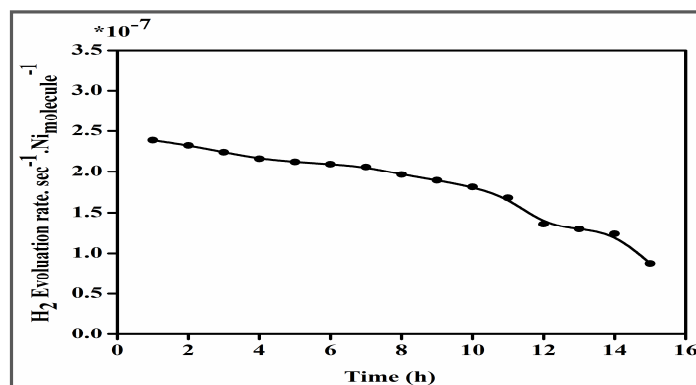

Figure 8. H$_2$-evoluation over 15NC catalysts on dehydrogenation Reaction conditions:
Weight of catalyst: 0.5g, Temperature: 300°C, Feed flow: 30 mL.h^{-1}.

analysis. TGA profiles of fresh and spent 15NC catalysts were presented in figure 9. The 15NC spent catalyst shows higher weight loss compared to the fresh 15NC catalyst. This weight loss is occurred is due to the deposition of carbonaceous species over the 15NC catalyst during time on stream study. CHNS analysis also confirms the presence of carbon in spent 15NC catalyst (68%) than in fresh 15NC catalyst (59%). TEM analysis of spent catalyst show an increase in the particle sizes of Ni after 16 h time on stream study. With these results, the decrease in the conversion of DC or the rate of H$_2$ evolution is due to the deposition of carbonaceous species and agglomeration of Ni over activated carbon.
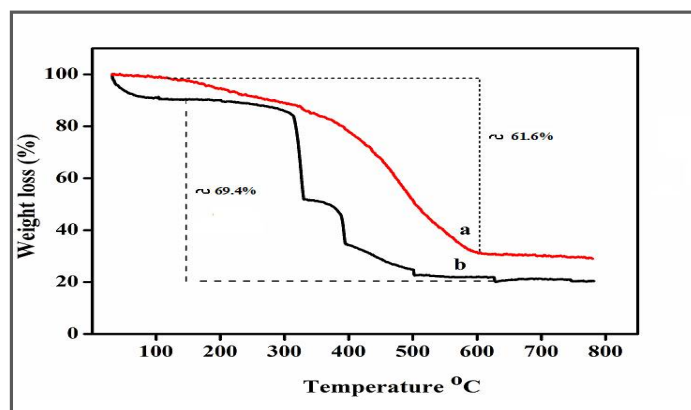
Figure 9. TGA profiles of a) Fresh 15NC, b) spent 15NC catalysts.

APPLICATION

The present activated carbon supported Ni catalytic system offers production of H_2 from liquid organic hydrides in fixed bed down flow reactor. It is noble metal free catalytic system.

CONCLUSION

In summary, activated carbon supported Ni catalysts are found to be efficient for the dehydrogenation of decalin in continuous process at atmospheric pressure. Among all the catalysts, 15 wt% Ni supported on activated carbon catalyst shows good conversion of decalin at 300°C which is attributed to the higher number of active metal sites and dispersion. During the time on steam studies a gradual decline in the catalytic activity is observed due to deposition of coke formed during the reaction and it is strongly evidenced by CHNS and TGA analysis.

ACKNOWLEDGEMENTS

REFERENCES

[1]. G. Cacciola, N. Giordano, G. Restuccia, Cyclohexane as a liquid phase carrier in hydrogen storage and transport, *International Journal of Hydrogen Energy*, **1984**, 9, 411-419.
[2]. G. P. Pez, A. R. Scott, A. C. Cooper, H. Cheng, Hydrogen storage by reversible hydrogenation of pi-conjugated substrates, US Patent No. 7101530.
[3]. R.H. Crabtree, Hydrogen storage in liquid organic heterocycles, Hydrogen storage in liquid organic heterocycles, *Energy Environ Sci.,* **2008**, 1, 134-138.
[4]. R.B. Biniwale, S. Rayalu, S. Devotta,M. Ichikawa, Chemical hydrides: A solution to high capacity hydrogen storage and supply, *International Journal of Hydrogen Energy*, **2008**, 33, 360-365
[5]. A. U. Pradhan, A. Shukla, J. V. Pande, S. Karmarkar, R. B. Biniwale, A feasibility analysis of hydrogen delivery system using liquid organic hydrides, *International Journal of Hydrogen Energy,* **2011**, 36, 680-688.
[6]. Y. Okada, E. Sasaki, E. Watanabe, S. Hyodo, H. Nishijima, Development of dehydrogenation catalyst for hydrogen generation in organic chemical hydride method, *Int. J. Hydrogen Energy,* **2006**, 31, 1348-1356.
[7]. S. Hodoshima, H. Arai, Y. Satio, Liquid-film-type catalytic decalin dehydrogeno-aromatization for long-term storage and long-distance transportation of hydrogen, *Int. J. Hydrog. Energy*, **2003**, 28, 197-204.

[8]. Y.G. Wang, N. Shah, G. P. Huffman, Pure Hydrogen Production by Partial Dehydrogenation of Cyclohexane and Methylcyclohexane over Nanotube-Supported Pt and Pd Catalysts, *Energy Fuels*, **2004**, 18, 1429-1433.

[9]. P. A. V. Trimpont, G. B. Marin, G. F. Froment, Kinetics of methylcyclohexane dehydrogenation on sulfided commercial platinum/alumina and platinum-rhenium/alumina catalysts, *Ind. Eng. Chem. Fundam.,***1986**, 25, 544-553.

[10]. A. C. Cooper, L. D. Bagzis, K. M. Campbell, G. P. Pez, Prepr. Symp.s*Am. Chem. Soc. Di* V. *Fuel Chem.* **2005**, 50(1), 271.

[11]. S. Hodoshima, S. Takaiwa, A. Shono, K. Satoh, Y. Satio, Hydrogen storage by decalin/naphthalene pair and hydrogen supply to fuel cells by use of superheated liquid-film-type catalysis, *Appl. Catal. A Gen.,* **2005***, 283, 235-242.

[12]. M. P. Lázaro, E. García-Bordejé, D. Sebastián, M. J. Lázaro, R. Moliner, In situ hydrogen generation from cycloalkanes using a Pt/CNF catalyst, *Catal. Today*, **2008**, 138, 203-209.

[13]. **S.** Hodoshima, H. Arai, Y. Satio, Liquid-film-type catalytic decalin dehydrogeno-aromatization for long-term storage and long-distance transportation of hydrogen, *Int. J. Hydrog. Energy*, 2003, 28, 197-204.

[14]. N. Jiang, K. S. Rao, M. J. Jin,S**.**E. Park, Effect of hydrogen spillover in decalin dehydrogenation over supported Pt catalysts, *Appl. Catal. A Gen.*, **2012**, 425-426, 62-67.

[15]. Z. Zhou,W. Zhou, S. Wang, G. Wang, L. Jiang, H. Li, G. Sun, Q. Xin, Preparation of highly active 40 wt.% Pt/C cathode electro catalysts for DMFC via different routes, *Catal. Today*, **2004**, 93–95, 523-528.

[16]. N. Kariya, A. Fukuoka, T. Utagawa, M. Sakuramoto, Y. Goto, M. Ichikawa, Efficient hydrogen production using cyclohexane and decalin by pulse-spray mode reactor with Pt catalysts, *Appl. Catal. A Gen.*, **2003**, 247, 247-259.

[17]. R. B. Biniwale, N. Kariya, M. Ichikawa, Dehydrogenation of Cyclohexane Over Ni Based Catalysts Supported on Activated Carbon using Spray-pulsed Reactor and Enhancement in Activity by Addition of a Small Amount of Pt*Catal. Let.,* **2005**, 105(1-2), 83-87.

[18]. F. T. Lechuga, C. G. Hill, M. A. Anderson, Effect of dilution in the experimental dehydrogenation of cyclohexane in hybrid membrane reactors, *J. Membr. Sci.,* **1996**, 118, 85-92.

[19]. T. S. Armadi, Z. L. Wang, T. C. Green, A. Henglein, M. A. El-Sayed, Shape-Controlled Synthesis of Colloidal Platinum Nanoparticles*Science,***1996**, 272, 1924-6.

[20]. L. G. Pratibha, R. Roper, M. G. White, *Curr. Opin.Solid State Mater.Sci.***2002**, 6, 401.

[21]. M. H. Yuan, C. Y. Chang, J. L. Shie, C. C. Chang, J. H. Chen, W. T. Tsai, Destruction of naphthalene via ozone-catalytic oxidation process over Pt/Al2O3 catalyst, *J. Hazard. Mater.***2010**, 175, 809-15.

[22]. Q. Zhou, P. Li, X. Wang, X. Zhou, D. Yang, D. Chen, Preparation of CNF-supported Pt catalysts for hydrogen evolution from decalin, *Mater ChemPhys,***2011**, 126, 41-45.

[23]. P. D. Tien, T. Satoh, M. Miura, M. Nomura, Efficient and Reusable Palladium Catalysts Supported on Activated Carbon Fibers for Dehydrogenation of Tetrahydronaphthalene, *Energy Fuels*, **2005**, 19, 731-735.

[24]. P. Sun, G. Gao, Z. Zhao, Ch. Xia, F. Li, Stabilization of Cobalt Catalysts by Embedment for Efficient Production of Valeric Biofuel, *ACS. Catal.,* **2014**, 4, 4136-4142.

[25]. M. Surendar, T. V. Sagar, B. HariBabu, N. Lingaiah, K. S. Rama Rao, P. S. S. Prasad, Glycerol steam reforming over La–Ce–Co mixed oxide-derived cobalt catalysts, *RSC. Adv.* **2015**, 5, 45184-45193.

[26]. G. J. B. Voss, J. B. Floystad, A. Voronov, M. Ronning, *Top. Catal.* **2015**, 58, 8964.