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ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (3): 939-947

(International Peer Reviewed Journal)

Pt-Ni/Al_2O_3 Bimetallic Catalysts for Vapor Phase Dehydrogenation of Decalin

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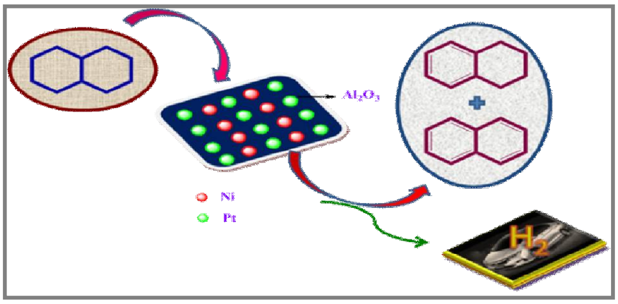
ABSTRACT

The present study investigates the promotional effect of bimetallic catalysts compared to the monometallic catalysts in vapor phase dehydrogenation of decalin. A series of Al_2O_3 supported Pt-Ni bimetallic and their monometallic catalysts were prepared by sequential wet impregnation and simple wet impregnation methods respectively. As synthesized catalysts were characterized by powder XRD, BET-surface area, Temperature programmed reduction (H_2-TPR), H_2-pluse chemisorption, TGA, CHNS analysis, SEM and TEM techniques. 1wt.% Pt-3 wt. % Ni/Al_2O_3 catalyst exhibited the highest dehydrogenation activity than corresponding monometallic catalysts due to the presence of more number of active metallic sites in the catalyst. The hydrogen evaluation rate over 1 wt.% Pt-3 wt. %Ni/ Al_2O_3 catalyst was about $30.32\times10^{-6}sec^{-1}$ during 10 h time on stream study.

Graphical Abstract



Keywords: Decalin, Pt-Ni, Bimetallic catalysts, Dehydrogenation.

INTRODUCTION

Hydrogen, a clean energy carrier has good prospects in hydrogen fuel cells and alternative energy sources. Storage and supply of hydrogen for fuel cell without CO is one of the promising solutions in transportation. The dehydrogenation of cyclic hydrocarbons such as decalin, tetralin, cyclohexane, and methylcyclohexane are receiving an increasing amount of attention as organic liquid hydrogen storage materials [1–3]. Among all the liquid organic hydrides, decalin is one of the best candidates because of its excellent hydrogen storage density of 7.2 wt%. Moreover, decalin is an environmentally friendly hydrogen carrier without CO and CO_2 emission in the dehydrogenation process [**4, 6-14**]. It is renowned that the decalin dehydrogenation reaction is an endothermic reaction. Many researchers have studied the dehydrogenation of these organic hydrides in vapour phase. Kariya et al. studied Pt-Re, Pt-Pd, and Pt-Rh catalysts for cycloalkane dehydrogenation and reported that bimetallic catalysts showed better catalytic performance than their monometallic counter parts [**5**]. Lei *et al.*, studied Pt and Ni supported on carbon catalysts for the dehydrogenation of decalin [**15**]. It has been demonstrated that the structure of the bimetallic surfaces plays a considerable role in controlling their electronic and catalytic properties. Often bimetallic catalysts demonstrate distinctly different electronic and chemical properties from those of the parent metals; offer the chance to design new catalytic materials with improved activity, selectivity and stability. In this context, a series of Pt and Ni and combination of Pt-Ni supported on Al_2O_3 were prepared by wet impregnation method and evaluated for the vapor phase dehydrogenation of decalin. Various reaction parameters were optimized and the catalytic activity was correlated with the characterization results.

MATERIALS AND METHODS

Catalyst preparation: Alumina (M/s. Sud-Chemie India Pvt. Ltd) supported Pt, Ni and Pt-Ni catalysts were prepared by wet impregnation method. In a typical method for mono-metallic catalysts, requisite amount of metal precursor ($H_2PtCl_6.6H_2O$ (M/s. Sigma Aldrich, 99.9%) or Ni $(NO_3)_2.6H_2O$ (M/s. Alfa Aeaser, 99.9%)) was dissolved in deionized water and γ-alumina support was added to the solution and heated on a hot plate at 344 K until to complete dryness. The solid was dried in hot oven at 373 K for 12 h and then calcined in air at 673 K for 3 h. The resultant solid was denoted as xNiAl or xPtAl where x indicates the weight percentage of the metal. In the same fashion, the Pt-Ni/Al_2O_3 catalysts were prepared in sequential impregnation method where Ni was impregnated first followed by Pt. The resultant solid was denoted as xPt-yNiAl where and y indicate the weight percentage of corresponding metal.

Catalyst Characterization: X-ray diffraction patterns of all the catalysts were obtained on an Ultima-IV (M/s. Rigaku Corporation, Japan) XRD unit and it is operated at 40 kV and 40 mA equipped with nickel-filtered Cu Kα radiation ($\lambda = 1.54056$ Å) and a 2θ value ranging from 10 to 80° at a scanning rate of 0.5 degree/min. BET specific surface areas, pore volumes and pore sizes was determined by using the N_2physisorption studies (M/s. Quantachrome Instruments, USA) by nitrogen adsorption at 77 K. Prior to measurement, the samples were degassed at 423 K for 2 h. The morphological studies of catalysts were carried out by scanning electron microscope (M/s. JEOL, Switzerland) and TEM images were obtained on a JEM 2000EXII apparatus (M/s. JEOL, Switzerland) operating between 160 and 180 kV respectively. Prior to TEM analysis, the catalyst sample was ultrasonicated in ethanol and a drop was placed onto a carbon coated copper grid, the solvent was then evaporated in an air oven at 353 K for 6 hours. Temperature programmed reduction (TPR) was performed in a laboratory-built equipment containing a quartz reactor with electrical heating and gas chromatograph equipped thermal conductivity detector (TCD). About 100 mg of catalyst placed at the centre of the quartz reactor between two plugs of quartz wool was pre-treated at 573 K for 1 h in Ar flow (60 mL min^{-1}). Then the catalyst was exposed to 5% H_2 balance Ar gas flow for 1 h at 373 K followed by raising the temperature of sample up to1123K at a heating rate of 10 K min^{-1}.

Catalytic activity: The vapor phase dehydrogenation of decalin was performed in a fixed-bed flow reactor. In a typical experiment, decalin was injected (0.5 mL h^{-1}) with a microfeeder to the reactor containing catalysts at different temperatures under nitrogen stream (20 mL min^{-1}). Before conducting the reaction all catalysts were reduced in H_2 stream with 40 mL/min. After the reaction, the condensed product mixture was collected in an ice cold trap periodically for every 1 h and analyzed by GC (Shimadzu-17A) equipped with FID detector and EB-5 capillary column (30 m Lx0.5 mm I.D). Prior to regular analysis, the products were identified by GC-MS (Shimadzu-QP 5050) equipped with DB-5 capillary column (30 mLx0.32 mm I.D).

$$\text{Conversion (\%0} = \frac{\text{Moles of reactant fed-Moles of reactant remaining}}{\text{Moles of reactant fed}}$$

$$\text{Selectivity (\%)} = \frac{\text{Moles of product formed}}{\text{Moles of reactant converted}} \quad \text{X } 100$$

$$\text{Rate (moles sec}^{-1}\text{ g}^{-1}) = \frac{\text{(Feed flow rate (moles/sec) x fractional conversion)}}{\text{Weight of the catalyst}}$$

RESULTS AND DISCUSSION

X-ray diffraction Analysis: The XRD analysis of calcined catalysts at 673 K was shown in figure1a. The peaks at 2θ values of 37.8, 45.7 and 67.6° are assigned to Al_2O_3 support. The reduced catalysts were presented in figure 1 did not show any characteristics peaks for platinum or nickel species suggesting that the fine PtO_2 and NiO particles are highly dispersed on support [16]. The metallic platinum diffraction peaks observed at 39.7, 46.3, 67.8 and 81.6° which can be assigned to the crystalline phases (111), (200), (220) and (311) planes [17, 18]. The diffraction peak at 2θ value of 52° indicates the presence of metallic Ni species. In all the catalysts, the intensities of diffraction peaks are less intense which represents the active metallic species are in highly dispersed form over the support Al_2O_3.

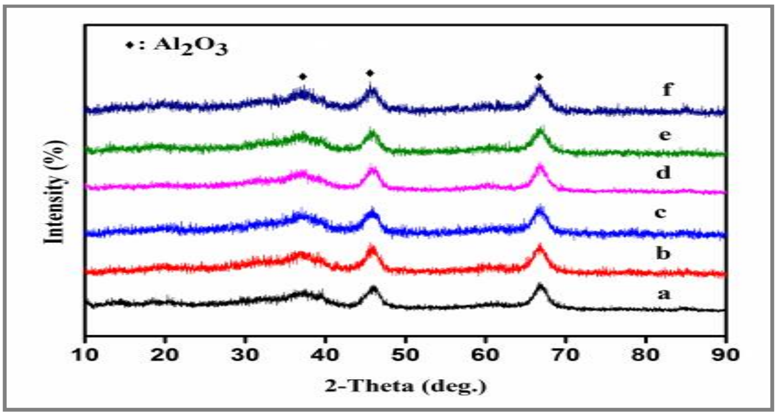


Figure1. Powder XRD patterns of a) Al_2O_3b) 3Ni/Al_2O_3, c) 5Ni/Al_2O_3, d) 1Pt/Al_2O_3, e) 1Pt-3Ni/Al_2O_3 andf) 1Pt-5Ni/Al_2O_3catalysts.

Table 1. Physico-chemical properties of alumina supported catalysts

Catalyst	BET Surface area ($m^2.g^{-1}$)	N_m (μ moles.g^{-1})	Metal surface area (m^2/g_{cat})	Average particle size (nm)	Dispersion (%)	Particle Size (nm)	
						XRD	TEM
Al_2O_3	242	-	-	-	-	-	-
3NiAl	165	19.99	2.14	5.2	19.5	4.73	-
5NiAl	182	21.33	2.29	4.9	20.8	3.69	-
1PtAl	196	23.99	2.57	4.4	23.4	4.46	-
1Pt-3NiAl	206	26.45	2.83	4.1	25.8	4.34	4.67
1Pt-5NiAl	197	22.15	2.38	4.7	21.6	4.38	-

Temperature programmed reduction analysis: To find out the improvement of catalytic performance over Pt-promoted Ni/Al_2O_3 catalysts, the interactions between Pt and Ni and interactions between metals and supportAl_2O_3 were investigated by the temperature programmed reduction (TPR). The monometallic supported Ni catalysts, the TPR curves show two sets of H_2 consumption peaks. The first set of peak was low temperature reduction peak obtained at temperatures lower than 873 K. These peaks were attributed to NiO species with different extent interactions with the support. Second set of peaks occurred around 800°C is high reduction peak corresponds to $NiAl_2O_4$ phases [19]. TPR profile of calcined bimetallic catalysts showed a low reduction peak belongs to the PtO_2 to Pt metallic state. The reduction peak at the range of 873-1017K corresponds to the reduction of Ni^{+2} ions deposited on the aluminate structure.

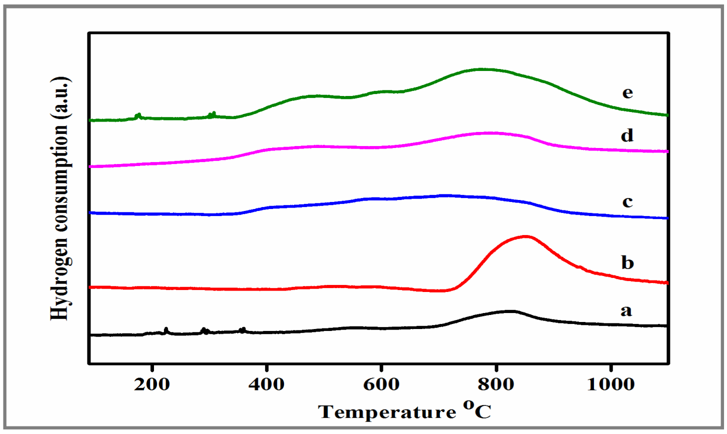


Figure 2. TPR patterns of a) 3Ni/Al_2O_3, b) 5Ni/Al_2O_3, c) 1Pt/Al_2O_3, d) 1Pt-3Ni/Al_2O_3 and e) 1Pt-5Ni/Al_2O_3catalysts.

Transmission Electron Microscopy (TEM) analysis: The typical SEM and TEM images were depicted in Fig. 3 and it can be seen the Pt-Ni alloy particles spread out uniformly on the surface of alumina support. The metal particle size was estimated to be 4.9 nm for fresh catalyst. The surface morphology was analyzed by Scanning Electron Microscopy. A representative SEM images fresh and used Pt–Ni catalyst has a high porosity and specific surface area, which offers more active sites and larger reaction zone for decalin molecules; therefore it is beneficial in terms of mass specific activity of Pt. After conducting reaction the metal content on the catalysts increases slightly, which is explained by the agglomeration of metal particles [20]. Both the metal agglomeration and coke formation contribute to deactivation of catalysts.

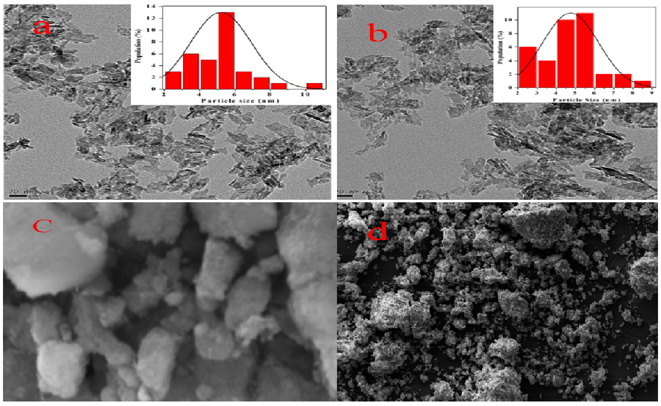
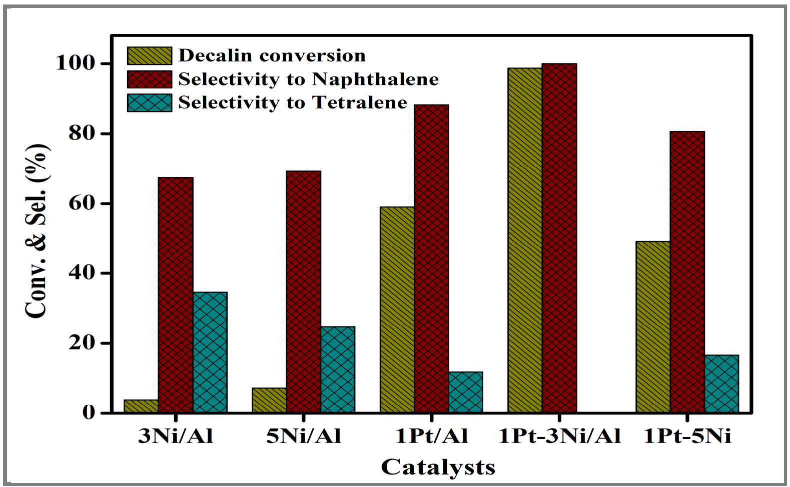


Figure 3. TEM and SEM image of 1Pt-3Ni/ Al_2O_3catalyst a, c) Reduced and b, d) Used.

Catalytic activity studies

The effect of mono and bimetallic catalysts: The catalytic activity over mono and bimetallic catalysts was studied and the results were presented in figure 4. The monometallic nickel catalysts (3Ni/Al and 5Ni/Al) showed more or less 20% conversion of decalin. On the other hand, the 1Pt/Al catalyst exhibited 59% conversion of decalin. By the addition of 3 wt. % Ni, the 1Pt-3Ni/Al catalyst reached a maximum conversion of decalin. Further addition of 5 wt. % Ni, 1Pt-5Ni/Al catalyst exhibited a down fall in conversion of decalin.



Reaction conditions: 300°C, 30 mL h^{-1} and 500 mg catalysts.

Figure 4. Dehydrogenation of decalin over monometallic catalysts with 1Pt- 3Ni/ Al_2O_3 catalyst.

These results can be ascribed to dispersion of active metallic sites over support. In the case of monometallic catalysts the dispersion is low, and the bimetallic catalysts possessed not only high dispersion but also the formation of synergetic effect between the Ni and Pt metallic species.

The effect of reaction temperature: The effect of reaction temperature on catalytic activity and selectivity was studied at temperature range of 498-573 K over 1Pt-3Ni/Al catalyst and results were presented in Fig. 5. The conversion of decalin increases with increase in temperature and product selectivity towards naphthalene is constant, but the intermediate tetralin was decreases with high temperature due to endothermic nature of decalin dehydrogenation reactions.

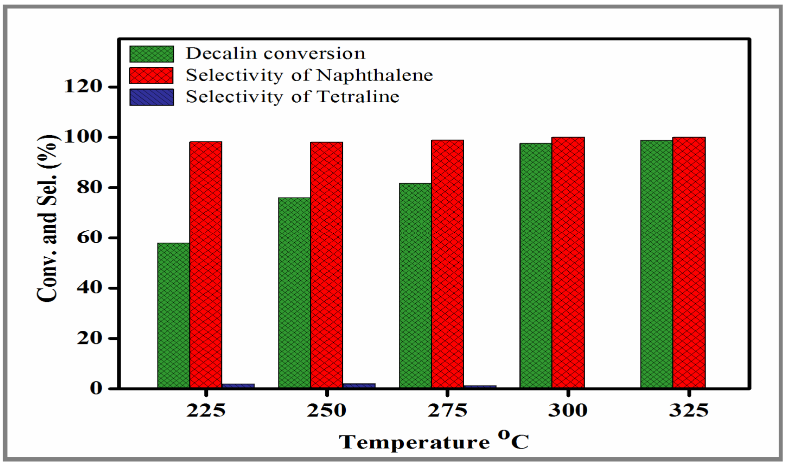
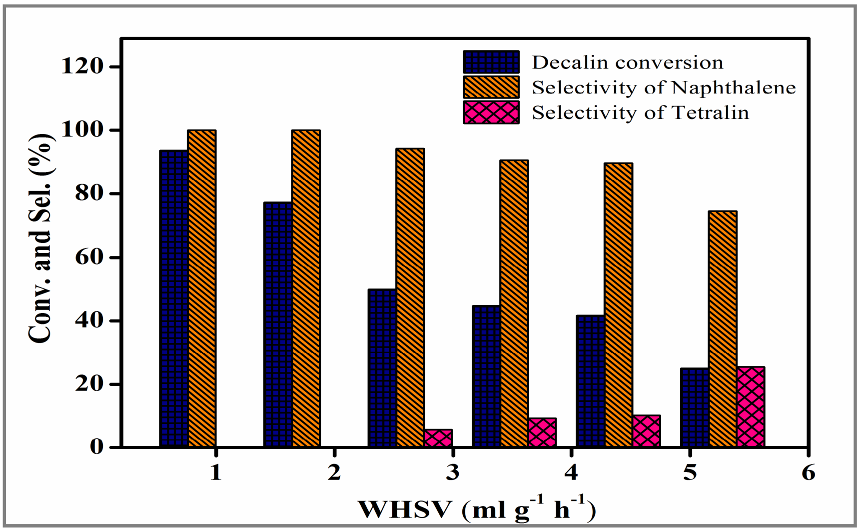


Figure 5. Effect of reaction temperature on decalin conversion and the selectivity of naphthalene and tetralin over 1Pt- 3Ni/ Al_2O_3 catalyst. Reaction conditions: 500 mg of catalyst, 30 mLh^{-1}, 20 mL min^{-1} of N_2 flow.

At reaction temperature of 498K the conversion of decalin is 58% and it reaches a maximum of 98% at reaction temperature of 573K. Beyond this reaction temperature there is no considerable change in the conversion and selectivity. Hence, the optimum reaction temperature for decalin dehydrogenation under these reaction conditions is 573K.

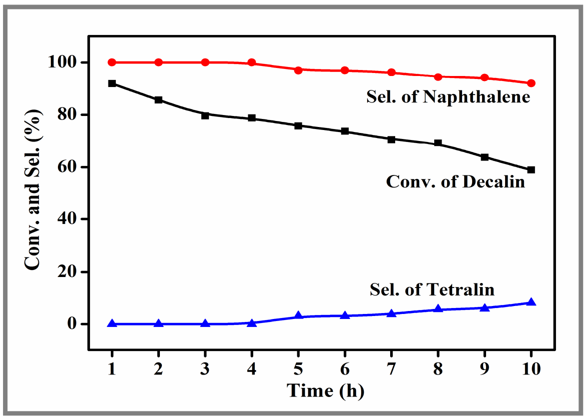
Effect of feed flow rate: The effect of flow rate of reactant on catalytic activity of 1Pt-3Ni/Al catalyst was examined and the results were shown in figure 6. At a WHSV of 0.879 h^{-1}, maximum conversion of decalin and selectivity's to naphthalene were observed and further increase in WHSV led to decrease in the conversion of decalin and slight decreases to the selectivity of naphthalene. The increase in WHSV increases the formation of tetralin and the selectivity to naphthalene also decreases. The low catalytic activity at high WHSVs is due to the increase in amount of reactant molecules per active metallic sites. The number of active metallic sites is low when compared to the amount of reactant molecules during the unit time of reaction.



Reaction conditions: Catalyst weight=0.5 g, Temperature=573 K,
WHSV=0.879 $ml.g^{-1}.h^{-1}$.

Figure 6. Effect of flow rate of reactant on the dehydrogenation of DC to NP over 1Pt- 3Ni/ Al_2O_3 catalyst.

Reaction evolution with time: In order to know the stability of 1Pt-3Ni/Al catalyst, time-on-stream studies were conducted and results were presented in figure 7. From the results, it can be observed that there is a decline in the catalytic activity during 10 h time on stream study. Based on the time on stream studies, the rate of H_2 evolution was calculated and presented in figure 9. The reason for decrease in the rate of H_2 evolution can be assessed by the characterization of the spent catalyst. 1Pt-3Ni/Al catalyst spent catalyst was characterized by Thermo Gravimetric Analysis (TGA), CHNS and TEM analysis. TGA profiles of fresh and spent 1Pt-3Ni/Al catalyst were presented in figure 8. The 1Pt-3Ni/Al spent catalyst shows higher weight loss compared to the fresh 1Pt-3Ni/Al catalyst. This weight loss is occurred is due to the deposition of carbonaceous species over the 1Pt-3Ni/Al catalyst during time on stream study. CHNS analysis also confirms the presence of carbon in spent 1Pt-3Ni/A catalyst (5.3%). TEM analysis of spent catalyst show an increase in the particle sizes after 10 h time on stream study. With these results, the decrease in the conversion of decalin or the rate of H_2 evolution is due to the deposition of carbonaceous species and agglomeration of metallic species over activated carbon.



Reaction conditions:0.5g of catalyst, 30 mL h^{-1}, 20 mL min^{-1} of N_2 flow, 573K of reaction temperature.

Figure 7. Effect of reaction time on decalin conversion, the selectivity of naphthalene and tetralin over 1Pt- 3Ni/ Al_2O_3 catalyst.

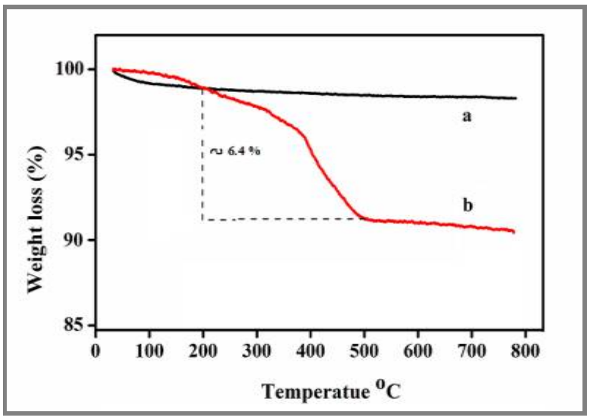


Figure 8. TGA data of 1Pt- 3Ni/ Al_2O_3 a) fresh and b) spent catalyst.

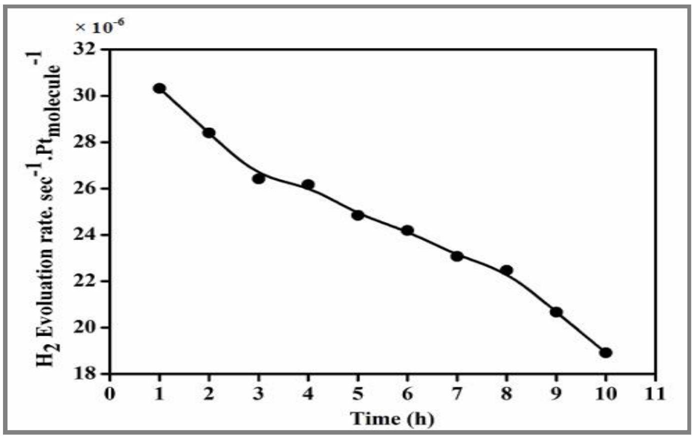


Figure 9. Hydrogen evaluation of 1Pt- 3Ni/ Al_2O_3 catalyst for 10 h.

Table 2. CHNS and TGA data of fresh and spent catalysts

Catalyst	Carbon (%)	
	CHNS	TGA
1Pt-3Ni (F)	0	0
1Pt-3Ni (U)	5.3	6.4

APPLICATION

The present sequential impregnation of bimetallic catalysts for catalytic system offers production of H_2 from liquid organic hydrides in fixed bed down flow reactor.

CONCLUSION

The catalysts of Al_2O_3 supported mono and bimetallic catalysts were synthesized by sequential wet impregnation method and adopted to decalin dehydrogenation by vapor phase conditions at atmospheric pressure. Among all the catalysts the 1Pt-3Ni/Al catalyst found to be the best catalyst for the decalin dehydrogenation. The 1Pt-3Ni/Al catalyst revealed excellent catalytic performance due to high dispersion and more surface area comparatively mono metallic catalysts. The impact of temperature on decalin dehydrogenation also studied and observed that at lower temperature the conversion of decalin is less. With the increase of temperature the conversion also found to increase and reaches maximum at 573 K over 1Pt-3Ni/Al catalyst. The decrease in conversion of decalin was observed during the time-on-stream which could be ascribed due to the coke formation and it is strongly evidenced by CHNS and TGA analysis.

ACKNOWLEDGEMENTS

The authors would like to thank CSIR, New Delhi, CSIR-IICT, Hyderabad and Osmania University for financing this work.

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