A comparative study of catalytic functionalities of Ni/RHSiO$_2$ and Ni/RHAC's for nitrobenzene hydrogenation

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Abstract

Highly dispersed nickel nanoparticles on supports such as rice extracted SiO$_2$, and Activated carbon's were prepared by impregnation and reductive deposition method by using hydrazine as reducing agent. The high light of this work is to compare the characteristics and activity of the catalysts prepared by both impregnation and reductive deposition method. All catalysts were characterized by various techniques such as BET, SEM, XRD, reduction behavior by using TPR technique. XRD results suggests that all the catalytic systems showing peaks corresponding to the supports as well as metal precursor. Ni/RHSiO$_2$, catalyst prepared by reductive deposition method show excellent conversion of nitrobenzene to aniline. This is due to the presence of higher number of well dispersed surface Ni species than other catalysts as evidenced by SEM studies. TPR results reveal the formation of metallic Ni species in the reductive deposition method.

Key words : Rice Husk, Silica, Activated Carbon, Nickel, Hydrogenation, Aniline

I. Introduction

It was found that Rice husk char contains amorphous silica in addition to amorphous carbon as the main constituents[1]. Many authors have concluded that rice husk is an excellent source of high grade amorphous silica[2-4]. This portion of the silica cannot be dissolved in alkali and can withstand very high temperatures[5]. Production of activated carbon from rice husk has also have peoples interests. Active carbon has good adsorption property, can be produced from a variety of raw materials, such as packing papers, plastic bottles, by-products of the timber industry (e.g. sawdust), straw, rice husk, seeds or fruit shells can be mentioned. Interest is growing on agricultural waste for the production of activated carbon. Production of activated carbon from rice husk is achieved through activation with chemical or physical means. Chemical impregnation with KOH, NaOH, ZnCl$_2$ or H$_3$PO$_4$ of

pyrolysed rice husk followed by activation at 650–850°C results in activated carbons with extremely high surface areas (750–3014m2/g)[6,7].

II. Literature Review

Recently, supported nickel catalysts were reported for various organic transformations such as hydrogenation[8,9], steam reforming reactions[10] reductive amination of alcohols[11] hydrodechlorination[12] partial oxidation[13], and dry reforming of methane[14]. Amongst, hydrogenation is of great interest for both industry and academia. The synthesis of aniline is generally done by the nitrobenzene hydrogenation. Aniline is an important raw material for synthesis of more than 300 different end products industrially, aniline is mainly used for the production of methylene diphenyl diisocyanate (MDI), a key compound in the production of polyurethane rigid and/or semi-rigid foams and elastomers. It is also used as a solvent, and has been used as an antiknock compound for gasoline[15,16]. Conversion of Levulinic acid to γ-Valerolactone was carried out by Srinivas et al by using the Ni catalysts coated on Silica extracted from rice husk[17]. Recently Feng et al studied Ni based catalysts for catalytic hydrogenation of p-nitrophenol[18]. Aniline finds application in various end-use markets including construction, rubber products, transportation, consumer, adhesives/sealants, packaging, agriculture, textiles, coatings, photography, dyes, and pharmaceuticals. A predominant proportion of the worldwide aniline production is utilized in the manufacture of polyurethanes, which are used in a wide array of applications including footwear, insulation and furniture. The global aniline market is projected to reach 6.2 million tons by the year 2015, due to the increasing demand from various end-user markets. In particular, the rising demand from methylene diphenyl diisocyanate (MDI), the chief ingredient in polyurethane foam, is expected to fuel consumption of aniline[19]. In present study activated carbons and silica extracted from rice husk are used as supports for preparation of hydrogenation catalysts

and synthesis of Ni catalysts by reductive deposition method without using any capping agent as an efficient catalyst for the hydrogenation of nitrobenzene at atmospheric pressure in vapour phase.

III. Experimental Procedure :
3.1 Preparation of Activated Carbons from rice husk:

A tubular furnace for carbonization provided with temperature programmer was used to prepare activated carbons. 10 gr of dried rice husk was heated in the furnace under nitrogen atmosphere at 10^0C/min. from room temperature to a 600^0C and maintained for an hour. After carbonization, the furnace was cooled to room temperature under continuous flow of nitrogen to avoid post oxidation process. Thus produced solids were washed with hydrochloric acid (1M) followed by thorough washing with hot distilled water to remove chloride ions and other residues until the pH became neutral. The purified solids were dried at 110^0C for 10 hr. Thus produced bio char is activated by using H_3PO_4 reagent to modify surface properties. 5 gr. of this bio char is first impregnated with 30 wt. % H_3PO_4 and then heated at 250^0C under air for 2 hr. Then the same sample is subjected to heating at 600^0C under nitrogen atmosphere for activation. This sample is named as RHAC.

3.2 Extraction of Silica from rice husk:

First, 10 g of pyrolytic rice husk char was pretreated with 200 ml of HCl (1 M) to remove most of the impurities and to improve the purity of silica. The char was introduced in a flask and the suspension was boiled for 3 hr. under reflux condenser and vigorous stirring. Then, the suspension was filtered and the solid was washed with distilled water until neutral pH. Finally the char recovered was dried for 15 hr. at 120°C. The next step was to remove the silica with a 15 wt. % Na_2CO_3 solution. The char and 200 ml of this solution were introduced in a flask and boiled for 4 hr. under reflux condenser. The suspension was flltered and the precipitate was washed with distilled water until the pH becomes neutral followed by drying at 120°C for 24 h. The precipitate is the resulting carbon material

from which activated carbon materials can be prepared by chemical activation process. The filtrate is a solution of sodium silicate, which was subjected to a carbonation process in order to recover the silica. Thus, the solution was heated to around 80°C under continuous flow of carbon dioxide. After 1 h, the carbon dioxide flow was stopped and the solution was cooled down. Finally, the silica precipitate was filtered and dried at 120°C for 24 hr. and labelled as $RHSiO_2$.

3.3 Catalyst preparation :
3.3.1 Preparation of supported nickel catalysts by impregnation:

Rice husk extracted AC and SiO_2 supported Ni catalysts were prepared by conventional impregnation (IM) method with 5 wt. % Ni. In this method, calculated amounts of aqueous metal precursor solution was added to supports and after allowing overnight adsorption, the excess water was removed by evaporation followed by drying at 393 K for 12 h and calcination at 723 K for 5 h. The catalysts were reduced in H_2 flow at 500°C for 4 h before its use for nitrobenzene hydrogenation reactions. These catalysts are designated as Ni/RHAC (I), Ni/RHSiO$_2$ (I)

3.3.2 Preparation of supported nickel catalysts by reductive Deposition method :

In the reductive Deposition method $RHSiO_2$ and RHAC supports were first dispersed into aqueous solution of $Ni(NO_3)_2.6H_2O$ containing 5wt % Ni with respect to the support. 1 M NaOH was slowly added to the solution containing the Nickel precursor and the support to get a PH value of the mixture to 10. Then N_2H_4 solution was added. The suspension was then maintained at the same pH for 1h. The resultant solid was filtered and washed with de-ionized water several times until no sodium ion was detected. The solid thus obtained was oven dried at 120 °C for 12 h. The catalysts were reduced in H_2 flow at 500°C for 4 h before its use for hydrogenation reaction. The catalysts are labelled as Ni/RHAC (R), Ni/RHSiO$_2$ (R).

3.4 Catalyst characterization :

All the above catalysts were characterized by XRD, BET method, TPR and SEM.

3.5 Activity studies :

A layer of silicon beads have been placed to act as a preheating zone, above catalyst bed taken in a fixed bed reactor. Isothermal conditions were ensured by diluting the catalyst bed with ground silica beads. Reaction temperature was continuously monitored by a thermocouple inserted in a thermowell which was placed within the catalyst bed. The liquid reactant was delivered to the reactor from a glass /Teflon air-tight syringe and Teflon tube using a microprocessor controlled infusion pump, at a required flow rate. NB and ultra-pure H_2 were maintained with an inlet NB flow $=1$ml h^{-1} and H_2 flow of 1 time in excess of the stoichiometric requirement (H_2/NB molar ratio $= 4$). In a blank test, passage of NB reactant along with stream of H_2 through an empty reactor or over the support alone did not result in any appreciable NB conversion. The product mixture was cooled in an ice cooled trap and the analysis were performed on a gas chromatograph, equipped with a flame ionization detector, with a OV-1 (30 m length 0.53 mm i.d., 0.33 mm film thickness) capillary column.

IV. Results and Discussion

4.1 Surface area & Pore size :

Surface area and pore size of the catalysts are determined by BET method with the help of nitrogen adsorption isotherms. Table-1 shows the details of the surface properties of pure supports and Ni coated catalysts. Silica supported Ni catalysts shows high surface area than Ni coated on activated carbon catalysts. However pore size in both the cases remains almost same. Catalysts in which Ni is incorporated through reductive deposition precipitation method shows higher surface area than the catalysts prepared by impregnation method. This indicates that the high surface area of Ni-RHAC (R) and Ni-RHSiO$_2$ (R) catalysts is due to better dispersion of nickel metal on surface of the support where nickel also contributes to the additional surface area.

Table 1. Surface area and pore size of Ni/RHAC and Ni/RHSiO$_2$ catalysts

| S.No.	Sample	Surface area (m^2/g)	Pore diameter (nm)
1	RHSiO$_2$	595.2	3.12
2	5Ni-RHSiO$_2$(I)	548.6	3.06
3	5Ni-RHSiO$_2$(R)	564.1	3.0
4	RHAC	462.0	2.86
5	5Ni-RHAC (I)	414.5	2.64
6	5Ni-RHAC (R)	429.3	2.76

4.2 Comparative study of XRD patterns of Ni on activated carbons and silica supports:

XRD patterns of all nickel-catalysts supported on activated carbon and silica are shown in Fig.1. The presence of NiO phase in these catalysts suggests the decomposition of nickel nitrate in air during the calcination results in the formation of NiO species. In the XRD profile of the Ni/RHSiO$_2$ catalyst a broad peak at 22° is due to amorphous silica. According to the literature, the reflection peaks at $2\theta = 37.28, 43.3, 62.8$ and $75.3°$ can be ascribed due to the NiO phase. Moreover the reflection peaks at $2\theta = 37.28$ and $62.8°$ can also be attributed to nickel silicate[20]. XRD patterns for the activated catalysts are presented in Fig. 1. Peaks at $2\phi = 26.8$ correspond to the graphite plane of carbon. Reflections appearing at 43.58, 52.88 and 79.58 correspond, respectively, to the planes of metallic nickel, which are consistent with an exclusive cubic geometry[21] and establish the presence of Ni0 before activation of catalyst. However there is no much difference between the XRD patterns for catalysts prepared by impregnation and reductive deposition precipitation method.
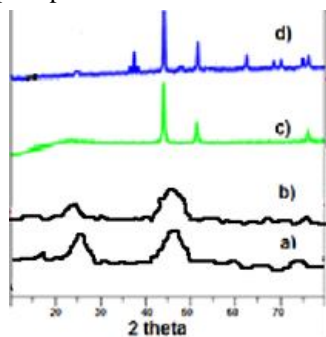
Fig.1 a) Ni/RHAC (I) b) Ni/RHSiO$_2$ (I) c) Ni/RHAC (R), d)Ni/RHSiO$_2$ (R)

4.3 SEM studies :

The SEM images of catalysts prepared by reductive deposition precipitation method (Fig. 2) shows the presence of well dispersed Ni particles than in the impregnated catalysts. The greater nucleation in the impregnation method leads to agglomeration of metal nanoparticles.
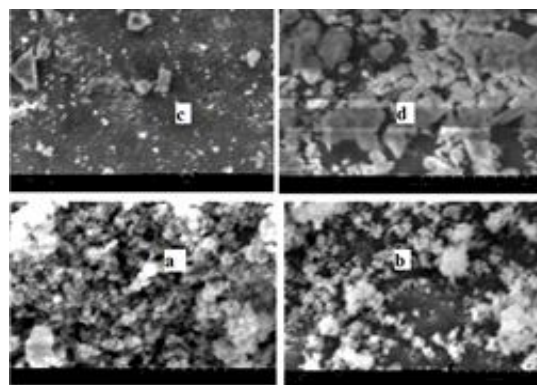
Fig. 2 SEM images a) Ni/RHAC (I), b) Ni/RHSiO$_2$(I) c) Ni/RHAC (R) d) Ni/RHSiO$_2$(R)

4.4 TPR studies :

TPR gives important information for the supported metal catalyst regarding the metal-support interactions and also the temperature at which the metal oxide gets reduced to metal. The TPR profiles of the nickel-based catalysts are shown in Fig. 3. Pompeo *et al.*, suggested that the TPR patterns of Ni/SiO$_2$ catalyst shows two reduction peaks at around 450 and 610°C [22]. The first of them is due to the presence of NiO species of low interaction with the support, while the signal at 610°C is due to the presence of nickel oxide interacting chemically with the support forming nickel silicate[22]. The strong interaction between the

nickel metal and silica could be probably due to an increased interfacial area. A hydrogen consumption peak at 347–357^{0}C is observed for Ni/RHAC catalyst. As this peak is absent in the case of the supports, it can be attributed to the reduction of NiO. A comparable reduction peak (Tmax = 300^{0}C) has been previously reported by Bitter et al. for a Ni/C prepared in a similar fashion[23]. While in case of reductive precipitation catalysts, no significant consumption of hydrogen was observed which clearly indicates the presence of Ni in metallic state,
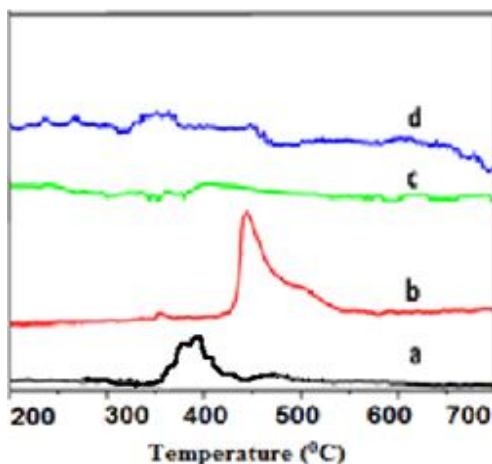

Fig. 3 - TPR profiles of all the Ni based catalysts
a) Ni/RHAC (I) b) Ni/RHSiO$_2$ (I) c) Ni/RHAC (R),
d)Ni/RHSiO$_2$ (R)

4.5 Effect of temperature :

The catalysts prepared by reductive deposition method are found to be efficient for the production of aniline than for the impregnated catalysts (Fig. 4). Moreover, among all the catalysts Ni/RHSiO$_2$ (R) catalyst prepared by reductive deposition method is found to be an efficient catalyst due to high Ni dispersion as well as smaller Ni particle size than the others. Additionally, the SEM result also supports the presence of smaller Ni particles on this catalyst. Among all the temperatures, 250°C is an optimum temperature for yielding the aniline at cent percent conversion. Because of reducible nature of SiO$_2$, strong metal support interaction (SMSI) prevails between the Ni and SiO$_2$. That's why Ni dispersion and thereby nitrobenzene conversion is higher with this catalyst than in the Ni/RHAC and others. The selectivity

towards aniline is 100%. Because of the exothermic nature of nitrobenzene hydrogenation reaction, decline in the activity (initial nitrobenzene conversion) at higher temperatures (above 250°C) is observed on both the catalysts. (Fig. 4). However, the selectivity to aniline remains at 100% on both the catalysts at all temperatures.
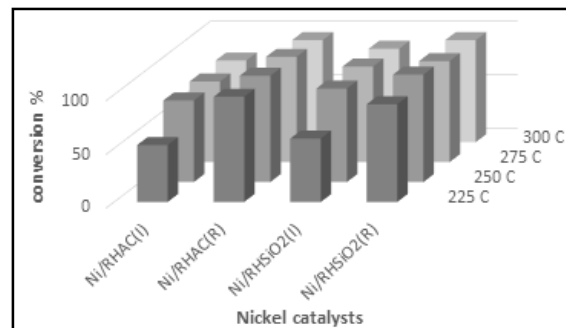

Fig. 4 Effect of support and preparation method on the NB conversion over Ni based catalyst

4.6 Effect of time on stream :

The stability of Ni/RHSiO$_2$ catalyst prepared by reductive deposition method can be observed from Fig. 5 during the time on stream for 10 h at 250°C. Silica supported Ni catalysts are showing better conversion rates and stability than activated carbon supported Ni catalysts. The conversion of nitrobenzene over this catalyst is decreasing slightly during the course of time, may be due to the condensation of reaction intermediates like water and coke formation. The formation of coke might be main cause for the deactivation of the catalyst during the course of reaction.
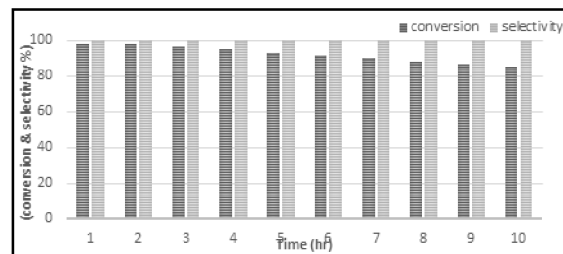

Fig.5 Time on stream study on Ni/RHSiO$_2$ (R) for the Nitrobenzene hydrogenation

Conclusions
- Extraction of silica and preparation of activated

carbon from rice husk adds value to agricultural bio waste materials.

- Preparation of nickel catalysts through reductive deposition method proves to be better one than the conventional impregnation method.
- TPR results shows hydrogen consumption which is ascribed to a reduction of the metal precursor in tandem with a Ni- catalyzed decomposition of surface active groups.
- The catalysts prepared by reductive precipitation method are found to be efficient for the hydrogenation of nitrobenzene.
- Among all the catalytic systems, Ni/RHSiO$_2$(R) catalyst shows good conversion of nitro benzene as well as selectivity towards aniline which is attributed to the high dispersion.
- Silica supported Ni catalysts are showing better conversion rates and stability than activated carbon supported Ni catalysts.
- Stability of these catalysts are also reasonably good.

Acknowledgments

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