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NICKEL CATALYTIC ACTIVITIES ON THE SUPPORTS OF SILICA AND ACTIVATED CARBON EXTRACTION FROM LOCAL RICE HUSK FOR NITROBENZENE HYDROGENATION: A COMPARATIVE STUDY

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ABSTRACT

Activated carbon (RHAC) and Silica ($RHSiO_2$) both were prepared from Rice Husk (RH) with very simple methods. These supports were used for the preparation of Ni catalyst for hydrogenation of nitrobenzene by wet impregnation and reductive deposition method. $Ni/RHSiO_2$ and Ni/RHAC catalysts are characterized by BET, XRD, SEM, and TPR techniques. Well, dispersion of Ni on these supports shows excellent conversion of nitrobenzene to Aniline.

Keywords: Rice Husk, Activated Carbon, Silica, $Ni/RHSiO_2$, and Ni/RHAC Catalyst.
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INTRODUCTION

Analysts found that the Rice husk roast is fundamentally created with formless silica and enacted carbon; it's a great wellspring of high evaluation silica.[1-4] this kind of SiO_2 can't blend in antacid and can be ready to remain at a high temperature.[5] Because of the good adsorption limit of enacted carbon from rice husk dominant part of individuals shows intrigue. All in all, actuated carbon is delivered from various kinds of crude materials, for example, papers, plastic jugs, seeds, or organic product shells, and further-more results from the timber industry (like sawdust), rice husk, and straw. In any case, specialists show their advantage and readiness to enact carbon from horticultural waste. From rice husk creation of initiated carbon should be possible by compound or physical actuation. General concoction impregnation with KOH, sodium hydroxide (NaOH), zinc chloride ($ZnCl_2$), or Ortho-phosphoric acid (H_3PO_4) of pyrolyzed RH followed by 650-850ºC outcomes in actuated carbons with amazingly high SA (750–3014 m^2g^{-1}).[6,7] At present, there are many natural responses and changes like hydrogenation, steam transforming responses, reductive amination of alcohols, hydro-dechlorination, incomplete oxidation, and dry improvement of methane completed over a bolstered nickel catalyst.[8-14] Over every one of these responses, hydrogenation is the most utilized one in both modern and research facilities. Elastomers, semi-inflexible and polyurethane (PU) created from fundamental compounds like Methylene diphenyl diisocyanate (MDI) and it is delivered from Aniline (AN). Aniline is likewise the primary crude material for an arrangement of more than 300 distinctive final results in businesses. Aniline is utilized likewise as a dissolvable and has been utilized as an antiknock compound for fuel.[15,16] Srinivas *et al.* announced that the Conversion of Levulinic corrosive to gamma-Valerolactone was completed by utilizing nickel impetus on SiO_2 arranged from rice husk.[17] As of late Feng, *et al.* read Ni-based catalyst for reactant hydrogenation of p-nitrophenol.[18] Aniline can be likewise utilized for uses of various end-use showcases

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like development, elastic items, transportation, customer, glues/sealants, bundling, horticulture, materials, coatings, photography, colors, and pharmaceuticals. Most of Aniline was utilized in the overall assembling of PU, which is utilized in a wide cluster of utilizations including footwear, protection, and furniture. In the year 2015, aniline created practically 6.2 million tons as a result of interest increment in different end-client showcases. For the most part aniline creation increments for the arrangement of Methylene diphenyl diisocyanate (MDI), the principle element for polyurethane (PU).[19] The current work is on the readiness of Silica and enacted carbon from rice husk; these are impregnation and reductive affidavit strategies with nickel. The bolstered nickel catalyst was utilized for the hydrogenation of nitrobenzene to aniline at atmospheric pressure in a vapor phase.

EXPERIMENTAL

Preparation of Activated Carbons from Rice Husk

A tubular furnace for carbonization provided with a temperature programmer was used to prepare activated carbons. 10 grams of dried rice husk were heated in the furnace under a nitrogen atmosphere at 10^{0}C/min. From room temperature to 600^{0}C and maintained for an hour. After carbonization, the heater was cooled to room temperature under the consistent progression of nitrogen to stay away from the 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 P^{H} became neutral. The purified solids were dried at 110^{0}C for 10 hr. Thus produced biochar is activated by using an H_3PO_4 reagent to modify surface properties. 5 gr. of this biochar is first impregnated with 30 wt. % H_3PO_4 and then heated at 250^{O}C under air for 2 hours. Then the same sample is subjected to heating at 600^{O}C under a nitrogen atmosphere for activation. This sample is named RHAC.

Fig.-1: Extraction of Silica and Activated Carbon from Rice Husk Image

Extraction of Silica (SiO_2) From Rice Husk

10g of RH char was preheated with 1 molar 200 mL hydrochloric acid to remove impurities and attractive the purity of Silica. Now char was transferred into a suspension flask and boiled for 3 hours under a reflux condenser with continuous stirring. Then solid is washed with double distilled water up to become neutral pH and dried at 120°C for 15 hours. After dried, it is introduced into the reflex condenser and treated with a 15wt% sodium carbonate solution for 4 hours to remove silica. Now suspension was filtered and the precipitate was washed with double distilled water up to become neural pH followed by dried at 120°C for 24 hours. The precipitate contains carbon material from which is activated carbon by chemical activation. The excess is a solution of Sodium silicate that is turned into silica by the carbonization process. The solution was heated at around 80°C under CO_2 gas flow. After 1 Hour CO_2 gas flow stopped and the solution cool down and reaches room temperature. Finally, the precipitated silica was filtered out and dried at 120°C for 24 hours, named $RHSiO_2$.

Catalyst Preparation

Preparation of Supported Nickel Catalysts by Impregnation

Rice husk extracted AC and SiO_2 supported "Nickel catalysts were prepared by conventional impregnation (IM) method with 5 wt. % Ni. In this method, calculated amounts of aqueous metal precursor solution were added to supports and after allowing overnight adsorption, the excess water was removed by evaporation followed by drying at 393 K for 12 hours and calculations at 723 K for 5 hours. The catalysts were cut down in H_2 flow at 500°C for 4 hours before their use for nitrobenzene hydrogenation reactions. These catalysts are designated as Ni/RHAC (I), and Ni/$RHSiO_2$ (I).

Preparation of supported nickel catalysts by Reductive Deposition method

In the reductive Deposition method, $RHSiO_2$, and RHAC supports were first dispersed into an aqueous solution of Ni $(NO_3)_2.6H_2O$ containing 5wt. % Ni for the support. 1 molar 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 strong was separated and washed with de-ionized water a few times until no sodium particle was recognized. The strong along these lines got was stove dried at 120 °C for 12 hours. The catalysts were decreased in H_2 at 500°C for 4 h before their utilization for hydrogenation response. The catalysts are marked as Ni/RHAC (R), and Ni/$RHSiO_2$ (R).

Catalysts Characterization

Catalysts were characterized by XRD, BET technique, TPR, and SEM. The XRD was recorded on Rigaku Ultima – IV X-ray diffractometer. The BET surface area of all catalysts is measured on Quadrasorb – SI. GC-17A with TCD, (Shimadzu Instrument Corporation, and Japan) was used for analyzing and recording the TPR profiles. The scanning electron micrograms of the selected catalyst samples were recorded on a Hitachi S-520 SEM. Product components were analyzed by an FID-equipped GC and also confirmed using GC-MS (SHIMADZU Instruments, Japan, model: QP-5050).

RESULTS AND DISCUSSION

BET Analysis of Surface Area and Pore Size

The surface area and pore size of the catalysts is determined by the 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 show high surface area than Ni coated on activated carbon catalysts. However, pore size in both cases remains almost the same. An impetus wherein Ni is consolidated through reductive affidavit precipitation strategy shows a higher surface region than the catalyst arranged by the impregnation technique. This demonstrates the high surface territory of Ni-RHAC (R) and Ni-$RHSiO_2$ (R) catalysts because of better scattering of nickel metal on the surface of the help whereas nickel likewise adds to the extra surface region.

Table-1: SA and Pore Size of Ni/RHAC and Ni/$RHSiO_2$ Catalysts

S. No.	Sample	Surface area(m^2/g)	Pore diameter (nm)
1	$RHSiO_2$	585.3	3.13
2	5% Ni/$RHSiO_2$(I)	546.5	3.08
3	5%Ni/$RHSiO_2$(R)	565.8	3.01
4	RHAC	470.1	2.85
5	5%Ni/RHAC(I)	415.8	2.71
6	5%Ni/RHAC(R)	430.5	2.65

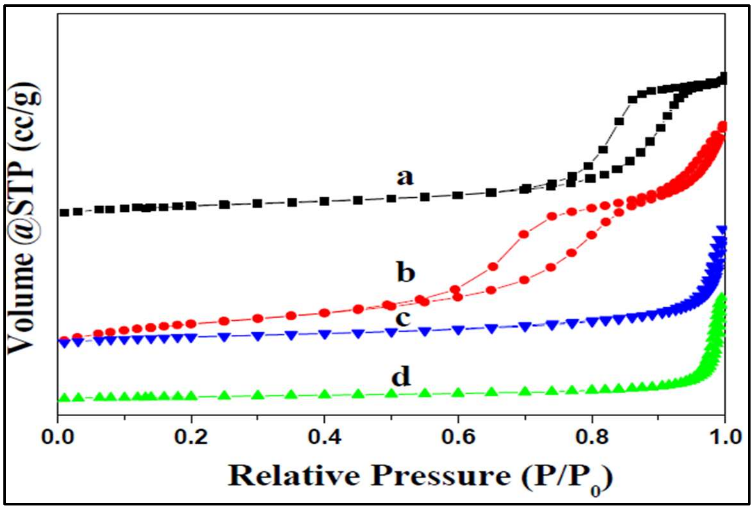

Fig.-2: N_2 Adsorption-Desorption Isotherms of Ni Catalysts (a)Ni/RHAC (I), (b) Ni/$RHSiO_2$ (I), (c) Ni/RHAC (R), (d)Ni/$RHSiO_2$ (R)

Comparative Study of XRD Patterns of Ni on Activated Carbons and Silica Supports

X-beam diffraction examples of all nickel-catalyst upheld on actuated carbon and silica have appeared in Fig.-3. The nearness of the NiO stage in these catalysts proposes the decay of Nickel nitrate in the air during the calculations bringing about the arrangement of NiO. In the X-beam diffractions of the Ni/$RHSiO_2$ catalysts, a wide top at 22° is because of indistinct silica. As indicated by the writing, the reflection tops at peaks of 37.28°, 43.3°, 62.8, and 75.3° can be attributed because of the NiO stage. In addition, the reflection tops at $2\Theta = 37.28°$ and 62.8° can likewise be credited to nickel silicate.[20] X-ray diffraction designs for the initiated catalysts are introduced in Fig.-3 Peaks at $2\Theta = 26.8°$ related to the graphite plane of carbon. Reflections showing up at 43.58, 52.88, and 79.58 compare, separately, to the planes of metallic nickel, which are reliable with a restrictive cubic geometry[21] and build up the nearness of NiO before the enactment of catalyst. Anyway, there is not a lot of distinction between the XRD designs for catalysts arranged by impregnation and reductive statement precipitation strategy.

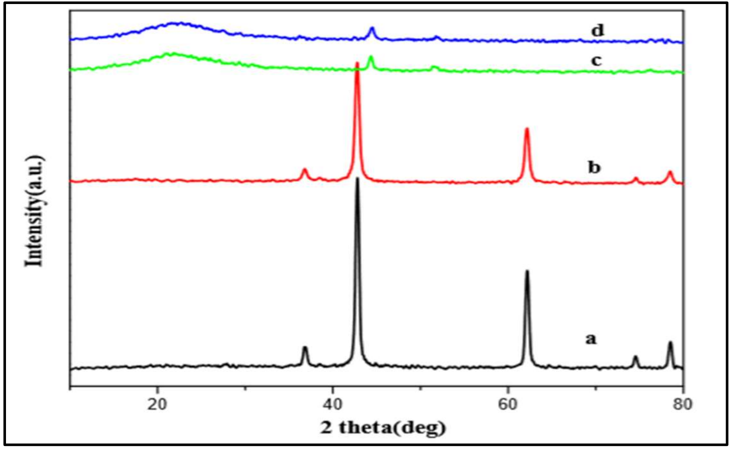

Fig.-3: XRD pattern (a) Ni/RHAC (I) (b) Ni/$RHSiO_2$ (I) (c) Ni/RHAC (R), (d)Ni/$RHSiO_2$ (R)

Scanning Electronic Microscopy (SEM) Studies

The SEM images of samples are prepared by the methods of impregnations and reductive deposition shown (Fig.-4) Ni/RHAC (I), Ni/$RHSiO_2$ (I), Ni/RHAC (R), Ni/$RHSiO_2$ (R). Among this reductive testimony of test, Ni/$RHSiO_2$ (R) is all around scattered nickel particles than the impregnated catalyst. The more prominent nucleation in the impregnation strategy prompts the agglomeration of metal nanoparticles.

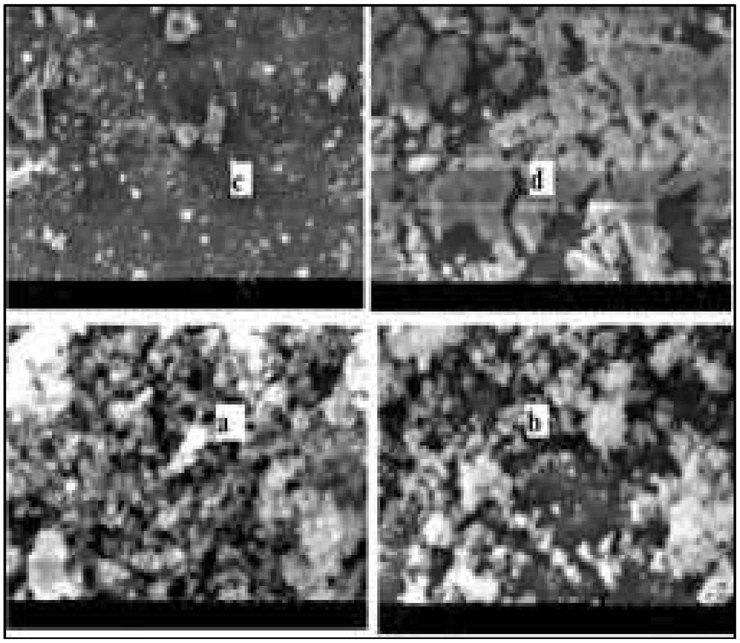

Fig: 4. SEM images (a) Ni/RHAC (I), (b) Ni/RHSiO$_2$ (I), (c) Ni/RHAC (R), (d) Ni/RHSiO$_2$(R)

TPR Studies

TPR gives significant data for the bolstered metal catalyst for the metal-bolster connections and the temperature at which the metal oxide gets to the metal. The TPR profiles of the nickel-based catalyst appeared in Fig.-5. Pompeo *et al.* proposed that the TPR examples of Ni/SiO$_2$ impetus show two decrease tops at around 450 and 610°C.[22] The first of them is because of the nearness of NiO types of low cooperation with the help, while the sign at 610°C is because of the nearness of nickel oxide associating synthetically with the help shaping nickel silicate.[23] The solid cooperation between the nickel metal and silica could be presumably because of an expanded interfacial zone. A hydrogen utilization top at 347^o to357^{o}C is watched for Ni/RHAC impetus. As this pinnacle is missing on account of the backings, it very well may be credited to the decrease of NiO. A practically identical decrease top (Tmax = 300^{o}C) has been recently announced by Bitter et al. for a Ni/C arranged along these lines.[21] While there should be an occurrence of reductive precipitation catalyst, no critical utilization of hydrogen was seen which plainly shows the nearness of Ni in the metallic state.

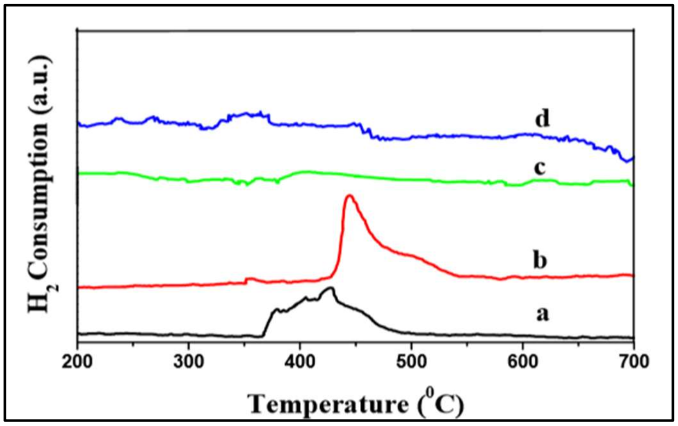

Fig.-5: TPR of the Ni Based Catalysts (a) Ni/RHAC (I) (b) Ni/RHSiO$_2$ (I) (c) Ni/RHAC (R), (d) Ni/RHSiO$_2$ (R)

Activity Measurements

Catalyst placed in fixed bed reactor having a silicon beads layer in preheating chamber. The reaction temperature was monitored by using a thermocouple. Reactant injected into fixed bed reactor using Teflon airtight syringe in a tube was controlled feed pump. Ultra-pure nitrobenzene and H$_2$ were tested for a black test with the required rate flow (NB is 1 ml /hr and H$_2$/NB =4). NB reactant with the steam of H$_2$

passed over catalyst support and converted to AN. The vapor was collected in an ice bath at particular time intervals and found by using GC with FID OV-1 having a capillary column (30 m length 0.53 mm ID., 0.33 mm film thickness).

Effect of Temperature on Reaction

The temperature impact on the change of nitrobenzene to aniline hydrogenation response 250^{0}C is an ideal temperature. At this temperature convert to aniline yielding limit is 100%, because the catalyst is set up by reductive affidavit strategy and impregnated technique. Among all these catalysts Ni/RHSiO$_2$ (R) is shown effective for the creation of aniline because of high Ni species scattering on help and molecule size of Ni is not exactly different examples. Simultaneously silica reducible nature and solid metal help connection among nickel and silica support. At temperatures above 250^{0}C change, the rate is diminished because of its exothermic nature. The selectivity to aniline is 100% at all temperatures and catalysts (Fig.-6).

$$Selectivity\% = \frac{amount\ of\ aniline\ formed\ (mole)}{Total\ amount\ of\ nitrodenzene\ converted\ (mole)} \times 100$$

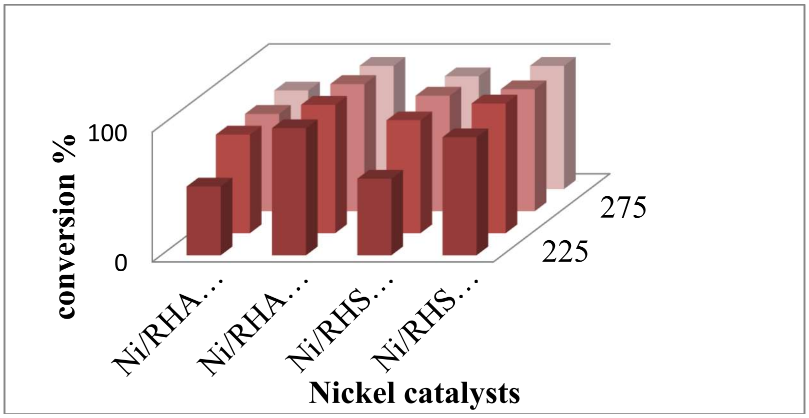

Fig.-6: Support and Preparation Method Effect on the NB Conversion Over Ni-Based Catalyst

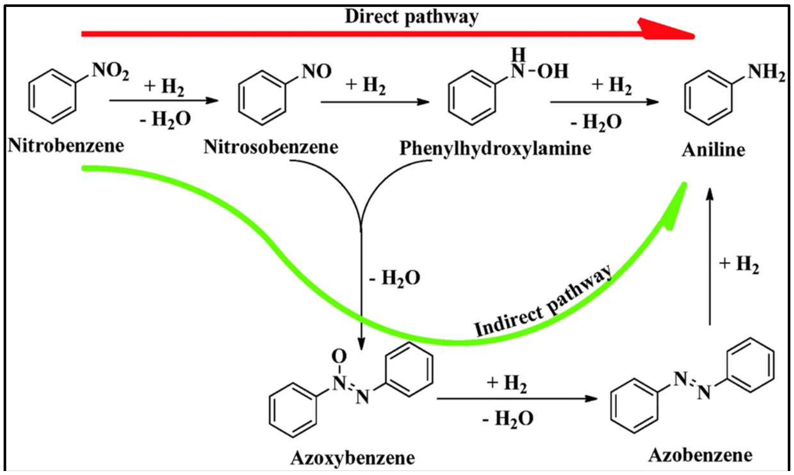

Fig.-7: Reaction Pathways for the Hydrogenation of Nitrobenzene

Effect of Time on Stream on Reaction

The time stream on the catalyst Ni/RHSiO$_2$ arranged by reductive testimony strategy which shows the strength, proficient aftereffects of change of nitrobenzene to aniline can be seen from Fig.-8 during the time on stream for ten hours at 250°C. The yielding limit may somewhat diminish because of the arrangement of coke and the buildup of the middle of the particles like H_2O in response. The coke arrangement may be a fundamental driver for the deactivation of the catalyst throughout response".[15]

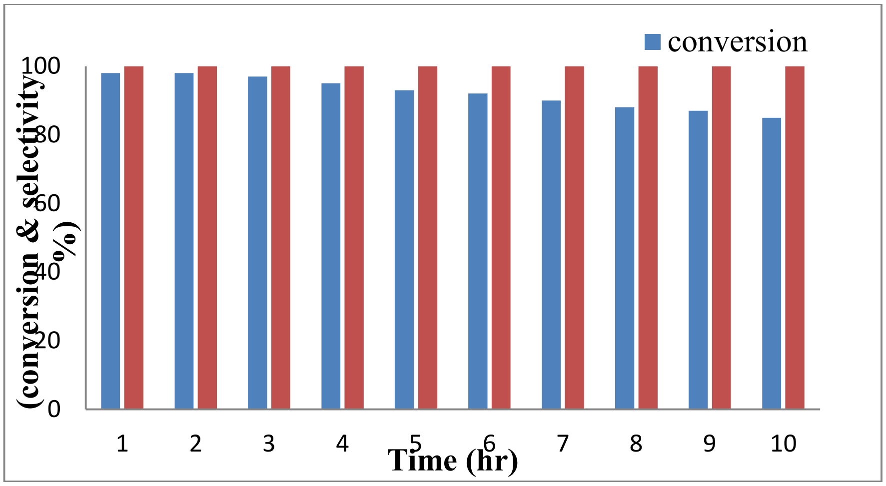

Fig.-8: Time on Stream Study Effect on Ni/$RHSiO_2$ (R) for the NB to AN

CONCLUSION

1. Extraction of silica and preparation of activated carbon from rice husk adds value to agricultural biowaste materials.
2. The preparation of nickel catalysts through the reductive deposition method proves to be a better one than the conventional impregnation method.
3. TPR results show hydrogen consumption which is ascribed to a reduction of the metal precursor in tandem with a Ni- catalyzed decomposition of surface-active groups.
4. Hydrogenation of nitrobenzene can be observed catalysts prepared by reductive deposition method are efficient. From all the catalytic samples Ni/$RHSiO_2$(R) catalyst shows good conversion of nitrobenzene as well as selectivity towards aniline which is attributed to the high dispersion.
5. Silica-supported Ni catalysts are showing better conversion rates and stability than activated carbon-supported Ni catalysts. The stability of these catalysts is also reasonably good.

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