Diazotization-azo coupling reaction of alphnaphthol over silica-sulfaric acid catalyst

Haneen Majed Saheb1, Elham Kadhim Hilal2, Kasim Mohammed Hello*1

1Chemistry Department, College of Science, Al-Muthanna University, Iraq
2Nursing College, Al-Muthanna University, Iraq

*1Corresponding author: kasimhillo@gmail.com; kasimhillo@mu.edu.iq

Abstract: Using agrowaste as a source of recycled materials is a hot topic among experts and technologists these days. Waste materials can be converted into energy and new products by using them. As a rice waste, rice husk (RH) is a rich source of pure silica that is recyclable. The pure silica in RH was sulfonated by agitating and reacting it with diluted sulfuric acid. Various sulfate concentrations were loaded on silica (5, 10, 15, and 20%), and the catalyst was designated as RHASO4. As the sulfate content increased, the specific surface area decreased. TEM analysis showed different forms of catalyst, including spherical, cylindrical, and fibbered forms. The catalyst was used for the in-situ generation of nitrose acid to prepare a diazonium salt for aromatic coupling reactions. Our experiment indicates that azo dyes can be produced at 68 percent over the catalyst at 10 degrees Celsius, while traditional catalysts cannot produce them above 5 degrees Celsius. For the highest yield of azo dyes, a 20% sulfate loading is optimum. A simple laboratory procedure is followed to reuse a catalyst without deteriorating its properties.

Keywords: Surface modification; Diazotization; Rice husk ash; Azo dyes; Coupling reaction.

1. Introduction

A variety of methods have been described to synthesize azo aromatic compounds, which have gained considerable popularity because of their variety of applications [1]. More than 0.7 million tonnes of dyes are produced worldwide every year [2]. As before, strong mineral acids (like H2SO4 and HCl) in aqueous solution have been the most prevalent method to synthesize azo aromatic compounds via diazotization-azo coupling reactions [3][4][5]. Using mineral acids in diazotization reactions clashes with the concept of green chemistry. Environmental incompatibility is the main factor in this process. Therefore, it is imperative to synthesize recyclable, solid catalysts as a replacement for unrecyclable liquid acid catalysts for the construction of a "green" artifice [6] [7].

An innovative form of p-xyllyl diimidazolium chloride-silica as a heterogeneous catalyst has been synthesized in our laboratory [8]. Through the catalyst, nitrous acid can be generated in-situ and produced as diazonium salt. Resulted in extremely high yields of azo dyes. In order to prepare the catalyst, rice husk was used.

Rice husk is available biomass that has distinctive characteristics because it has low quality, high chemical resistance, and sustainability [9] [10]. Rice husks can be converted into many different substances, such as catalysis [11], activated carbon, and zeolites [12]. When rice husk is burned under managed prerequisites, it yields noncrystalline silica. By alkaline hydrolysis, silica is transformed into sodium silicate. A sodium silicate can be functionalized in a one-pot method with alkyl silylation
retailers to be a starting material for extraordinary applications [13]. We have organized many catalysts using this technique in our laboratory, such as esterification [14, 15], acetalization of glycerol with benzaldehyde [16], cellulose hydrolysis [17], and production of monosaccharide [18]. Using a simple and more inexperienced technique for acidifying silica surfaces with sulfuric acid has been developed to create a heterogeneous catalyst that can be used to produce azo dyes via in situ techniques of nitroso acid to form diazonium salt.

2. Experimental

2.1. Raw materials

The chemicals used in this study were nitric acid (Systerm, 65%), Sodium hydroxide (Systerm, 99%), Sulfuric acid (Sigma- Aldrich, 98%), Sodium nitrite (BDH Chemical, 96%), Aniline (GCC, 99.5%), 1-Naphthol (SCR, ≥ 99 %), p-Aminopheno (Sigma- Aldrich, 98 %), 4-Hydroxy-1-aminonaphthalene (Sigma-Aldrich, 99%). Rice husk was collected from the mail of Samawah city, south of Iraq.

2.2. Preparation of solid silica-sulfuric acid

In this study, rice husk was converted into rice husk ash (RHA) according to the procedure reported [8] [19]. RHASO₄ was once prepared via handled of 3.0 gm silica with 5, 10, 15, and 20% (25 mL) sulfuric acid for 24 h to provide a strong acidic catalyst at room temperature. The solid was once filtered and dried at 110 °C for overnight. About 2.9 gm of the catalyst used to be amassed and stored on the container for different functions

2.3. Catalyst activity

Mixture A: aniline 1.0 mL (10 mmol) combined with 5.0 mL of H₂O then 200 mg of catalyst was once delivered to the mixture. Mixture B: Sodium nitrate 0.69 gm (10 mmol) used to be dissolved in distilled water (5.0 mL). The subsequent step combination A was once introduced to the combination B very slowly beneath stirring for 24 h, whilst the temperature in no way goes above 15 °C. Thereafter, the catalyst used to be eliminated through easy filtration. About 200 mg of alpha-Naphthol which was once dissolved in two mL of 10% NaOH and then 5.0 mL distilled water used to be added. The combination color used to be changed immediately which indicated the endpoint of the reaction. The equation below was once followed to calculate the last yield.

\[ \text{Yield} \% = \left( \frac{W_{t_{ex.}}}{W_{t_{theo.}}} \right) \times 100 \% \]

Where (Wt_{ex.}) is the experimental weight, (Wt_{theo.}) is the theoretical weight.

2.4. Equipment's

Nitrogen adsorption-desorption evaluation has been determined on Micro Active for TriStar II plus Version 2.03, surface area, and pore dimension analyzer. The samples had been outgassed for about 12 h at a hundred and five celsius underneath vacuum (at 3–10 mm Hg) in the degassing port of the adsorption analyzer. The specific surface area has once calculated the usage of the BET method. The pore diameter and pore measurement distribution of the substances have been acquired from the desorption branch of the isotherms by using the Barrett–Joyner–Halenda (BJH) method. The floor morphology of the amorphous silica was once analyzed employing the use of a scanning electron microscope (SEM) ((FEI Nova SEM 450). The dimension was once carried out at excessive vacuum mode with the accelerating voltage of 20 kV. EM 208 Philips instrument was once used for TEM images. Acetone used to be used to suspended powder material. One droplet of the suspension was once dropped on a carbon film lined with four hundred mesh copper grid and allowed to stand for 1–3 min, dried by a piece of filter paper, and examined.
3. Results and discussion

3.1. Synthesis of RHASO

Silica used to be extracted from rice husk via burning the rice husk at a managed temperature. The silanol groups (Si-OH) onto silica have been successful to changed via different molecules under crucial situations. Sulfuric acid used to be reacted with silica to functionalize its surface (which is mainly silanol groups) to sulfate groups (Si-OSO$_3$H). Various analysis for identified the catalysts was once carried which include surface area, SEM, and TEM and others as in the subtitle below.

3.1.1. Scanning Electron Microscopy (SEM) for RHASO

In Figs. 1 (a & b), rough surfaces with cylindrical shapes can be seen arranged randomly. In Fig 1 (c), microtubes, which are 10%RHASO$_4$, are collapsed together on a smooth surface. In Fig 1 (d), the surface of 10%RHASO$_4$ was rock surface where clearly visible. In Fig 1 (e), microtubes were visible on the surface. Fig 1 (f-i) displays the SEM images of 20%RHASO$_4$, but no specific shapes could be seen.

3.1.2. Transmission Electron Microscopy (TEM) RHASO

As shown in Fig. 2 (a, b, c, and d) the TEM images for 5%RHASO$_4$ showed the irregular particles were observed. Some of the spherical particles were found. The TEM of 10% RHASO$_4$ in Fig. 2 (e, f, and g) showed spherical nanoparticles. The calculations showed that the particles were less than 35 nm in diameter. The estimation was done beside Fig. 2 (f). Fig. 2 (h, i, and j) shows the TEM images of 15% RHASO$_4$. All TEM images showed spherical shapes irregular distributed. Fig. 2(k, l, and m) shows the TEM images of 20% RHASO$_4$ at different magnification. Similarly to other loadings, nano spherical shapes were seen.

Fig. 1: The SEM images topography of % RHASO$_4$; (a, b) SEM of 5%RHASO$_4$; While (c, d) for 10%RHASO$_4$; (e) for 15%RHASO$_4$; (f-i) SEM images of 20%RHASO$_4$. 

Fig. 2: The TEM images of % RHASO$_4$; (a, b) TEM of 5%RHASO$_4$; While (c, d) for 10%RHASO$_4$; (e) for 15%RHASO$_4$; (f-i) TEM images of 20%RHASO$_4$. 

3.1.3. Analysis of Catalysts

Various analysis were used to identify the catalysts such as surface area, SEM, TEM, and others as in the subtitle below.

Fig. 3: The TEM images of % RHASO$_4$; (a, b) TEM of 5%RHASO$_4$; While (c, d) for 10%RHASO$_4$; (e) for 15%RHASO$_4$; (f-i) TEM images of 20%RHASO$_4$. 

3.1.4. Catalytic Activity

The catalytic activity of RHASO$_4$ was measured using a fixed-bed reactor. The results showed that the activity increased with the increase in catalyst loading. The highest activity was observed for the 20%RHASO$_4$ loading.
Fig. 2: TEM images topography to surface of % RHASO₄. (a, b, c, and d) the TEM images for 5%RHASO₄; While (e, f, and g) for 10%RHASO₄; (h, i, and j) for 15%RHASO₄; (k, l, and m) the TEM images of 20%RHASO₄.

3.1.3. Nitrogen adsorption– desorption for different loading of RHASO₄

The BET finds out showed a unique surface area of 20% RHASO₄ used to be 8.20 m² gm⁻¹, whilst the specific surface area of 15% RHASO₄ was once 40.03 m² gm⁻¹. 10% RHASO₄ recorded 53.6 m² gm⁻¹ as a specific surface area, whilst 5% RHASO₄ confirmed 69.6 m² gm⁻¹ specific surface area. It used to be mentioned that when the charging of acid decreased the specific surface area used to be increased this could be due to the surface became crowded with the sulfate groups and lead to a limit in the
surface area. Fig. 3 (a, and b) gives the nitrogen adsorption isotherm of 5% RHASO₄ and 10% RHASO₄, in both the models of hysteresis loops, was type H1. For both loading 15% RHASO₄ and 20% RHASO₄ the hysteresis loops was type H3 as in Fig. 5 (c, and d). In all loading the hysteresis loop seen in the range of 0.5 < P/P₀ < 1.0. This was correlated with capillary condensation according to the IUPAC division. The pores of all loading of RHASO₄ Fig. 4 is found to be less than 5.0 nm. These pores fall in the microporous range.

**Fig. 3:** The nitrogen adsorption– desorption isotherm of (a) 5%RHASO₄, (b) 10%RHASO₄, (c) 15%RHASO₄, and (d) 20%RHASO₄.
3.2. Catalytic study

Diazonium salt was made over RHASO₄ by *in–situ* formations of nitrous acid (Scheme 1). The first aniline is dissolved in water which was before mixed with RHASO₄ catalyst. Sodium nitrite solution was added to that mixture. This step was *in–situ* generated nitrous acid. The aniline attacks by nitrous acid for producing diazonium salt. The catalyst was removed by filtration through filter paper. Diazonium salt was coupled with alpha-naphthol for production azo dyes. The subtitle below were discussed the bath followed to reach the optimum condition of the catalyst.

\[
\text{NH}_2 + \text{RHASO}_4 \rightarrow \text{NH}_3 \text{RHASO}_4
\]

\[
\text{N}=\text{N} + \text{OH}
\]

\[
\text{N}_2 + \text{RHASO}_4
\]

\[
\text{OH}
\]

Scheme 1: Coupling reaction of alpha-naphthol with diazonium salt over RHASO₄

---

**Fig. 4:** The different loading pores of RHASO₄.
3.2.1. Optimization of reaction conditions

Different loadings of acid (5, 10, 15, and 15 %) onto silica have been tested with inside the manufacturing of the azo dye to optimize the excellent acid loading. About 0.1 gm of the catalyst becomes used at 0-15 °C. Table 1 confirmed the yield of azo dyes over the RHASO₄ catalyst. It become observed that the yield of azo dyes become improved while the acid loading increased. The maximum yield becomes 42.5% over 20% RHASO₄. Therefore, 20% RHASO₄ was selected to be the optimum catalyst as the excellent acid loading onto silica.

Different masses of 20%RHASO₄ were analyzed on the coupling reaction of the diazonium salt with alpha-naphthol. 50, 100, 150, and 250 mg of 20%RHASO₄ were applied to discover the best mass of catalyst as shown in Table 1. About 67.95% of azo dyes yield was obtained when the reaction is carried out using 0.25 gm of 20%RHASO₄ at 10 °C. The yield was decreased at catalyst mass was less than 250 mg. According to our experiment, 250 mg was the optimum catalyst mass.

It was well known that nitrous acid is very sensitive to temperature. Therefore, it was very critical to control the reaction temperatures to not be up than 15 °C. This was to avoid nitrous acid decomposition. In our previous study [8], it was shown that it can design a catalyst capable of producing nitrous acid at a reaction temperature equal to 15 °C. Similarly, it was found that RHASO₄ was able to keep nitrous acid active at reaction temperatures less than 15 °C. Our experiment (Table 1) showed that the yield increased by only 3.0 % when the reaction temperature increased from 5 to 10 °C. While the yield was decreased when the reaction temperature decreased due to the decomposition of nitrous acid.

The water, methanol, ethanol, n-propanol, and n-butanol were used as reaction solvents and the results were shown in Table 1. The yield obtained was 68% when water was used as a reaction solvent. Other solvents were shown to yield very close to each other and less than water. The selected solvents were capable of forming hydrogen bonds with the reactant over the catalyst surface. The catalyst bonding with the reactants could increase the reaction possibility and this could lead to yield increases.

20%RHASO₄ was classified as a heterogeneous catalyst and because of this nature it was isolated from the reaction by simple filtration and reused several times without loss of it is activity. The recycling results are given in Table 1.

Table 1: The effects of different parameters on the production of azo dyes over 20%RHASO₄ catalysts were shown.

| Entry | Parameters | Variants | Yield (%) |
|-------|------------|----------|-----------|
| 1     | Catalyst mass | 50       | 43        |
|       |             | 100      | 51        |
|       |             | 200      | 55        |
|       |             | 250      | 66        |
| 2     | Solvent effects | Water | 68        |
|       |             | methanol | 52        |
|       |             | ethanol | 45        |
|       |             | propanol | 57        |
|   | n-butanol |   |
|---|-----------|---|
| 3 | Reaction  | 5 |
|   | temperature| 10 |
|   | (°C)      | 15 |
| 4 | Derivatives |   |
|   | ![Chemical Structure](image1) | 66 |
|   | ![Chemical Structure](image2) | 68 |
|   | ![Chemical Structure](image3) | 64 |
|   | ![Chemical Structure](image4) | 67 |
| 5 | Recycle   | Fresh in methanol |
|   | Run 1     | 55 |
|   | Run 2     | 52 |
4. Conclusions

RHA classified as a source of silica which could become sodium silicate. This silicate was treated with different loading of sulfuric acid and resulted in solid silica with $-\text{SO}_3\text{H}$ end groups. The adsorption of nitrogen study revealed that the catalysts prepared have a low surface area with a narrow pore size as loading of sulfate increased. Micrograph study indicated that the catalysts had very regular nano shapes. Some of these shapes were spherical others had fiber-like shapes. The catalysts were applied successfully in-situ to generations of nitrous acid. Nitrous acid was a precursor to a produced diazonium salt. 20% RHASO$_4$ was found the optimum loading of acid onto silica. When this catalyst was used, the azo yield was reached 68% at 10 °C. Our results indicated that the catalyst was stable, safe to handle, and could be reused actively many times.

5. Acknowledgement

The Authors would like to thank Al-Muthanna University, Republic of Iraq for financial support.

References

[1] N. Koukabi, S. Otoke, E. Kolvari, A. Amoozadeh, 2016. Convenient and rapid diazotization and diazo coupling reaction via aryl diazonium nanomagnetic sulfate under solvent-free conditions at room temperature. Dyes and Pigments, 124, pp. 12-17.
[2] M.P. Shah, 2014. An application of bioaugmentation strategy to decolorize & degrade reactive black dye by pseudomonas spp. Int. J. Environ. Bioremediation Biodegrad, 2 (2), pp. 50-54.
[3] F. Hamon, F. Djedaini-Pilard, F. Barbot, C. 2009. LenAzobenzenes—synthesis and carbohydrate applications, Tetrahedron, 65 (49), pp. 10105-10123.
[4] A.D. Towns, 1999. Developments in azo disperse dyes derived from heterocyclic diazo components, Dyes Pigm, 42 (1), pp. 3-28.
[5] E. Merino, 2011. Synthesis of azobenzenes: the coloured pieces of molecular materials, Chem Soc Rev, 40 (7), pp. 3835-3853.
[6] K. Wilson, H. Clark James, 2000. Solid acids and their use as environmentally friendly catalysts in organic synthesis, Pure Appl. Chem., p. 1313.
[7] J. H. Clark, 2002. Solid acids for green chemistry, Acc. Chem. Res., 35 (9), pp. 791-797.
[8] K. M. Hello, N. G. Fahad, 2019. Generation of diazonium salt over silica imidazole catalyst for dyes production, Bulletin Chem. Reaction Eng. Catal., 14 (2), p. 249.
[9] Z. Shamsollahi, A. Partovinia, 2019. Recent advances on pollutants removal by rice husk as a bio-based adsorbent: A critical review, J. Environ. Manag., 246, 314-323.
[10] S. Afewerki, A. Franco, A. M. Balu, T. Cheuk-Wai, R. Luque, and A. Córdova, 2020. Sustainable and recyclable heterogenous palladium catalysts from rice husk-derived biosilicates for Suzuki-Miyaura crosscoupoungs, aerobic oxidations and stereoselective cascade carbocyclizations” Scientific Rep., vol. 10, No. 6407, 2020. DOI: https://doi.org/10.1038/s41598-020-63083-8.
[11] D.M. Hasan, K.M. Hello, 2021. Fabrication of sodium hydrogen sulfate onto silica from waste for biomass energy. Chemistry Africa. https://doi.org/10.1007/s42250-021-00279-z.
[12] X.-G. Chen, S.-S. Lv, S.-T. Liu, P.-P. Zhang, A.-B. Zhang, J. Sun, Y. Ye, 2012.
Adsorption of methylene blue by rice hull ash, Separ. Sci. Technol., 47, pp. 147-156.

[13] F. Adam, Kasim Mohammed Hello and H. Osman, 2009. The immobilization of 3-(chloropropyl)triethoxysilane onto silica by a simple one-pot synthesis, J. colloid interface Sci., 331, pp. 143-174.

[14] Adam F., Hello K., Osman H., 2009. Esterification via saccharine mediated silica solid catalyst, Appl. Catal. A, 365, pp. 165-172.

[15] Adam F., Hello K. M., Chai S., 2012. The heterogenation of L-phenylalanine-Ru(III) complex and its application in esterification reaction, Chem. Eng. Res. Design, 90, pp. 633-642.

[16] Adam F., Hassan H., Hello K. M., 2012. The synthesis of N-heterocyclic carbene-silica nano particles and its catalytic activity in the cyclization of glycerol, J. Taiwan Inst. Chem. Eng., 2012, 43, pp. 619-630.

[17] Hello K., AbdulKarim-Talaq M., Sager A., 2017. Solid urea sulfate catalyst for hydrolysis of cellulose, Waste Biomass Valor., 8, pp. 2621–2630.

[18] Hello K., Mihsen H., Mosa M., Modification of silica with 2,4-dinitrophenylhydrazanomethylphenol for monosaccharide productions, 2014. Iran. J. Catal., 4, pp. 195-203.

[19] Hello K. M. and Hlial E. K., 2019. Modification of silica with sulfuric acid and phosphoric acid for cellulose hydrolysis, J. Phys.: Conf. Ser. 1294, 052013.