***Acknowledgment***

 In the name of Allah, the first who deserves all thanks and appreciation for granting me with health, strength and by his help, this research has been accomplished.

 I.would.like..to..thank.the.deanship.of.the.College.of.Science.

Al-Muthanna .University .and .Department. of .Chemistry.for providing the necessary facilities during this study.

 I would like to express my special appreciation and special thanks, to ***Prof. Dr. Kasim Mohammed Hello***  for his supervision and providing me valuable & necessary observation and advices in this work. I want to thank Mr. Mohammed Adil and Mr. Haider radi and my friends in department of Chemistry for their helping and support.

Nahla…

**ABSTRACT**

 In this study, silica was extracted from rice husk via washing rice husk many time with distilled water, and then treated with 1.0 M of Nitric acid; finally, it was burned in an oven at 800 oC. The ash was converted to sodium silicate and reacted with chloropropyltriethoxysilane to form RHACCl. Imidazole with *p*-xylylene dichloride was loaded onto RHACCl in the form of *p*-xylylbisimidazole to form solid catalyst donated RHAPrIM. Various analytical techniques were well characterize the catalyst including CHN analysis, TGA/DTA, FT-IR, N2-adsorption desorption study, 29Si &13C MAS NMR spectra TEM, SEM and EDX. According to the CHN results, it was noticed that the carbon percentage increased from (11.70%) in RHACCl to (16.704%) in RHAPrIM; also the results were showed a present of nitrogen in RHAPrIM which was not present in RHACCl. Silicon solid-state nuclear magnetic resonance showed Q4, Q3, T3, and T2 chemical shifts at expected position. 13C spectrum showed different peaks at different chemical shifts related to the carbon structures of the organic moieties. Thermal analysis showed that the catalyst could be used safely up to 277 ºC. TEM images of RHAPrIM showed regularly shaped particles with an estimated size 5 nm. Some particle seems to be smooth in shape, while the others showed a porous shape. The catalytic activity of RHAPrIM was examined in–situ preparation of nitrous acid which was used in the preparation of diazonium salt. The RHAPrIM was used to produce nitrous acid via it’s reaction with nitrite ions. Nitrous acid is the key start materials for dyes preparation via diazonium salt. Coupling reaction of aromatic compounds was carried out with a diazonium salt to yield a mono azo dye. All dyes were characterized by elemental analysis, FT- IR, and UV–Visible spectra. Both calculated and found results of elemental analysis of prepared azo compound were match with each other. The catalyst was stable and regenerated within a simple experimental procedure.

|  |
| --- |
| **List of Contents** |
| I | Acknowledgements |
| II | Abstract |
| III | List of Contents |
| VI | List of Tables |
| VII | List of Figures |
| VIII | List of Schemes |
| IX | List of Appendix |
| X | List of Abbreviations |

|  |
| --- |
| **Subject** |
| **No.** | **Chapter One: Introduction** | **Pages** |
| 1.1 | Wastes Recycle | 1 |
| 1.2 | Rice Husk | 2 |
| 1.3 | Chemical Structure of Rice Husk Ash | 4 |
| 1.4 | Modification of Silica with Silylating Agents | 5 |
| 1.5 | General Applications of Rice Husk Ash | 5 |
| 1.6 | Catalysis | 11 |
| 1.7 | Diazonium Salts | 12 |
| 1.8 | Mechanism of Diazonium Salts | 14 |
| 1.9 | Diazonium Salts Reactions | 15 |
| 1.10 | Azo Dyes | 16 |
| 1.11 | Theory of Catalysis  | 17 |
|  | Objectives of the Present Study | 19 |
| **Chapter Two : Experimental part** |
| 2.1 | Raw Materials and Chemicals | 20 |
| 2.2 | Instrumentation | 21 |
| 2.2.1 | Fourier Transform- Infrared Spectrophotometer | 21 |
| 2.2,2 | UV-Visible Spectrophotometer | 22 |
| 2.2.3 | Elemental Analysis (C.H.N) | 22 |
| 2.2.4 | 1H &13C NMR | 22 |
| 2.2.5 | Thermogravimetric Analysis (TGA/Differential Thermal Analysis ( DTA) | 22 |
| 2.2.6 | Nitrogen Adsorption-Desorption Analysis | 23 |
| 2.2.7 | Scanning Electron Microscopy /Energy Dispersive X-ray (SEM/ EDX) | 23 |
| 2.2.8 | Transmission Electron Microscopy (TEM) | 23 |
| 2.2.9 | 29Si MAS NMR Spectroscopy | 23 |
| 2.3 | Preparation of Starting Materials | 24 |
| 2.3.1 | Extraction of Silica from Rice Husk | 24 |
| 2.3.2 | Preparation of RHACCl | 24 |
| 2.3.3 |  Preparation of *p-*xylylbisimidazole(Bis-Imi) | 25 |
| 2.4 | Synthesis..of .Heterogeneous..catalyst...*p*-xylylbisimidazolium Chloride-Silica Catalyst (RHAPrIM)  | 25 |
| 2.5 | Catalyst Activity on Synthesis of Azo Dye | 26 |
| 2.6 | The Optimization of the Reaction Condition | 26 |
| 2.6.1 | The Optimization of the Catalyst Mass | 26 |
| 2.6.2 | The Optimization of the Reaction Temperature | 26 |
| 2.6.3 | The Solvent’s Effect | 27 |
| 2.6.4 | Regeneration of the Catalyst | 27 |
| **Chapter Three : Results and Discussion** |
| 3.0 | Materials Synthesis | 29 |
| 3.1 | The Synthesis of *p-*xylylbisimidazole | 29 |
| 3.1.1 | Fourier Transforme Infrared Spectroscopic Analysis of Bis-Imi | 30 |
| 3.1.2 | The Elemental Analysis of Bis-Imi | 31 |
| 3.1.3 | The 1H NMR Analysis of Bis-Imi | 31 |
| 3.1.4 | The 13C NMR Analysis of Bis-Imi | 32 |
| 3.2 | The Synthesis of Solid *p*-xylylbisimidazolium chloride-Silica Catalyst (RHAPrIM) | 33 |
| 3.2.1 | FTIR of RHAPrIM Catalyst | 35 |
| 3.2.2 | Elemental Analysis for RHA, RHACCl, and RHAPrIM | 36 |
| 3.2.3 | Thermogravimetric Analysis (TGA)/Differential Thermal Analysis (DTA) for RHAPrIM | 37 |
| 3.2.4 | Nitrogen Adsorption–Desorption Analysis | 39 |
| 3.2.5 | Scanning Electron Microscopy(SEM) | 41 |
| 3.2.6 | Transition Electron Microscopy (TEM) | 42 |
| 3.2.7 | The 29Si MAS NMR Spectroscopy Analysis | 44 |
| 3.2.8 | The 13C MAS NMR Spectroscopy Analysis | 46 |
| **Chapter Four :Catalytic Activity** |
| 4.0 | Catalytic Performances | 48 |
| 4.1 | Influence of Catalyst’s Mass | 48 |
| 4.2 | Influence of Temperature | 50 |
| 4.3 | Influence of Solvent Effect | 51 |
| 4.4 | Catalyst’s Recycle | 52 |
| 4.5 | FT-IR Analysis of Reused Catalyst RHAPrIM  | 53 |
| 4.6 | Thermal. Analysis of Reused Catalyst | 54 |
| 4.7 | Proposed Mechanism | 55 |
| 4.7.1 | Elemental Analysis and Melting Points of Derivatives Dyes | 56 |
| 4.7.2 | UV-Vis Spectra | 57 |
| 4.7.3 | FT-IR Spectra | 58 |
| **Chapter Five: Conclusions and Recommendations** |
| 5.1 | Conclusions | 59 |
| 5.2 | The Slight Deactivation in the Activity of the Catalyst | 60 |
| 5.3 | Recommendations | 61 |
|  | **References** | 62 |
| **List of Tables** |
| **No.** | **Title of Tables** | **Pages** |
| 1.1 | Typical analysis of raw rice husk | 3 |
| 1.2 | Organic composition of RH contine silica | 3 |
| 2.1 | Chemicals with their purity and the manufacture companies.  | 20 |
| 3.1 | Elemental an Elemental analysis for RHA, RHACCl, RHAPrIM. The EDX data between brackets.  | 37 |
| 3.2 | The nitrogen adsorption–desorption parameter for RHA, RHACCl, RHAPrIM | 41 |
| 4.1 | The effect of catalyst mass on the production of azo dyes over RHAPrIM catalyst | 49 |
| 4.2 | The effects of reaction temperatures on the production of azo dyes over RHAPrIM catalyst | 50 |
| 4.3 | The effect of different solvents on the reaction of benzyl diazonium chloride with Resorcinol over RHAPrIM at 10°C | 52 |
| 4.4 |  FT-IR spectrophotometer results of fresh and reused catalyst | 53 |
| 4.5 | The physical properties, elemental analysis, and FT-IR of azo dye derivatives prepared over RHAPrIM. | 58 |
| **List of Figures** |
| **No.** | **Title of Figures** | **Pages** |
| 1.1 | Rice husk (byproduct of rice) | 2 |
| 1.2 | Different types of silanol group in surface of silica | 4 |
| 3.1 |  The FT-IR spectrum of Bis-Imi | 30 |
| 3.2 | The 1H NMR spectrum of Bis-Imi in d3-CD3CN | 32 |
| 3.3 | The 13C NMR spectrum of Bis-Imi in d3-CD3CN. | 33 |
| 3.4 |  The FT-IR spectra of RHACCl, RHAPrIM and the differential spectrum | 35 |
| 3.5 | Thermogravimetric analysis and differential thermal analysis of RHAPrIM. | 39 |
| 3.6 | The nitrogen adsorption–desorption isotherm of RHAPrIM. The inset shows the corresponding pore size distribution | 40 |
| 3.7 | The SEM images of RHAPrIM at different magnifications | 42 |
| 3.8 | The TEM images for RHAPrIM at different magnifications | 43 |
| 3.9 | The solid state 29Si MAS NMR spectrum. (a) RHA , (b) RHACCl, (C) RHAPrIM | 45 |
| 3.10 | The solid state 13C MAS NMR spectrum of (a) RHACCl, (b) RHAPrIM | 47 |
| 4.1 | The effect of catalyst mass on the production of azo dyes over RHAPrIM catalyst | 49 |
| 4.2 | The effect of the reaction temperature on the preparation of dyes | 51 |
| 4.3 | The reusability of the catalyst | 52 |
| 4.4 | FTIR spectrum of reused catalyst RHAPrIM | 54 |
| 4.5 | Thermogravimetric analysis and differential thermal analysis of reused catalyst RHAPrIM. | 55 |
| 4.6 |  The UV-Vis of the monoazo dyes derivatives prepared over RHAPrIM | 57 |
| **List of Schemes** |
| **No.** | **Title of Schemes** | **Pages** |
| 1.1 | The simple reaction sequence for the modified with CPTES in a one-pot synthesis. The product was libeled as RHACCl | 6 |
| 1.2 | Synthesis of silica-imidazole catalyst | 7 |
| 1.3 | Synthesis of N-butylimidazole-silica heterogeneous catalyst from RHACCl | 7 |
| 1.4 | Sulfanilic acid immobilized onto RHACCl | 8 |
| 1.5 | Synthesis of RHACP-PDA and RHAC-DTO from the reaction ofdithiooaxamide (DTO) and *P*-phenylenediamine with RHACCl | 8 |
| 1.6 | The reaction sequences and the possible structure of the hybrid organo-silica materials | 9 |
| 1.7 | The simple reaction sequence and the structure for RHAPrNH2 and RHNH3SO4H | 10 |
| 1.8 | The first step in mechanism is the nucleophilic attach amine onto nitrosonium ion. The second step shows the formation of diazonium salts | 14 |
| 1.9 | An example of diazonium salt reaction to form azo dyes | 15 |
| 2.1 | Research progress during the catalyst preparation | 28 |
| 3.1 | The synthesis of *p*-xylyl bis (N-imidazole) (Bis-Imi) | 29 |
| 3.2 | The simple sequence of reactions and the possible structure for RHAPrIM | 34 |
| 4.1 | The generation of diazonium salt over RHAPrIM | 56 |
| **List of Appendix** |
| **No.** | **Title of Appendix** | **Page** |
| 1 | FT-IR Spectrum of 4-( phenyl azo) -1-Naphthol | 74 |
| 2 | FT-IR Spectrum of 2-( phenylazo) Resorcinol | 75 |
| 3 | FT-IR Spectrum of 2-(phenyl azo) *-*4-Bromo benzaldehyde | 76 |
| 4 | FT-IR Spectrum of 2-(phenyl azo) benzene | 77 |
| 5 | FT-IR Spectrum of 2-( phenyl azo) m-crysol | 78 |
| 6 | FT-IR Spectrum of 2-(phenyl azo)4-(N,N-dimethyl) benzaldehyde | 79 |