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بسم الله الرحمن الرحيم

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صدق الله العلي العظيم

سورة طه الآية /١١٤

الخلاصة

في هذه الدراسة تم استخلاص السيلكا من قشور الرز عن طريق غسل قشور الرز مرات عديدة بالماء المقطر، ثم عوملت مع محلول (١مولاري) من حامض النتريك، بعد ذلك أحرقت في فرن بدرجة حرارة ٨٠٠ درجة مئوية ، تم تحويل السليكا الناتجة الى سيليكات الصوديوم بعد ذلك تم مفاعلتها مع CPTES ينتج سليكا ذات مجموعة وظيفية -CH_2Cl- رمز لها بالرمز RHACCl. تم تحميل الاميدازول المتفاعل مع كلوريد بارا زايلين على سطح RHACCl لتكوين العامل المساعد غير المتجانس رمز له RHAPrIM. تم تشخيص العامل المساعد بعدة تقنيات منها تحليل العناصر والتحليل ألوزني الحراري TGA/DTAوتحليل امتزاز النتروجين ومطيافية الأشعة تحت الحمراء FT-IR وكذلك أطياف الرنين النووي المغناطيسي للحالة الصلبة لنواة ذرتي الكربون والسيليكون (^{13}C MAS NMR , ^{29}Si) وكذلك المجهر الالكتروني الماسح SEM والمجهر الالكتروني النافذTEM. طبقا إلى نتائج CHN ،EDX لوحظ زيادة نسبة الكربون أكثر مما هي عليه في RHACCl وبين التحليل كذلك وجود نسب من النتروجين والتي لم تكن موجودة سابقا في المركبRHACCl. اظهر تحليل الرنين النووي المغناطيسي للحالة الصلبة لنواة ذرة السيليكون ^{29}Si وجود إزاحات كيميائية تعود إلى Q^4، Q^3، T^3، T^2 عند إزاحات كيميائية في الطيف حسب الأدبيات. أما تحليل الرنين النووي المغناطيسي للحالة الصلبة لنواة ذرة الكربون^{13}C اظهر حزما عند مواقع كيميائية مختلفة تعود لذرات الكربون في العامل المساعد المحضر. في حين بينت نتائج التحليل الحراري TGA/DTA أمكانية استخدام العامل المساعد حتى ٢٧٧ درجة مئوية دون أن يتفكك . وطبقا لصور المجهر الالكتروني النافذ TEM ظهرت دقائق ذات أشكال منتظمة وبحجم ٥ نانومتر ، بعضها ملساء والأخرى كانت مسامية.درست الفعالية التحفيزية للعامل المساعدRHAPrIM في حمل ايون النتريت لتحضير حامض النتروز المستخدم في تحضير أملاح الدايزونيوم . يعتبر حامض النتروز المادة الاساسبة لتحضير الأصباغ ، حيث حظرت أصباغ مختلفة عن طريق تفاعل الازدواج بين المركبات الاروماتية وأملاح الدايزونيوم. شخصت الأصباغ المحضرة بواسطة تحليل العناصر، FT-IR وأطياف UV-Vis . لوحظ تطابق النتائج العملية والمحسوبة لتحليل العناصر لمركبات الازو المحضرة. تم أعادة استخدام العامل المساعد عدة مرات و بثباتية عالية.

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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, N_2-adsorption desorption study, ^{29}Si &^{13}C 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 Q^4, Q^3, T^3, and T^2 chemical shifts at expected position. ^{13}C 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.

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ntroduction

1.1 Waste Recycle

The waste continuously increasing every year due to the large development happens in a world. Waste recycling can be defined as a process that converts waste materials into new uses materials, which lead at last reduced accumulation of wasted materials [1]. In general, many advantages were obtained from the process of waste recycle, lowering level of consumption of raw materials, decrease energy usage, lowering air and water pollution due to gas emissions such as (NO_2, CO_2 and NO) that could happen via reducing the need for conventional unwanted materials [1, 2]. Apotential waste material is rice husk, that was represented the bulk of agricultural product via the milling process causing a problem and risk to the environment, it was available almost everywhere, and it is also highly resistant to natural degradation [3]. Besides to these problems, RHA is usually dumped through water streams, that was precipitate pollution. However, it was estimated that RHA makes a good supported as a mineral admixture of concrete [4]. Tangchirapat *et al.* [5] proved that the utilization of ground RHA in recycled aggregate concrete enhances compressive strength. Also, it was estimated that about 20 million tons of RH are result every year as waste in disposal sites in eastern and western Asia [6]. This is not only a great waste but it also causes an environmental threat as there are potential risks of pollution for the surrounding land where it is discarded. There have been a number of studies to do this in an environmentally friendly way. Additionally, Rice husk was used in the production of silicon, which was used for the production of lithium-ion battery anodes [7].

1.2 Rice Husk

Rice is grown in more than 77 countries [8]. Rice husk (RH) is an agro-biomass resulted during the refining of rice [9], so it was a thin sheath that is a product on the rice grains through their growth [10] (Fig.1.1). It was reported that about 0.23 ton of husk has resulted after every ton of rice product, and every ton of husk results about 0.041 tons of ash, according to the variety, climatic system, chemical nature of the soil, crop year, and geographical location [11]. RH was contained 75-90 % organic volatile material, and 20 % of RH was converted into ash (RHA) after the burning process. The percentage of inorganic compounds in RHA approximately 95% (wt) of silica, the remaining percentage 5% can be listed in (Table 1.1) [12].While the organic constituents of RH was reported by Sharma *et al.* [14] as in (Table 1.2).



Fig. 1.1: Rice husk (byproduct of rice) [13].

Table 1.1: Typical analysis of raw rice husk [12].

Components	Content (wt. %)
Organic material and moisture	73.87%
Al_2O_3	1.23
Fe_2O_3	1.28
CaO	1.24
MgO	0.21
SiO_2	22.12
MnO_2	0.074

Table 1.2: Organic composition of RH contine silica [14].

Components	Percentage present in RH wt %
A-cellulose	43.30
Lignin	22.00
D-xylose	17.52
L-arabinose	6.53
Methyl glucuronic acid	3.27
D-galactose	2.35

1.3 Chemical Structure of Rice Husk Ash

Silicon dioxide $(SiO_2)_n$ known as a silica [15,16] is the major component of RHA. Silica is an inorganic polymer. It has a melting point of 1440 ˚C [17]. The natural amorphous silica

could be found as sols, powders, gels, porous glass, and particle. Silicon atom in silica has a tetrahedral arrangement with four covalent bonds to oxygen atoms. All of the oxygen atoms are covalently bonded to one silicon atom in order to form siloxane groups, Si–O–Si, or silanol groups, Si–OH [18,19]. It was found a different type of silanol group onto silica surface. First, one is isolated groups which a single hydroxyl group bonded to a silicon atom. Second a geminal groups; two hydroxyl group bonded to same silicon atom [19]. Vicinal silanol groups or bridged silanol groups, in which two single silanol groups, bonded in hydrogen bond to different silicon atoms (Fig. 1.2).

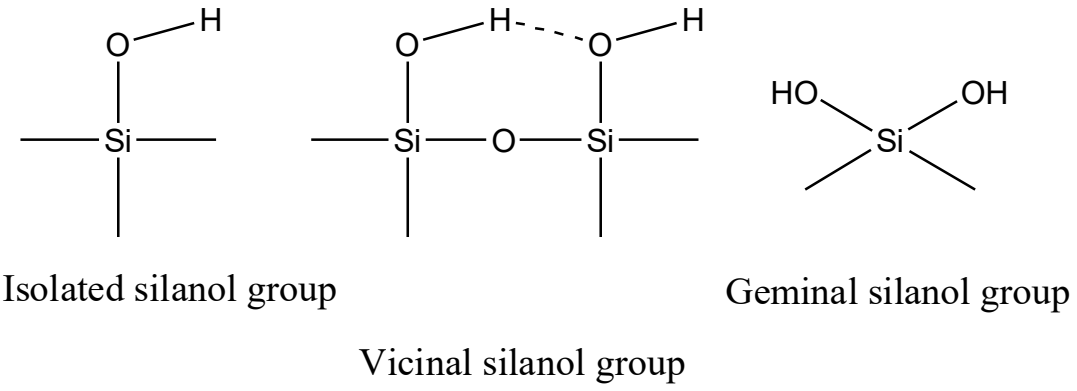


Fig. 1.2: Different types of silanol group in surface of silica [19].

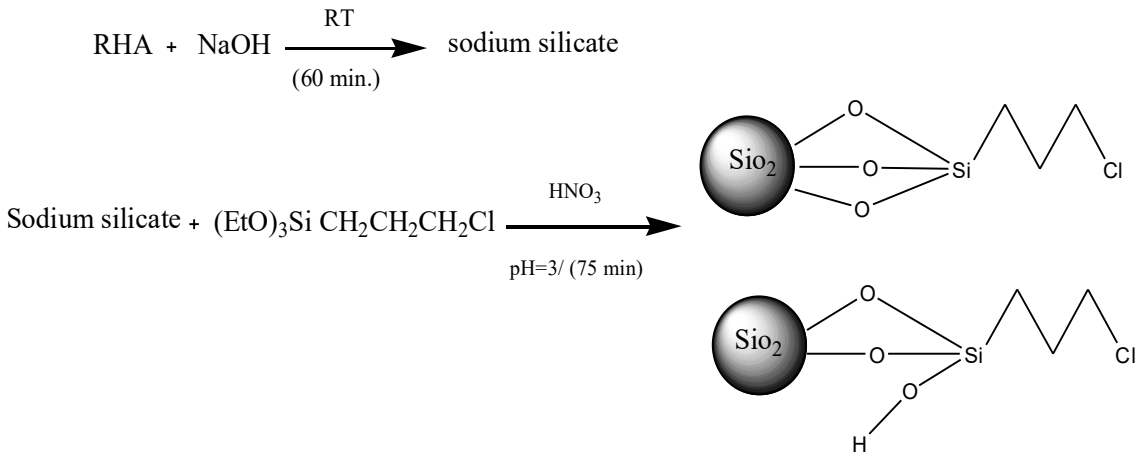
1.4 Modification of Silica with Silylating Agents

The functionalization of silica is mostly done using organic materials to modify its surface [20]. Silylating agents are chemically reactive with free silanol groups onto silica surface. RO_3SiR^* was the general formula of the silylating agents (alkoxysilanes), R represents methyl or ethyl groups, R* refers to an alkyl carbon series containing functional end groups, halogen, amine or sulfur group [21]. Functionalized silica with the silylating agent is the best method to

produce primary groups which anchored pendant chain [22]. One important advantage of functionalized silica with organic groups is to make the immobilized organic group high resisting to remove from silica surface by many organic solvents and water [23]. High thermal and hydrolytic stability and accessibility to the active center is another advantage of this functionalized [22].

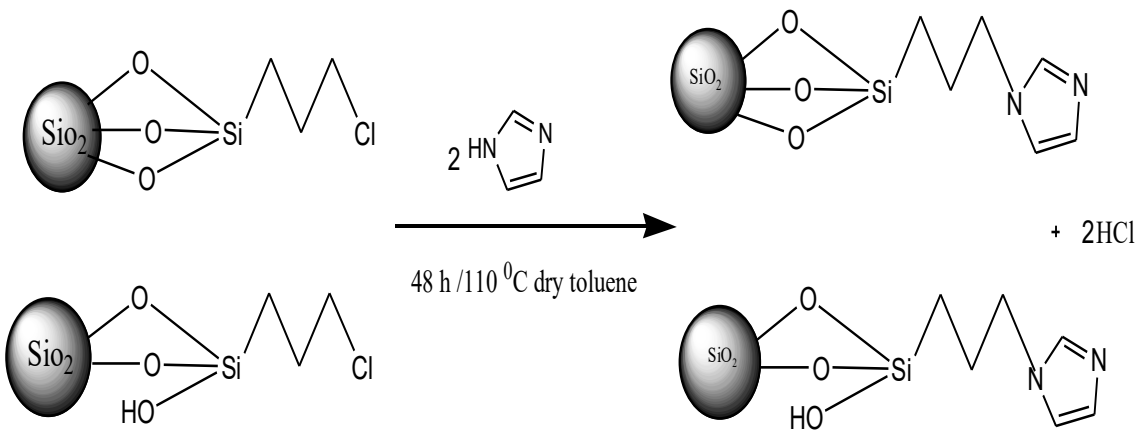
1.5 General Applications of Rice Husk Ash

Silica from RHA has very good properties, such as amorphous structure, large specific surface area, large pore volume, and high reactivity. There is many application of RHA [24, 25] such as catalysis [26], adsorption [27], and for different chemical synthesis [28]. The functionalization of silica surface that extracted from rice husk with 3-chloropropyltriethoxysilane (CPTES) [29] was carried out in a solid-liquid mixed phase reaction (Scheme 1.1). Adam *et al.* [30] the first groups who mentioned the ability of silica to immobilize with CPTES via simple sol-gel method, (Scheme 1.1) in aqueous solution. This method is simple, no toxic reagents involved and short time to reach the products without needed to high refluxing temperature. This technique includes a one-pot synthesis of silica – CPTES complex by using sodium silicate resulted from RHA. Many research has followed this technique, due to it was simple and resulting high yield.



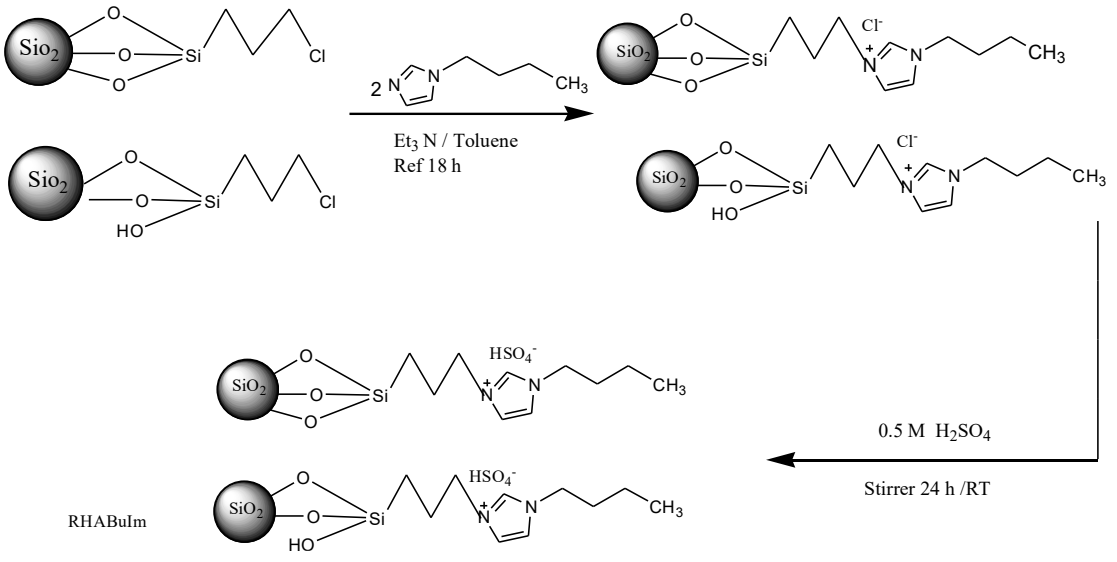
Scheme 1.1: The simple reaction sequence for the modified with CPTES in a one-pot synthesis. The product was labeled as RHACCl.

Many types of research were depended on using RHACCl as a starting point in their researches. Farook *et al.* [31] were used RHACCl in prepared heterogeneous catalyst during the reaction between RHACCl and imidazole, as in (Scheme 1.2). The product was used as catalysis, separation and in electronic technologies.



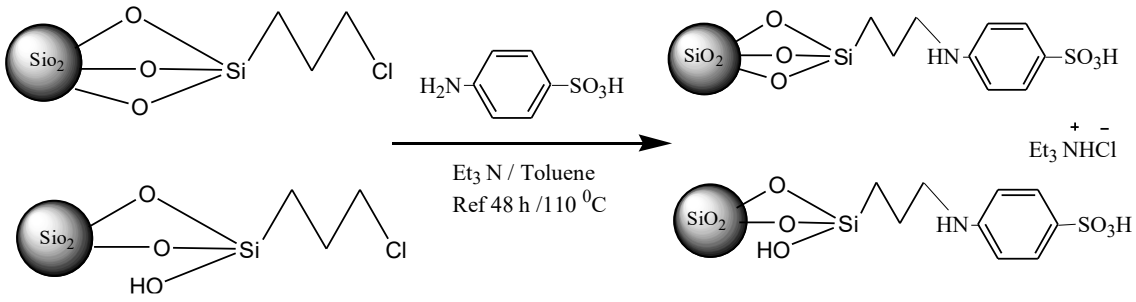
Scheme 1.2: Synthesis of silica-imidazole catalyst.

Farook *et al.* [32], were used RHACCl in the synthesis of a heterogeneous catalyst by the reaction between butyl imidazole and RHACCl (Scheme 1.3). The catalytic activity was studied in the cyclization reaction of glycerol to cyclic acetals.



Scheme 1.3: Synthesis of N-butylimidazole-silica heterogeneous catalyst from RHACCl.

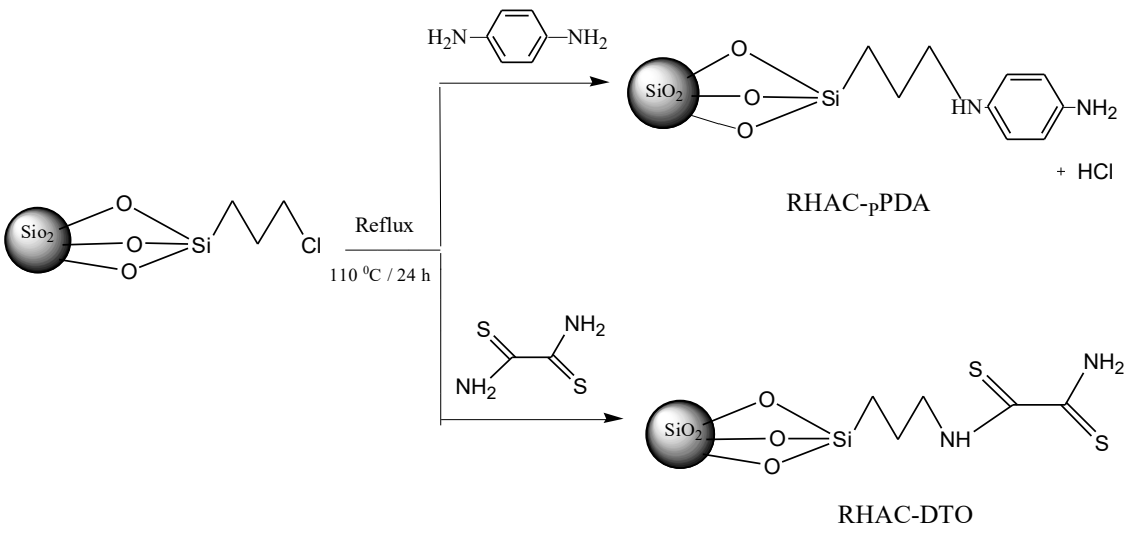
Sulfanilic acid was also immobilized onto RHACCl to synthesis solid acidic catalyst (Scheme 1.4). The catalytic activity was studied in the alkylation of phenol. The catalyst shows high reusability and used several times with little loss of the catalytic activity [33].



Scheme 1.4: Sulfanilic acid immobilized onto RHACCl.

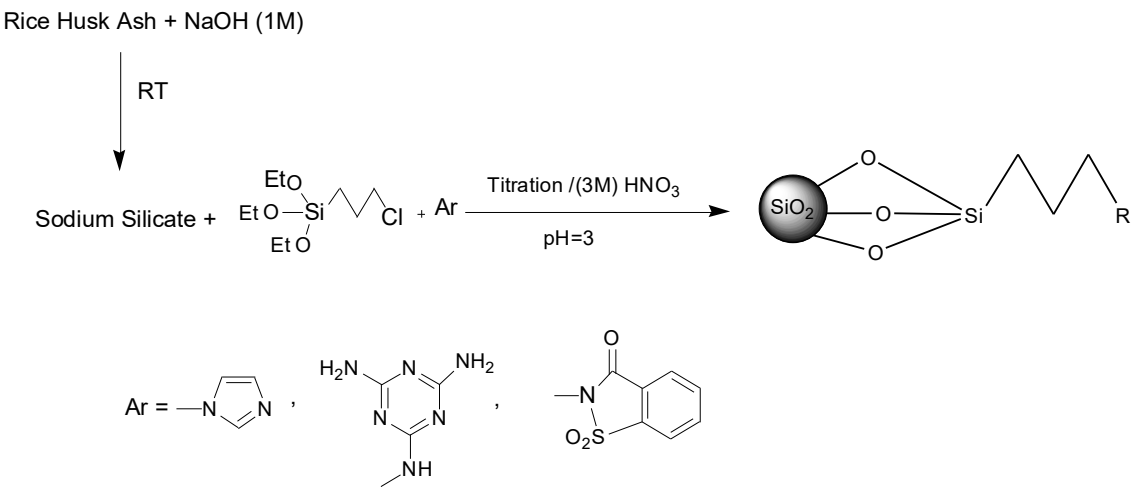
Thana [34] showed the reaction between RHACCl and dithiooxamide (DTO) and *P*-phenylenediamine (*P*-PDA) in dry toluene and Et_3N (Scheme 1.5). The catalytic activity was

studied in the esterification of ethyl alcohol with acetic acid.



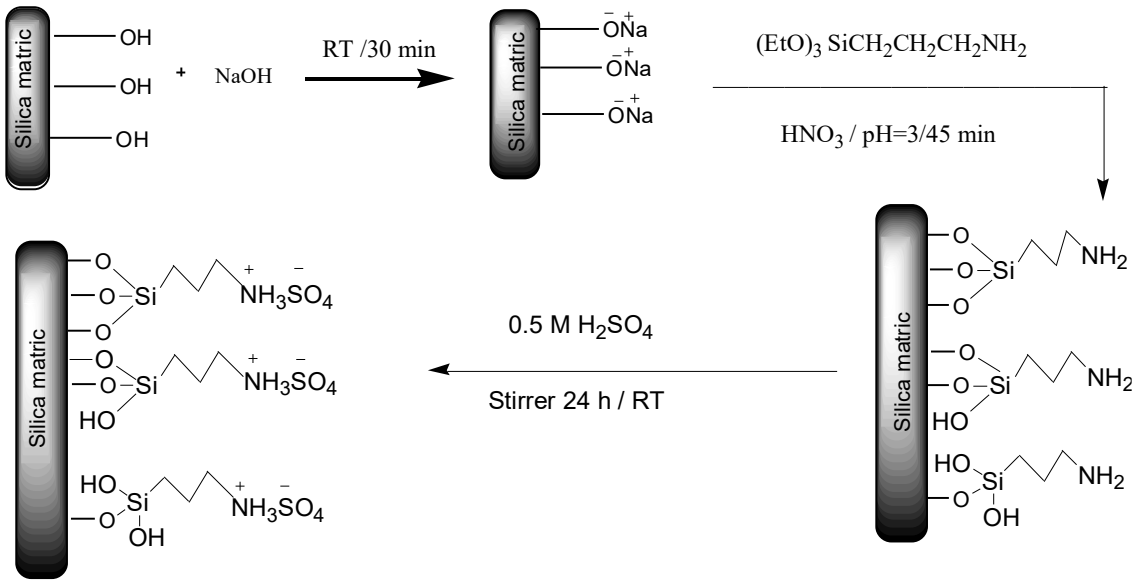
Scheme 1.5: Synthesis of RHAC$_P$-PDA and RHAC-DTO from the reaction of *P*-phenylenediamine and dithiooxamide (DTO) with RHACCl.

Hello *et al.* (2018) [35] shows that the CPTES successfully reacted with imidazole (in a separate experiment with melamine and saccharine) and sodium silicate from RHA in a purely homogenous method using water as a solvent. The material had ordered mesoporous straight-channels which were like the MCM-41. The surface areas of the materials were very high compared with the materials which have similar structure prepared by the traditional method. The synthesis procedure is simple, repeatable with different organic ligands and does not require toxic solvents or multiple steps with high products yield.



Scheme 1.6: The reaction sequences and the possible structure of the hybrid organo-silica materials.

Solid ammonium sulfate was synthesized by the reaction of 3-aminopropyltriethoxysilane with silica rice husk ash (Scheme 1.7). The catalytic activity was studied in the hydrolysis of cellulose which was extracted from the waste of rice husk [36].



Scheme 1.7: The simple reaction sequence and the structure for $RHAPrNH_2$ and $RHNH_2SO_4H$.

1.6 Catalysis

Catalysis was discovered by Berzelius in 1836 in order to speed up many chemical reactions [37, 38]. It was defined as the substances that used in the reaction without being consumed with reactants. In general, the effect of catalysis was noticed in increasing the reaction rate to reach the equilibrium between the reactants and products [39, 40] and lowering reaction time due to decreasing the activation energy [38]. The first catalysts were generally solid minerals or mineral complexes, prepared from soluble acids or bases in organometallic systems [41]. Catalysts were very important materials in scientific research and technological development. Nowadays the research of catalysis shifts from traditional applications to the marketing applications such as in the oil field, medicine, agricultural chemicals, and environmental protection systems [42]. Because of these malti applications, the research of catalysis was very important in many different scientific types of research. There were two kinds of catalysis could be recognized, the natural catalyst such as Enzymes which were large proteins react in specific active site [43]. The second type was unnatural catalysis. Unnatural catalysis was divided into two kinds homogeneous and heterogeneous catalyst. It's known that homogenous catalysts were in the same phase with the reactant and products usually in the liquid phase. Heterogeneous catalysts were the catalyst in a different reaction phase, usually in solid phase [43]. The heterogeneous catalyst had a weak internal bond, the reactants chemisorb on the surface of a solid catalyst that leads at last easyly formation of new bonds with other reactants. In a homogenous catalyst, the linkage of the catalyst with the reactant was stronger. Another advantage of heterogeneous catalyst was the lower affinity of the product, so it was released into a liquid phase [44]. Although many chemical reactions could be promoted with two types of catalyst homogenous and heterogeneous catalyst, the better type of catalyst that

allows for little waste, no toxic reagents, and has the ability for recycling [45]. Additionally, heterogeneous catalysts were preferred as compared with homogeneous catalysts because of many reasons, the first simple method of separation from the product and secondly high ability of regeneration [46]. The separated catalyst could be reused multi times with the same activity. Generally, the advantages and main characteristics of the heterogeneous catalysts are as easy separation from the reaction mixture [47], the solid structure avoids the aggregation to the active catalyst [42], high thermal stability, resistance solubility in organic solvents [48], the ability of storage for a long time, convenient to handle [49,50] and high selectivity (include multiple binding sites) [51].

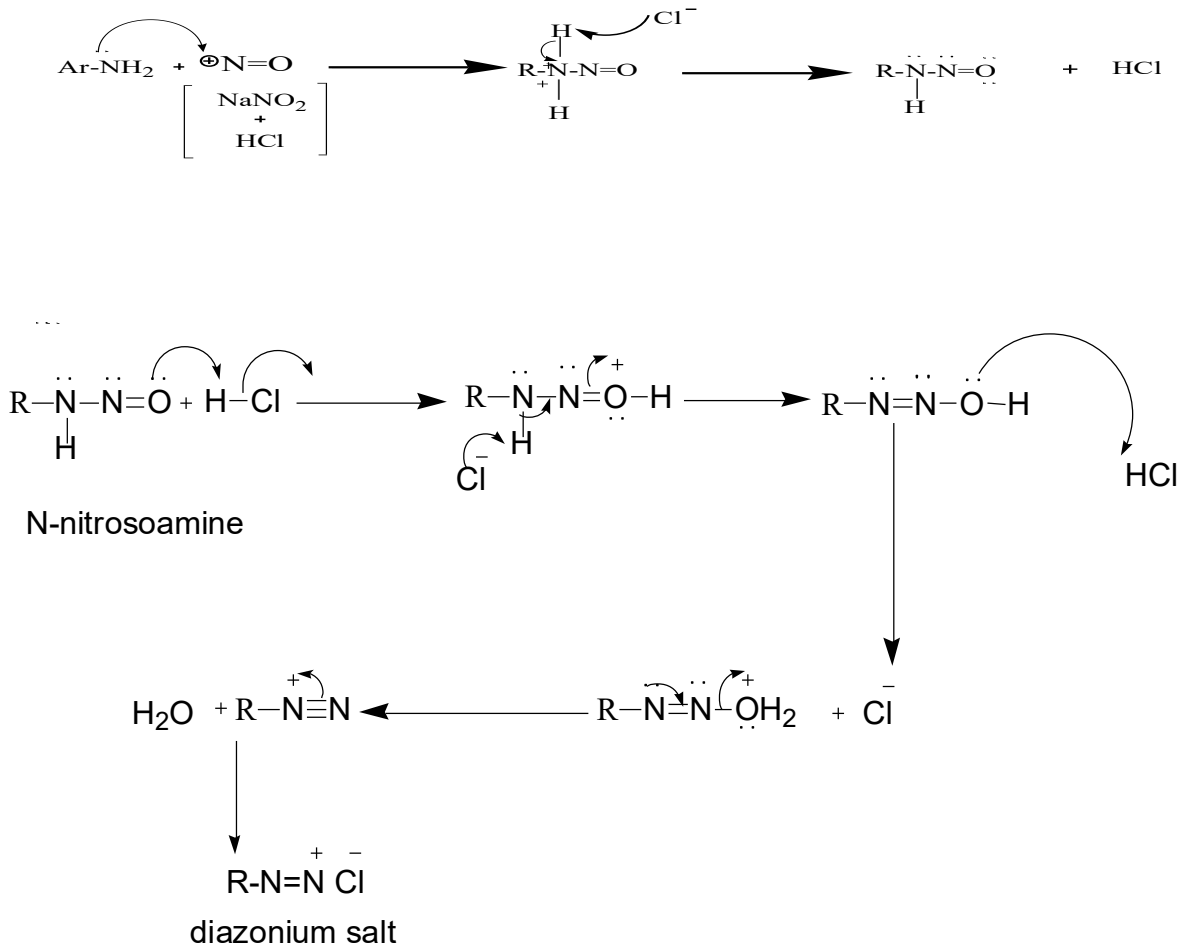
1.7 Diazonium Salt

Diazotization reactions normally proceed via the reaction of primary aromatic amines, aniline and it's related derivatives, with nitrous acid to form diazonium salt. The formed diazonium salts were capable to couple with organic benzene molecules yielding azo dyes. Besides dyes preparation, aromatic diazonium salts could also reacted by different procedures to give different materials for various purposes such as sensor [52], carbon nano tubes [53], polymers [54], and waste by-products treatment [55], which were relevant to many fields of life such medicine, industry, environment, etc. Numerous methods/ techniques, for preparation of diazonium salt required homogenous acid as a catalyst. Normally concentrated HCl or H_2SO_4 was used as homogenous catalyst in the synthesis of diazonium salt at low temperature [56, 57]. The environmental incompatibility is the main limitation of such catalysts. Simultaneously, the production of diazonium salts without using homogenous concentrated acids was not mentioned in the literatures. Recently, diazotization reactions of various aromatic compounds in aqueous acidic phase such as hydrochloric acid under mild conditions were taken place over the new silica immobilized with nano nitrite [58]. During the use of homogenous catalysts, the main challenging problem could be the productions of azo dyes over silica in heterogeneous phase catalyst. Additionally, there was no clean method for production of azo dyes support the green chemistry. Diazonium salt was investigated by German Scientist Peter

Griess in 1858 [59]. The general structural formula of diazonium salts ($R{-}N_2^+X^-$). R, refer to any organic residue like alkyl or aryl and X, represent an inorganic or organic anion like a halogen. Salts could be defined as the product obtained from the neutralization reaction of acid and base, so it is neutral compounds [60]. Diazonium salts could be described as an unstable compounds, high sensitive, so it was breakdown under near UV or violet light [61]. It is a very important synthetic reagent, it is a starting point in the synthesis of different aromatic compounds like dyes and drugs. Diazonium could be reduced into radicals which were an application in the covalent surface modification of carbon [62], semiconductors [63], and metal [64]. An important application of diazonium salts was the synthesis of azo dyes by coupling reaction [65, 66]. Nitrous acid was used for the diazotization of many aniline derivatives in acidic condition. The source of nitrous acid was sodium or potassium nitrite as result of the instability of free nitrous acid. Another source of nitrous acid was organic nitrite ester as ethyl nitrite and t-butyl nitrite in the organic solvent [67].

1.8 Mechanism of Diazonium Salts

The mechanism of diazonium salts involves several steps. Firstly, a nucleophilic attack of amine onto nitrosonium ion to form N–nitroso amine and loss of H_2O. Secondly the formation of diazonium ion through a series transformations which lead at last loss of H_2O (Scheme1.8).



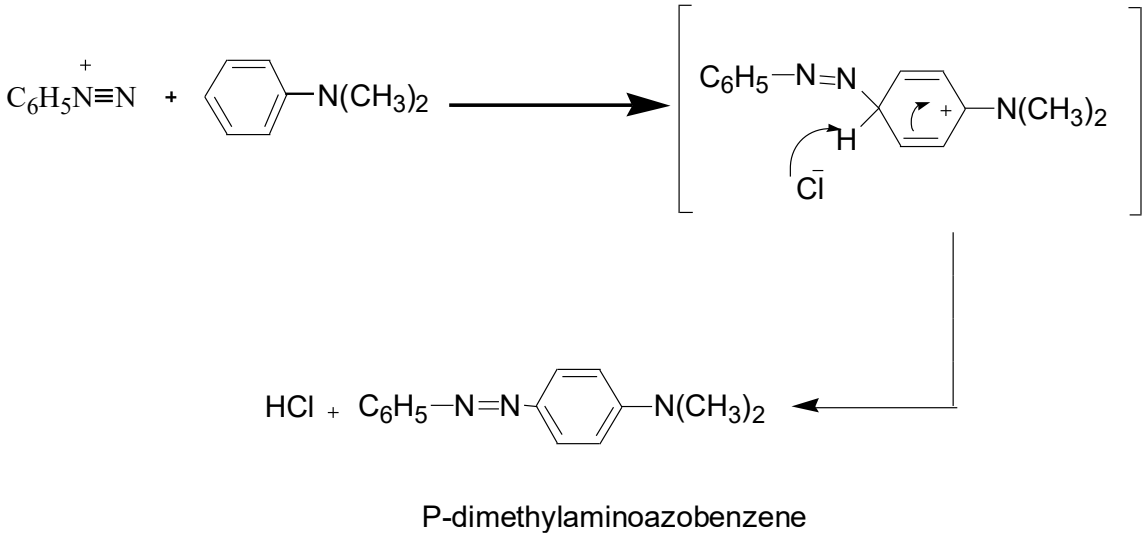
Scheme 1.8: The first step in mechanism is anucleophilic attack amine onto nitrosonium ion. The second step shows the formation of diazonium salts.

Diazotization is the manner of formation diazonium salt of the reaction of sodium nitrate, inorganic acid and primary aromatic amine in ice-chilled solution.

1.9 Diazonium Salts Reactions

There are two types of diazonium salts reactions. First one was the replacement reaction in which nitrogen atoms were replaced with different organic materials groups such as (hydroxyl, halogen, cyano-group, nitro-group, arsenic acid ASO_3H_2, aryl group). The second type was coupling reaction in which nitrogen atoms were grasped. The mechanism of coupling reaction involves electrophilic substituent with different benzene ring through the diazonium cation. This cation is weak electrophilic than the nitronium ion, therefore, they attack activated benzene ring only. For instance this phenol or aniline in order to form an azo compound

(Scheme 1.9) [68]. In general, the diazonium cation and phenoxide ion or free amine was an essential part of the coupling reaction mechanism [69].



Scheme 1.9: An example of diazonium salt reaction to form azo dyes.

1.10 Azo Dyes

Azo dyes include at least one nitrogen-nitrogen double bond (N=N), in general, there are several desirable structures [70]. Mono azo dyes in which one N=N double bond are a present. In common, the azo groups were bonded to aromatic rings. It could be bonded to aromatic heterocyclic or aliphatic groups. The side groups had a great role for color developing in the dye, with various different shades possible. Because of various models of dye components available for preparation, extremely different structure of azo dyes exists and widely used in industry [71]. Worldwide production of organic dyes were currently calculated approximately 450,000 tons, with 50,000 tons being lost in effluents during use and manufacture [72]. Dyes and pigments are defined as the important colorants that used to add a color or to change the color of the substrate [73, 74, 75, 76]. However, they were strongly colored compounds; they could be yellow, red, orange, blue or green, according to the present structure of the molecule.

Because of their color, azo compounds were important as dyes and also as pigments for a long time. In general, today half of the dyes that use in industry are azo dyes, which were prepared from diazonium salts [77]. The chemical structural of organic compounds, that often produce color are C=C, –N=O, –N=N–, aromatic rings, C=O and $–NO_2$. Most importantly, the groups that strongly produce color are the azo (–N=N–) and nitroso (–N=O) [78]. Moreover, azo dyes had wide application because of their excellent thermal and optical properties. Aromatic azo compounds were used as acid-base indicators, also they were used as optical recording medium [79], toner, In kjet printing, and oil-soluble lightfast dyes. Nowadays, azo compounds as organic dyes have also attracted attention because of their interesting electronic features for the connection and their application in molecular memory storage, nonlinear optical elements, and organic photoconductors, biomedical uses [80]. However, the importance of azo dyes was represented in preparation of dyes that were used extensively in the industry [81]. Dyes were widely used because to the easily preparation of azo-function group, it was used in Couple polymers [82], Nanoelectronic properties [83, 84],Mechanical motion [85], Linking group [86],Biomacromolecules and nanoparticles to the surface [87],To introduce light switching [88],To control wettability and swelling properties [89], Photomediated trans-to cis-interconversion of azo type [90], Development in a wealth of photo-responsive materials, involving reversible gel-sol systems [91], Polymers,Molecular switches [92], and Modified proteins[93]. A dye should be soluble in different medium, often water, while pigments are the colorants composed of particles that are insoluble in the application medium [94].

1.11 Theory of Catalysis

Theories of catalysis explain the influence of the catalysts upon the rate of a reaction by describing the detailed mechanism by which the catalyst is involved in the steps of the chemical reaction [95]. The following theories are proposed to explain the mechanism of catalysis.

(1) **Intermediate compound formulation theory**:

According to this theory one of the reactants combines with catalyst to form intermediate product, which carries out the reaction, E.g.

$$A + C \rightarrow AC$$
$$AC + B \rightarrow AB + C$$
$$A + B + C \rightarrow AB + C$$

where A and B are reactants, C is the catalyst and AC is the intermediate product.

$$4KClO_3 + 2MnO_2 \rightarrow 2KMnO_4 + 2KCl + Cl_2 + 4O_2$$
$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$
$$K_2MnO_4 + Cl_2 \rightarrow 2KCl + MnO_2 + O_2$$

$$or\ 2KClO_3 \overset{MnO_2}{\rightarrow} 2KCl + 3O_2$$

(2) **Adsorption theory:**

According to this theory, reactants are adsorbed on the surface of the catalyst and form a film. Due to high concentration of the reactants on the film, reaction proceeds at a faster rate.

(3) **Modern adsorption theory:**

According to this theory, reactants are adsorbed at the active centers i.e. free valencies etc. on the solid surface and form activated complex which under strain forms new molecules and leaves the surface. This explains, why the finely divided catalyst has greater activity.

(4) **Energy activation theory:**

According to this theory, catalyst changes the value of activation energy which can be crossed by the reactants easily and consequently products are formed.

Objectives of the Present Study

The main objectives of this research are:

1. Preparation a new heterogeneous catalyst that environmental friendly by available and cheap rice husk materials.

2. Characterization the structure of prepared catalyst by different spectroscopic, microscopic and other analytical techniques including TGA, CHNS analysis, N_2 adsorption-desorption, ^{29}Si and ^{13}C MAS NMR, FT-IR, SEM/EDX, and TEM.

3. The catalytic activity of the prepared catalyst was evaluated by the preparation of Azo dyes.

4. Optimization parameters and conditions of the catalyst in the diazonium generation for dyes preparation.

2.1 Raw Materials and Chemicals

All chemicals were of analytical grade or high purity and used directly without further purification. The rice husk was collected from a rice mill in Al Muthanna governorate, Iraq. The chemical materials that used in this thesis with their manufacturing companies and purity percentage were shown in (Table 2.1).

Table 2.1: Chemicals with their purity and the manufacture companies.

Entry	Chemical	Company	Purity %
1	Acetone	GCC	99

2	Aniline	BDH	98
3	Benzene	Merck	98
4	3-(chloropropyl)triethoxysilane	Sigma	98
5	Diethyl ether	GCC	99
6	DCM	Merck	99
7	α,α′-Dichloro-*p*-xylene	Aldrich	98
8	Ethanol	GCC	99
9	Imidazole	GCC	99
10	*m*-crysol	DH Scientific	98
11	N,N-dimethyl benzaldehyde	BDH	98
12	1-Naphthol	SDFCL	99
13	Nitric acid	Scharlau	65
14	*p*-Bromo benzaldehyde	BDH	99
15	Potassium carbonate	SDFCL	99
16	Resorcinol	SDFCL	99
17	Sodium hydroxide	Systerm	99
18	Sodium nitrite	Aldrich	99
19	Toluene	Fluka	99

2.2 Instrumentation

Some of analytical were done at School of Chemical Sciences, University Sains Malaysia, Malaysia. The other analytical such as (FT-IR, UV, TGA, and CHN) were done in College of Science, Al-Muthanna University, Iraq.

2.2.1 Fourier Transform- Infrared Spectrophotometer

FT-IR spectra done by using Fourier transformed infrared spectrophotometer (Shimadzu-8400S) using KBr disc and scanned from 400 to 4000 cm^{-1} in College of Science, Al-Muthanna University.

2.2.2 UV-Visible Spectrophotometer

The scanning spectra were measured using UV-Visible spectrophotometer (1650 pc Shimadzu) to identify the absorption of the dyes in College of Science, Al-Muthanna University.

2.2.3 Elemental Analysis (C.H.N)

The percentage of each C, H, and N was determined by elemental analysis using Perkin Elemer 2400 CHNS/O Series II System, Al-Muthanna University.

2.2.4 ^{1}H &^{13}C NMR

^{1}H&^{13}C NMR spectra were recorded on bruker 400 MHz at School of Chemical Sciences, University Sains Malaysia, Malaysia. The D_2O was used as solvent.

2.2.5 Thermogravimetric Analysis (TGA)/ Differential thermal analysis (DTA)

Thermogravimetric analysis (TGA) was recorded by using a TGA/DTA instrument; nearly 20.0 mg of the sample was heated from (100-900) ˚C at a heating rate of 20 ˚C min^{-1} under nitrogen flow. TGA/DTA was carried out in Iraq, College of Science, Al- Muthanna University.

2.2.6 Nitrogen Adsorption-Desorption Analysis

Nitrogen adsorption was recorded using (Nova 2200e, Surface area and pore size analyzer). The measurement was done at the School of Chemical Sciences, University Sains Malaysia, Malaysia.

2.2.7 Scanning Electron Microscopy /Energy Dispersive X-ray (SEM/EDX)

The scanning electron microscopy (SEM) was recorded using (Leica Cambridge S360). The measurement was done at the School of Biology Sciences, University Sains Malaysia, Malaysia.

2.2.8 Transmission Electron Microscopy (TEM)

The transmission electron microscopy (TEM) was obtained using Philips CM12 equipment. The measurement was done at the School of Biology Sciences, University Sains Malaysia, Malaysia .

2.2.9 ^{29}Si MAS NMR Spectroscopy

^{29}Si MAS NMR analysis for RHAPrIM were done to know the chemical environmental of Si atoms. The analysis was performed at a magnetic field of 400MHz on a Bruker AV400 WB solid state NMR equipped with a magic angle-spinning (MAS) unit. The ^{29}Si was recorded at 59.62 MHz with 15.0 sec recycle and 5385 scans.

2.3 Preparation of Starting Materials

2.3.1 Extraction of Silica from Rice Husk

The source of amorphous silica was the rice husk RH as it was available in abundance. The extraction of silica from RH according to the method reported [96]. 35 gm of rice husk was washed with enough amount of water and rinsed with distilled water. After drying at room temperature, 35 gm of rice husk was stirred with 1.0 M (750 mL) nitric acid at room temperature for about 24 h, then washed with distill water and drying at 110 ˚C. The cleaned RH was pyrolyzed in a muffle furnace (Carbolite, UK, Model AAF 11/7) at 800 ˚C for 6 h. The white ash was washed with distilled water and was used as the source of silica [97]. The white ash was labeled as RHA.

2.3.2 Preparation of RHACCl

The immobilization of CPTES on the silica was done according to the method reported [30]. 3.0 gm from RHA was added to 100 mL of 1.0 M NaOH and stirred for 60 min at room temperature to form sodium silicate. The prepared sodium silicate was filtered to remove undissolved particles, then 6.0 mL of 3-chloropropyltriethoxylsilane was added to the solution. Under constant stirring the solution was titrated slowly (1.0 mL min^{-1}) with 3.0 M Nitric acid. The change in pH was monitored by a pH meter. In pH 9 a white gel was started to form. When the pH of the solution reached 3.0, the titration was stopped and the gel was kept covered to the next day at room temperature. The separation process was done by using centrifuge at 4000 rpm for 15 min, the seperation process was repeated 6 times and washed with distilled water, last washed was done with acetone. After that, the sample was dried at 110 ˚C for 24 h. A fine powder was weighted (6.7 gm) and labeled as RHACCl [29].

2.3.3 Preparation of *p*-xylylbisimidazole (Bis-Imi)

A mixture of *p*-xylylene dichloride (8.0 mmol, 1.5 gm) and (16.0 mmol, 1.16 gm) of imidazole were mixed and stirred with 30 mL ethanol in an oil bath and refluxed for 24 h at (70-80) ˚C. The product was cooled in ice bath until the crystal appeared, and then the solvent

was removed. The product was washed by diethyl ether and dissolved in 30 mL (6 %) potassium carbonate for 3 days. The product was filtered and recrystallized in water. The white product was dried in an oven at 50 ˚C for 24 h. The product was labeled as (Bis-Imi). The yield was 76.0 %.

2.4 Synthesis of Heterogeneous Catalyst *p*-xylylbisimidazolium Chloride-Silica Catalyst (RHAPrIM)

The resulting solid, RHACCl, was used as support to the *p*-xylylbisimidazole onto the silica. RHAPrIM was synthesis by mixing (5.0 mmol, 1.0 gm) of *p*-xylylbisimidazole with (1.0 gm) of RHACCl in 30 mL of dry toluene. The reaction mixture was refluxed at 110 ˚C in an oil bath for 24 h. The catalyst was filtered, washed with three different solvent toluene, DCM, ethanol. The catalyst was dried at 110 ˚C for 24 h. Finally, a fine powder of catalyst was labeled as (RHAPrIM).

2.5 Catalyst Activity on Synthesis of Azo Dye

100 mg of RHAPrIM were mixed with 1.0 mL (10 mmol) of aniline which was soluble in 5.0 mL of distilled water. About 0.69 gm (10 mmol) of sodium nitrite was dissolved in 5.0 mL of distilled water then added to the catalyst-aniline mixture very slowly and stirring for 24 h, while the temperature never goes above 15 ˚C. Thereafter, the catalyst was removed by simple filtration. About 0.2 gm of resorcinol which was dissolved in 2.0 mL of 10 % NaOH and then 5.0 mL distilled water were added. The mixture color was changed directly which indicated to the end point of the reaction.

2.6 The Optimization of the Reaction Conditions

2.6.1 The Optimization of the Catalyst Mass

The catalytic activity with different mass of catalyst (50, 100, 200, and 250) mg was studied in the same procedure in Section 2.5. The comparison between the results was done to reach the optimum mass.

2.6.2 The Optimization of the Reaction Temperature

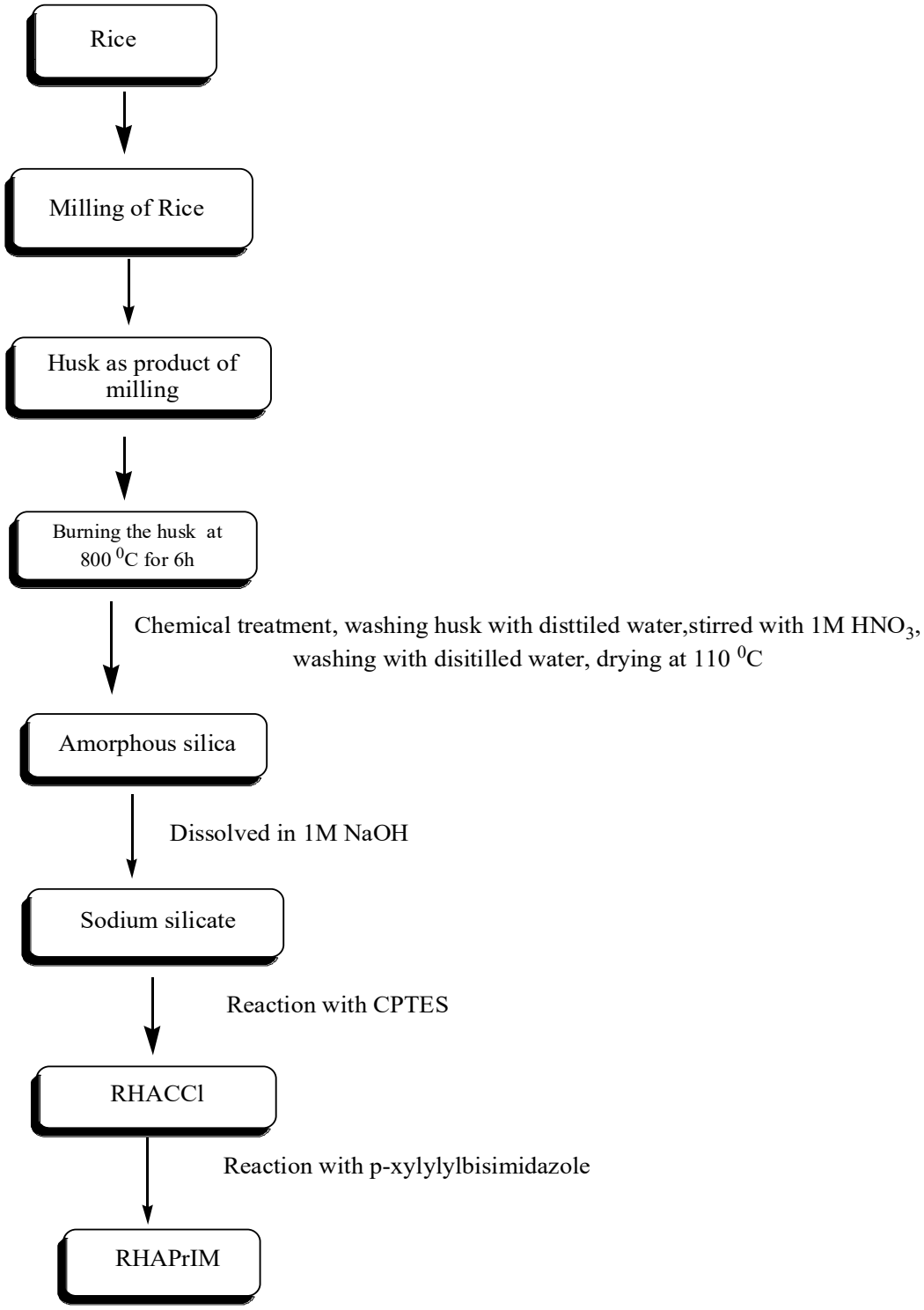
The catalytic activity with different temperature (5, 10, and 15) ˚C was studied in the same procedure in Section 2.5. The optimum temperature is the temperature which gives high yield of dyes.

2.6.3. The Solvent's Effect

The catalytic activity with different solvent such as (water, diethyl ether, ethanol, and benzene) was studied in the same procedure in Section 2.5. The high yield of dyes is the key to know the best solvent which is suitable for this reaction in presence of RHAPrIM.

2.6.4 Regeneration of the Catalyst

Reusability experiment was conducted by running the reaction with the catalyst under the optimum conditions. The reaction was first run with the fresh catalyst to complete conversion and then the catalyst was filtered and washed with ethanol and dried at 110 ˚C for 24 h. After regeneration, the catalyst was reused for second and third times under the optimized reaction conditions.



Scheme 2.1:Research diagram for the catalyst preparation

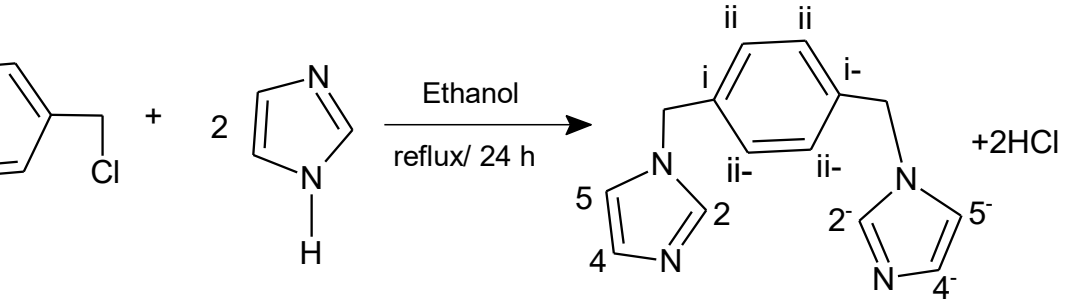
3.0 Materials Synthesis

A solution of *p*-xylylenedichloride and imidazole was refluxed to form *p*-xylyl bisimidazole (Bis-Imi). Formation of Bis-Imi basically depends on the replacement of chloride in *p*-

xylylenedichloride with imidazole under refluxed condition Scheme 3.1. CPTES was necessary for functionalization of silica from RHA. The product of this treatment resulted with CH_2–Cl as the end group on the solid. Immobilization procedure via proton abstraction from the amine group in imidazole and alkyl chloride bonded to silica propyl chain was taken place in Scheme 3.2. This reaction was anchored Bis-Imi to silica via the connection to propyl chain in organosilane.

3.1 The Synthesis of *p*-xylylbisimidazole

The preparation of Bis-Imi was carried out by the reaction between *p*-xylylene dichloride and two moles imidazole under reflux conditions for 24 h as shown in Scheme 3.1. Deep analysis for the *p*-xylylbisimidazole was carried including ^{1}H & ^{13}C NMR, elemental analysis, and FT-IR as in the subtitle below [97].



Scheme 3.1: The synthesis of *p*-xylylbisimidazole (Bis-Imi).

3.1.1 Fourier Transforme Infrared Spectroscopic Analysis of Bis-Imi

The FT-IR spectrum of *p*-xylylbisimidazole Fig.3.1. showed a band at 3200 cm^{-1} attributed to the stretching vibration of aromatic C–H bond [98]. The stretching vibration of C–H aliphatic was observed around 2978 cm^{-1}. The band at 1660 cm^{-1} was attributed to the stretching vibration of imine C=N bond [99]. The band at 1448 cm^{-1} was attributed to bending

vibration of N=C–H bond. The stretching vibration of C–N bond was observed around 1379 cm^{-1}.

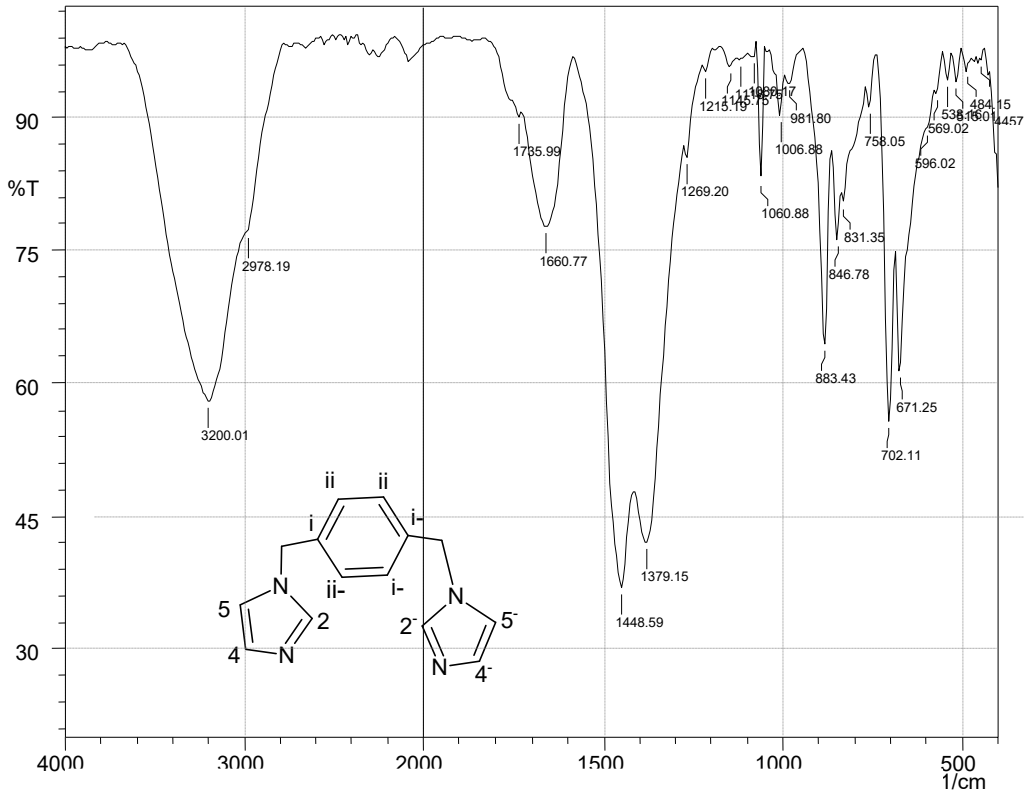


Fig. 3.1: The FT-IR spectrum of Bis-Imi.

3.1.2 The Elemental Analysis of Bis-Imi

The elemental analysis of Bis-Imi showed 70.82 % percent of carbon and 5.61 % percent of hydrogen. The analysis showed 19.63 % of nitrogen. While the theoretical percentage of carbon 70.58 %, hydrogen 5.88 %, and nitrogen 23.52 %. The experimental and calculated percentage compositions of the elements agreed within each other. This indicate successfull formation of *p*-xylylbisimidazole.

3.1.3 The ^{1}H NMR Analysis of Bis-Imi

Fig. 3.2 shows ^{1}HNMR spectrum of the Bis-Imi. There were different chemical shifts at many position observed. ^{1}H NMR spectrum shows the presence of imidazole protons H_2, $H_{2'}$ signal (N–CH–N) at chemical shift 7.7 ppm. This chemical shift is consistent with the chemical shifts of common imidazole salts [100]. The singlate chemical shift at 5.1 ppm due to four protons of two methylene groups (–CH_2). Two proton of imidazole rings labeled as H_5, H_{5-} were shown douplit peaks at 6.9 ppm. While H_4 ,$H_{4'}$ protons of imidazole rings were shown a chemical shifts at 7.2 ppm. The chemical shift at 7.4 ppm was due to the four protons of aromatic ring (Hii,Hii^{-}).

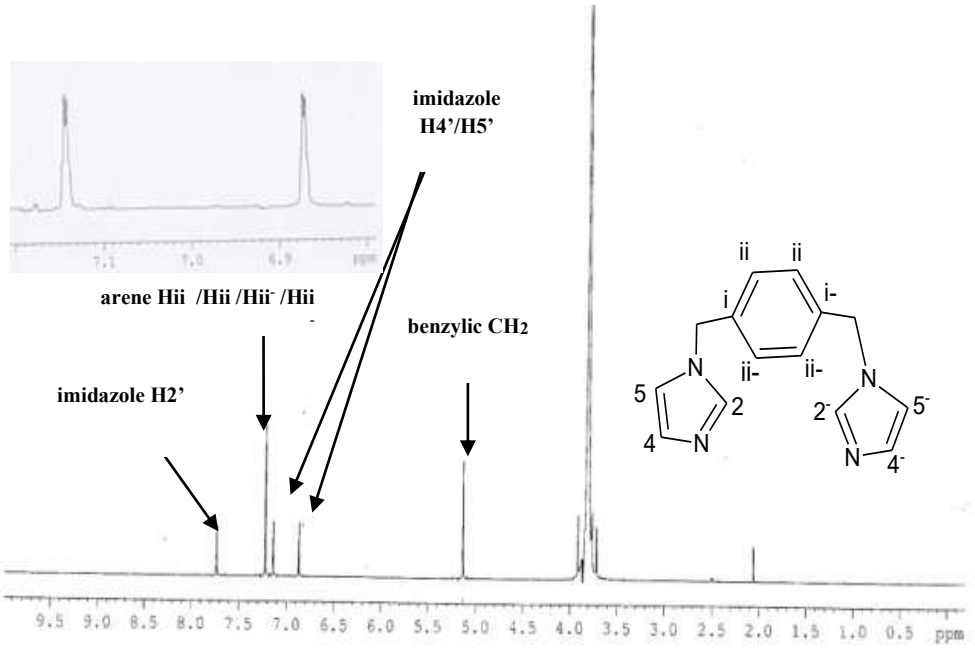


Fig. 3.2: The ^{1}H NMR spectrum of Bis-Imi in d_3-CD_3CN

3.1.4 The ^{13}C NMR Analysis of Bis-Imi

Fig. 3.3 shows the ^{13}C NMR analysis of the Bis-Imi. It showed several sharp chemical shifts at 120.39, 128.68, 129.62 and 138.18 ppm which were assigned to the aromatic carbon in the benzene ring and the imidazole rings. The chemical shift at 120.39 ppm should be due to the two carbon atoms labeled (i, i^{-}) in the benzene ring. The chemical shift at 128.68 ppm due to the carbon atoms labeled (ii, ii^{-}) (four carbon atoms of the benzene ring). The chemical shift at 129.62 ppm was due to the two carbon atoms of the imidazole labeled as 4, 5, 4^{-}, 5^{-}. Both carbons limite of resonate very closely even be indistinguishable by NMR. The chemical shift at 138.18 ppm was assigned to the imidazole carbon (NCN) labeled 2, 2$^{/}$ and the chemical shift at 49.96 ppm was assigned to the alkyl carbon (Bz–CH_2–N). The chemical shift centered at 40.31 ppm was assigned to the solvent CD_3CN.

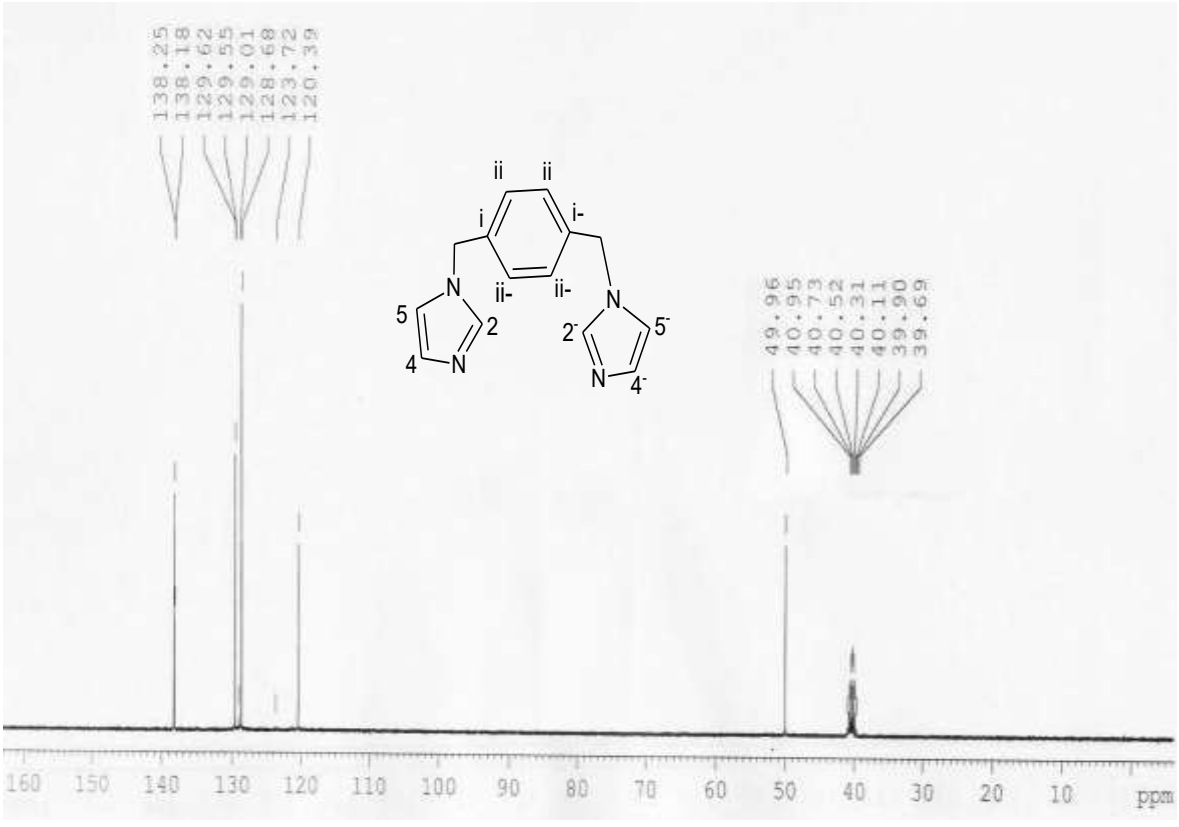
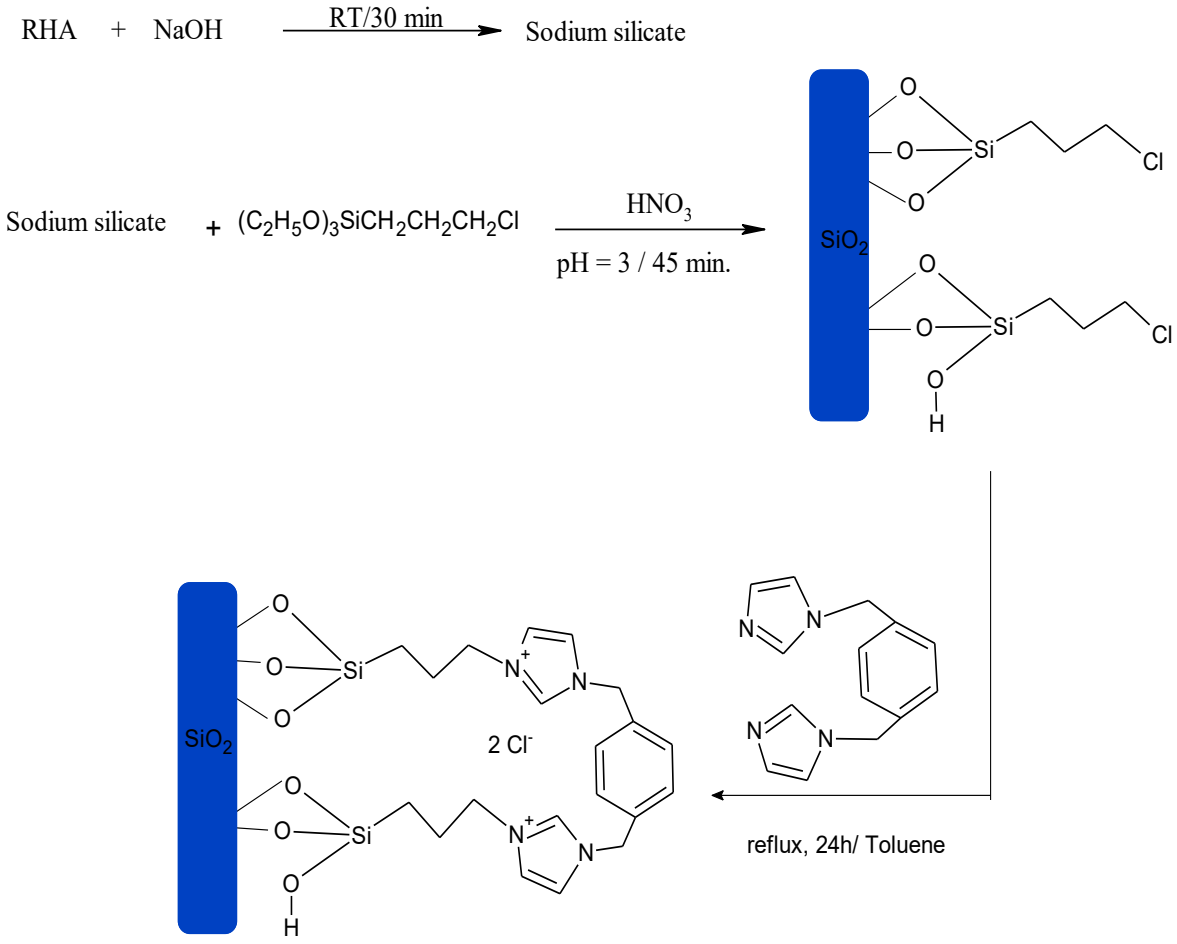


Fig. 3.3: The ^{13}C NMR spectrum of Bis-Imi in d_3-CD_3CN

3.2 The Synthesis of Solid *p*-xylylbisimidazolium Chloride-Silica Catalyst (RHAPrIM)

The silica from RHA was extracted by the method previously published in literature [101,102]. The RHA was treated with sodium hydroxide to form sodium silicate which was used to immobilize CPTES onto the silica surface by a simple sol-gel method as shown in Scheme 3.2. The resulting product was labeled as RHACCl.

p-xylylbisimidazolium chloride-silica, RHAPrIM nano solid catalyst was prepared via the reaction between RHACCl and *p*-xylylbisimidazole. Both the reactants were suspended in the toluene medium. Scheme 3.2 shows the schemetic reaction for the preparation of RHAPrIM.



Scheme 3.2: The simple sequence of reactions and the possible structure for RHAPrIM catalyst.

FT-IR of RHAPrIM Catalyst 3.2.1

The spectra of RHACCl, RHAPrIM with differential are given in Fig. 3.4. The FT-IR spectra allowed to observe the bands characteristic of most functional groups of mesoporous RHAPrIM. A previous studies had been described the Si–O–Si vibrations of RHA which appeared at 1101 cm^{-1}[103].The vibration is observed to shift to 1082 cm^{-1} in RHACCl and to 1061 cm^{-1} in RHAPrIM. Silanol groups (SiO–H) and absorbed water (HO–H) appeared as a broad band around 3458 cm^{-1} [104]. At 3225 cm^{-1} in the differential the absorption band corresponds to the imidazole C–H bond vibration was appeared. Benzene ring identified by vibration of C=C stretching at 1566 cm^{-1}. While in the differential spectrum the vibration at 1618 cm^{-1} was due to the imine groups C=N. The vibration at 1225 cm^{-1} was due to Si–C covalent bond. All these vibrations for the expected functional groups FT-IR refers that Bis-Im molecules were loaded onto silica via RHACCl.

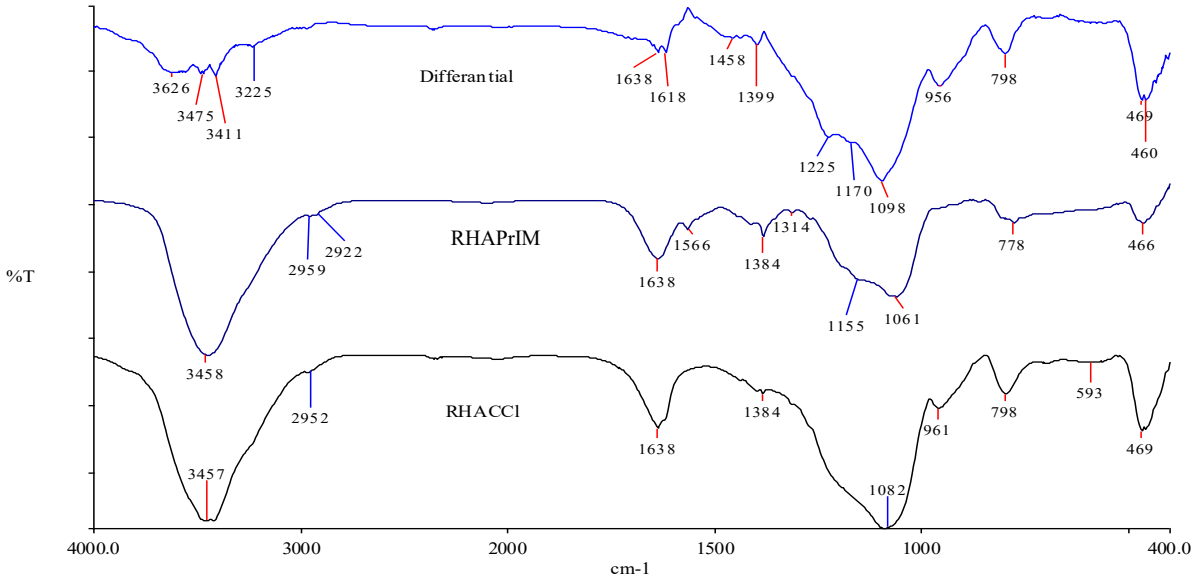


Fig. 3.4: The FT-IR spectra of RHACCl, RHAPrIM and the differential spectrum.

Elemental Analysis for RHA, RHACCl, and RHAPrIM 3.2.2

Table 3.1 shows the elemental analysis results of RHA, RHACCl, and RHAPrIM. The result of EDX analysis are shown in brackets. The percentage of carbon and hydrogen in RHACCl was found to be 11.7 % and 1.76 % respectively. The percentage of carbon and hydrogen in RHACCl was more than of RHA. From the increased amount of C, this indicated that CPTES was incorporated onto RHA silica to produce RHACCl. Similar conclusion was made by Hello *et al.* (2010) and Brunel *et al.* (1999) [30]. Carbon content of RHAPrIM 16.74 %, (30.22 % according to the EDX) was slightly higher than RHACCl, as a result of immobilization of Bis-Imi. Nitrogen composition showed of 1.91 %, (3.30 % according to the EDX). The elemental data analysis reflects that the Bis-Imi was indeed incorporated on the silica. Elemental analysis showed the presence of N in RHAPrIM catalyst, but it was not found in RHA and RHACCl. It had been a good indication to conclude that the *p*-xylylbisimidazole was successfully incorporated to form RHAPrIM catalyst.

Table 3.1: Elemental analysis for RHA, RHACCl, RHAPrIM. The EDX data between brackets.

Sample	Elemental analysis (%)				
	C	H	N	Cl	Si

RHA	0.84	1.6	-	-	- (29.09)
RHACCl	11.70 (23.93)	1.76 -	- -	- (3.07)	- (23.47)
RHAPrIM	16.74 (30.22)	2.34 (-)	1.91 (3.30)	- (3.8)	- 16.69

3.2.3 Thermogravimetric Analysis (TGA)/Differential Thermal Analysis (DTA) for RHAPrIM

Several informations can be deducted from the TGA/DTA analysis. The moisture content, the percentage of inorganic and organic materials immobilized onto the surface of the silica, it's decomposition point, the stability of the catalyst, and determined the range in which the catalyst can be used. Some reactions require temperatures higher than the temperature range of the catalyst, that leads to decomposition of the catalyst and loss of catalytic activity. Fig. 3.5 shows the TGA/DTA graphs of the RHAPrIM catalyst .

The analysis was carried out in the range of 39 - 908 °C. The TGA analysis of RHAPrIM showed four characteristic decomposition stages. The first mass loss of ca. 7.1 % at 100 °C was due to the loss of surface absorbed water. The second mass loss of ca. 19.3 % between 200 to 270 °C was assumed to be associated with the decomposition of the propyl and *p*-xylylbisimidazol which was immobilized onto the silica surface. The third mass loss of ca. 7.7 % from 280 to 400 °C was due to the decomposition of the residual organic groups deep within the pore system. The fourth mass loss (ca. 1.1 %) at 514 °C, attributed to the formation of siloxane groups as a result of silanol groups condensation and the condensation of neighboring silanol in order to form siloxane bonds and releasing water in the process.

The DTA curve shown in Fig. 3.5 shows four exothermic transformations. The first one occurs in the rang 30-100. It could be due to the loss of absorbed water. The second exothermic occurs between 200-277 ˚C with a maximum at 258 ˚C. The third exothermic occurs between 277- 410 ˚C with a maximum at 344 ˚C and the fourth in the rang (410 - 560) ˚C with a maximum at 514 ˚C. The second and the third transformation were attributed to the arrangement of the organic structure of the catalyst [105]. The fourth attributed to the formation of siloxane groups as a result of silanol groups condensation. Thus, according to the TGA/DTA analysis, it was concluded that Bis-Imi was incorporated onto the silica surface.

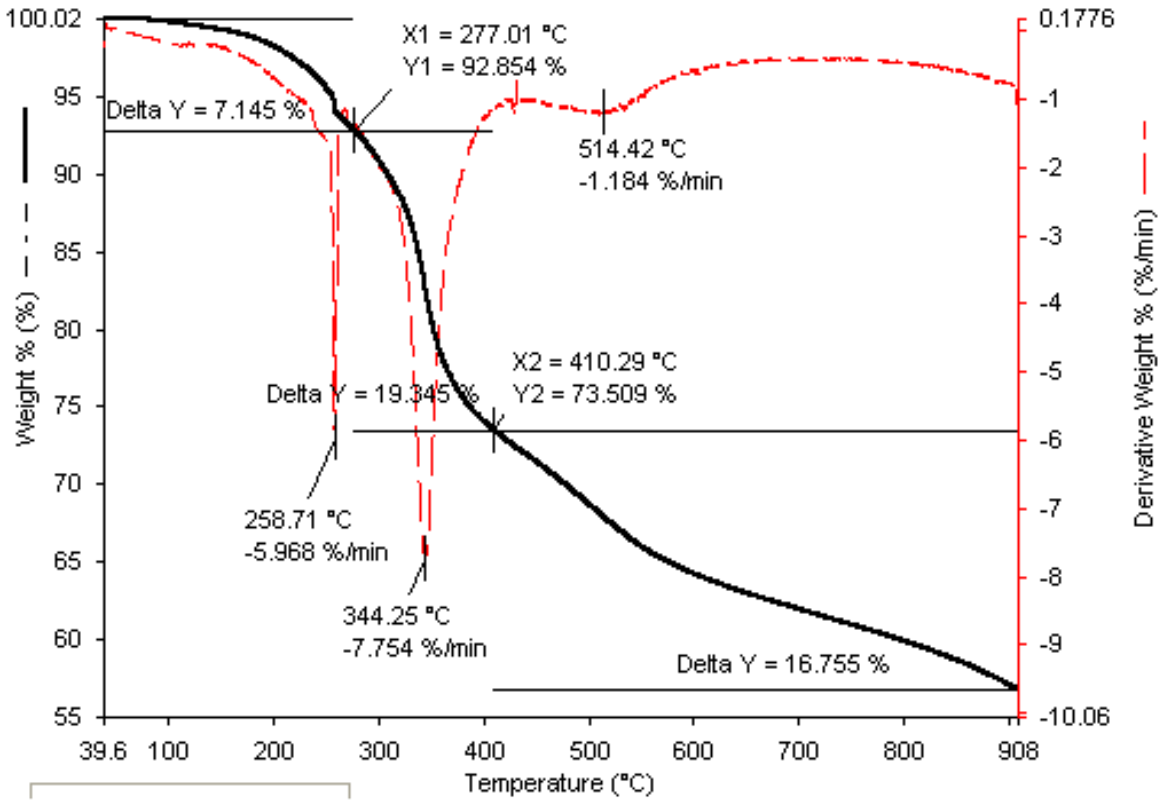
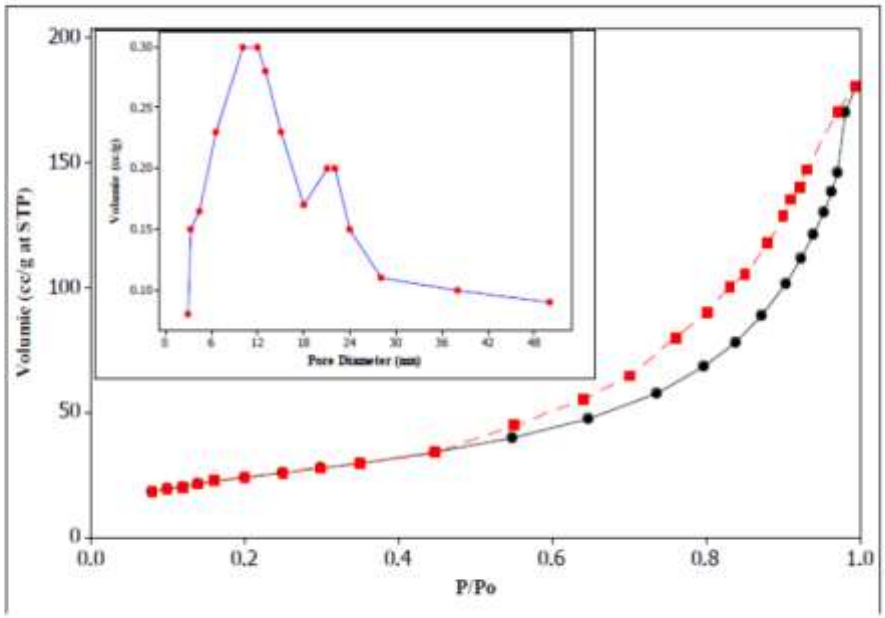


Fig. 3.5: Thermogravimetric analysis and differential thermal analysis of RHAPrIM.

3.2.4 Nitrogen Adsorption–Desorption Analysis

Nitrogen adsorption analysis Brunauer-Emmett-Teller (BET) method has been used to determind the specific surface area, pore diameter and pore volume of the prepared materials [34]. Fig. 3.6 shows the nitrogen adsorption isotherm for RHAPrIM with the inset showing the pore size distribution curve. The rang of the hysteresis loop was $0.70 < P/P0 < 0.85$. This was associated with capillary condensation according to IUPAC classification. The isotherm exhibited by RHAPrIM was type IV with H1 hysteresis loop, indicating a highly ordered mesoporous structure [106].

The specific surface area of RHAPrIM was found to be 91.2 $m^2 g^{-1}$ while it was 347 $m^2 g^{-1}$ for RHA [98], 633 $m^2 g^{-1}$ for RHACCl [29]. In RHAPrIM however, the pendent group was too large and restricts the availability of adsorption sites resulting in a drastic reduction in the specific surface area. The average pore volume was 0.24 $cm^3 g^{-1}$. It had decreased as compared to RHA and RHACCl. It was attributed to the presence of Bis-Imi on the surface which blocked the pores in the silica matrix. The pore size distribution of RHAPrIM was found to be narrow at ca. 10.9 nm which was in the mesoporous range. The data of the nitrogen adsorption–desorption analysis is shown in Table 3.2.



Fig

3.6: The nitrogen adsorption–desorption isotherm of RHAPrIM. The inset shows the corresponding pore size distribution.

Table 3.2: The nitrogen adsorption–desorption parameter for RHA, RHACCl, RHAPrIM.

Sample	Surface area (m^2/gm)	Averge pore diameter (nm)	Averge pore volume (cm^3/gm)
RHA	347	10.4	0.87
RHACCl	633	6.04	0.70
RHAPrIM	91.16	10.9	0.24

Scanning Electron Microscopy (SEM)3.2.5

Fig. 3.7 shows the SEM analysis of RHAPrIM. Close observation of the image (Fig. 3.7 (c, and d)) at higher magnification, revealed the presence of aggregate particles that may be

associated with its highly porous nature surface. The SEM images also show irregular shapes arranged randomly on a smooth surface. No specific geometrical shapes are observed.

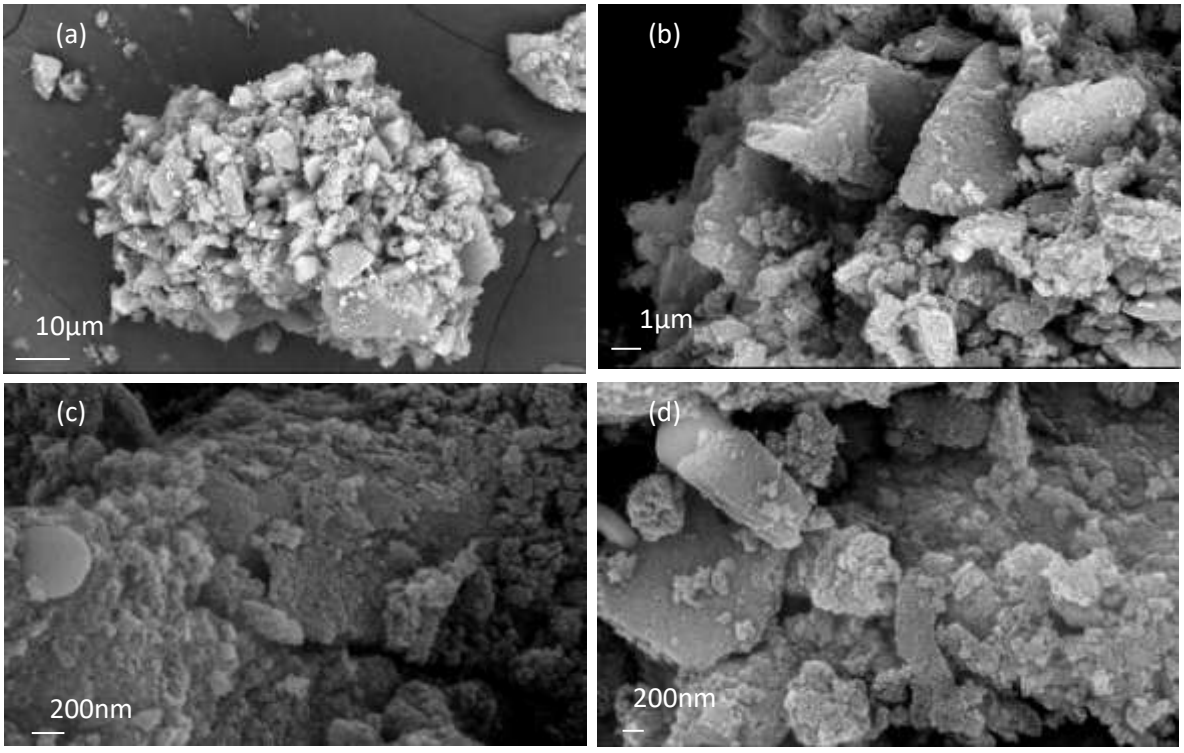


Fig. 3.7: The SEM images of RHAPrIM at different Magnifications.

Transition Electron Microscopy (TEM) 3.2.6

Fig. 3.8 shows the TEM images for RHAPrIM which appeared as spherical particles. However, on higher magnification these spherical particles appeared to have a rough surface resulting in the highly porous surface. As clearly shown that the RHAPrIM consist two types

of spherical particles. Both those particles have approximately size of ca. 5 nm. The first type of particle seems to be smooth in shape, while the second one shows porous shape. The particles sizes were in nano range which might have important characterization besides having a catalyst.

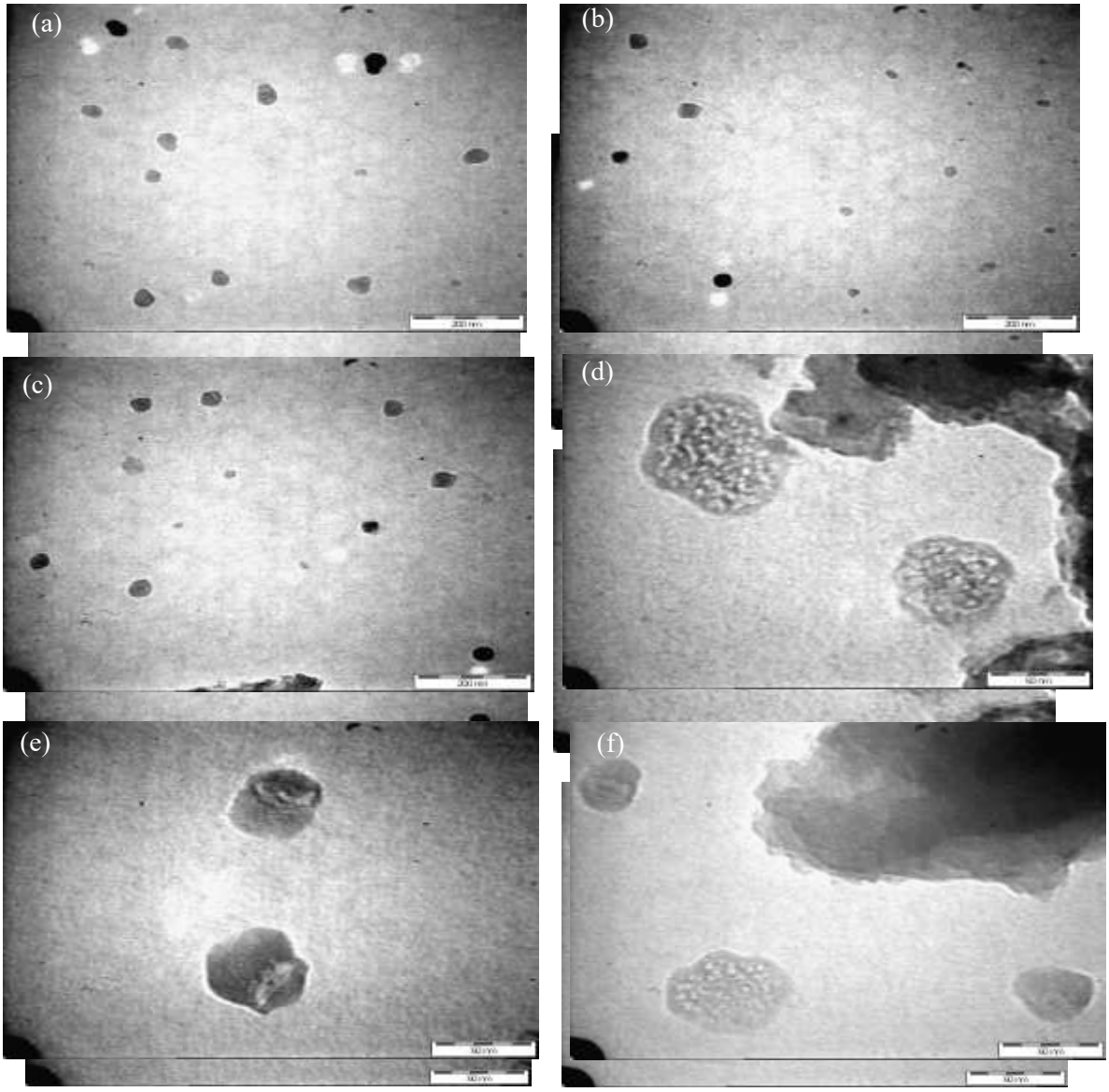
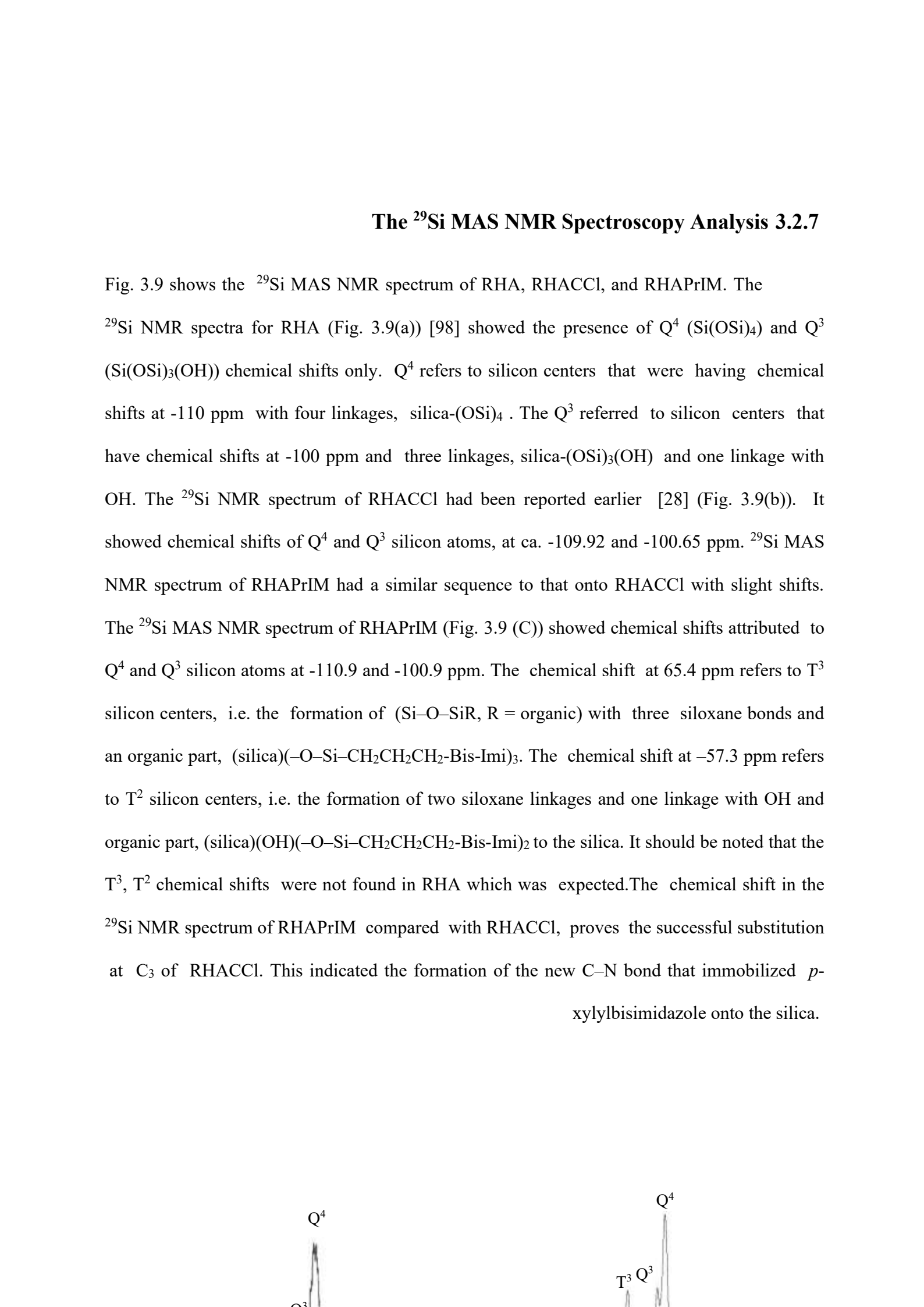


Fig. 3.8: The TEM images for RHAPrIM at different magnifications.

The ^{29}Si MAS NMR Spectroscopy Analysis 3.2.7

Fig. 3.9 shows the ^{29}Si MAS NMR spectrum of RHA, RHACCl, and RHAPrIM. The ^{29}Si NMR spectra for RHA (Fig. 3.9(a)) [98] showed the presence of Q^4 ($Si(OSi)_4$) and Q^3 ($Si(OSi)_3(OH)$) chemical shifts only. Q^4 refers to silicon centers that were having chemical shifts at -110 ppm with four linkages, silica-$(OSi)_4$. The Q^3 referred to silicon centers that have chemical shifts at -100 ppm and three linkages, silica-$(OSi)_3(OH)$ and one linkage with OH. The ^{29}Si NMR spectrum of RHACCl had been reported earlier [28] (Fig. 3.9(b)). It showed chemical shifts of Q^4 and Q^3 silicon atoms, at ca. -109.92 and -100.65 ppm. ^{29}Si MAS NMR spectrum of RHAPrIM had a similar sequence to that onto RHACCl with slight shifts. The ^{29}Si MAS NMR spectrum of RHAPrIM (Fig. 3.9 (C)) showed chemical shifts attributed to Q^4 and Q^3 silicon atoms at -110.9 and -100.9 ppm. The chemical shift at 65.4 ppm refers to T^3 silicon centers, i.e. the formation of (Si–O–SiR, R = organic) with three siloxane bonds and an organic part, (silica)(–O–Si–$CH_2CH_2CH_2$-Bis-Imi)$_3$. The chemical shift at –57.3 ppm refers to T^2 silicon centers, i.e. the formation of two siloxane linkages and one linkage with OH and organic part, (silica)(OH)(–O–Si–$CH_2CH_2CH_2$-Bis-Imi)$_2$ to the silica. It should be noted that the T^3, T^2 chemical shifts were not found in RHA which was expected.The chemical shift in the ^{29}Si NMR spectrum of RHAPrIM compared with RHACCl, proves the successful substitution at C_3 of RHACCl. This indicated the formation of the new C–N bond that immobilized *p*-xylylbisimidazole onto the silica.



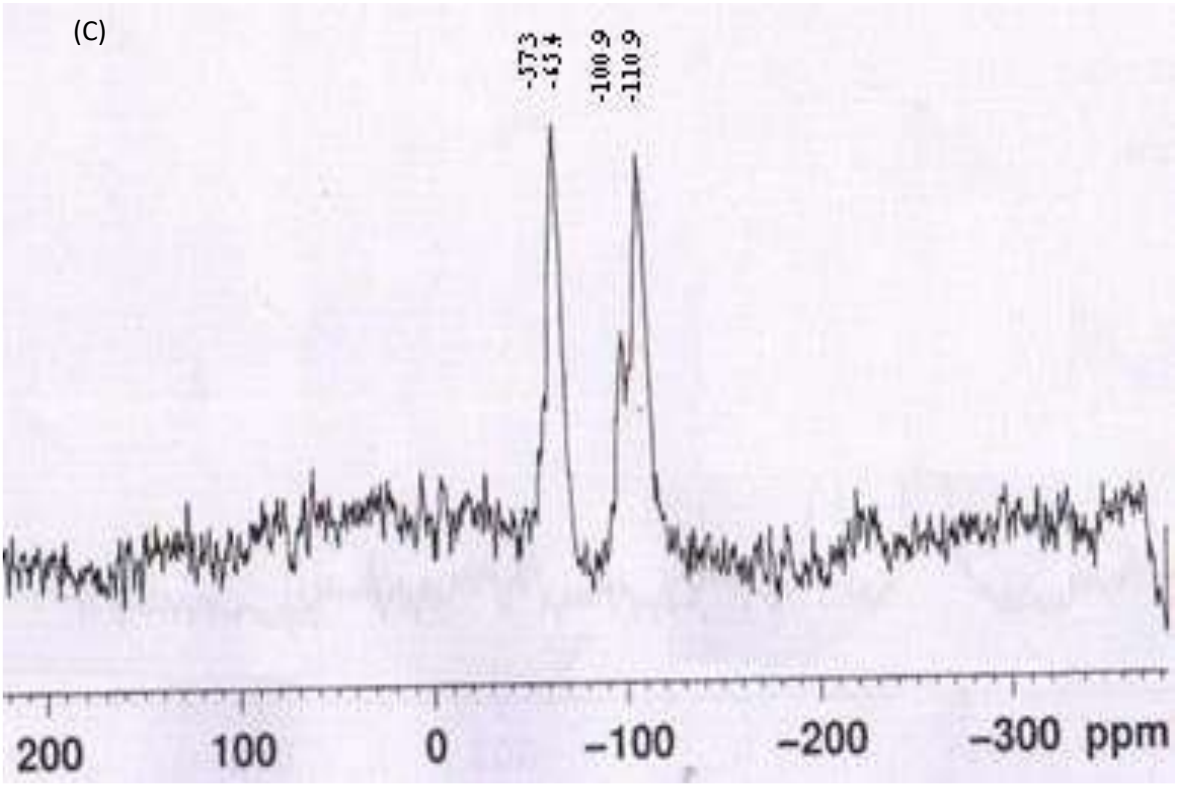


Fig. 3.9: The solid state ^{29}Si MAS NMR spectrum. (a) RHA [adapted from Ahmed & Adam (2007) [98]], (b) RHACCl [adapted from Hello (2010)[30]], (C) RHAPrIM.

The ^{13}C MAS NMR Spectroscopy Analysis 3.2.8

Fig. 3.10 shows the solid state ^{13}C NMR of RHACCl, and RHAPrIM. The carbon bonded to silicon is shown at 10.4 ppm (C_1 carbon). At 26.6 ppm the peak is assigned to the C_2

carbon, while the C_3 carbon is observed at 47.69 ppm. Comparing to the ^{13}C NMR of RHACCl (Fig. 3.10 (a))[30] those chemical shifts were down field shifted. The peaks at 52.9 and 64.3 ppm were corresponding to the two CH_2 groups. Imidazole carbons ring C_4, C_5, $C_{4'}$& $C_{5'}$ (Scheme 3.1) chemically equivalent are shown at 122.3 ppm. Benzene ring (4 × ArC) was appeared at 128.9, 130.8 ppm. The chemical shift at 135.2 ppm is related to the two aromatic carbons which they bonded to the CH_2 groups. The chemical shifts at 134.6 and 136.1 ppm were referred to the imidazole carbon atom C_2, $C_{2'}$ (Scheme 3.1).

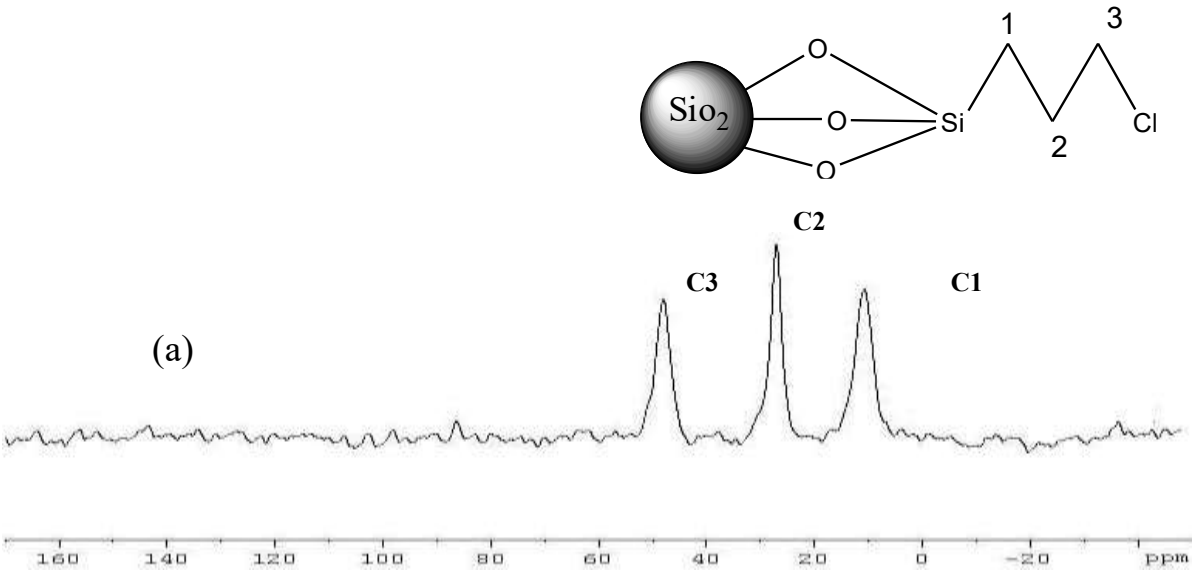




Fig. 3.10: The solid state ^{13}C MAS NMR spectrum of (a) RHACCl [adapted from Hello (2010)[30]], (b) RHAPrIM.

4.0 Catalytic Performances

The catalytic activity of RHAPrIM was examined in–situ preparation of nitrous acid which was used to prepare diazonium salt. In the case of it's reaction with aniline, the aniline was first dissolved in water at the presence of RHAPrIM catalyst. To that mixture, a solution of sodium nitrite was added. This reaction produced in–situ nitrous acid which attacks aniline and forming diazonium salt. After the formation of diazonium salt, simple filtration was necessary to remov the catalyst. The final reaction was a coupling of the diazonium salt with resorcinol as a model substrate to produce azo dyes.

4.1 Influence of Catalyst's Mass

The activity of RHAPrIM was analyzed at different masses of catalyst. Coupling reaction of the diazonium salt with resorcinol was a common method to synthesize azo dye. Four different mass of RHAPrIM were used (50, 100, 200, and 250 mg) to reach the optimum mass of catalyst as shown in Table 4.1 (Fig. 4.1). The yield reached to its maximal 59% when the reaction is carried out using 100 mg at 0-5 $^{\circ}$C. The increases of the catalyst mass to 250 mg, however, the yield does not change. At catalyst

mass of less than 100 mg, it was observed that the yield decreased to be 40 %. Thus, the 100 mg of catalyst mass was selected to be optimum.

Table 4.1: The effect of catalyst mass on the production of azo dyes over RHAPrIM catalyst.

Variants (mg)	Azo Dyes Yield (%)	Temperature (˚C)
50	40	
100	59	0-5
200	52	
250	55	

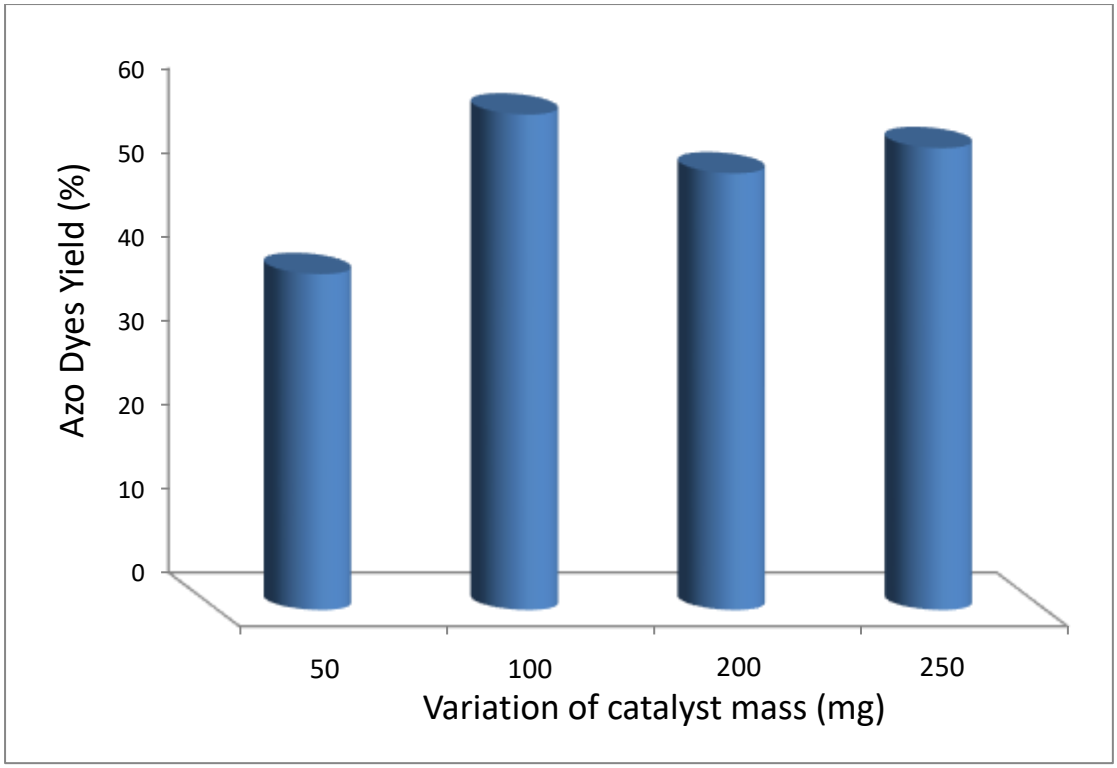


Fig. 4.1: The effect of catalyst mass on the production of azo dyes over RHAPrIM catalyst.

4.2 Influence of Temperature

Temperature is the very important factor in the reaction due to the fact that the sensitivity of nitrous acid, therefore the reaction temperatures was controlled to be not more than 15 ˚C. Clearly found that when the reaction temperature increased from 0 to 10 ˚C, the yield increased from 59 to 92%. At temperature of 15 ˚C the azo dye yield decreased to be 76 % as shown in Table 4.2. As the temperature reached 15 ˚C the nitrous acid decomposition may be the main reason for the yield decreasing of azo dye.

Table 4.2: The effects of reaction temperatures on the production of azo dyes over RHAPrIM catalyst.

Variants	Azo Dyes Yield

(°C)	(%)
5	59
10	92
15	76

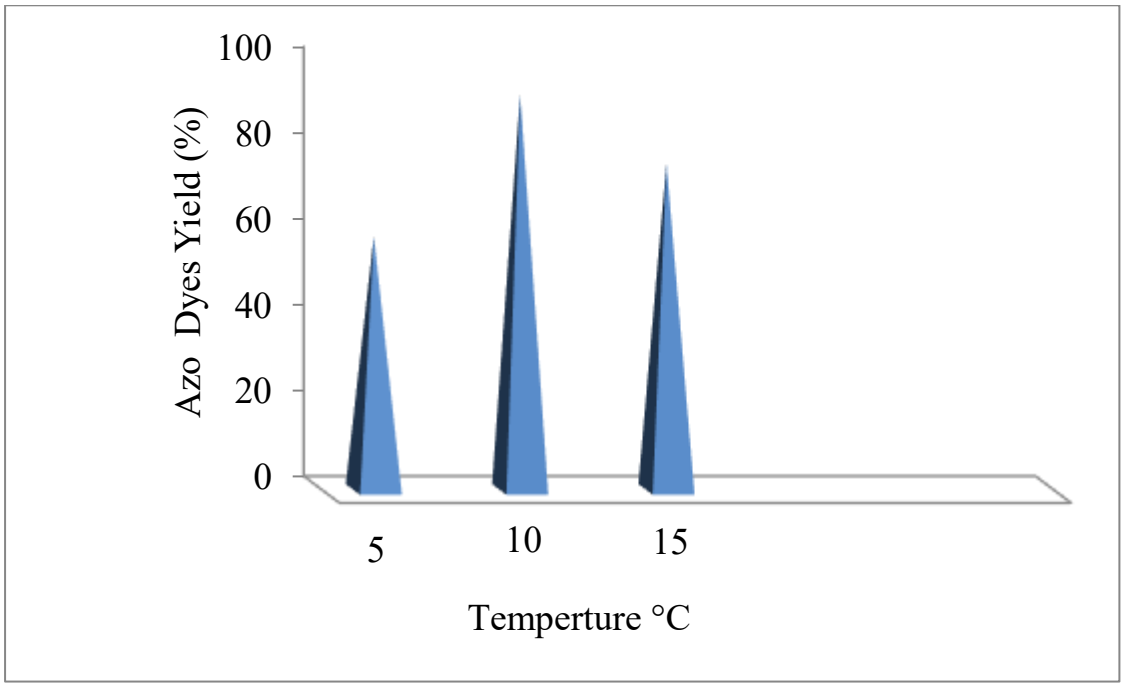


Fig. 4.2:The effect of the reaction temperature on the preparation of Azo dyes.

4.3 Influence of Solvent Effect

Solvents effects on the azo dye yield were studied and the results were listed in Table 4.3. The water, ethyl alcohol, benzene, and diethyl ether were used as reaction solvents. During the experiment, water was found the best solvent for this reaction with 92 % yield of azo dye. It was found that the yield of azo dye decrease in the medium of ethyl alcohol to reached 61 %, 57 % in diethyl ether and 52

% in benzene. Water is capable to form hydrogen bonding with the reactant over the catalyst surface and this could lead to the high percentage of yield. In case of using ethyl alcohol, the probability to form a hydrogen bonding became less and the yield could reduce.

Table 4.3: The effect of different solvents on the reaction of benzyl diazonium chloride with Resorcinol over RHAPrIM at 10 °C.

Solvent	Azo Dyes Yield (%)
Water	92
Ethanol	61
Diethyl ether	57
Benzene	52

4.4 Catalyst's Recycle

After the end of the reaction, RHAPrIM was easily recovered and reused at least two times with minimum loss in activity. It should be noted that the activity was reduced after the third run of the reaction and reached to be 89 % (Fig. 4.3). It was deduced that the RHAPrIM might be poisoning by the solvent used via forming a hydrogen bonding with the solvent and this could block the pore off.

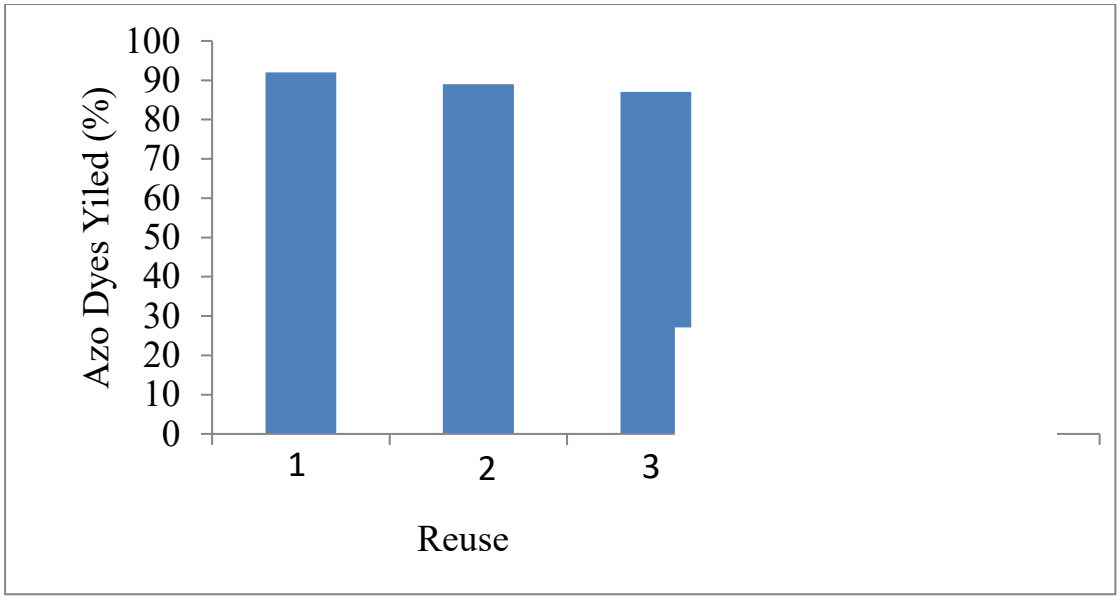


Fig. 4.3: The reusability of the catalyst.

4.5 FT-IR Analysis of Reused Catalyst RHAPrIM

The FT-IR spectrum of RHAPrIM after the second usage is shown in Fig. 4.4. All catalyst functional groups are shown at the expected position as compared to the fresh catalyst (Fig. 3.4, pp. 35). The vibration of Si–O–Si is observed at 1068 cm^{-1} and 1061 cm^{-1} in the fresh catalyst. Silanol groups and absorbed water appeared as a broad band around 3410 cm^{-1}. This peak is becoming broader and slightly shifted as compared to the fresh catalyst as a result of using the catalyst in water. The imidazole C5–H bond vibration has appeared at 3138-3101 cm^{-1}. The vibration at 1562 cm^{-1} related to the benzene ring. Vibrations at 1647- 1626 cm^{-1} are due to the imine groups, C=N. The results of FT-IR spectra of fresh and reused catalyst are listed in (Table 4.4).

Table 4.4: FT-IR Spectrophotometer results of fresh and reused catalyst

Functional groups	Observed .Absorption (cm^{-1}) for Fresh catalyst	Observed. Absorption (cm^{-1}) for reused catalyst
Si-OH	3458	3410
Si-O-Si	1061	1068

C5-H imidazole	3225	3138-3101
C-H aliphatic	2922	2960
C=C aromatic	1566	1562
C-N	1384	1383
C=N	1638	1647-1626
Si-C	1155	1151

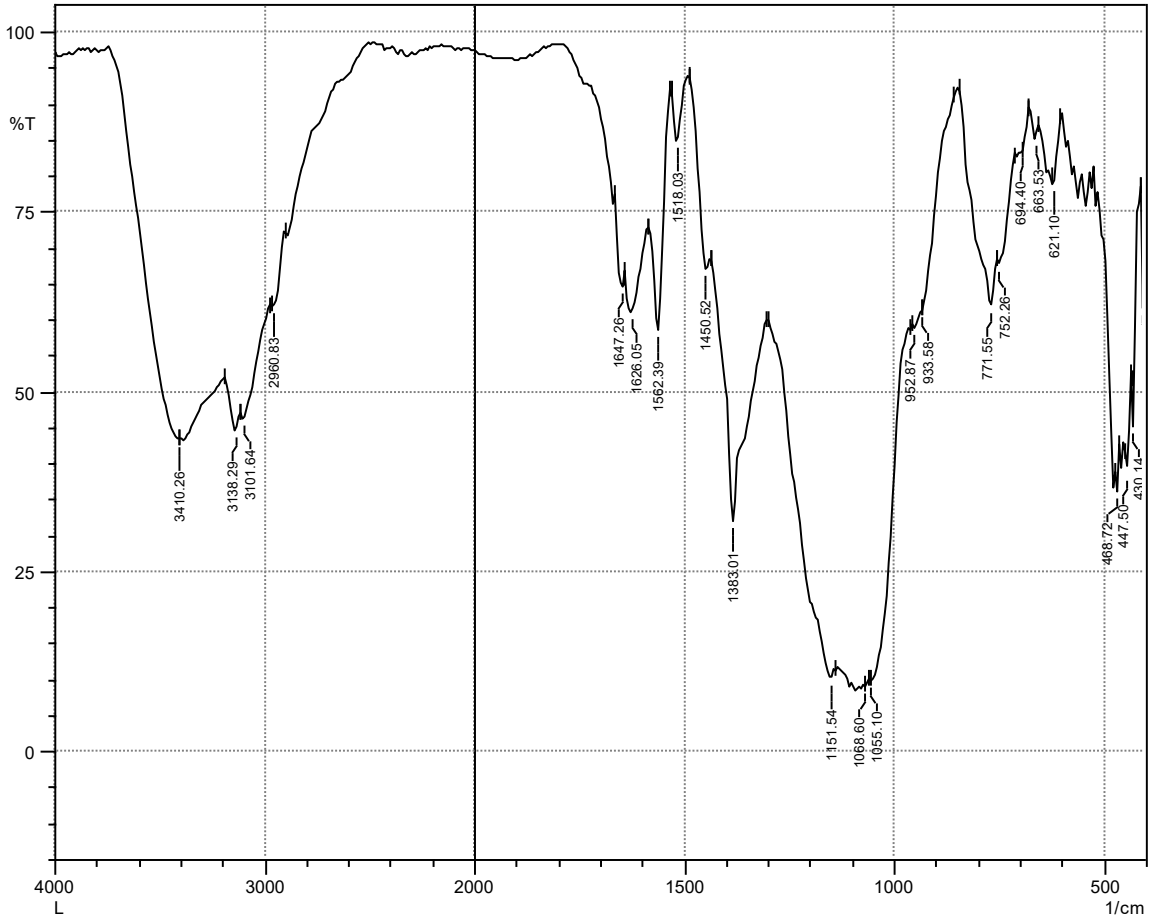


Fig.4.4: FTIR spectrum of reused catalyst RHAPrIM

٤,٦ Thermal Analysis of Reused Catalyst

TGA/DTA curve of RHAPrIM after the second reused is shown in Fig.4.5. The sequence of characteristic decomposition stages is observed similar to the fresh catalyst (Fig 3.5, pp. 39). First mass loss of water adsorbed started at 39 ºC with the maximum at 115 ºC as in DTA curve. The amount of this mass loss becomes 12.1 % as compared to the fresh one (7.1 %, Fig. 3.5). The rest mass losses are not changed too much as compared to the fresh catalyst.

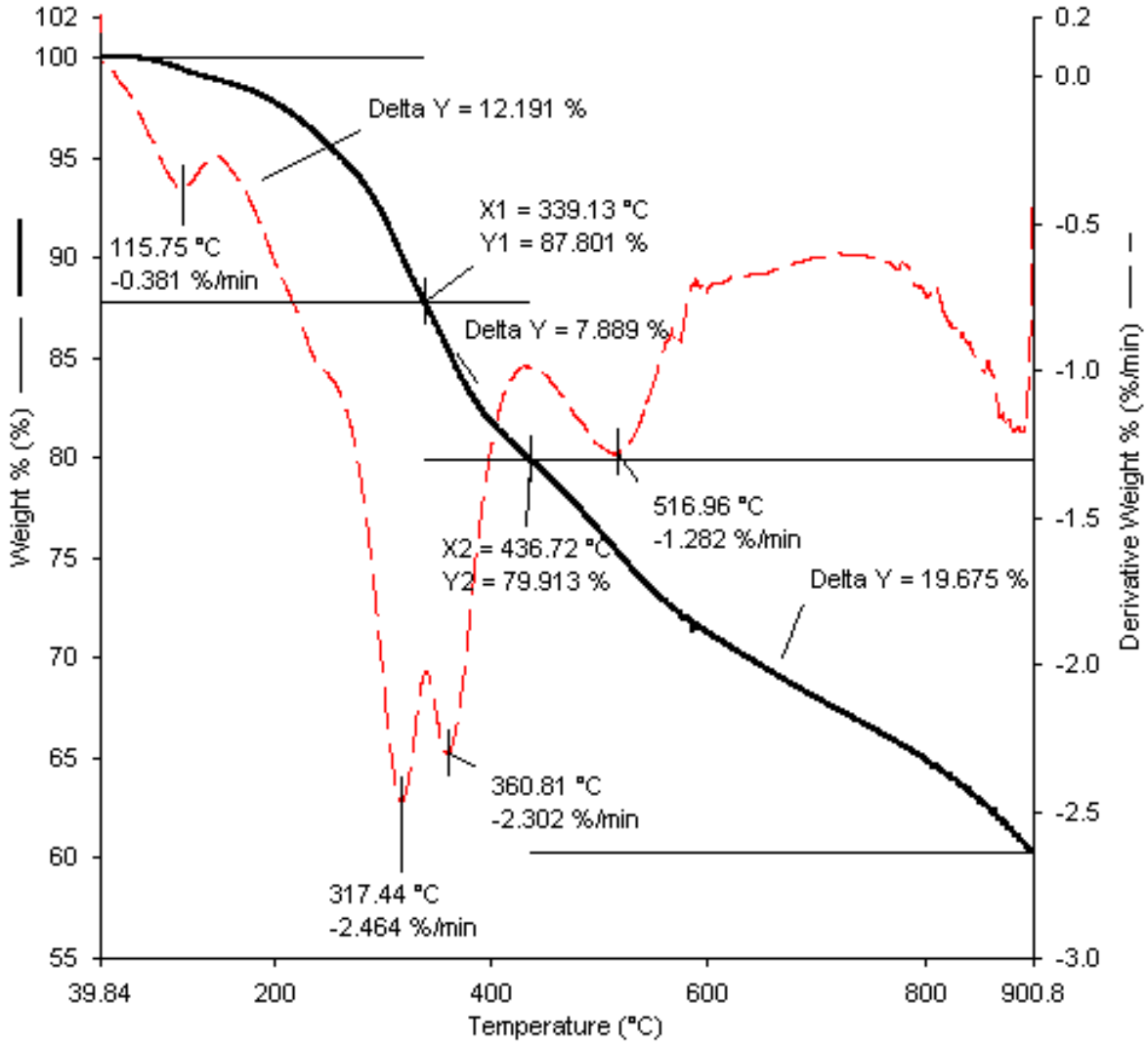
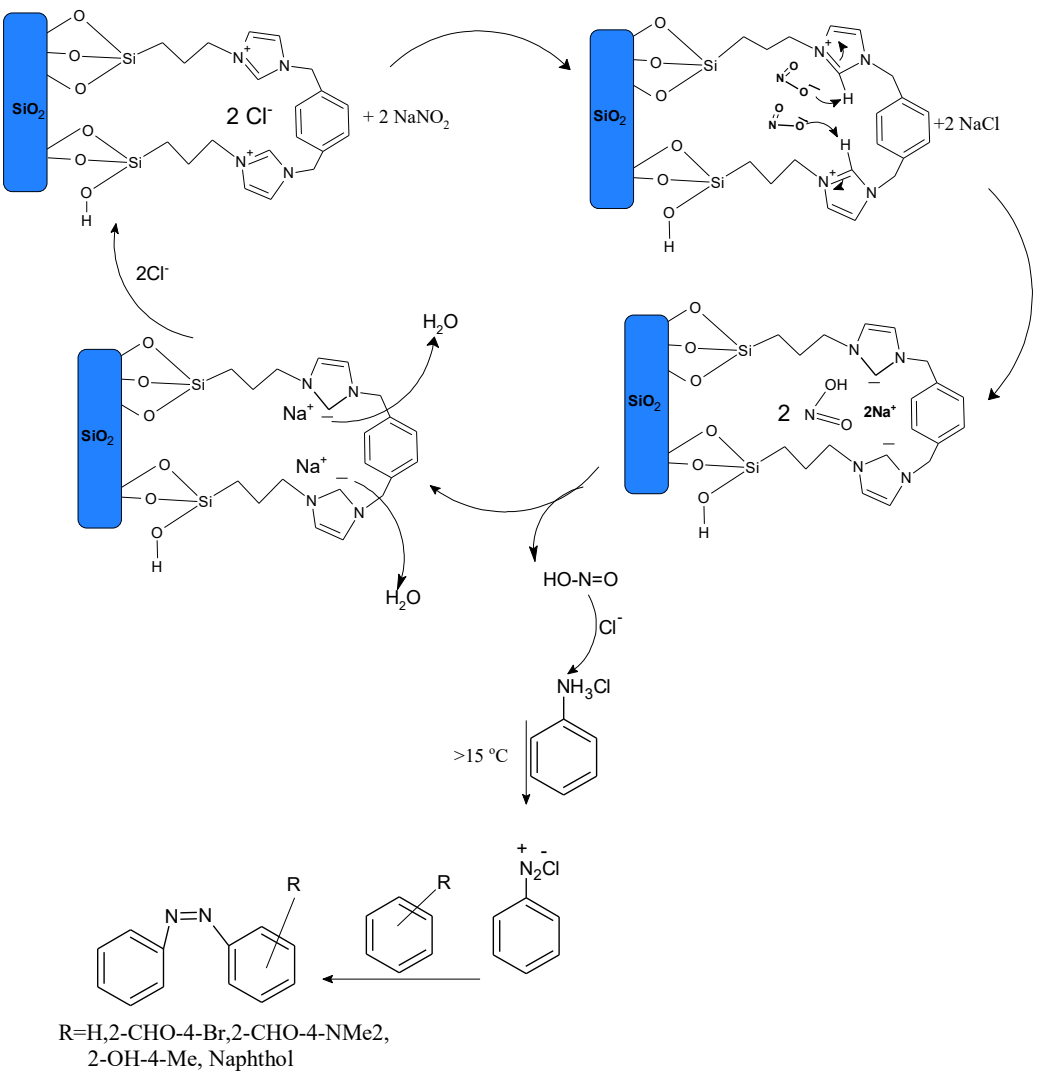


Fig.4.5: Thermogravimetric analysis and differential thermal analysis of reused catalyst RHAPrIM.

4.7 Proposed Mechanism

A mineral acid is usually used to generate the nitrous acid by acidification of aqueous solutions sodium nitrite. The RHAPrIM has imidazole acidic hydrogen able to acidification of sodium nitrite in

situ. Free nitrous acid is liberated and attack aniline rapidly to form the diazonium salt. The formed diazonium salt is able to couple with an aromatic molecule to produced azo dyes. While the fresh catalyst is continued for catalyzing new reaction as in Scheme 4.1.



Scheme 4.1: The generation of diazonium salt and azo dye over RHAPrIM.

4.7.1 Elemental Analysis and Melting Points of Derivatives Dyes

Six different derivatives of dyes were prepared as it was showed in Table 4.5. The derivatives were characterized by using FT-IR, UV, CHN, and melting point. Elemental analyses were clearly shown the abundant between the theoretical and found values Table 4.5. The melting points of prepared dyes were also match with their values in the literatures [107, 108, 109].

4.7.2 UV-Vis Spectra

The UV-Vis spectra (Fig. 4.6) exhibit strong absorptions of π-π* transition for the azo moiety at wavelength 271, 268, 238, 242, 278, and 273 nm, respectively. The type of auxochrome groups on the azo derivatives are clearly affected on the absorptions. Red shifts were observed on those aromatic containing electron-donating substituent.

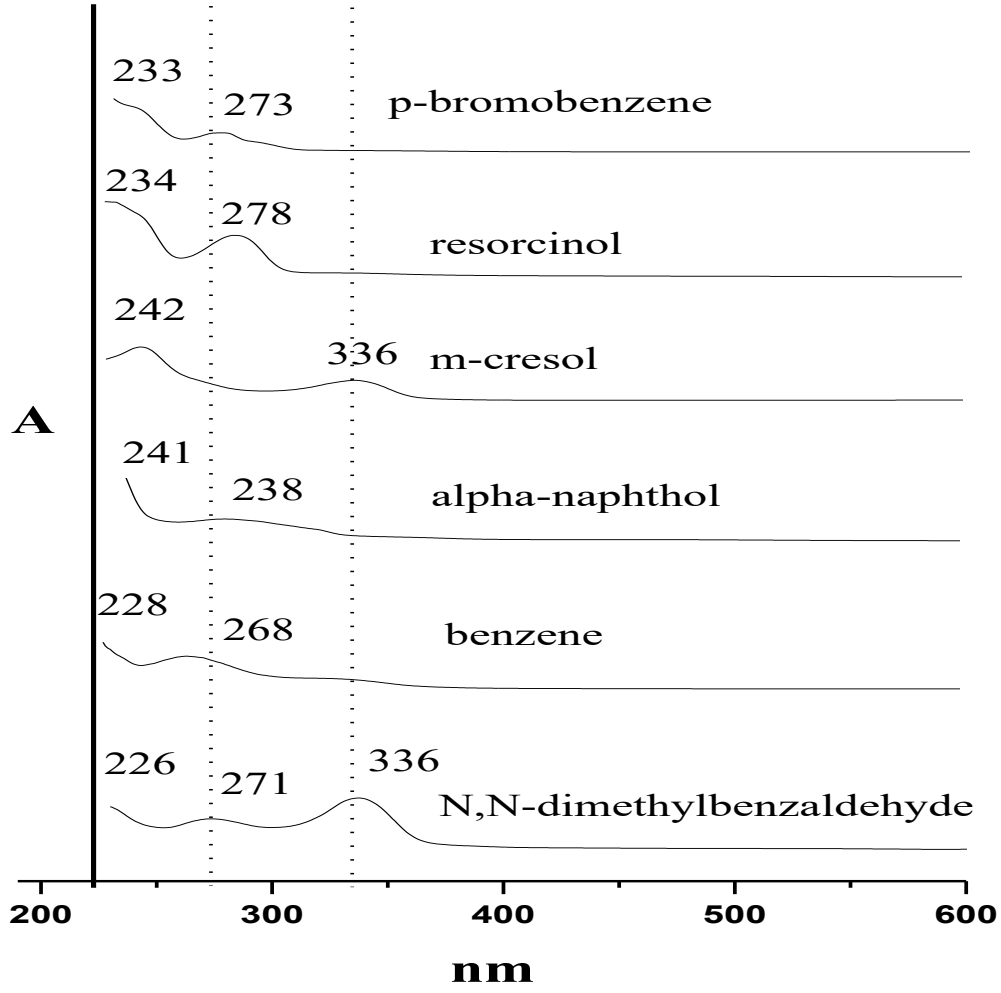
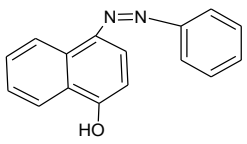
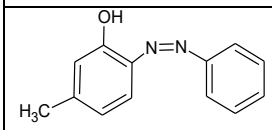
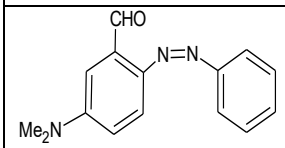


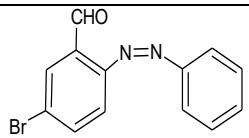
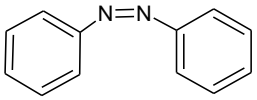
Fig. 4.6: The UV-Vis of the mono azo dyes derivatives prepared over RHAPrIM.

4.7.3 FT-IR Spectra

The FT-IR (see appendix) are listed in Table 4.5. The effective bands are those due to the azo chromophore (-N=N-), and other bands, e.g. C=C and C-H of aromatic ring, and carbonyl were clearly shown on FT-IR spectra.

Table 4.5: The physical properties, elemental analysis, and FT-IR of azo dye derivatives prepared over RHAPrIM.

Compound	Color	m. p °C		Elemental analysis %		FT-IR cm^{-1}
		Liter.	found	Calculated	found	
	Red	129-132	128-131	C:77.4, H:4.87; N:11.28	C:77.66, H:5.0, N:11.0	3486 (O-H), 3041 (CH)Ar 1578 (N=N),
	Brown	125-128	128-130	C:72, H:5; N:10	C:71.6, H:5.62; N:11.28	3436 (O-H), 3037 (C-H)Ar 1577 (N=N),
	Orange	130-132	129-130	C:71, H:5.5; N:16	C:69.99, H: 5.53; N:12.77	3060 (C-H)Ar 2950(CH)alph 1530 (N=N), 1610 (C=O)

	Yellow	100-113	113-115	C:53, H:3; N:9	C:52.76, H:2.87; N:8.33	3090 (C-H)Ar, 1570 (N=N), 1680 (C=O)
	White	88-90	90-92	C:78.23; H: 6.57; N:15.21	C:78.23; H: 6.57; N:15.21	3100 (C-H)Ar, 1510 (N=N)

5.1 Conclusions

The functionalization of silica with different silylating agents was an important starting point to synthesize many different types of silica-based materials. The functionalization process produced silica with a -CH_2Cl end group which played a great role in synthesis many kinds from heterogeneous catalysts via substitution Cl by different organic molecules. In this study *p*-xylylbisimidazole was immobilized onto silica surface in order to synthesize a strong heterogeneous catalyst. FT-IR spectroscopy showed presence absorption bands of the most functional groups in the catalyst at the expected range. CHNS and EDX analysis of RHAPrIM shows that nitrogen was present within the catalyst structure. The specific surface area of the catalyst was found to be 91.61 m^2 /gm. According to TGA/DTA analysis, RHAPrIM showed high thermal stability with three characteristic decomposition stages. Thermal analysis shows that the catalyst can used safely up to 277 ◦C. The ^{29}Si NMR spectrum of RHAPrIM were showed several chemical shifts attributed to Q^4,Q^3, T^3, and T^2 silicon atoms. ^{13}C NMR spectrum for RHAPrIM was showed chemical shifts assigned to the aromatic carbon in benzene and imidazole rings. The catalytic activity of the catalyst was studied in the preparation of dyes. High yield was achieved under the optimum reaction conditions. The yield of the preparated dyes was reached to 92% when 100 mg of catalyst mass at 10 ◦C.

5.2 The slight deactivation in the activity of the catalyst

It was deduced that the RHAPrIM might be poisoned by the solvent used by forming a hydrogen bonding with the solvent and this could block the pore of the catalyst. The hydrogen bonding was formed between the reactants and the solvent over the catalyst active center. Beside this, a hydrogen bonding could also be formed between the active centers and the solvent (in case of using water). The TGA shows that the catalyst is able to capture the moisture from the air (about 7.1 % of water for each 10 mg of catalyst was deducted). This phenomena clearly shows that the catalyst surface is highly hydrophilic. This will be decreased in the other solvent Ethanol which has one hydroxyl groups able to form hydrogen bonding, and less in diethyl ether (which has not any hydroxyl groups). Therefore there is no deactivation of the catalyst in case of using diethyl ether and ethanol. After the catalyst used, a TGA\DTA was running and the result has shown that the moisture became (12.1%) which clearly support that the poisoning of the catalyst by the solvent which may explain the minimum reducing of the activity after the third run.

5.3 Recommendations

The purpose of heterogeneous catalyst during this research was managing RH as a source of silica. The pure silica was performed by burning the RH at a high temperature. As a result of critical conditions, silica was transferred to sodium silicate followed by immobilizing with alkyl silylating agents in a simple one-pot synthesis. Finally, the material was treated with *p*-xylylbisimidazole to form a heterogeneous catalyst which was used successfully to generate diazonium salt for azo dyes production.

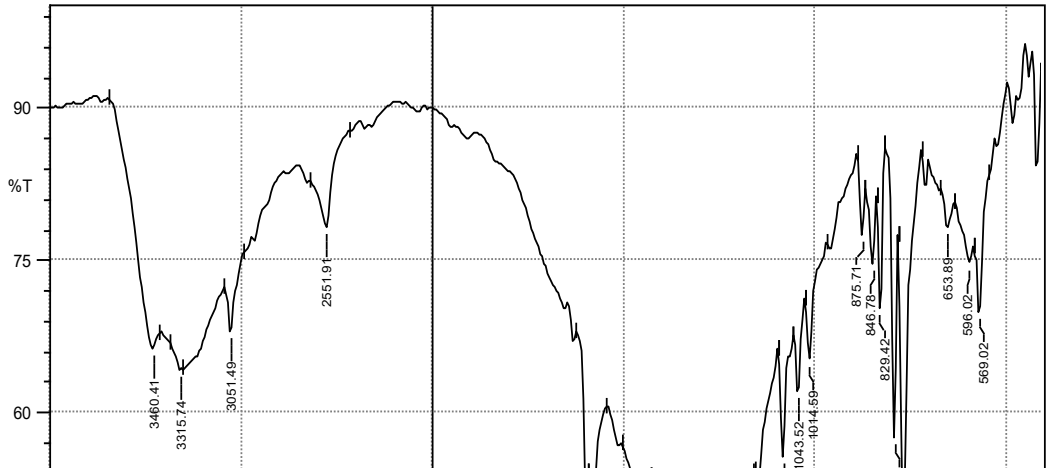
1. As the research used RH which was accounting as a wanted waste, therefore, this research is an attempt to recycle agriculture waste. The silica was extracted from RH by the classical method, therefore, an extraction of silica from RH by new methods are required.

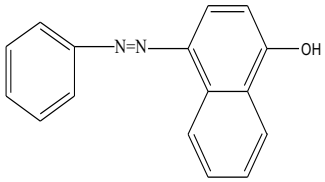
2. Due to the excellent results of the prepared catalyst, RHAPrIM it may have promising uses in the manufacturing of dyes. More studies are needed to apply this study in the marketing.

3. More study to prove the mechanism is required.

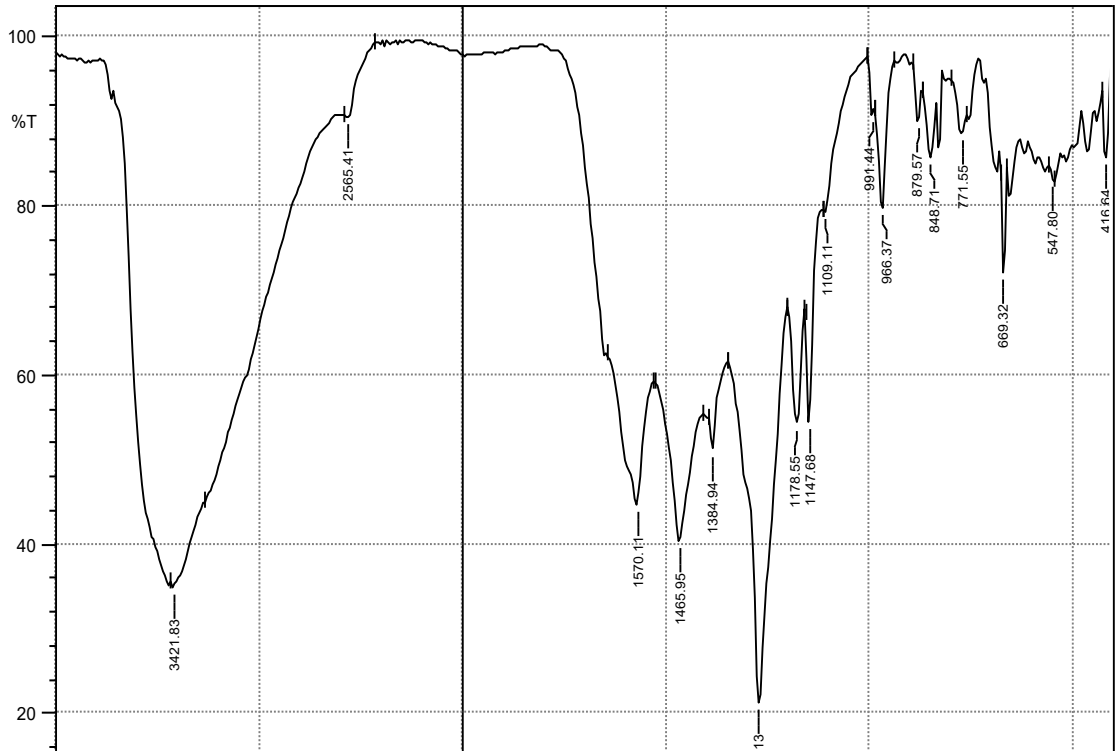
Characterization of Dyes

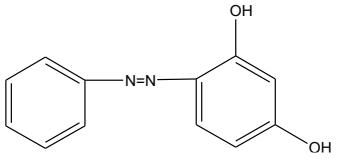
Fourier Transformed Infrared Spectroscopic Analysis



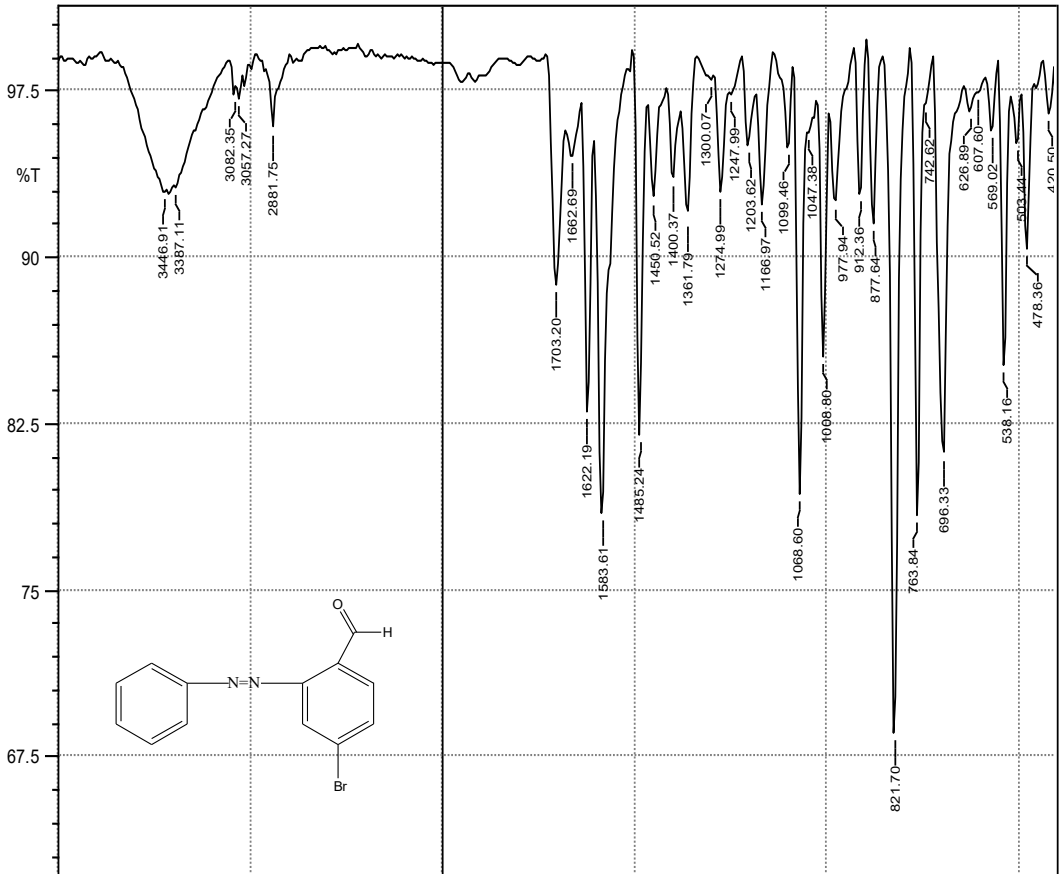


Appendix1: FT-IR Spectrum of 4-(phenyl azo) -1-Naphthol

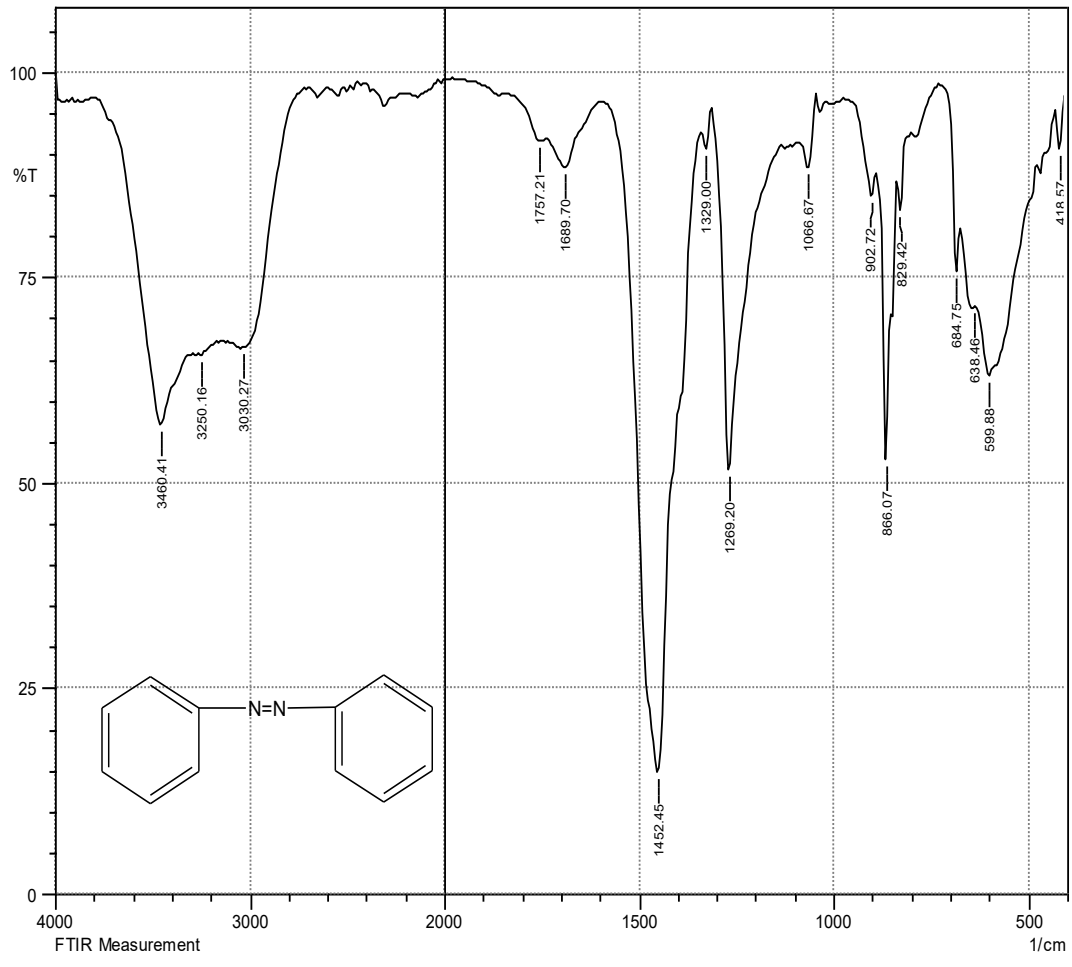




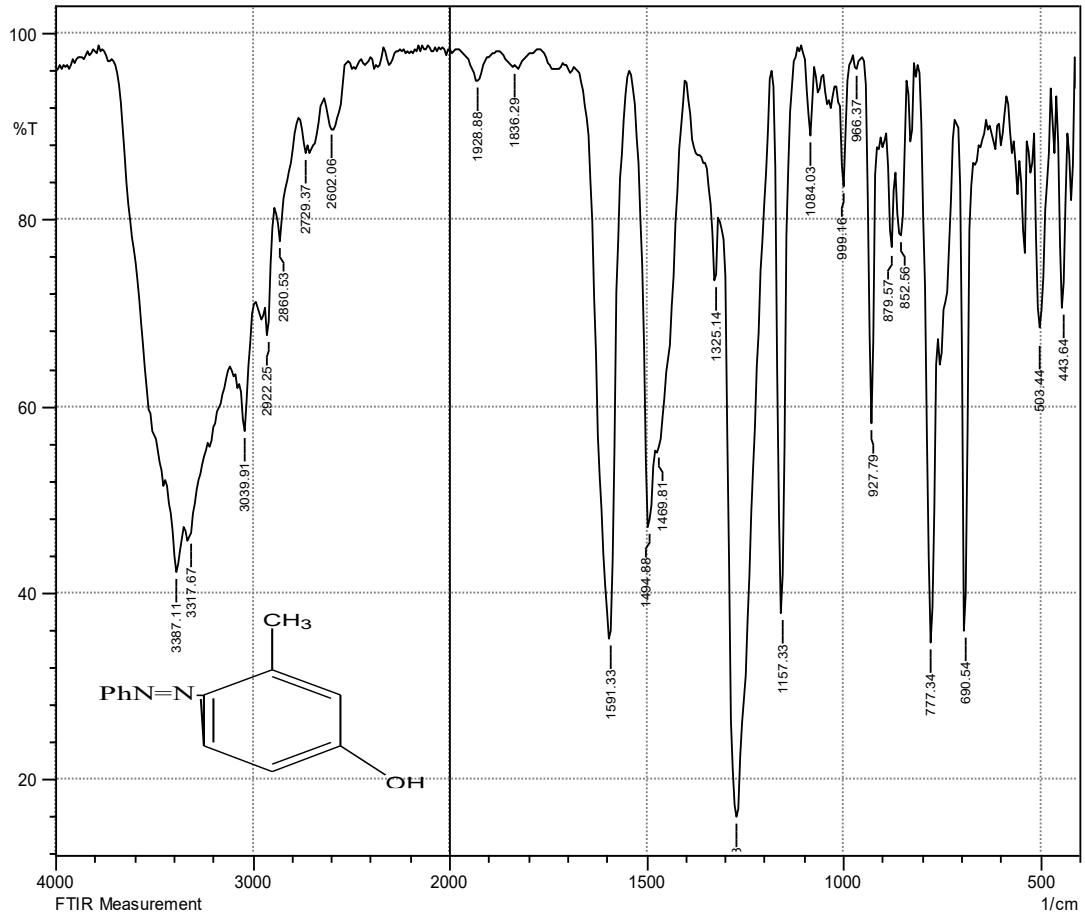
Appendix 2: FT-IR Spectrum of 2-(phenylazo) Resorcinol.



Appendix 3: FT-IR Spectrum of 2-(phenyl azo) -4-Bromo benzaldehyde

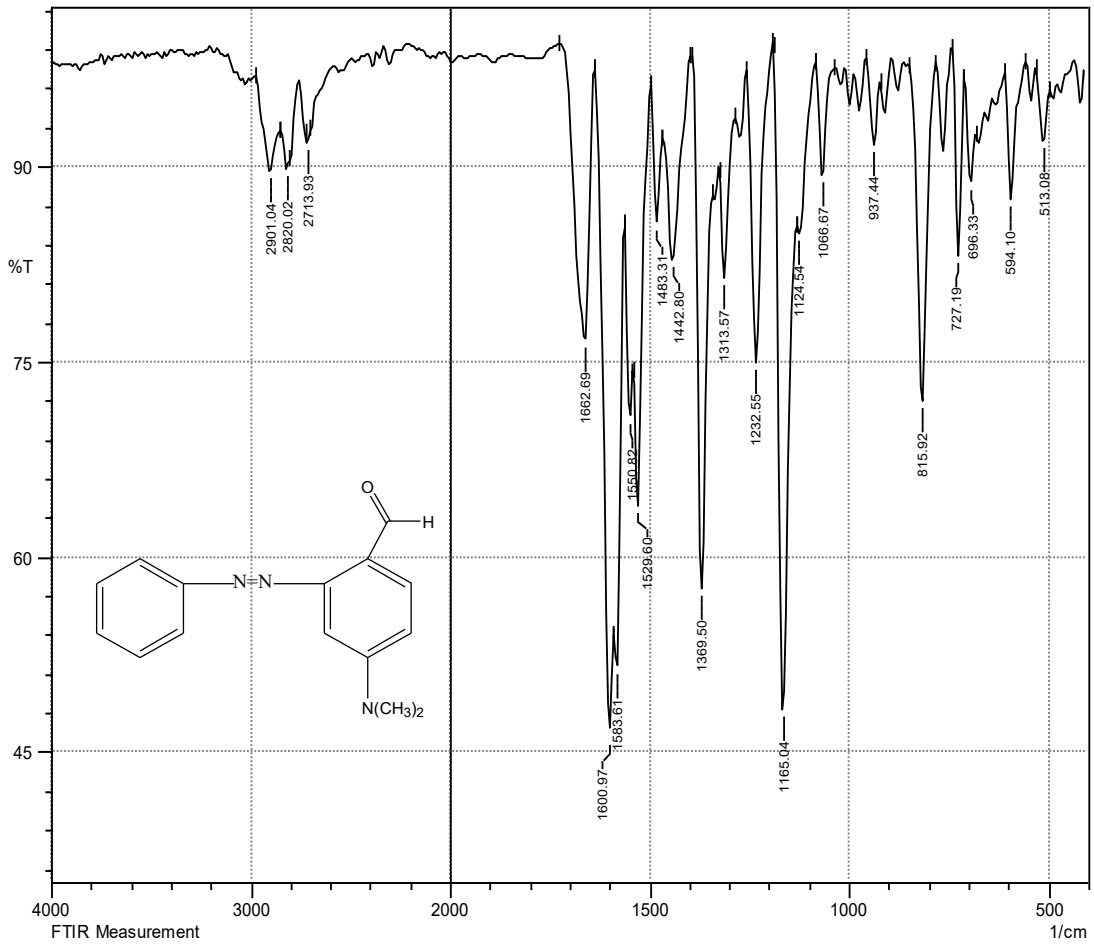


Appendix 4: FT-IR Spectrum of 2-(phenyl azo) benzene



Appendix 5: FT-IR Spectrum of 2-(phenyl azo) m-crysol

List of Symbols and Abbreviations



Appendix 6: FT-IR Spectrum of 2-(phenyl azo) 4-(N,N-dimethyl) benzaldehyde

Abbreviation	Term
BET	Brunauer-Emmett-Teller
Bis-Imi	*p*-xylylbisimidazole
Bz	Benzene ring
CD_3CN	Acetonitrile- dutrate
CHNS	Carbon , hydrogen, nitrogen and sulfur elemental analysis
CPTES	3-(Chloropropyl) triethoxysilane
DTA	Differential Thermal Analysis
EDX	Energy Dispersive X–ray
FT–IR	Fourier Transform Infrared
DCM	Dichloro methane
NMR	Nuclear magic resonance
MAS	Magic angle spectroscopy
MCM-41	Mobil composition of Matter
rpm	Recycle per minute
RH	Rice Husk
RHA	Rice Husk Ash
RHACCl	Silica-3-(chloropropyl)triethoxysilane
RHAPrIM	*p*-xylylbisimidazoliumchloride-silica
SEM	Scanning Electron Microscopy

Sol	Colloidal suspension
Si-OH	Silanol group
Si-O-Si	Siloxane group
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis

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