Available online at BCREC website: https://bcrec.id

Bulletin of Chemical Reaction Engineering & Catalysis, 14 (2) 2019, 247-259

Research Article

In-situ Nitrous Acid Generation over Silica Imidazole Catalyst for Dyes Production

Kasim Mohammed Hello*, Nahla Ghaze Fahad

Chemistry Department, College of Science, Al-Muthanna University, Iraq

Received: 3rd May 2018; Revised: 5th November 2018; Accepted: 9th November 2018; Available online: 30th April 2019; Published regularly: 1st August 2019

Abstract

The objective of this research is to prepare a new type of heterogeneous catalyst and to study its usage for in-situ nitrous acid generation to form a diazonium salt. The high pure silica (> 95%) was produced by burning the clean rice husk at 800 °C. After that, the silica was transferred to sodium silicate using 1.0 M of NaOH, followed by immobilizing with 3-(chloropropyl)triethoxysilane in a simple one-pot synthesis. Finally, the material was refluxed with (0.015 mol) of p-xylyl di-imidazolium chloride. The silicon solid-state nuclear magnetic resonance shows the Q^4, Q^3, T^3, and T^2 chemical shifts at expected position. Carbon solid-state nuclear magnetic resonance spectrum shows different peaks at different chemical shifts related to the carbon structures of the organic moieties. The catalyst is stable up to 277 °C according to the thermal analysis. TEM images show smooth and porous regularly shaped particles with an estimation size of ca. 5 nm. Coupling reaction of aromatic compounds was carried out with a diazonium salt of aniline to yield a monoazo dye. All dyes were showed matching the elemental analysis with the theoretical calculation. Besides this, the spectrum of FT-IR and UV-Visible were recorded. The catalyst was stable, easy separation from the reaction mixture, and reusable by a simple experimental procedure. The catalyst could be used successfully for the nitrous acid generation.

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

How to Cite: Hello, K.M., Fahad, N.G. (2019). In-situ Nitrous Acid Generation over Silica Imidazole Catalyst for Dyes Production. *Bulletin of Chemical Reaction Engineering & Catalysis*, 14 (2): 247-259 (doi:10.9767/bcrec.14.2.2617.247-259)

Permalink/DOI: https://doi.org/10.9767/bcrec.14.2.2617.247-259

1. Introduction

Diazotization reactions normally prepared via the reaction of primary aromatic amines, aniline, and its related derivatives, with nitrous acid to form a diazonium salt. The formed diazonium salts were capable to couple with organic azobenzene molecules yielding azo dyes. Besides dyes preparation, aromatic diazonium salts can also be reached by different procedures to give different materials for various purposes such as sensor [1], carbon nanotube [2], polymer [3], and waste by-products treatment [4], which are relevant to many fields of life such medicine, industry, environment, etc. Numerous methods / techniques, for preparation of diazonium salt, required homogeneous acid as a catalyst. Normally concentrated HCl or H_2SO_4 was used as a homogeneous catalyst in the synthesis of diazonium salt at low temperature [5,6]. The environmental incompatibility is the main limitation of such catalysts. Simultaneously, the production

*Corresponding Author.
Email: kasimhello@gmail.com, kasimhillo@mu.edu.iq (M.H. Kasim),
Telp. +9647801274886

of diazonium salts without using homogeneous concentrated acids did not mention in the literature.

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 [7]. During the use of homogeneous catalysts, the main challenging problem could be the productions of azo dyes over silica in a heterogeneous phase catalyst. Additionally, there is no clean method for production of azo dyes support the green chemistry. Consequently, this work proposing a new type of heterogeneous catalyst to achieve a greener synthetic alternative, due to the increase of interest in the catalysis greener synthetic for dyes production. The heterogeneous catalyst, synthesized in this study, is by utilizing rice husk (RH) as a source of silica. The high pure silica was produced by burning the RH at a high temperature. As a result of severe conditions, silica was transferred to sodium silicate followed by immobilizing with alkyl silylating agents in a simple one-pot synthesis [8]. Finally, the material was treated with *p*-xylylene di-imidazolium chloride to form a heterogeneous catalyst which was used successfully to generate diazonium salt for azo dyes production.

2. Materials and Method

2.1 Chemicals

The reagents were imidazole (Sigma-Aldrich, 98.0%), sodium hydroxide (Systerm, 99.0%), nitric acid (Systerm, 65.0%), 3-(chloropropyl) triethoxysilane (CPTES) (Sigma-Aldrich, 99%), benzene (Merck, 99%), dioxane (Riedel-De Haen, 99.5%), acetone (Sigma, 98%), *p*-xylylene dichloride (Sigma, 98%), ethyl alcohol (HmbG Chemical, 99.7%), aniline (Sigma-Aldrich, 99%), α-naphthol and N,N-dimethyl benzaldehyde (Sigma-Aldrich, 99%), diethyl ether (GCC, 99%), potassium carbonate (Sigma-Aldrich, 99%), *p*-bromobenzaldehyde (Sigma-Aldrich, 99%), and dichloromethane (Sigma-Aldrich, 99%). The rice husk (RH) was collected from the rice mill in Samawah city, south of Iraq.

2.2 Materials Synthesis

2.2.1 Synthesis of *p*-xylyl bisimidazole (bis-imi)

A solution of *p*-xylylene dichloride (1.22 g, 7.0 mmol) and imidazole (1.25 g, 18.0 mmol) was refluxed at (70-80 °C) in ethanol (30 mL) for 24 h. The product was washed with diethyl ether then dissolved in potassium carbonate (K_2CO_3) solution (6%, 30 mL). After standing for 3 days, a white solid precipitated separated out from the solution. This solid was collected and recrystallized from water that produced white crystals. The yield was 1.61 g (97.0%), m.p.: 153-154 °C. ^{1}H NMR (400 MHz, d_3-CD_3CN): δ 5.1 (s, 4H, 2 × CH_2), 6.9 (2H, d, 2 × imidazolium H5), 7.2 (2H, d, 2 × imidazolium H4′), 7.4 (d, 4H, ArH), 7.7 (s, 2H, 2 × imidazolium H2′); ^{13}C NMR (400MHz, d_3-CD_3CN): δ 49.9 (CH_2), 120.3 (imidazolium C4, C5, C4′ & C5′), 128.6 (4 × ArC), 129.6 (2 × ArC), 138.1, 138.2 (imidazolium C2 and C2′). Elemental analysis (CHNS): Analytical calculation for $C_{14}H_{14}N_4$: (C, 70.57, H, 5.2, N, 23.51) %. Experimental: (C, 70.06, H, 5.1, N, 23.74) %.

2.2.2 Catalyst preparation, RHAPrIM

Rice husk was converted to rice husk ash (RHA) and subsequently immobilized with CPTES to produced solid product donated as RHACCl by following the method published in reference [8]. In general, bis-imi (2.0 g, 0.015 mol) was mixed with (2.0 g) of RHACCl in 30 mL of dry toluene. After that, the mixture transferred to an oil bath and then refluxed at 110 °C. After 24 h of reflux, the reaction mixture was filtered. The solid products washed with three different solvents (toluene, dichloromethane, and ethanol) to remove the unreacted organic. The product was transferred to the oven for drying at 100 °C for 24 h. About 1.80 gm was yield from applied this method.

2.3 Catalyst Activity

100 mg of RHAPrIM were mixed with 1.0 mL (10 mmol) of aniline which was soluble in 5 mL of distilled water. About 0.69 g (10 mmol) of sodium nitrite was dissolved in 5 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 filtrating about 250 mg of resorcinol which was dissolved in 2.0 mL of 10% NaOH and then 5.0 mL distilled water was added. The mixture color was changed directly which indicated to the end point of the reaction. As the reactants and the product are solid phase, the calculation of yield (conversion) was done by dividing the experimental weight (Wt_{ex}) on the theoretical weight (Wt_{theo}) multiplying by 100% as shown in the formula below (Equation (1)).

$$Yield\ \% = (Wt_{ex} / Wt_{theo}) \times 100\% \quad (1)$$

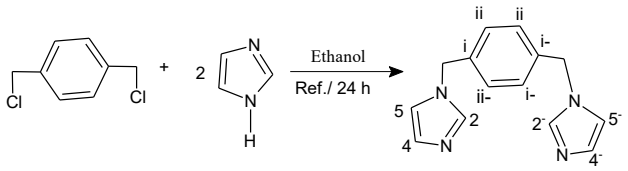
2.4 Sample Characterization

2.4.1 Elemental analysis and nitrogen adsorption desorption

The percentage of each carbon, hydrogen, and nitrogen was determined by CHN analyzer (Perkin Elmer-2400). Surface parameters were analyzed by physical adsorption of nitrogen in automatic physisorption porosimeter (Autosorb-1 CLP, Quantachrom, USA).

2.4.2 X-ray diffraction patterns (XRD)

The powder XRD of the sample was done on a Siemens diffractometer, D5000, Kristalloflex. The diffraction angle was scanned for 2 h at a rate in 6.0 °.min^{-1}.



Scheme 1. The synthesis of 1,4-bis(imidazole-1-ylmethyl)benzene (Bis-Imi)

2.4.3 FT-IR spectroscopy

The FT-IR spectra were obtained using Shimadzu 8400s spectrophotometer. A 0.5 mg of KBr to the 0.1 mg of sample was taken and grained to make the KBr discs.

2.4.4 Thermogravimetric analysis TGA / Differential thermal analysis DTA

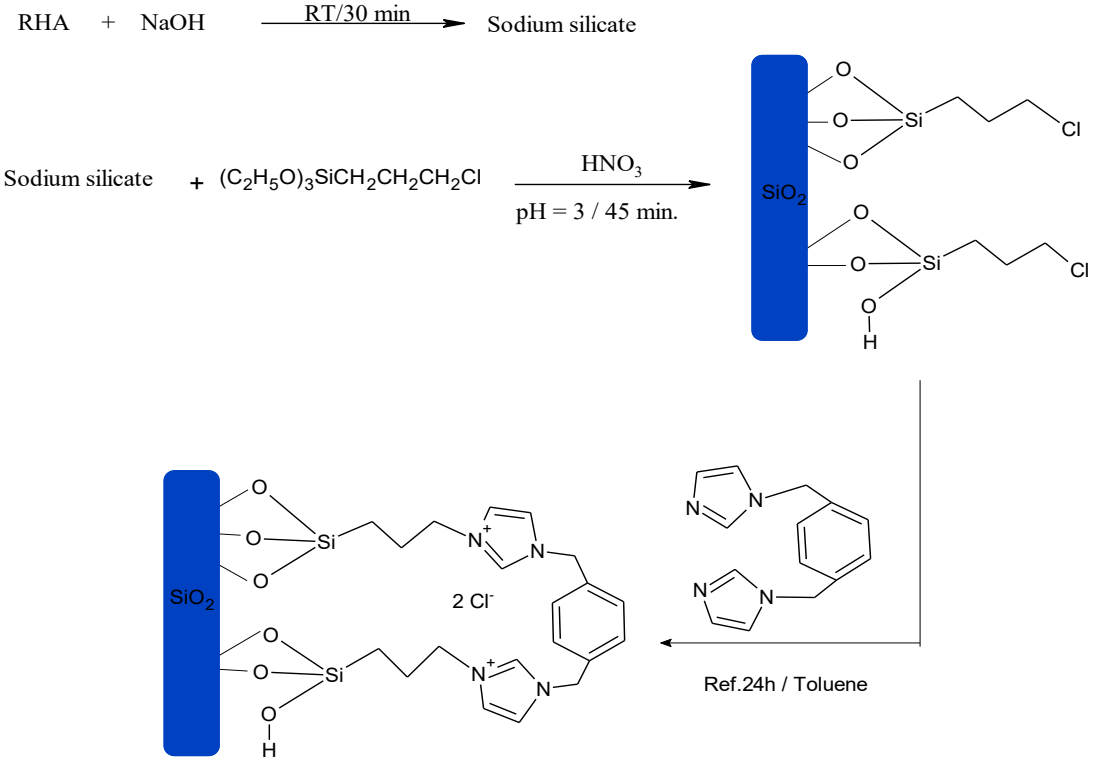
TGA/DTA was performed using a dual-purpose instrument type Perkin Elmer TGA-4000; about 10.0 mg of sample was heated from 40 °C to 900 °C at 20 °C/min under nitrogen flow.

2.4.5 ^{29}Si and ^{13}C MAS NMR

The ^{29}Si and ^{13}C MAS NMR were recorded by using Bruker machine type (DSX-300) was used to obtained ^{29}Si and ^{13}C MAS NMR.

2.4.6 TEM and SEM micrographs

The SEM images were carried out using Leica Cambridge S360 machine. The machine was provided with EDX type Falcon System. While the TEM images were deducted by Philips CM12 equipment. In general the sample was suspended in absolute ethanol and



Scheme 2. The reaction sequence and the possible structures for RHAPrIM as suggested by different techniques.

then droplet on carbon film coated with 400 mesh copper grid and left for 1-3 min.

3. Results and Discussion

3.1 Synthesis of Bis-Imi

Formation of bis-imi basically depends on the replacement of chloride in *p*-xylylene dichloride with imidazole in dioxane under refluxed condition Scheme 1. The ^{1}H and ^{13}C NMR spectra and elemental analysis (CHN) are nicely monitored the successful formation of the bis-Imi. ^{1}H NMR spectrum of bis-imi in Figure 1(a) shows the presence of imidazolium proton H2′ signal (N–CH–N) at chemical shifts of 7.7 ppm. This chemical shift is consistent with the chemical shifts of common imidazolium salts [9]. The carbene carbon resonances of imidazole (C2, C2′) led to downfield signals at δ of 138.2 and 138.1 ppm, respectively (Figure 1(b)). Aromatic carbons (i) and (i-) are observed at 129.55 and 129.6 ppm, while other chemical shifts of aromatic carbons, (ii), (ii-), are observed at 128.6 and 129.01 ppm, the car-

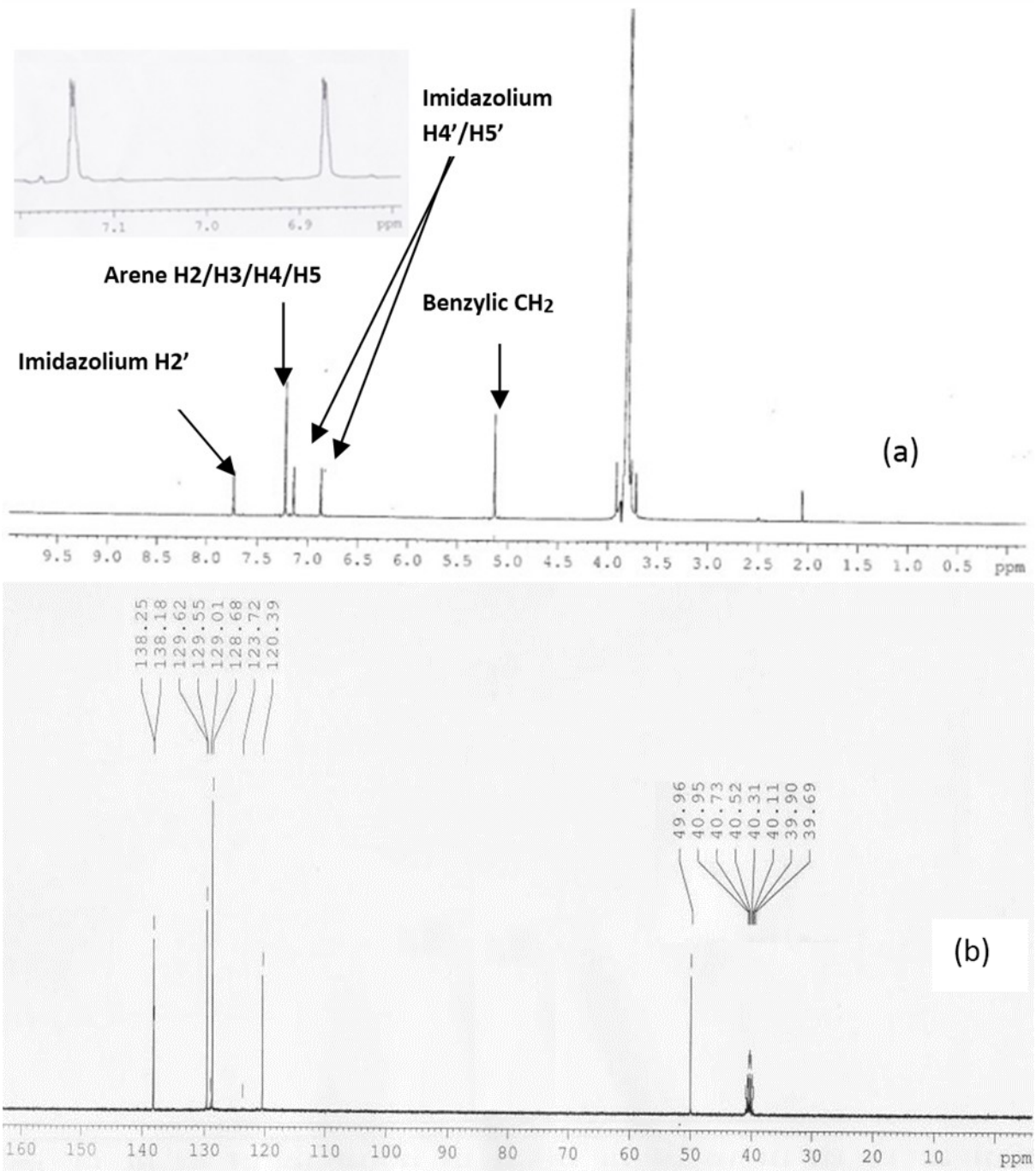


Figure 1. The NMR spectrum of bis-imi in d3-CD3CN. (a) ^{1}H NMR, (b) ^{13}CNMR.

bons of C3, C4, C3′, and C4′ are observed at 120.3 ppm. Methylene group's (CH_2) is shown at chemical shift 49.9 ppm. It is also found that the experimental elemental analysis of the synthesis bis-imi is in agreement well with calculated one. This data clearly indicates the significant synthesis of the bis-imi.

3.2 Synthesis of RHAPrIM

CPTES was necessary for functionalization silica from RHA. The bis-imi immobilization proceeds via proton abstraction from amine group in imidazole and alkyl chloride bonded to silica propyl chain Scheme 2. This reaction is anchored bis-imi to silica via the connection to propyl chain in organosilane. Deep analysis for the prepared catalyst was carried including solid-state NMR, stability, surface area and others as in the subtitle below.

3.2.1 Elemental analysis

To monitor the new elements onto silica the elemental data were used by the combination of elemental analysis (CHN) and energy dispersive X-ray analysis (EDX) analysis (shown in bract) Table 1. Elemental analysis percentages of RHACCl (not shown) showed the C and H content are 11.70 and 1.90%, respectively [8]. Carbone content of RHAPrIM 16.74% (30.22% according to the EDX) is slightly higher than RHACCl, as a result of immobilization of bis-imi. Nitrogen composition showed 1.91%, (3.30% according to the EDX). The elemental data analysis reflects that the bis-imi is indeed incorporated on the silica.

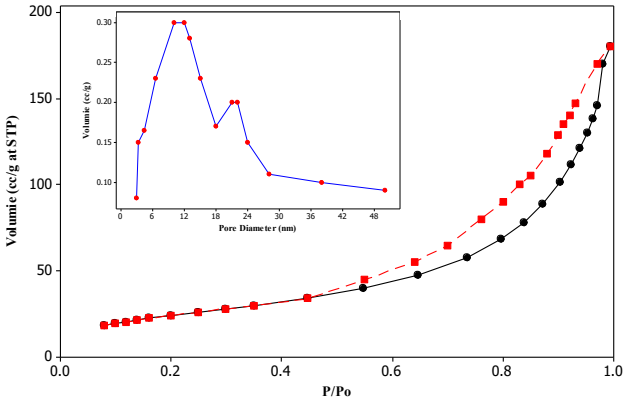


Figure 2. Nitrogen adsorption-desorption isotherms of RHAPrIM with pore size distribution

3.2.2 X-ray diffraction pattern (XRD) and nitrogen adsorption-desorption analysis

An amorphous phase is shown by XRD pattern (not shown) of RHAPrIM due to the presence of broadband at $2\theta = 22°$. This result reflects that no change in phases after the immobilization of bis-imi onto silica. In the previous study both of RHA and RHACCl shows amorphous phase [8,10].

The nitrogen adsorption-desorption isotherm and pore size graphs for RHAPrIM are given in Figure 2. According to IUPAC classification, the isotherm is of type IV with H1 hysteresis loop [11]. The isotherm at P/P_o form 0.70-0.85 the adsorption curve shows a sharp elevation. This is due to the presence of uniform size pores. According to the Brunauer-Emmett-Teller (BET) method RHAPrIM had 91.16 $m^2.g^{-1}$ surface areas. This surface area is less that of RHACCl (633 $m^2.g^{-1}$) [8]. The bis-imi ligand has larger molecules and presumably could block the pores and reduces the surface area of RHAPrIM. The RHAPrIM shows two types of pores the first is ranged from 4 to 15 nm and the second from 18 to 24 nm. Both pores fall in the mesoporous range (Table 1).

3.2.3 FT-IR spectroscopy

The spectra of RHACCl and RHAPrIM with the differential of both catalysts are giving in Figure 3. The FT-IR spectra allowed us to observe the bands characteristic of most functional groups of mesoporous RHAPrIM. Our previ-

Table 1. The physical parameters obtained for RHAPrIM. The C, H, and N contents determined by a combination of elemental and EDX analysis (shown in bract). The results of Nitrogen adsorption-desorption analysis are also shown

Elemental analysis (%)					Specific Surface area ($m^2.g^{-1}$)	Average pore volume ($cm^3.g^{-1}$)	Average pore diameter (nm)
C	H	N	Cl	Si			
16.74 (30.22)	2.34 (-)	1.91 (3.30)	- (3.8)	- (16.69)	91.16	0.24	10.9

ous studies had been described the Si–O–Si vibrations of RHA which appeared at 1101 cm^{-1} [8]. 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 broadband around 3485 cm^{-1} [12]. At 3225 cm^{-1} in the differential the absorption band corresponds to the imidazole C5–H bond vibration has appeared. Benzene ring identified by vibration of C=C stretching at 1566 cm^{-1}. While in the deferential spectrum the vibration at 1618 cm^{-1} are due to the imine groups, C=N and vibration at 1225 cm^{-1} is due to Si–C covalent bond. All these vibrations for the expected functional groups FT-IR refer that bis-im molecules are loaded onto silica via RHACCl.

3.2.4 The solid state ^{29}Si and ^{13}C NMR

Our previous study [13] found that the ^{29}Si MAS NMR of RHA which has only the presence of quadrant (Q^4) and tripartite (Q^3) at −110 and −100 ppm, respectively. Beside those Q^4, Q^3 silicon atom the RHACCl shows T^3, and T^2 [8]. The values of those chemical shifts are found –109.9, –100.6, –65.2, and –57.4 ppm, respectively.

^{29}Si MAS NMR spectrum of RHAPrIM has a similar sequence to that onto RHACCl with slight shifts (Figure 4(a)). Q^4, Q^3 silicon atoms appear at δ = –110.9 and –100.9 ppm. Another chemical shift at –65.4 ppm is observed indicates the formation of T^3, while a chemical shift at –57.3 ppm indicates the formation of T^2. The data from ^{29}Si NMR spectrum reveal that bis-imi molecules are successfully incorpo-

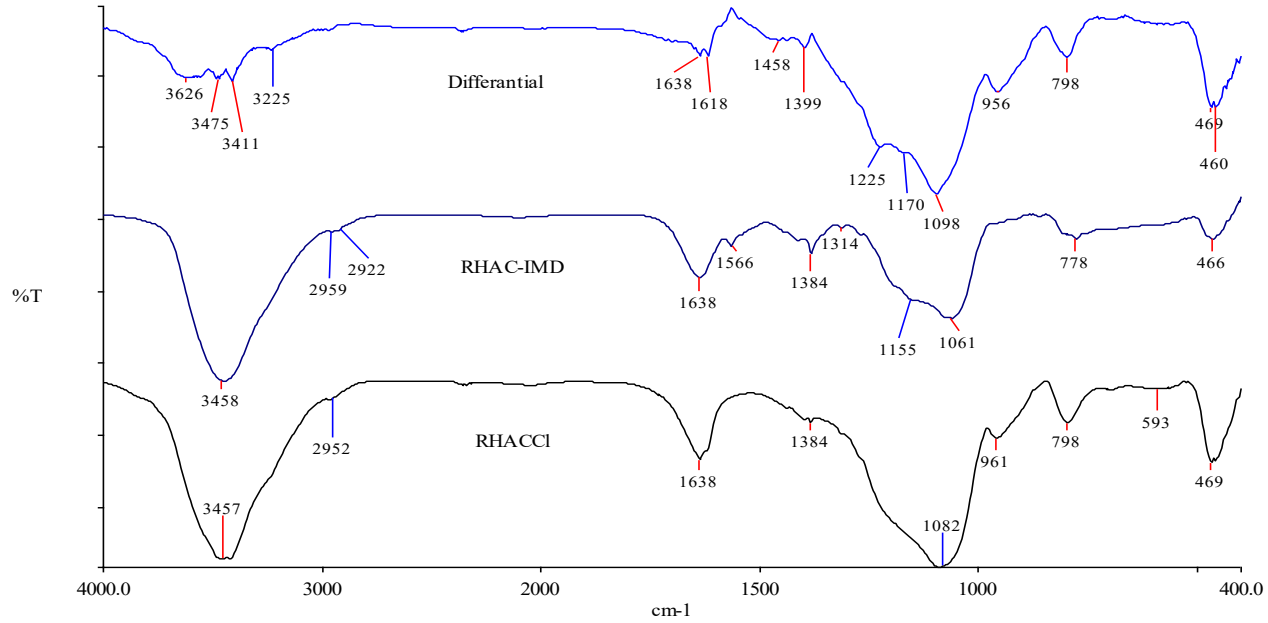


Figure 3. The FT-IR spectra of RHACCl, RHAPrIM and the differential spectrum

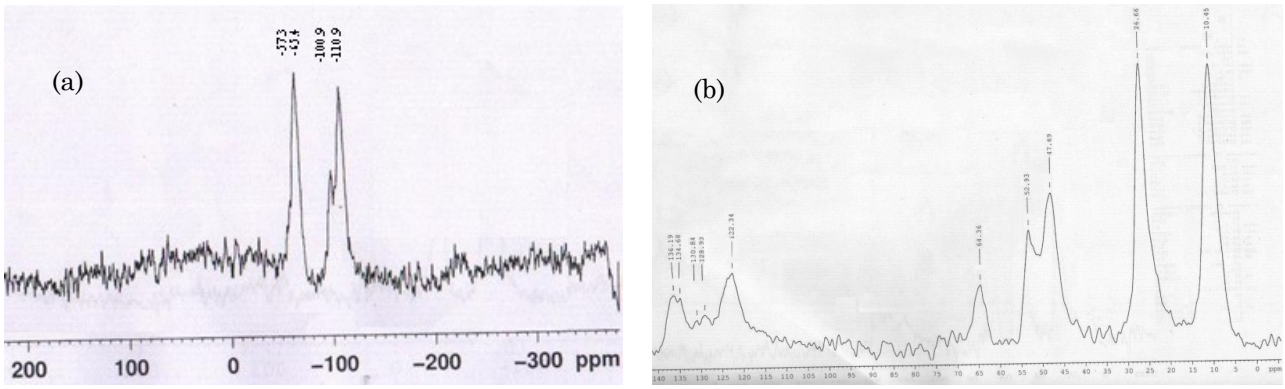


Figure 4. The solid sate NMR spectra of RHAPrIM. (a) The ^{29}Si MAS NMR spectrum (b) The ^{13}C MAS NMR spectrum

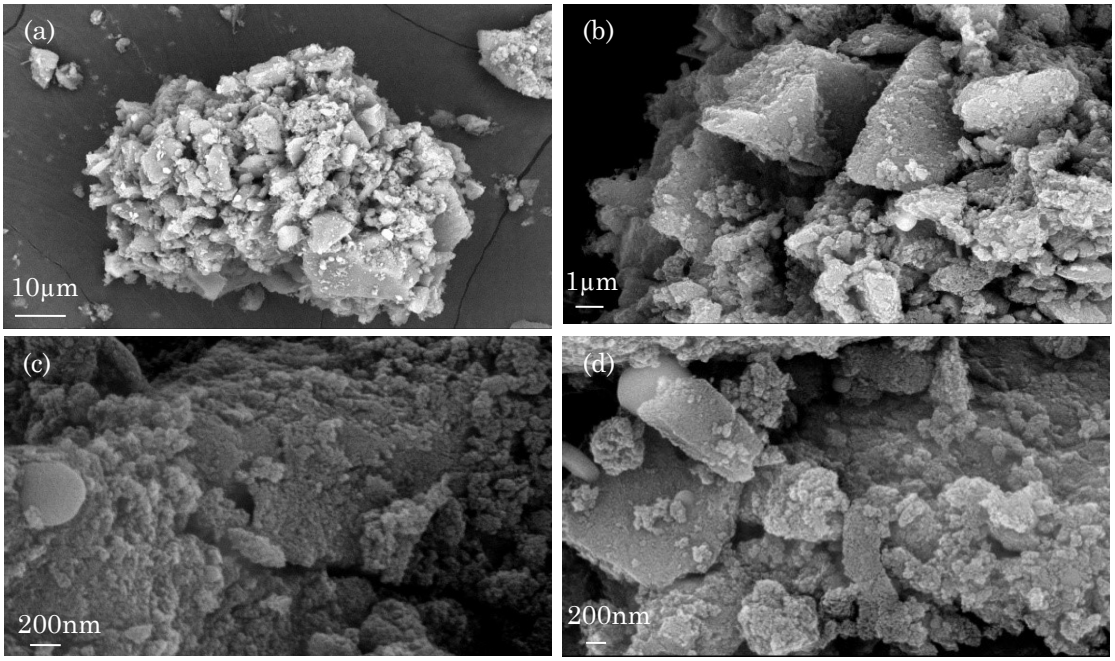
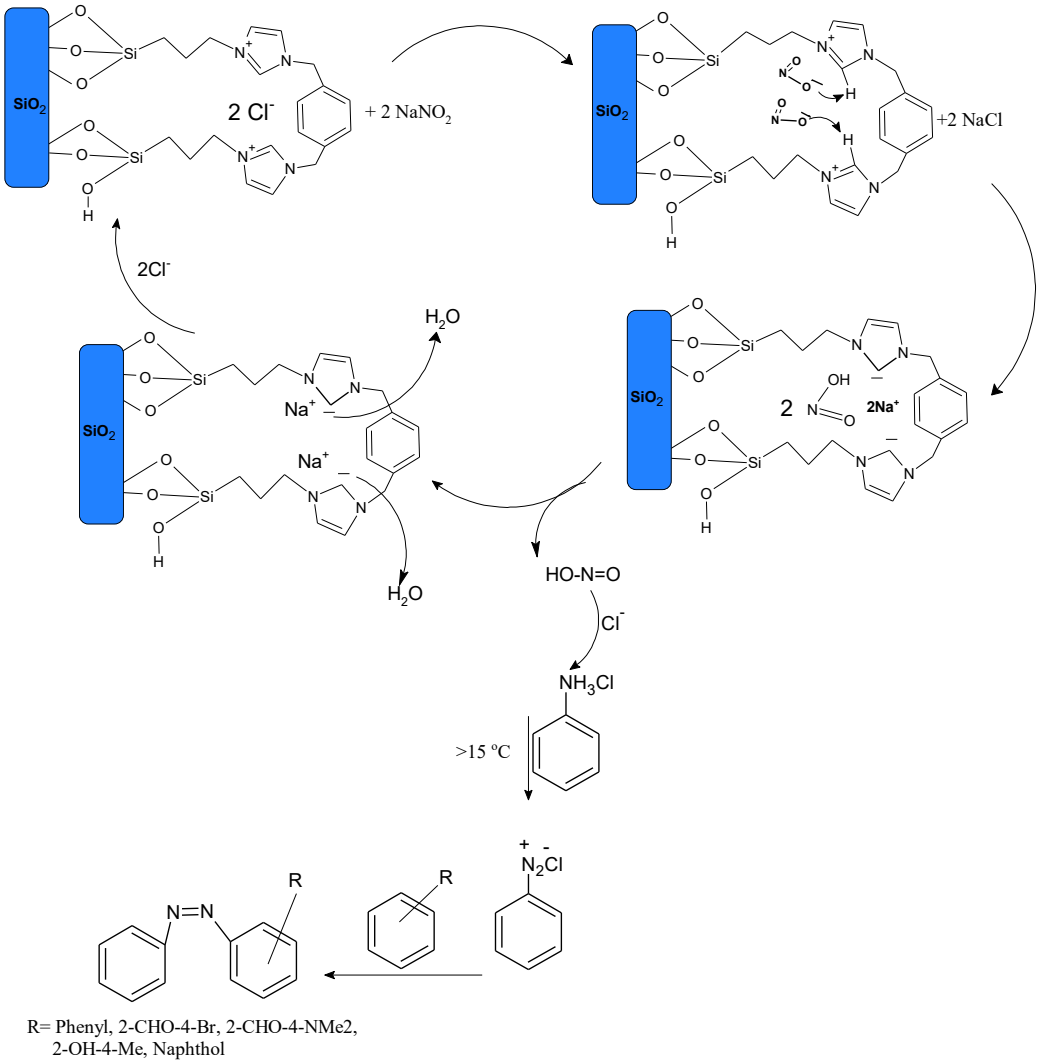


Figure 5. The SEM images RHAPrIM



Scheme 3. The generation of diazonium salt over RHAPrIM

rated with RHACCl. It is also saved to conclude that RHAPrIM has two type of structures as suggested in Scheme 2.

Figure 4(b) shows the solid-state ^{13}C NMR of RHAPrIM. The carbon bonded to silicon is shown at 10.4 ppm (C1 carbon). At 26.6 ppm the peak is assigned to the C2 carbon, while the C3 carbon is observed at 47.69 ppm. Comparing to the ^{13}C NMR of RHACCl [8] those chemical shifts are downfield shifted. The peaks at 52.9 and 64.3 ppm are corresponding to the two CH_2 groups. Imidazole carbons ring C4, C5, C4′, and C5′ (Scheme 1) chemically equivalent are shown at 122.3 ppm. Benzene ring (4 × ArC) appears at 128.9 and 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 refer to the imidazole carbon atom C2 and C2′ (Scheme 1).

3.2.5 Electron microscopy study

The SEM images (Figure 5) show irregular shapes arranged randomly on a smooth surface. No specific geometrical shapes are observed.

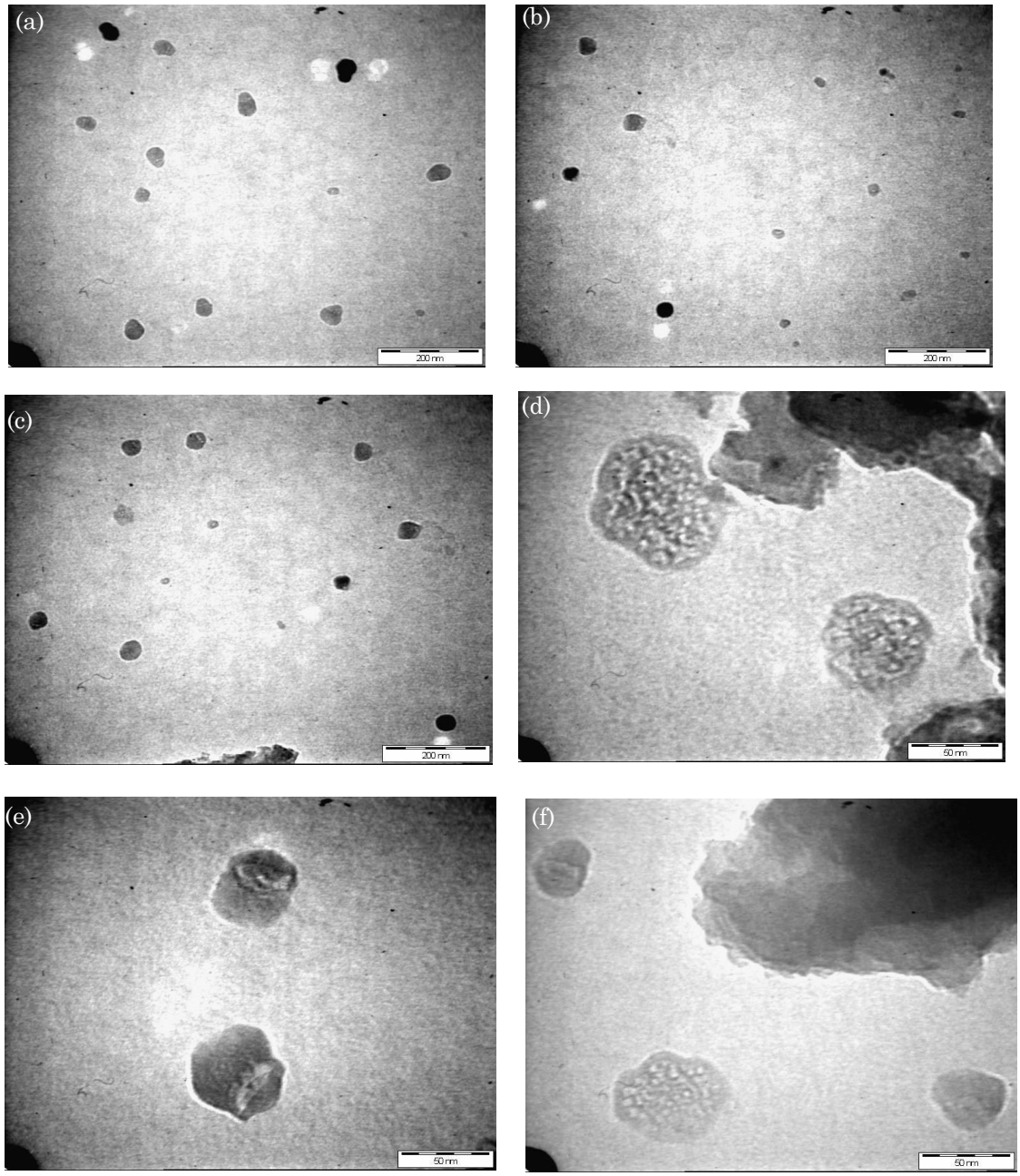


Figure 6. The SEM images for the RHAPrIM at different magnifications

Figure 6 shows the TEM images of RHAPrIM. Regularly shaped particles of RHAPrIM are observed. The RHAPrIM consists of two types of spherical particles. Both those particles have an approximate 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 are in nano range which might have important characterization besides having a catalyst.

3.2.6 Thermal analysis TGA/DTA

TGA/DTA curve of RHAPrIM is shown in Figure 7. Four characteristic decomposition stages are observed. First mass loss of water adsorbed started at 39 ºC. Second mass loss (ca. 5.9%) at 277 ºC, and third mass loss (ca. 7.7%) at 344 ºC, due to the organic moiety decomposition anchored onto silica. The fourth mass loss (ca. 1.1%) at 514 ºC, attributed to the formation of siloxane groups as a result of silanol groups condensation.

3.3 Catalytic Performances

The catalytic activity of RHAPrIM is examined *in-situ* preparation of nitrous acid which was used to prepare diazonium salt. In the case of its reaction with aniline, the aniline is first dissolved in water at the presence of RHAPrIM catalyst. To that mixture, a solution of sodium nitrite is added. This reaction produced *in–situ* nitrous acid which attacks aniline and forming the diazonium salt Scheme 3. After the formation of diazonium salt, simple filtration is necessary to remove the catalyst. The final reaction is a coupling of diazonium salt with resorcinol as a model substrate to produce azo dyes.

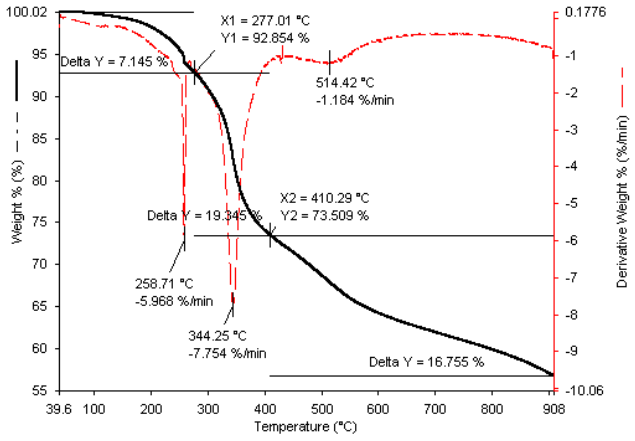


Figure 7. TGA/DTA curve of RHAPrIM

3.3.1 Optimization of reaction conditions

The activity of RHAPrIM was analyzed at different masses of catalyst, solvents, and temperatures (Table 2). Coupling reaction of the diazonium salt with resorcinol was a common method to synthesized azo dye. Four different masses of RHAPrIM were used (50, 100, 150, and 250 mg) to reach the optimum mass of catalyst as shown in Table 2. The yield reached its maximal 59% when the reaction is carried out using 100 mg at 0-5 °C. The increases of the catalyst mass to 250 mg, however, the yield does not change. At catalyst mass less than 100 mg it was observed that the yield decreased to be 40%. Thus, the 100 mg of catalyst mass is selected to be the optimum.

Temperature is a very important factor in the reaction due to the fact that the sensitivity of nitrous acid, therefore the reaction temperatures were 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% and a temperature of 15 °C the azo dye yield decrees to be 76% as shown in Table 2. As the temperature reached 15 °C the nitrous acid decomposition may be the main reason for the yield decreasing of azo dye.

Solvents effects on the yield of azo dye were studied and the results were listed in Table 2. The water, ethyl alcohol, and diethyl ether

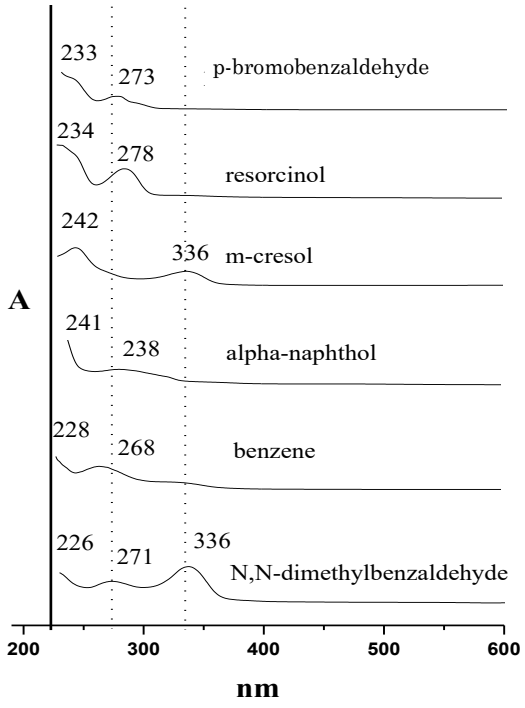
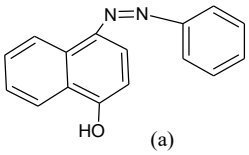
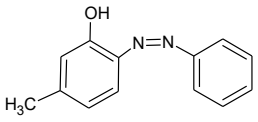
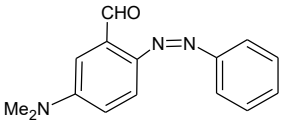
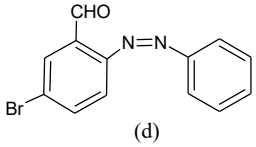
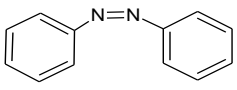


Figure 8. The UV-Vis of the monoazo dyes derivatives prepared over RHAPrIM

were used as reaction solvents. The structures of those solvents are the main reason behind their used. During the experiment, water is 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% and 57% in diethyl ether. 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 diethyl ether, the probability to form a hydrogen bonding became less and the yield could reduce.

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 is reduced after the third run of the reaction and reached to be 89 %. It was deduced that the RHAPrIM might be poisoning by the solvent used by forming a hy-

Table 2. The effects of different parameters on the production of azo dyes over RHAPrIM catalyst were shown

Entry	Parameters	Variants	Azo Dyes Yield (%)	Temperature (°C)
1	Variation of catalyst mass (mg)	50	40	0-5
		100	59	
		200	52	
		250	55	
2	Variation of solvent effects	Water	92	10
		Ethanol	61	
		Diethyl ether	57	
3	Variation of reaction temperature (°C)	5	59	–
		10	92	
		15	76	
4	Variation of benzene derivatives	 (a)	67	10
		 (b)	23	10
		 (c)	76	10
		 (d)	73	10
		 (e)	52	10
5	Catalytic cycle	Fresh	92	
		Run 1	89	
		Run 2	87	

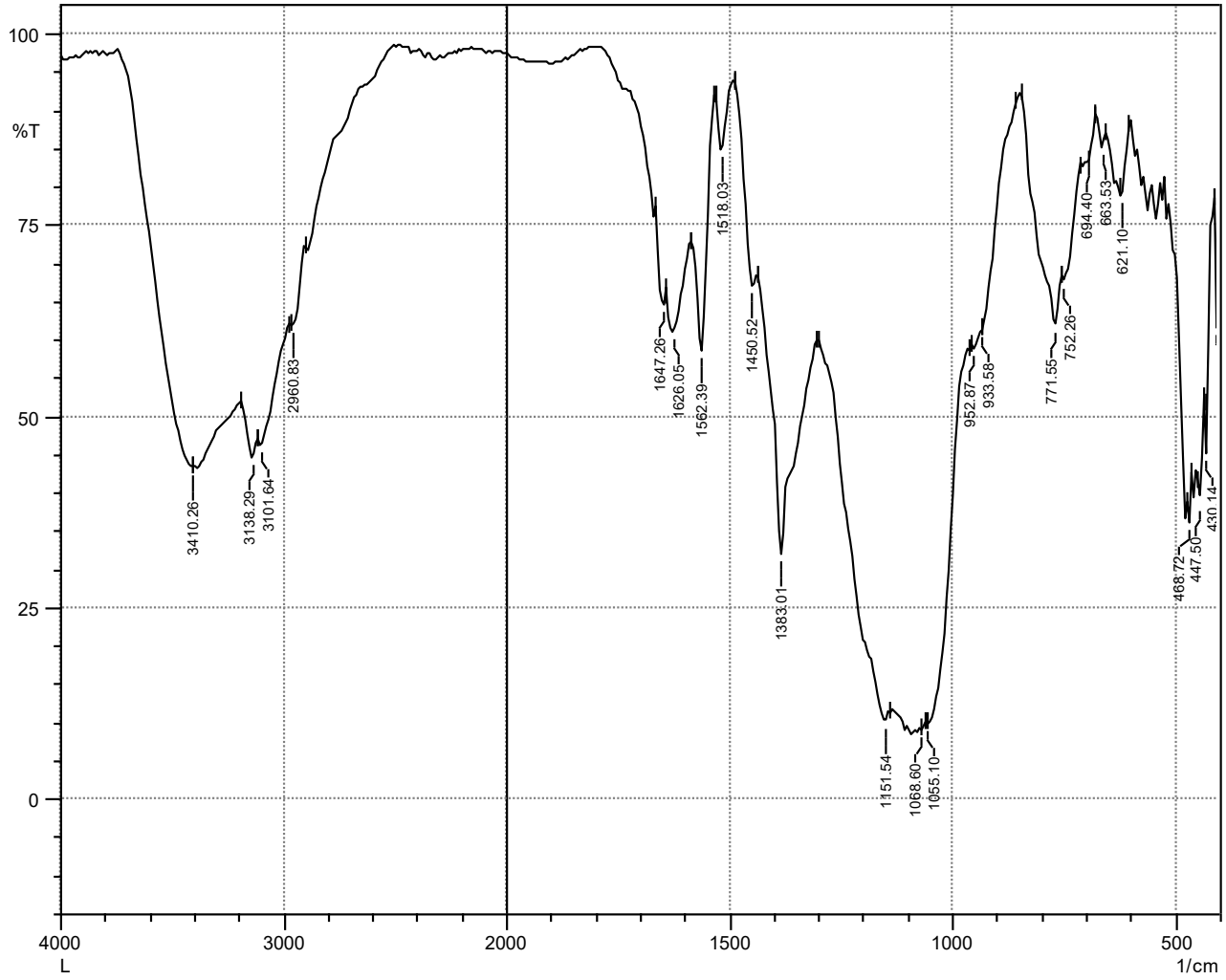


Figure 9. The FT-IR spectrum of RHAPrIM after the second used

Table 3. The physical properties, elemental analysis, and FT-IR of azo dye derivatives prepared over RHAPrIM

Compound	m.p (°C)	Elemental analysis (%)		FT-IR (cm^{-1})
		Calculated	found	
a	122	C:77.4, H:4.87; N:11.28	C:77.66, H:5.0, N:11.0	3486 (O-H), 3041 (C-Har), 1578 (N=N),
b	130	C:72, H:5; N:10	C:71.6, H:5.62; N:11.28	3436 (O-H), 3037 (C-Har), 1577 (N=N),
c	150	C:71, H:5.5; N:16	C:69.99, H:5.53; N:12.77	3060 (C-H_{Ar}), 2950 (C-Hal), 1530 (N=N), 1610 (C=O)
d	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)
e	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)

drogen 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 5.9% of water for each 10 mg of catalyst was deducted). This phenomena clearly shows that the catalyst surface is highly hydrophilic. This will be decried in the other solvent of 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 supported that the poisoning of the catalyst by the solvent which may explain the minimum reducing of the activity after the thread run.

3.3.2 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 3.

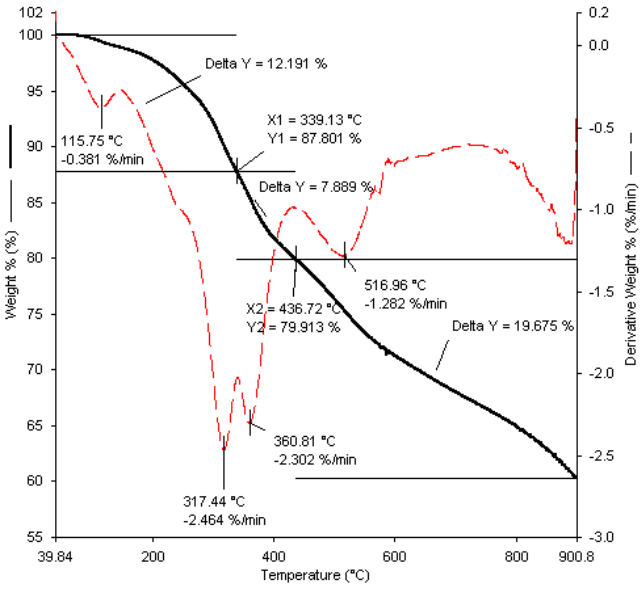


Figure 10. The TGA/DTA curve of RHAPrIM after the second used

3.3.3 Characterization of azo dyes

To give general applicability of RHAPrIM catalyst, various aromatic benzene derivatives were used to couple with the diazonium salt. Azo dyes derivatives were characterized by different techniques and the results listed in Table 3. Elemental analyses are clearly shown the abundant between the theoretical and found values Table 3. The UV-Vis spectra (Figure 8) 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 an electron-donating substituent. The FT-IR (not shown) is listed in Table 3. The effective bands are those due to the azo chromophore (–N=N–), and other bands, e.g. C=C and C–H of the aromatic ring, and carbonyl were clearly shown on FT-IR spectra.

3.4 Characterizations of the Reused Catalyst

The FT-IR spectrum of RHAPrIM after the second reused is shown in Figure 9. All catalyst functional groups are shown at the expected position as compared to the fresh catalyst (Figure 3). The vibration of Si–O–Si is observed at 1068 cm^{-1} and to 1061 cm^{-1} in the fresh catalyst. Silanol groups and absorbed water appeared as a broadband around 3410 cm^{-1}. This peak is becoming broader and slightly shifted as compared to the fresh catalyst as a result of the using the catalyst in water. The imidazole C5–H bond vibration has appeared at 3138-3110 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.

TGA/DTA curve of RHAPrIM after the second reused is shown in Figure 10. The sequence of characteristic decomposition stages is observed similar to the fresh catalyst (Figure 7). 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 (5.9%, Figure 7). The rest mass losses are not changed too much as compared to the fresh catalyst.

4. Conclusions

Silica from RHA was transferred to sodium silicate followed by immobilizing with CPTES in a simple one-pot synthesis. The material resulted was treated with p-xylyl di-imidazolium chloride to form a solid heterogeneous catalyst. Various spectroscopic methods were well char-

acterized the catalyst such as elemental analysis, TGA/DTA, FT-IR and ^{29}Si &^{13}C MAS NMR spectra. The presence of Q^4, Q^3, T^3, and T^2 silicon center in ^{29}Si MAS NMR and several peaks at a different position in ^{13}C MAS NMR spectrum are a good sign for silica modification with ligands. Thermal analysis shows that the catalyst can be used safely up to 277 ºC. TEM images of RHAPrIM showed regularly shaped particles with an estimation size of ca. 5 nm. Some particle seems to be smooth in shape, while the others show porous shape. The catalytic activity of RHAPrIM was examined *in–situ* preparation of nitrous acid which was used to the prepared diazonium salt. The RHAPrIM was used to produces nitrous acid via its 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 monoazo dye. All dyes were characterized by elemental analysis, IR, and UV-Visible spectral studies. The catalyst was stable and reusable in short reaction times with a simple experimental procedure.

Acknowledgement

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

References

[1] Serafína, V., Torrente-Rodríguez, R.M., González-Cortésa, A., de Frutos, P.G., Sabaté, M., Campuzano, S., Yáñez-Sedeño, P., Pingarrón, J.M. (2018). An electrochemical immunosensor for brain natriuretic peptide prepared with screen-printed carbon electrodes nanostructured with gold nanoparticles grafted through aryl, diazonium salt chemistry. *Talanta*, 179: 131-138.

[2] Mammeri, F., Teyssandiera, J., Darche-Dugaret, C., Debacker, S., Le Bourhis, E., Chehimi, M.M. (2014). Carbon nanotube–poly (methyl methacrylate) hybrid films: Preparation using diazonium salt chemistry and mechanical properties. *J. Colloid Interface Sci.*, 433: 115-122.

[3] Wang, J., Li, S., Liang, R., Wu, B., He, Y. (2018). Synthesis and characterization of water-soluble PE Gylated lignin-based polymers by macromolecular azo coupling reaction. *Chin. Chem. Lett.*, 29: 143-146.

[4] Fioresi, F., Vieillard, J., Bargougui, R., Bouazizi, N., Nkuigue, P., Emmanuel, F., Woumfo, D., Brunc, N., Mofaddel, N., Le Derf, F. (2017). Chemical modification of the cocoa shell surface using diazonium salts. *J. Colloid Interface Sci.*, 494: 92-97.

[5] Son, Y.A., Park, Y.M., Shin, C.J., Kim, S.H. (2007). Self-assembly multi-layer of diazonium resin and its coupling reaction with J-acid and H-acid. *Dyes Pig.*,72: 345-348.

[6] Dabbagh, H.A., Teimouri, A., Chermahini, A.N. (2007). Green and efficient diazotization and diazo coupling reactions on clays. *Dyes Pig.*, 73: 239-244.

[7] Valizadeh, H., Amiri, M., Hosseinzadeh, F. (2012). Nanoparticles of organosilane-based nitrite ionic liquid immobilized on silica for the diazotization of aniline derivatives and subsequent synthesis of azo dyes. *Dyes Pig.*, 92: 1308-1313.

[8] Adam, F., Osman, H., Hello, K.M. (2009). The immobilization of 3-(chloropropyl) triethoxysilane onto silica by a simple one-pot synthesis. *J. Colloid Interface Sci.*, 331: 143-147.

[9] Salman, A.W., Ur Rehman, G., Abdullah, N., Budagumpi, S., Endud, S., Abdallah, H.H. (2015). Synthesis, characterization, density function theory and catalytic performances of palladium(II)–*N*-heterocyclic carbene complexes derived from benzimidazol-2-ylidenes. *Inorg. Chim. Acta*, 438:14–22.

[10] Yalçin, N., Sevinç, V. (2000). Studies on silica obtained from rice husk. *Ceram. Int.,* 27: 219-224.

[11] Brunaure, S., Deming, L.S., Deming, W.E., Teller, E. (1940). On a Theory of the van der Waals Adsorption of Gases. *J. Am. Chem. Soc.*, 62: 1723-1732.

[12] Adam, F., Balakhrisnan, S., Wong, P.L. (2006). Rice husk ash silica as a support material for ruthenium based heterogenous catalyst. *J. Phys. Sci.*, 17: 1-13.

[13] Hello, K.M. (2010). The heterogenation of saccharin, melamine, and sulfonic acid onto rice husk ash silica and their catalytic activity in esterification reaction. *PhD Dissertation*, School of Chemical Science, University Sains Malaysia, Malaysia.