Arabian Journal of Chemistry (2017) 10, S1492–S1500

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Catalytic esterification via silica immobilized *p*-phenylenediamine and dithiooxamide solid catalysts

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Received 24 October 2012; accepted 29 April 2013
Available online 9 May 2013

KEYWORDS

Rice husk ash;
Surface modification;
Dithiooxamide;
p-Phenylenediamine;
Esterification

Abstract The *p*-phenylenediamine (PDA) and dithiooxamide (DTO) were immobilized onto silica from rice husk ash (RHA) using 3-chloropropyltriethoxyilane (CPTES) to form a solid catalyst denoted as RHAPDA and RHADTO, respectively. BET measurements of the catalysts showed the surface area to be 145 and 9.7 $m^2 g^{-1}$ with an average pore diameter of 9.8 and 10.9 nm, respectively. The catalytic performance of RHAPDA and RHADTO was tested in the esterification of ethyl alcohol with acetic acid. A conversion of 48% and 69% was achieved, respectively with 100% selectivity toward ethyl acetate.

1. Introduction

In recent years, the study of heterogenization of important organic ligands including important homogeneous catalysts onto suitable supports has seen increased interest due to the demand for green chemistry and environmentally friendly technologies (Hello, 2010).

The heterogeneous catalyst offers many advantages to chemical processes such as improved selectivity and ease of catalyst separation from reaction mixture, reducing the number of process stages and generation of wastes (Borges and Diaz, 2012). These are the main reasons why nowadays new methods are being developed to produce heterogeneous catalysts. In this respect the heterogenization of several organic molecules, i.e. saccharine (Adam et al., 2009a), melamine (Adam et al., 2010), 7-amino-1-naphthalene sulfonic acid (Adam et al., 2012a), sulfanilic acid (Adam et al., 2011) and chiral catalyst (Adam et al., 2012b) onto silica support was studied.

Esters, which include a wide category of organic compounds ranging from aliphatic to aromatic, are generally used as plasticizers, solvents, perfumery, and flavor chemicals, and also as precursors for many pharmaceuticals, agrochemicals, biodiesel production and other fine chemicals (Bhorodwaj and Dutta, 2010). *p*-Phenylenediamine (PDA) and dithiooxamide (DTO)

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2013.04.030

are primary amines (Scheme 1). DTO has two different hetero atoms within its molecule, i.e. S and N, while PDA has only N atom. These atoms have lone pair electrons, which together could in essence act as catalytic sites imparting a certain degree of selectivity. These heteroatoms can also be used to form coordinating bonds with transition metals that can be utilized further for catalysis. In this regard, heterogeneous catalysts which have secondary amine groups as the main active site gave a significantly higher conversion (in esterification reaction) compared to the homogenous catalyst which has primary amine as the main active site (Adam et al., 2010). Similar finding has been observed when using 7-amino-1-naphthalene sulfonic acid (Adam et al., 2012a) as a catalyst for esterification reaction. However, the systematic study of esterification using PDA and DTO as homogeneous or heterogeneous catalysts has not been reported to the best of our knowledge.

Rice husk (RH) is an agricultural waste material abundantly available in rice producing countries. The economic viability of RH as a source of silica is due to its high silica content. It is the objective of the current study to incorporate the PDA and DTO molecules onto silica to produce a hybrid with a silica-PDA and silica-DTO architecture that can be used beneficially in catalytic processes.

2. Experimental

2.1. Raw materials

The chemicals used were sodium hydroxide (Fluka, 99%), nitric acid (BDH, 65%), 3-chloropropyltriethoxyilane (CPTES) (Sigma–Aldrich, 95%), *p*-phenylenediamine (PDA) (Fluka, > 99%), dimethylformamide (DMF) (Fluka, > 99%), dithiooxamide (DTO) (Fluka, > 99%), toluene (Fluka, 99%), triethylamine (R&M Chemical, 99%), dimethylsulfoxide (DMSO) and methanol (Fluka, 99%), dichloromethane (DCM) (BDH, 99%), ethanol (Fluka, > 99%), absolute ethanol (Fluka, > 99%) and acetic acid (BDH, 99.5%). The RH was collected from a rice mill in Najaf, Iraq. All other chemicals used were AR grade or of high purity and were used directly without further purification.

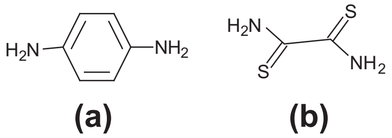
2.2. Extraction and modification of silica from RHA

2.2.1. Source of silica

The rice husk ash (RHA) was chosen as the source of amorphous silica as it was available in abundance. The silica was extracted from rice husk using a previously reported method (Adam and Chua, 2004; Ahmed and Adam 2007).

2.2.2. Preparation of RHAPDA

RHA silica was functionalized with CPTES according to the method reported elsewhere (Adam et al., 2009b, Scheme 2(a)).



Scheme 1 The structure of (a) *p*-phenylenediamine (PDA) and (b) dithiooxamide (DTO).

The resulting solid RHACCl was used as the support to immobilize PDA onto the silica surface. RHAPDA was prepared by adding PDA (2.0 g, 18.5 mmol) to a suspension of RHACCl (1.0 g) in dry toluene (30 mL) and triethylamine (Et_3N 2.3 mL, 18.5 mmol, Scheme 2(b)). The reaction mixture was refluxed at 110 °C in an oil bath for 24 h. The solid phase was filtered and washed with acidic ethanol, methanol, DMSO and then with DCM. The solid sample was then dried at 100 °C for 24 h. Finally, it was ground to produce a fine powder. About 1.2 g of the product was collected.

2.2.3. Preparation of RHADTO

RHADTO was prepared by adding DTO (2 g, 16.6 mmol) to a suspension of RHACCl (1.0 g) in dry toluene (30 mL) and Et_3N (2.3 mL, 16.6 mmol, Scheme 2(c)). The reaction mixture was refluxed at 110 °C in an oil bath for 24 h. The solid phase was filtered and washed with DCM and then with DMF. The sample was then dried at 100 °C for 24 h. Finally, it was ground to produce a fine powder. About 1.1 g of the product was collected.

2.3. Sample characterization

RHAPDA and RHADTO were characterized by elemental analysis (EuroEA Elemental Analyser), powder X-ray diffraction (XRD-6000, Shimadzu), and nitrogen adsorption porosimetry (Nova 2200e, surface area and pore size analyzer). Thermogravimetric analyses (TGA-DTA) were performed using a TGA SDTA851 instrument from 30 to 900 °C at a heating rate of 20 $°C\ min^{-1}$ under nitrogen flow. The catalytic reactions were analyzed by GC (SRI 8610 C, Buck Scientific, Inc.).

2.4. Esterification reaction

The esterification was carried out in a 50 mL round bottomed flask, equipped with a magnetic stirrer and water condenser. Ethyl alcohol (11.8 mL, 0.2 mol) was transferred by pipette into the round bottomed flask containing 200 mg of the catalyst (pre-dried at 110 °C for 24 h and cooled in a desiccator to minimize moisture content). After the reaction temperature reached 85 °C, acetic acid (12.9 mL, 0.2 mol) was added. The reaction mixture was refluxed for 9 h. Samples for analysis (~0.5 mL) were withdrawn at regular intervals from the reaction mixture and 10.0 μL of toluene (as internal standard) was added to the mixture. This mixture was then analyzed by gas chromatography.

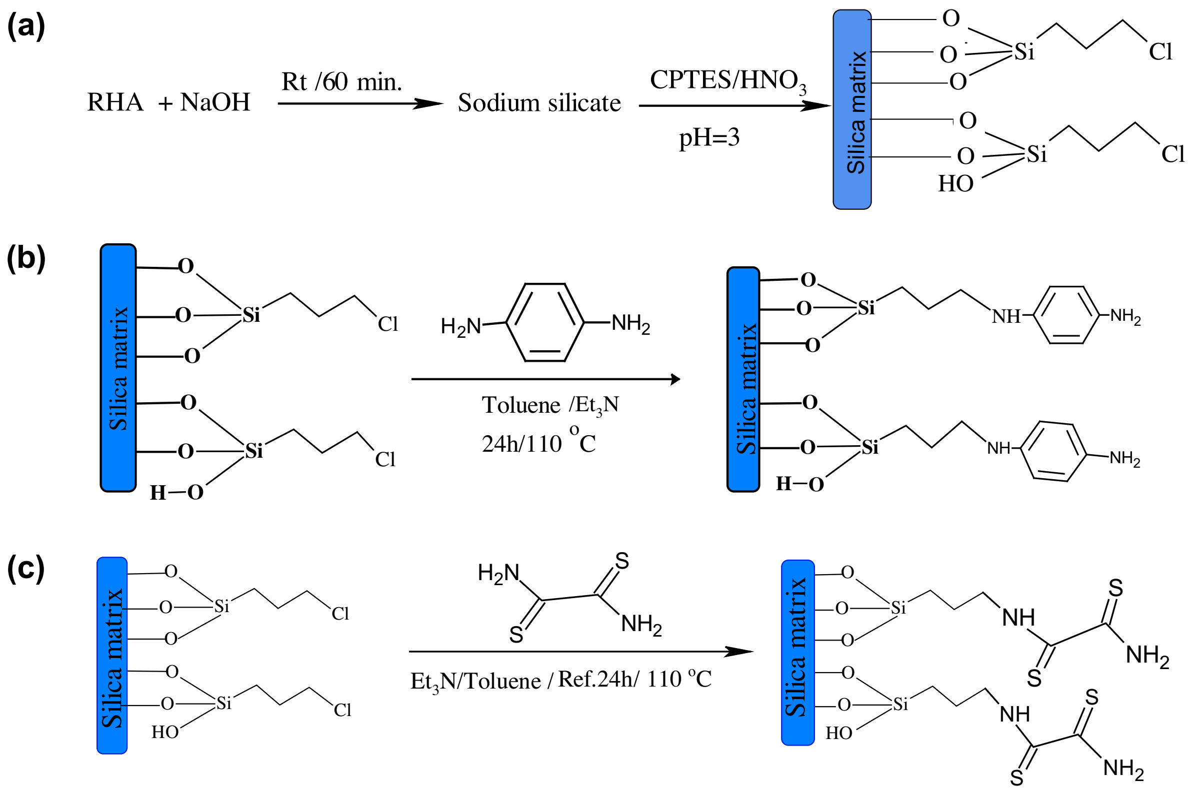
Catalytic activity with different mass of catalyst (100, 150, 200, and 250 mg), different temperatures (65, 75, and 85 °C) and different mole ratios 1:1, 1:2, 1:3, was studied as described above.

3. Results and discussion

The schematic representation for the synthesis of RHAPDA and RHADTO is shown in Scheme 2. The characterizations are discussed in detail in the following sections.

3.1. Elemental analysis

The elemental analysis of RHA and RHACCl was reported elsewhere (Ahmed and Adam, 2007; Adam et al., 2009b). The elemental analysis of RHAPDA and RHADTO had a nitrogen



Scheme 2 The reaction sequence for the synthesis of (a) RHACCl (Adam et al., 2009b), (b) RHAPDA, and (c) RHADTO. The possible structures of the catalyst and the approximate times taken for the completion of the experimental process are also shown.

composition of 3.3% and 6.0%, respectively (Table 1). RHADTO also shows it contained 12.6% S. The percentage of C and H were 13.9% and 2.0% for RHAPDA, while RHADTO showed 11.3% and 1.7%, respectively. These results were significantly higher than those in RHACCl and RHA (Adam et al., 2009b), as was expected. These results clearly indicate that the PDA and DTO were successfully immobilized onto RHACCl.

The percentage loading of PDA onto RHACCl was calculated according to the method used by Rahman et al. (2008). The grafting amount of PDA onto RHACCl was found to be 29.2%. The surface coverage by PDA was found to be 1.16 μmol m^{-2}. The grafting amount of DTA onto RHACCl was found to be 45.8%. This resulted in a surface coverage by DTA of 1.77 μmol m^{-2}.

3.2. Powder X-ray diffraction (XRD) and nitrogen adsorption analysis

The XRD diffraction pattern of RHAPDA and RHADTO (not shown) did not show sharp diffraction pattern. Only one broad band at 2θ angle of 22° was observed which was typical for amorphous silica.

Adsorption and desorption isotherms of RHAPDA are shown in Fig. 1(a) with the inset showing the corresponding pore size distribution graph. RHAPDA exhibited a type IV adsorption with H3 hysteresis (Thommes, 2010). The specific surface area of RHAPDA was 145 $m^2\,g^{-1}$ (Table 1). The decrease in the surface area of RHAPDA compared with RHACCl (Adam et al., 2009b) (which has a surface area of 633 $m^2\,g^{-1}$) could be due to the immobilization of large molecules of PDA on the silica surface causing the surface to be over crowded with the ligand network on the surface and thus blocking the pores. Fig. 1(a) shows two types of pore size distribution. The first pore range was observed between 1 and 5 nm which is in the microporous range. The second pore range was observed between 6 and 10 nm which is in the mesoporous range.

Adsorption and desorption isotherms of RHADTO are shown in Fig. 1(b) with the inset showing the corresponding pore size distribution graph. RHADTO exhibited a type IV adsorption isotherm with H3 hysteresis. The specific surface area of RHADTO was found to be only 9.7 $m^2\,g^{-1}$ (Table 1). The specific surface area of RHADTO had undergone a drastic change compared to the specific surface area of RHA (347 $m^2\,g^{-1}$) and RHACCl (633 $m^2\,g^{-1}$). Such drastic decrease in the surface area might be due to the cross linking of the −OH groups on the silica surface with the S and N atoms on the DTO ligand. As a result of this the pore size distribution of RHADTO (Fig. 1(b)) was observed to be in a very wide range of 1–20 nm. However, the observed pore sizes are within the mesoporous range.

3.3. Fourier transformed infrared spectroscopy analysis (FT-IR)

Fig. 2(a) shows the FT-IR spectra of RHA, RHACCl, and RHAPDA. The spectrum of RHA and RHACCl has been reported earlier (Adam et al., 2009b). RHAPDA spectrum show transmission bands at 3421–3325 cm^{-1} which were due to the stretching vibration of the NH_2 group (Adam et al., 2010). The transmission band at 3214 cm^{-1} could be due to the stretching vibration of the N−H bond (Mureseanu et al.,

Table 1 The physical parameters obtained for RHACCl, RHAPDA and RHADTO. The elemental content was determined by a combination of elemental and EDX analyses. The average values obtained from EDX analysis are shown in brackets. The results of BET analysis are also shown.

Sample	Elemental analysis (%)				Specific Surface area ($m^2\ g^{-1}$)	Average pore volume ($cc\ g^{-1}$)	Average pore diameter (nm)
	C	H	N	S			
RHA (Ahmed and Adam, 2007)	0.4	1.7	–	–	347	0.8	10.4
RHACCl (Adam et al., 2009b)	11.7	1.9	–	–	633	0.7	6.0
RHAPDA	13.9	2.0	3.3	–	145	0.8	10.4
RHADTO	11.3	1.7	6.1	12.6	9.7	0.005	3.5

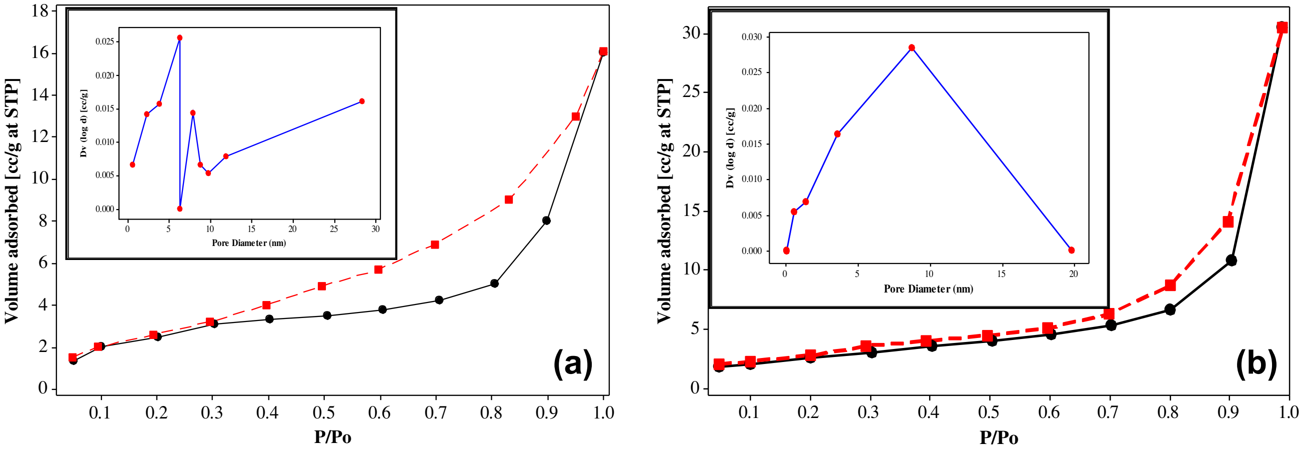


Figure 1 The nitrogen adsorption–desorption isotherms of (a) RHAPDA, (b) RHADTO. The inset shows the corresponding pore size distribution.

2008). A transmission band at 3022 cm^{-1} was assigned to the C–H aromatic stretching vibration. The band at 1630 cm^{-1} was due to the bending vibration of adsorbed H_2O (Adam et al., 2006). The transmission bands at 1609 and 1515 cm^{-1} were assigned to the stretching vibration of the aromatic ring carbons and N–H bending in the secondary amine, respectively (Silverstein et al., 1981).

The silanol (Si–OH) stretching vibration appeared at 3421 cm^{-1}. The stretching vibration of the siloxane (Si–O–Si) appeared at 1111 cm^{-1} which had clearly shifted as compared with the spectra of RHA (1099 cm^{-1}) and RHACCl (1092 cm^{-1}) (Adam et al., 2009b). The presence of NH_2, N–H, C–H aromatic and carbon-carbon aromatic vibration bands in RHAPDA spectrum indicated that the PDA was successfully immobilized onto RHACCl.

RHADTO spectrum in Fig. 2(b) showed transmission bands at 3433–3301 cm^{-1} which were due to the stretching vibration of NH_2 groups and also could be due to the overlapping of the Si–OH stretching vibration. The broad peak at 3133 cm^{-1} belongs to N–H vibration and adsorbed water in silica (Mureseanu et al., 2008). The absorption band at 2918 cm^{-1} was assigned to the stretching vibration of C–H bond. Furthermore, the transmission band at 1631 cm^{-1} could be due to the bending vibration of adsorbed H_2O. The transmission band at 1583 cm^{-1} was assigned to the bending vibration of N–H in the secondary amine (Adam et al., 2010). While the bending vibrations of the CH_2 groups (symmetrical and asymmetrical vibrations) can be seen at 1428 cm^{-1} (Adam et al., 2012b). The broad band at 1053 cm^{-1} was assigned to the Si–O–Si vibration. From these characteristic bands it can be concluded that the DTO was successfully incorporated onto RHACCl.

3.4. Thermogravimetric analysis (TGA)/differential thermal analysis (DTA)

A 10.5 mg of RHAPDA was used to study the thermal analysis and the result is presented in Fig. 3(a). The TGA of RHAPDA showed three distinct decomposition stages: the first starting at 30–160 °C, assigned to the loss of physisorbed water (ca. 4.40%, 0.46 mg); the second mass loss (ca. 19.2%, 2.0 mg) was observed between 160 and 433 °C, assigned to the decomposition of PDA on the silica surface. In accordance to this mass loss, it was calculated that 0.66 mmol of PDA was loaded on 10.5 mg of RHAPDA. The third continuous mass loss (ca. 16.9%, 1.7 mg) occurred between 433 and 898 °C, and was attributed to the decomposition of organic groups deep within the pore system and the condensation of neighboring silanol to form siloxane bonds, releasing water molecules.

The TGA of RHADTO is shown in Fig. 3(b). The first mass loss occurred between 30 and 124 °C (ca. 3.8%, 0.4 mg) was attributed to the loss of adsorbed water. The second mass loss (ca.14.4%, 1.5 mg) was from 124 to 247 °C, while the third mass loss (ca 18.8%, 1.9 mg) was from 247 to 497 °C. Both these mass loses were due to the degradation of propyl chain

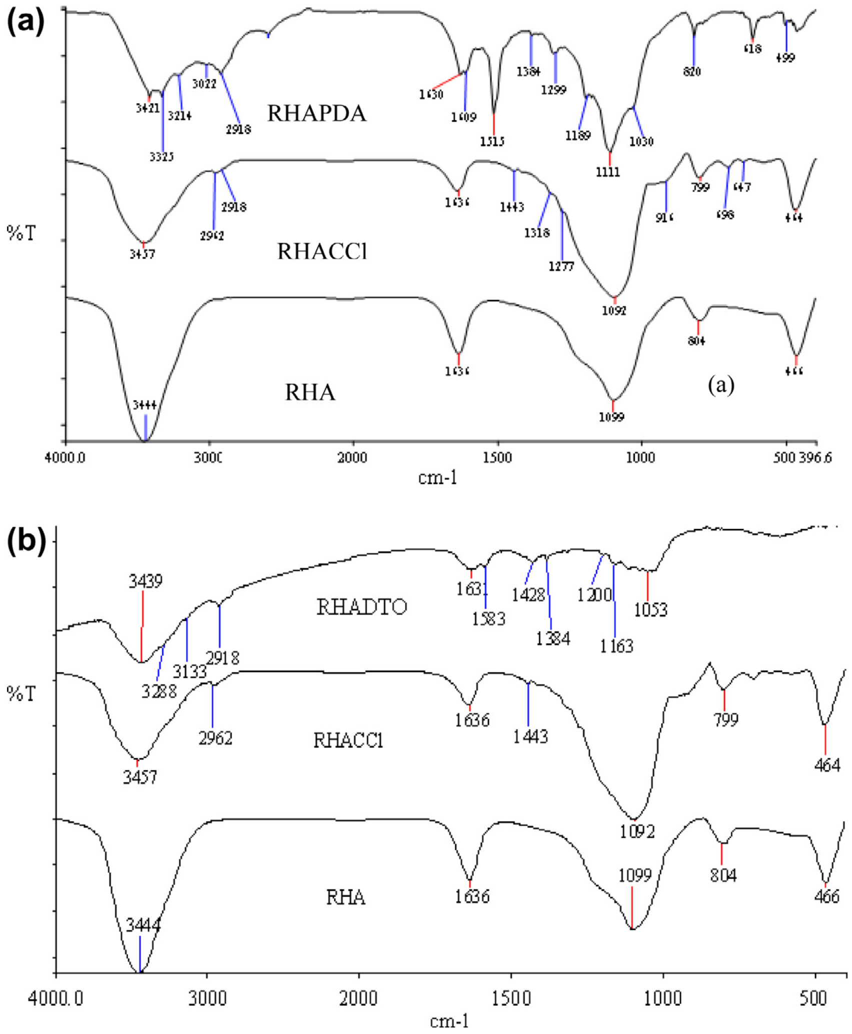


Figure 2 The FT-IR spectra of (a) RHA, RHACCl, and RHAPDA. (b) RHA, RHACCl, and RHADTO.

attached to the silica matrix and also due to the removal of DTO moiety. The continuous mass loses between 497 and 898 °C (ca. 13.3%, 1.4 mg) correspond to the condensation of silanol groups.

In the DTA curve for RHAPDA shown in Fig. 3(a), there were three exothermic transformations. The first peak occurred between 30 and 160 °C, with a maximum at 80 °C and the second occurred between 166 and 433 °C, with a maximum at 315 °C. The third occurred between 433 and 898 °C with a maximum at 525 °C. In the DTA curve of RHADTO shown in Fig. 3(b), the first peak occurred between 30 and 124 °C, with a maximum at 60 °C and the second occurred between 124 and 247 °C, with a maximum at 210 °C. The third occurred between 247 and 497 °C with a maximum at 260 °C. The TGA-DTA provided further evidence for the successful immobilization of PDA and DTO on RHA via RHACCl.

3.5. Esterification over RHAPDA, RHADTO, PDA, and DTO catalysts

3.5.1. Influence of reaction time

The effect of reaction time on the conversion of ethyl alcohol over RHAPDA, PDA, RHADTO, DTO, RHA-Blank and RHACCl-Blank is shown in Fig. 4. The reaction was carried out using 200 mg of catalyst with an acetic acid: ethanol ratio of 1:1 at 85 °C. The conversion of ethyl alcohol over RHAPDA during the second hour was 28% and it increased to a maximum of 48% in 4 h. However, there was no change in the conversion of ethyl alcohol after that time. It was decided to use 4 h as the optimum reaction time. The conversion of ethyl alcohol over RHADTO during the second hour was 20% and it increased to a maximum of 69% in 6 h. There was no change in the conversion of ethyl alcohol after 6 h. Therefore, the optimum reaction time was 6 h. The conversion over RHA-Blank and RHACCl-Blank was less than 25% in 6 h of reaction.

PDA (0.072 mg, 0.66 mmol) and DTO (0.066 mg, 0.55 mmol) were also used as homogeneous catalysts for the esterification reaction under the same conditions (Fig. 4). It was found that the conversion was less than 20% when PDA was used as the catalyst as compared with the heterogeneous RHAPDA catalyst. No change in the conversion was observed after 4 h of reaction. The esterification using DTO as catalyst showed 15% conversion in 2 h. No change in the conversion was observed after the second hour. The heterogeneous catalyst (RHADTO) showed a significant catalytic activity in comparison with the homogeneous catalyst and RHA-Blank. The low conversion over the PDA as compared with RHAPDA

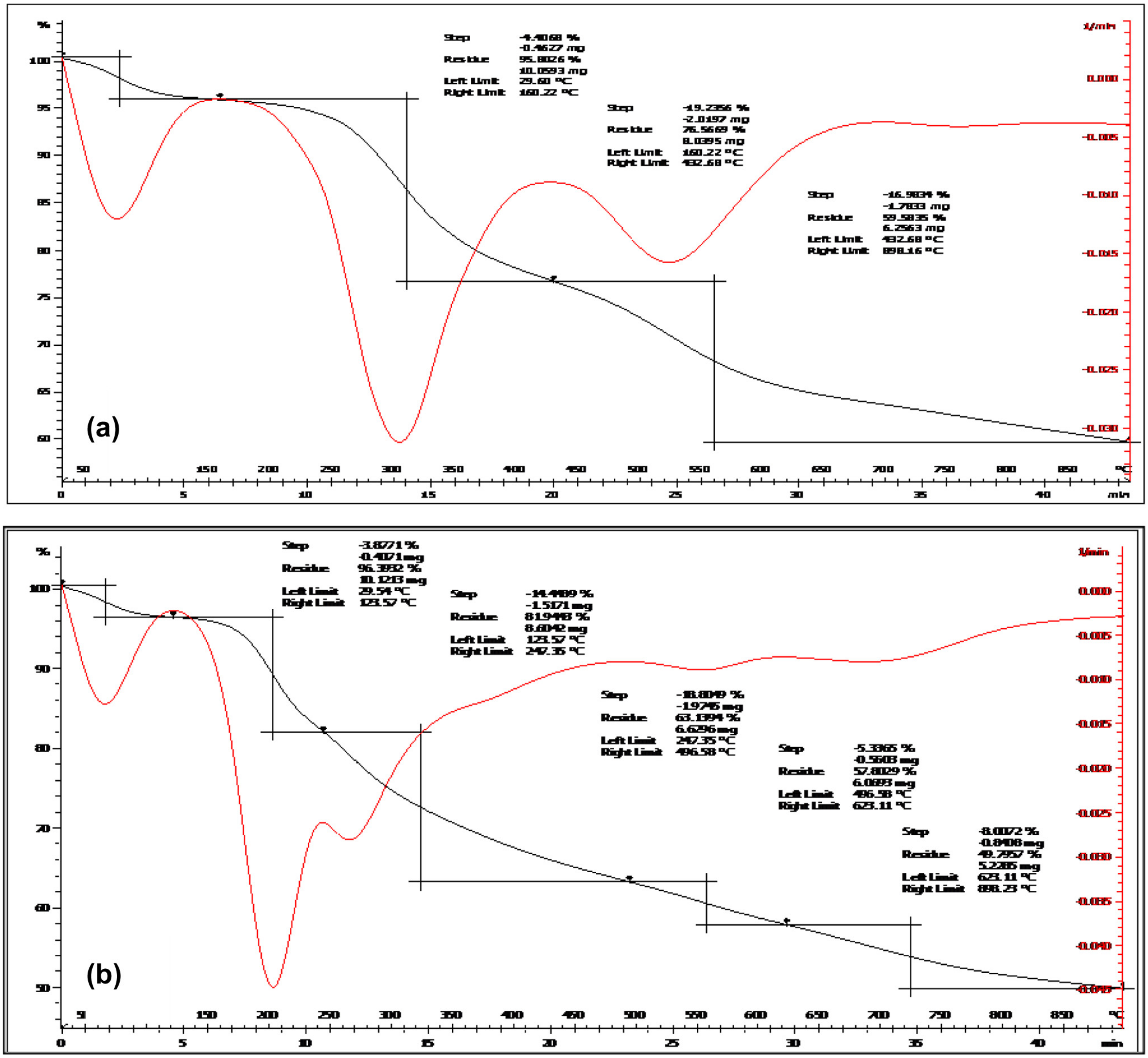


Figure 3 The TGA/DTA curves of (a) RHAPDA and (b) RHADTO.

could be due to the type of active centers on the catalyst. The amine group could act as the active center of the catalyst. The primary amine which is the main active center on PDA has very low basicity as compared with the secondary amine which is the main active center on RHAPDA (Adam et al., 2010). Therefore, the immobilization of PDA could generate secondary amine which can increase the catalytic activity of the heterogeneous catalyst RHAPDA.

3.5.2. Effect of catalyst mass

The esterification reaction was carried out by varying the amount of RHAPDA and RHADTO between 100 and 250 mg, while the alcohol: acid ratio was fixed at 1:1 for 4 h (over RHAPDA) and 6 h (over RHADTO) at 85 °C. The effect of the amount of catalyst on the ethyl alcohol conversion is shown in Table 2 (entry 1). When the catalyst mass of RHAPDA was increased from 100 to 200 mg, the conversion of ethyl alcohol increased from 30% to 48%. Further increase in the catalyst mass reduced the conversion to 29%. At this point it is not possible to say why such a decrease was observed when the catalyst mass was increased to more than 200 mg.

The esterification over RHADTO showed that when the catalyst mass was increased from 100 to 200 mg, the conversion was maximum at 69%. Therefore, 200 mg was taken as the optimum mass of catalyst in this study.

3.5.3. Influence of molar ratio of the reactants

The effect of molar ratio of the reactants on the conversion of ethyl alcohol over RHAPDA and RHADTO is shown in Table 2 (entry 2). The molar ratio of reactants acid: alcohol varied between 1:1 and 1:3. The reverse mole ratio of 1:1 to 3:1 of acid: alcohol was also studied. The best conversion of ethyl

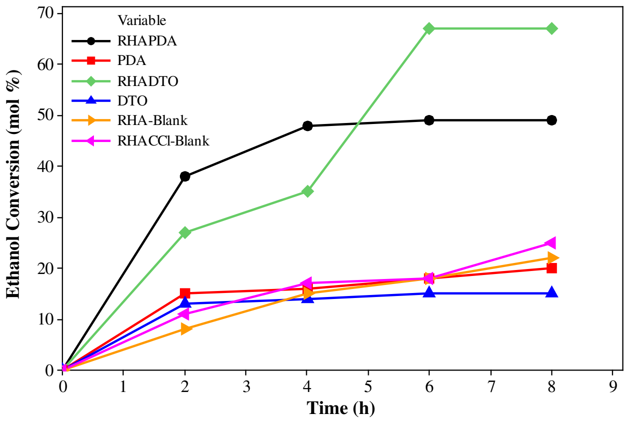


Figure 4 The percentage conversion versus time in the esterification of ethyl alcohol with acetic acid over RHAPDA, RHADTO, RHACCl-Blank and RHA-Blank (heterogeneous) and homogeneous (PDA and DTO). The reaction conditions were: The catalyst mass of RHAPDA, RHADTO, RHACCl-Blank and RHA-Blank was 200 mg, PDA (0.66 mmol, 0.072 mg) and DTO (0.066 mg, 0.55 mmol), mole ratio of acetic acid: ethanol = 1:1 and reaction temperature (85 °C).

alcohol over RHAPDA was 48% with 1:1 mol ratio of ethyl alcohol to acid. It was observed that increasing the acid could increase the conversion, while increasing the alcohol reduced the conversion of ethyl alcohol. This could be due to the basicity of the active sites of the catalyst which may adsorb the acid molecules on the catalyst surface by forming hydrogen bonding and increasing the conversion. The best conversion of ethyl alcohol over RHADTO was 69% when the mole ratio was 1:1 (acid: alcohol).

3.5.4. *Influence of reaction temperature*

The effect of the reaction temperatures on the conversion of ethyl alcohol over RHAPDA and RHADTO is shown in Table 2 (entry 3). The conversion increased when the reaction temperature was increased from 65 to 85 °C. The conversions recorded were 48% over RHAPDA and 69% with RHADTO at 85 °C. Higher temperatures were not studied due to the low boiling point of the alcohol.

3.5.5. *The turnover number and turnover frequency calculations*

Calculation of turnover number (TON) and turnover frequencies (TOF) provides a comprehensive way to make comparisons based on a per active site basis. The TON and TOF were calculated using the basic site density of PDA in RHAPDA of 0.66 mmol g^{-1}, and the basic site density of DTO in RHADTO of 0.55 mmol g^{-1}. These values have been calculated from the TGA data. Initial TON and TOF values were calculated using Eqs. (1) and (2), respectively. The results are shown in Table 3. On a per active site basis, the catalytic activity of RHADTO was greater than that of RHAPDA. Table 3 shows the TON and TOF and the conversion for each catalyst at the optimum reaction time.

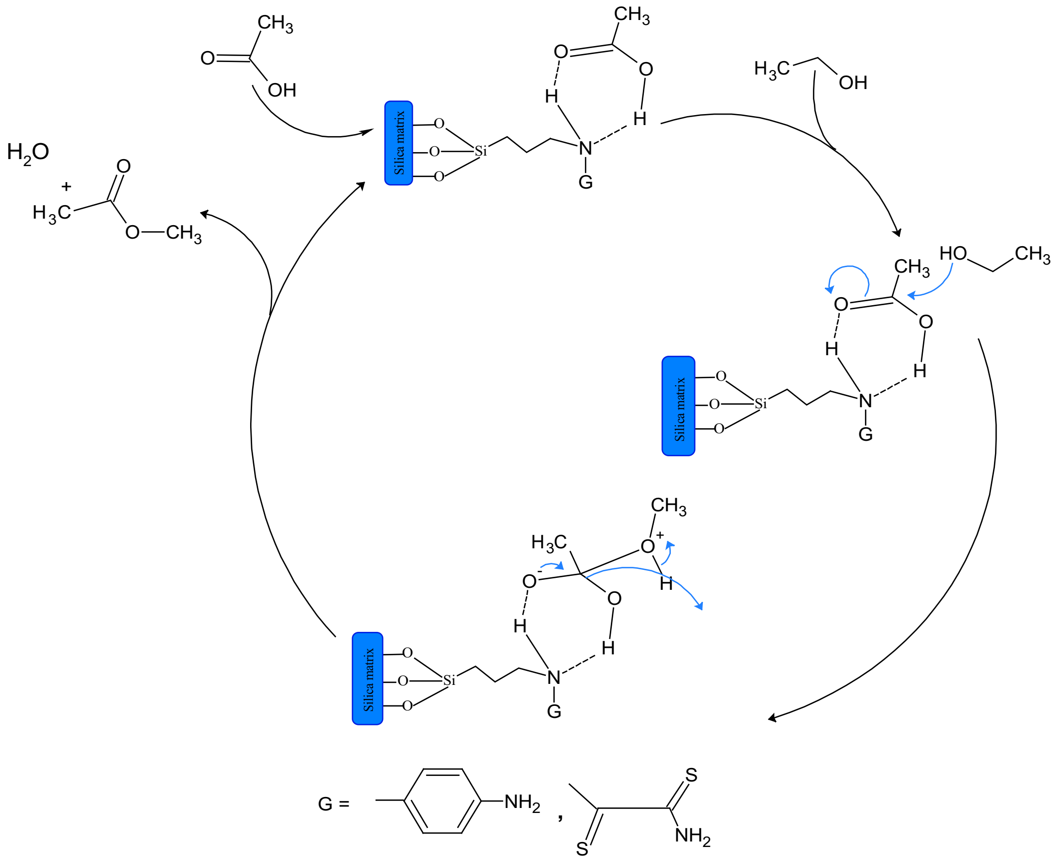
$$\mathrm{TON} = \frac{\text{The amount of products(mol)}}{\text{The amount of catalytic active sites(mol)}} \tag{1}$$

Table 2 The effect of different parameters on the conversion of alcohol into ester with RHAPDA and RHADTO.

Entry	Parameter	Variants	Conversion (%)	
			RHAPDA	RHADTO
1	Variation of catalytic mass (mg)	100	30	63
		150	34	58
		200	48	69
		250	29	40
2	Variation of molar ratio acid: alcohol	1:1	48	69
		1:2	25	23
		1:3	18	20
		2:1	24	45
		3:1	47	58
3	Variation of reaction temperature (°C)	65	23	28
		75	38	30
		85	48	69
4	Reusability with 200 mg of catalyst	Fresh catalyst	48	69
		1st reuse	39	51
		2nd reuse	45	50

Table 3 TON and TOF values calculated for different heterogeneous and homogenous catalysts catalyzed on the conversion of alcohol into ester at 85 °C.

Catalyst	Reaction time (h)	Active side × 10^{-3} (mol)	Conversion (mol)	TON × 10^3	TOF × 10^3(h^{-1})
RHAPDA	4	0.6	48	72.7	18.2
PDA Homogenous	4	0.6	20	30.3	7.6
RHADTO	6	0.5	69	125.4	20.9
DTO Homogenous	2	0.5	15	72.7	13.6



Scheme 3 The proposed reaction mechanism for the esterification of ethyl alcohol with acetic acid on the surface of RHAPDA and RHADTO. The fixation of the acid on the catalyst is via the formation a stable six member ring transition structure.

$$\mathrm{TOF} = \frac{\text{The amount of products(mol)}}{\text{The amount of catalytic active sites(mol)X Time (h)}} \qquad (2)$$

3.5.6. The reaction of methyl alcohol with acetic acid with RHAPDA and RHADTO as the catalyst

Esterification of methyl alcohols with acetic acid was tested over RHAPDA and RHADTO catalysts to give more applicability for the catalysts. The reaction was run under the optimum conditions of the catalysts determined for ethyl alcohol. The temperature of the reaction was fixed (65 °C) due to the low boiling point of methyl alcohol. It was found that the conversion of methyl alcohol was 31%, which is higher than the conversion of ethyl alcohol 23% at the same temperature 65 °C. However, it was found that the conversion of methyl alcohol over RHADTO was 35%, which is higher than the conversion of ethyl alcohol (28%) at the same temperature of 65 °C.

3.5.7. The reusability studies

The catalytic reusability is illustrated in Table 2 (entry 4). The catalysts were regenerated by washing with ethanol and drying at 135 °C (for RHAPDA) and 125 °C (for RHADTO) for 24 h before each reuse. In the case of RHAPDA, the conversion deceased from 48% to 45% over three runs. While for RHADTO, the conversion decreased from 69% to 50% over the same number of runs. The slight deterioration in the catalytic activity observed can be attributed to catalyst poisoning by the liberated water which also has a strong affinity to the active sites on the catalysts.

3.5.8. The proposed reaction mechanism

The proposed mechanism of the esterification over RHAPDA and RHADTO is shown in Scheme 3. The first step in the mechanism involves the adsorption of the acid on the basic nitrogen center via hydrogen bonding with the catalyst. This results in the formation of a hydrogen bonded stable six member ring transition state. This was followed by nucleophilic attack by the lone pair electrons of the alcohol on the carbonyl carbon of the adsorbed acid. This results in the formation of the expected products followed by the release of the free catalyst to continue the reaction.

4. Conclusion

In this work, we have designed a heterogeneous catalyst using a simple procedure which was used to functionalize RHA with CPTES and then with PDA or DTO. The procedure is simple and environmental friendly. The spectroscopic evidence obtained in this study showed that the PDA and DTO molecules had been successfully anchored on the silica. RHAPDA and RHADTO showed good catalytic activity toward esterification of ethanol and methanol with acetic acid. A conversion of 48% and 69% was achieved over RHAPDA and RHADTO, respectively with 100% selectivity toward ethyl acetate. The catalysts could be reused several times after a simple regeneration procedure. The catalyst is easy to prepare, environmentally friendly and promotes green chemistry.

Acknowledgment

We would like to thank Baghdad University, Republic of Iraq for financial support.

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