



# The heterogenation of melamine and its catalytic activity

Farook Adam\*, Kasim Mohammed Hello, Hasnah Osman

School of Chemical Sciences, University Sains Malaysia, 11800 Penang, Malaysia

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## ABSTRACT

The immobilization of melamine (Mela) onto silica extracted from rice husk ash (RHA) has been done via 3-chloropropyltriethoxysilane (CPTES). The resulting catalyst was designated as RHAPrMela. The melamine loading on the silica was found to be ca. 65.74%. The  $^{29}\text{Si}$  MAS NMR showed the presence of T<sup>2</sup>, T<sup>3</sup>, Q<sup>3</sup> and Q<sup>4</sup> silicon centers. The  $^{13}\text{C}$  MAS NMR showed that RHAPrMela had three chemical shifts at 14.83, 31.17 and 52.24 ppm, consistent with the three carbon atoms, and two chemical shifts at 161.52 and 169.67 ppm with double spinning side bands, indicating that the three carbon atoms in melamine ring are not equivalent in RHAPrMela. The catalytic potential of RHAPrMela was tested for the esterification of acetic acid with several alcohols. A conversion of 73% was achieved with 100% selectivity for the respective esters. The catalyst was easily regenerated and could be reused many times without loss of catalytic activity.

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## 1. Introduction

The important rule in the design of any heterogeneous catalyst should be its ease of synthesis. The cost should be low and the catalyst recoverable, hence reusable and environment friendly. In this respect, a simple one-pot synthesis developed by Adam et al. [1] allowed the immobilization of 3-chloropropyltriethoxysilane (CPTES) onto silica extracted from rice husk ash (RHA). These hybrid organic–inorganic materials with an organic functionality as part of the solid network have important and unique properties and many possible applications due to the high surface area and the presence of the organic end group, CH<sub>2</sub>–Cl. We had recently reported the synthesis of a saccharine–silica (RHAC–Sac) catalyst by nucleophilic substitution of the chlorine atom of the CH<sub>2</sub>–Cl end group with saccharine. This catalyst was shown to be an excellent heterogeneous catalyst for the esterification of acetic acid with ethanol [2].

Melamine (1,3,5-triazine–2,4,6-triamine) is a chemical intermediate originally used to manufacture amino resins and plastics [3] and has several industrial uses. Since it became commercially available in the late 1930s, it has been used in a wide range of products, i.e. in combination with formaldehyde to produce melamine resin as a durable thermosetting plastic, and melamine foam as a polymeric cleaning product [4]. However, it must be acknowledged that the recent misuse of melamine in tainted infant milk powder raised people's awareness of its many possibilities. It also raised our interest due to the presence of a high number of heteroatoms in the

melamine molecule, which we thought could be put to beneficial use.

It is the objective of the current study to incorporate the melamine molecules onto RHA to produce a hybrid with a silica–melamine architecture that could give beneficial catalytic properties. The melamine immobilized catalyst (RHAPrMela) was used as a heterogeneous catalyst for the esterification of several alcohols with acetic acid. To the best of our knowledge, the use of melamine as a homogeneous or a heterogeneous catalyst has not been reported.

## 2. Experimental

### 2.1. Raw materials

Sodium hydroxide (System, 99%), nitric acid (System, 65%), CPTES (Sigma–Aldrich, 95%), toluene (J.T. Baker, 99.8%), absolute ethanol (HmbG Chemical, 99.74%), 1-propanol and 1-butanol (R&M Chemical, 99.5%), benzyl alcohol (Unilab, 97%), tert-butanol (Merck, 99%), 2-propanol (Unvasol, 99%), acetic acid (System, 99.5%), triethylamine (R&M Chemical, 99%), melamine (Acros Organics, 99%). The rice husk (RH) was collected from a rice mill in Penang, Malaysia. 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. Sources 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 according to a reported method [5,6].

\* Corresponding author. Tel.: +60 4 6533567; fax: +60 4 6574854.  
E-mail addresses: [farook@usm.my](mailto:farook@usm.my), [farook.dr@yahoo.com](mailto:farook.dr@yahoo.com) (F. Adam).

### 2.2.2. Preparation of silica–melamine catalyst, RHAPrMela

RHA silica was functionalized with CPTES according to a method reported elsewhere [1]. The resulting solid, RHACCl, was used as the support to immobilize the melamine onto the silica surface. The synthesis of silica–melamine catalyst was carried out by adding melamine (2.0 g, 0.015 mol) to a suspension of RHACCl (2.0 g) in dry toluene (30 mL) and triethylamine ( $\text{Et}_3\text{N}$ ) (2.1 mL, 0.015 mol). The  $\text{Et}_3\text{N}$  was used as a deprotonating agent in order to increase the efficiency of the reaction and also to trap the HCl released during the reaction. The reaction mixture was refluxed at  $110^\circ\text{C}$  in an oil bath for 24 h. The solid phase was filtered and washed with hot acidic distilled water then by ordinary distilled water. The solid sample was then dried at  $100^\circ\text{C}$  for 24 h. Finally, it was ground to produce a fine powder. The sample was labeled as RHAPrMela. Yield = 1.80 g.

### 2.3. Sample characterization

The RHAPrMela was characterized by Powder X-ray Diffraction. The measurement was carried out using a Siemens Diffractometer D5000, Kristalloflex. Nitrogen adsorption porosimetry was carried out using an Automatic physisorption, Autosorb-1 CLP, Quantachrom, USA. The FT-IR spectra were recorded using a Perkin Elmer System 2000. The  $^{29}\text{Si}$  and  $^{13}\text{C}$  MAS NMR were recorded using Bruker, DSX-300 nmr instrument. The scanning electron microscopy (SEM) was carried out using a Leica Cambridge S360 and energy dispersive spectrometry, EDX, was carried out by Edax Falcon System. The TEM micrograph was obtained using Philips CM12 equipment. Thermogravimetric analysis (TGA) was performed using a (TGA SDTA851 $^\circ$ ) instrument: 10.337 mg of the samples were heated from 30 to  $900^\circ\text{C}$  at a heating rate of  $20^\circ\text{C min}^{-1}$  under nitrogen flow. The emission was recorded on a FT-IR.

### 2.4. Esterification reaction

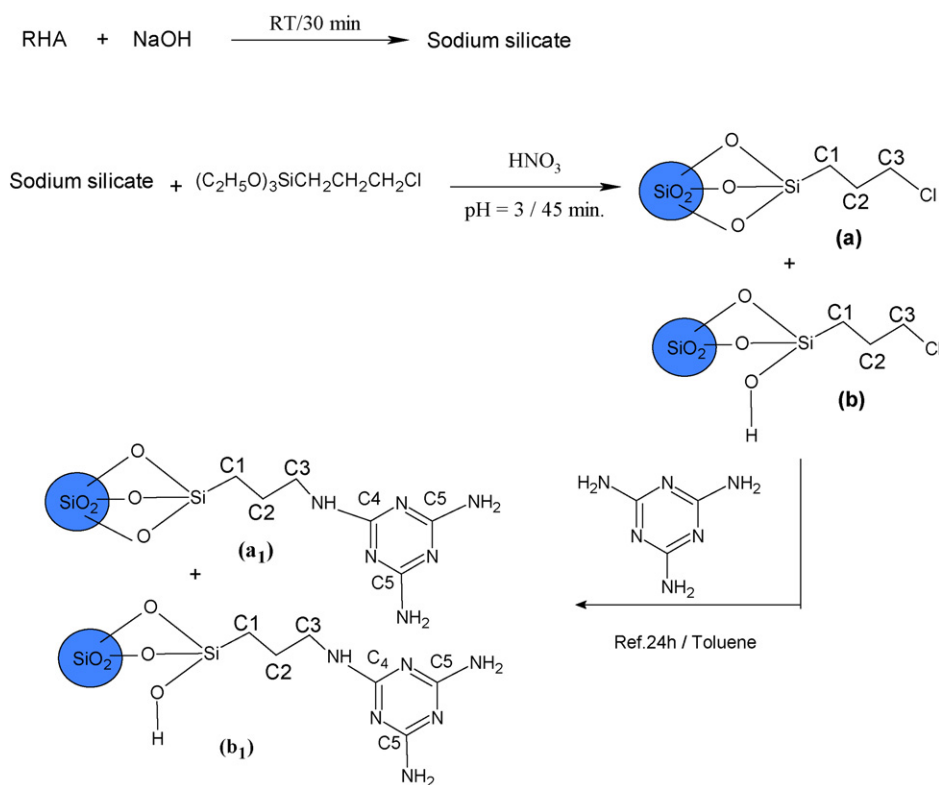
The esterification was carried out in a 50 mL round bottom flask, equipped with a magnetic stirrer and water condenser. Ethyl alcohol (12.0 mL, 0.20 mol) was transferred by pipette into the round bottom flask containing 0.10 g of the catalyst (pre-dried at  $110^\circ\text{C}$  for 24 h and cooled in a desiccator to minimize moisture content). After the reaction temperature reached  $85^\circ\text{C}$ , 12.9 mL (0.20 mol) of acetic acid was added. The reaction mixture was refluxed for 9 h. Samples for analysis ( $\sim 0.50$  mL) were withdrawn at regular intervals from the reaction mixture and 10.2  $\mu\text{L}$  of toluene (as internal standard) was added to the mixture. This mixture was then analyzed by gas chromatography.

Catalytic activity with different masses of catalyst (0.05, 0.1, 0.2, and 0.25 g), different temperatures (31, 65, 75, and  $85^\circ\text{C}$ ) and different mole ratios 1:1, 1:2, 1:3, and 1:4 of ethanol:acid and acid:ethanol was studied by conducting the experiment as described above.

The products of the catalytic reactions were analyzed by GC (Clarus 500, Perkin Elmer) and identified by GC–MS (Clarus 600, Perkin Elmer). A 30 m wax capillary column was used in the GC and GC–MS. The column and injector port temperatures were maintained at  $200^\circ\text{C}$ . In both cases, the oven temperature was programmed from  $34^\circ\text{C}$  with 6 min hold, then to  $160^\circ\text{C}$  at  $20^\circ\text{C min}^{-1}$  increment.

## 3. Results and discussion

The synthesis of RHAPrMela is shown in Scheme 1. The immobilization of melamine on RHACCl was carried out in a heterogeneous reaction. The reflux was carried out in dry toluene for 24 h, yielding the products as shown in Scheme 1.



**Scheme 1.** The reaction sequence and the possible structures for RHAPrMela as suggested by MAS NMR and FT-IR. (a, a1) T<sup>3</sup> – three siloxane bonds to a silicon atom in the silica. (b, b1) T<sup>2</sup> – two siloxane bonds to a silicon atom in the silica. It also shows C1, C2, C3, C4 and C5 (two carbon atoms are labeled as C5 due to their similar chemical environment) as identified in the solid-state  $^{13}\text{C}$  MAS NMR spectrum. The approximate times taken for the completion of the experimental processes are also shown.

**Table 1**  
The result of BET analysis for RHA, RHACCl and RHAPrMela.

Sample	Specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Average pore volume ( $\text{cc g}^{-1}$ )	Average pore diameter (nm)
RHA [6]	347	0.872	10.4
RHACCl [1]	633	0.705	6.07
RHAPrMela	235	0.41	7.09

### 3.1. CHN analysis

The elemental analysis of RHACCl showed that the percentages of C and H were 11.70 and 1.90%, respectively [1]. RHAPrMela showed a nitrogen composition of 1.57%. The C content for RHAPrMela (13.17%) was slightly higher than RHACCl, which was expected. The EDX analysis also showed the presence of nitrogen (3.65%) in RHAPrMela, from which we can further conclude that the melamine was indeed to be incorporated on the silica. From the amount of Cl present in the EDX of RHACCl (3.07%) and RHAPrMela (1.06%), the percentage loading of melamine on the silica was calculated to be 65.74%. This result is in close agreement to the percentage loading of melamine calculated by the equation in the literature [7], which is 65.99%. The surface coverage of melamine in RHAPrMela was calculated to be  $2.28 \mu\text{mol m}^{-2}$ .

### 3.2. Nitrogen adsorption analysis

The XRD spectrum of RHAPrMela was found to be amorphous. There was no phase change on immobilization of melamine onto RHACCl. This was similar to the observation made for amorphous silica from RHA [2,8]. The nitrogen adsorption isotherm obtained for RHAPrMela (not shown) gave a hysteresis loop observed in the range of  $0.4 < P/P_0 < 1.0$ ; this is associated with capillary condensation according to IUPAC classification. The isotherm was of type IV and exhibited an H1 hysteresis loop [9]. The sharp elevation of the adsorption curve from 0.70 to 0.85  $P/P_0$  indicates the presence of uniform sized pores. The BET analysis showed the specific surface area of RHAPrMela was  $235 \text{ m}^2 \text{ g}^{-1}$ , while the specific surface areas of RHA and RHACCl were reported to be 347 and  $633 \text{ m}^2 \text{ g}^{-1}$  [1,6], respectively. The decrease in the surface area of RHAPrMela, however, could be due to the reduction of the surface sites due to the immobilization of melamine causing the surface to be over crowded with the ligand network on the surface and thus blocking the pores. The RHAPrMela showed a narrow pore size range from 4

to 7 nm which is in the mesoporous range. The result obtained by BET nitrogen adsorption–desorption analysis of RHA, RHACCl and RHAPrMela are summarized in Table 1.

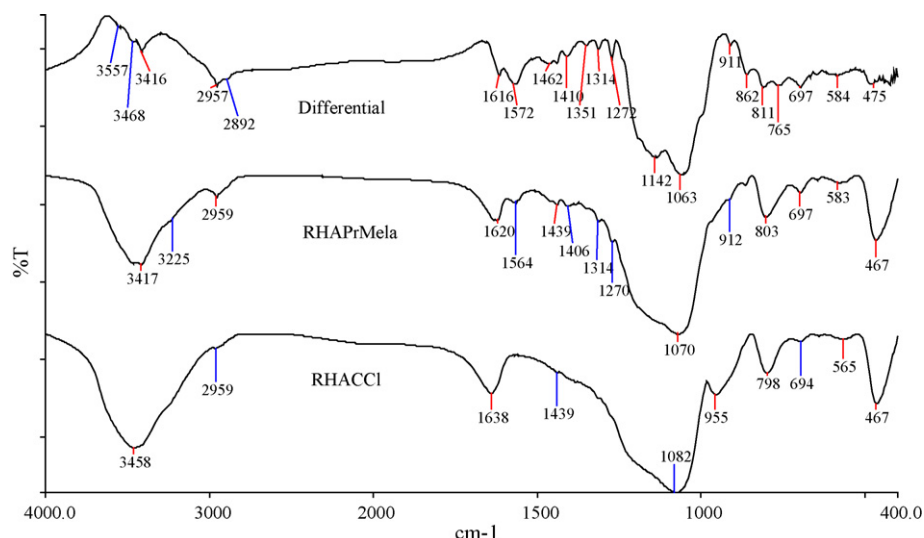
### 3.3. Fourier transformed infrared spectroscopy analysis

The FT-IR spectra of RHACCl, RHAPrMela and the differential are shown in Fig. 1. The FT-IR spectrum of RHA had been described previously by Ahmed and Adam [6]. The Si–O–Si vibrations appear at  $1101 \text{ cm}^{-1}$ , associated with the condensed silica network in RHA silica. This vibration was observed to shift to  $1082 \text{ cm}^{-1}$  in RHACCl and to  $1070 \text{ cm}^{-1}$  in RHAPrMela. This reflects the chemical transformation taking place adjacent to the –Si–O–Si– framework by the initial immobilization of CPTES and later by the melamine. The broad band around  $3557 \text{ cm}^{-1}$  is usually assigned to the O–H vibration from SiO–H and HO–H of absorbed water [10]. The melamine ring identified by the appearance of the  $\text{NH}_2$  band at  $3468\text{--}3416 \text{ cm}^{-1}$  and the stretching vibration of C–N at  $1572 \text{ cm}^{-1}$  are very clear in the differential spectrum. The band at  $1616 \text{ cm}^{-1}$  is due to the imine, C=N vibration, while the band at  $1272$  and  $1142 \text{ cm}^{-1}$  in the differential corresponds to the Si–C bond vibration. The appearance of vibrations due to  $\text{NH}_2$ , C–N and C=N groups indicate the successful incorporation of the melamine molecule with the RHACCl, forming the new catalyst, RHAPrMela.

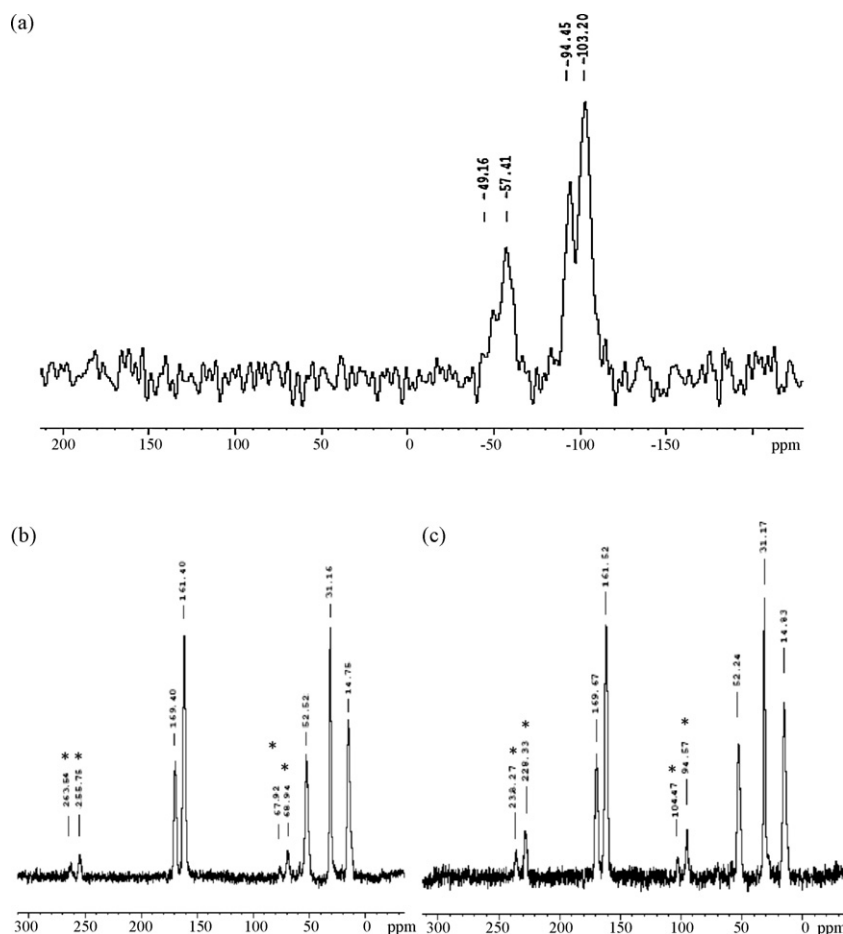
### 3.4. The $^{29}\text{Si}$ MAS NMR spectroscopy analysis

The  $^{29}\text{Si}$  MAS NMR solid-state spectra of RHA [6] showed only the presence of  $\text{Q}^4$  ( $\text{Si}(\text{OSi})_4$ ) and  $\text{Q}^3$  ( $\text{Si}(\text{OSi})_3(\text{OH})$ ) silicon centers [ $\text{Q}^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$ ] having chemical shifts at  $-110$  and  $-100$  ppm, respectively. The  $\text{Q}^3$  species are associated with single SiOH groups (silanol) which can also be H-bonded. The  $^{29}\text{Si}$  NMR spectrum of RHACCl had been reported elsewhere [1]. It showed chemical shifts attributed to  $\text{Q}^4$  and  $\text{Q}^3$  silicon atoms, i.e. at  $\delta = -109.92$  and  $-100.65$  ppm.

The  $^{29}\text{Si}$  NMR spectrum of RHAPrMela in Fig. 2(a) showed chemical shifts attributable to  $\text{Q}^4$ ,  $\text{Q}^3$  silicon atoms at  $\delta = -103.20$  and  $-94.45$  ppm. These are significant shifts compared to RHACCl. A chemical shift at  $-57.41$  ppm indicates the formation of Si–O–Si linkage via three siloxane bonds:  $(\text{SiO}_2)(-\text{O}-)_3\text{Si}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Mela}$  ( $\text{T}^3$ ). The chemical shift at  $-49.16$  ppm indicates the formation of two siloxane linkages, i.e.  $(\text{SiO}_2)(-\text{O}-)_2\text{Si}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2-\text{Mela}$  ( $\text{T}^2$ ), to the silica. Similar



**Fig. 1.** The FT-IR spectra of RHACCl, RHAPrMela and the differential spectra.



**Fig. 2.** The solid-state NMR of RHAPrMela. (a) The  $^{29}\text{Si}$  MAS NMR spectrum, (b) the  $^{13}\text{C}$  MAS NMR spectrum at 7 KHz and (c) the  $^{13}\text{C}$  MAS NMR spectrum at 5 KHz.

observations were made for RHACCl with chemical shifts at  $-65.2$  ( $\text{T}^3$ ) and  $-57.4$  ( $\text{T}^2$ ). The chemical shifts in the  $^{29}\text{Si}$  NMR spectrum of RHAPrMela with respect to RHACCl indicate the successful substitution at C3 of RHACCl, which essentially indicates the formation of the new C–N bond that immobilized the melamine onto the silica.

### 3.5. The $^{13}\text{C}$ MAS NMR spectroscopy analysis

The  $^{13}\text{C}$  MAS NMR of RHAPrMela is shown in Fig. 2(b). The chemical shift at 14.83 ppm was assigned to the C1 carbon directly bonded to a Si atom (Scheme 1). The chemical shift at 31.17 ppm was assigned to the C2 carbon, while the chemical shift at 52.24 ppm was assigned to the C3 carbon bonded to a –NH fragment. These chemical shifts for the propyl carbons were shifted down field compared to RHACCl [1]. The  $^{13}\text{C}$  MAS NMR shows two strong chemical shifts at 161.52 and 169.67 ppm with their respective spinning side bands (marked \*), indicating that the carbon atoms in melamine are not equivalent. To prove the existence of the spinning side bands, we carried out the  $^{13}\text{C}$  MAS NMR at different spin frequency of 7 MHz (Fig. 2(b)), and 5 MHz (Fig. 2(c)). The result clearly showed the shifting in the spinning side bands while the main chemical shifts of the melamine ring were not affected. Similar spinning side bands in the  $^{13}\text{C}$  NMR of melamine were also observed by Hayashi et al. [11]. The chemical shift at 161.52 ppm was assigned to the two carbon atoms with free amine groups C5 (Scheme 1) which are chemically equivalent. The second chemical shift at 169.67 ppm was assigned to the carbon atom of the melamine ring which is bonded to the propyl group C4 (Scheme 1) through the C3 carbon atom.

### 3.6. Transmission electron microscopy

The SEM images of RHAPrMela showed it to be made up of irregular particles arranged as layers. The layer structure is consistent with the BET analysis suggesting a swelling characteristic. On lower magnification, a smooth surface was revealed which resulted in a lower specific surface area compared to RHA.

Fig. 3 shows the TEM micrograph of RHAPrMela. It can be seen that the RHAPrMela consists of hollow nanotubes of rectangular cross-section. The outer surface of these rectangular nanotubes seems to be perforated either with pores or just indentations which may not open into the cavity of the nanotubes. On closer inspection at higher magnification, the nanotubes were found to be transparent with a smooth outer layer. It is possible that the sample consists of nanotubes with different types of surfaces. However, all the nanotubes observed had rectangular cross-section.

### 3.7. Thermal analysis TGA

A 10.337 mg of sample was used to study the thermal analysis curve of RHAPrMela (not shown). The FT-IR spectrum of the gasses evolved from RHAPrMela (not shown) was used to characterize each mass loss. The TGA of RHAPrMela showed four characteristic decomposition stages: the first starting at 30–110 °C, assigned to water loss (ca. 2.81%) which was confirmed by the FT-IR; the second mass loss (ca. 8.08%) occurred between 159 and 372 °C, assigned to the decomposition of the unreacted chloropropyl group anchored on the silica. The FT-IR spectrum of the evolved gasses showed the presence of  $-\text{C}_2\text{H}_3-$  and  $\text{H}_2\text{O}$  moieties; the third continuous mass

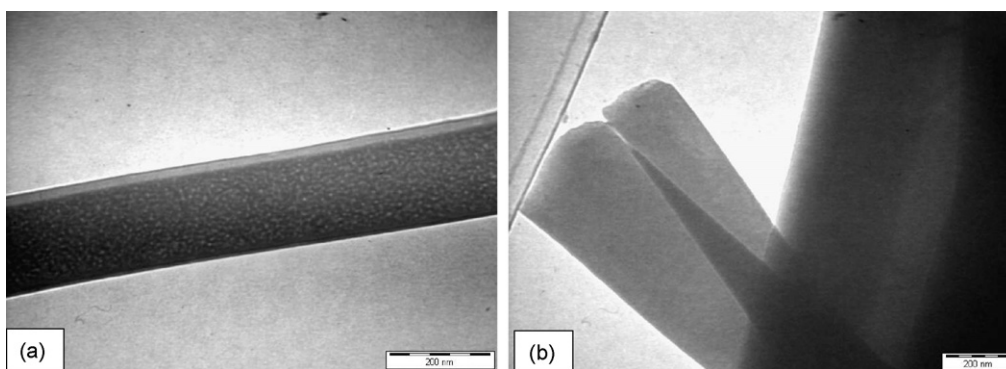


Fig. 3. The TEM images of RHAPrMela at different magnification: (a) 85 K magnification, (b) 500 K magnification.

loss (ca. 8.83%, 0.9103 mg) occurred between 372 and 505 °C, was attributed to the decomposition of melamine ring. The FT-IR for this mass loss showed the presence of CHNO moiety. In accordance to this mass loss, it was calculated that 0.0072 mmol/g of melamine was loaded on 10.337 mg of RHAPrMela. The fourth mass loss (ca. 7.82%) between 505 and 896 °C was attributed to the decomposition of the propyl group (loss of  $-C_2H_3-$  moiety) that was connected to the melamine and also the condensation of silanol groups, to yield siloxane groups by losing water.

### 3.8. Esterification with RHAPrMela as the catalyst

#### 3.8.1. Influence of reaction time on the catalytic activity

The effect of reaction time on the conversion of ethyl alcohol over RHAPrMela is shown in Fig. 4. The reaction was carried out with 0.10 g of the catalyst using alcohol/acid ratio of 1:1 at 85 °C. The initial conversion of ethyl alcohol during the first hour was 35% and it increased to a maximum of 73% in 9 h. Surprisingly, the reaction catalysed by 8.8 mg (0.069 mmol) of melamine (homogeneous) also showed 44% conversion in the same time. We believe that this is the first report of melamine being used as a catalyst in a chemical reaction. The heterogeneous reaction gave a significantly higher conversion compared to the homogenous catalyst.

The secondary amine on the silica support presents a strong basic center compared with the non-immobilized melamine which has only free primary amine groups ( $-NH_2$ ) and tertiary amine within the melamine ring: both of these are weak basic centers. It had been shown that some types of secondary amines are nearly

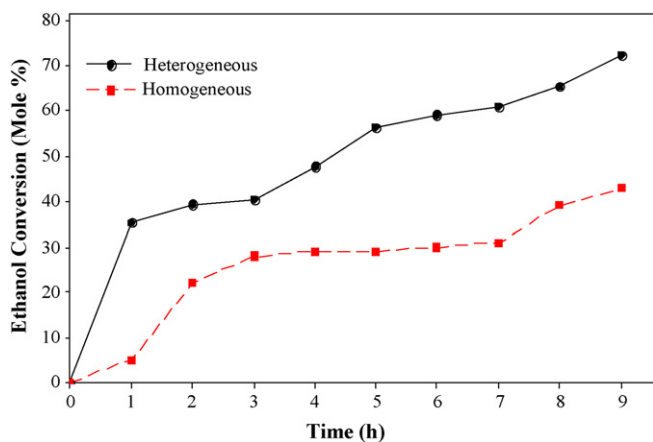


Fig. 4. The conversion of ethyl alcohol in the esterification with acetic acid over RHAPrMela and homogenous melamine as a function of reaction time. Reaction condition: catalyst 0.1 g (RHAPrMela) and 0.0088 g (melamine), mole ratio of reactant acid/alcohol = 1:1 at 85 °C.

Table 2

The effect of different parameters on the conversion of alcohol to ester with RHAPrMela.

Parameter	Variants	Percentage conversion (%)
Variation of catalyst mass with alcohol:acid = 1:1	0.05 g	56
	0.10 g	73
	0.20 g	65
	0.25 g	66
Variation of temperature of reaction	31 °C	3
	65 °C	27
	75 °C	57
	85 °C	73
Reusability with 0.1 g of catalyst	Fresh catalyst	73
	1st reuse	69
	2nd reuse	73
	3rd reuse	70

as basic as NaOH [12]. The strong basic character of RHAPrMela can be due to this similarity to the secondary amines, which resulted in the higher conversion compared to the homogeneous melamine. The selectivity towards ethyl acetate was 100% in all cases.

An equilibrium is generally established in esterification. Therefore, 100% conversion may not be possible due to this reason. However, a 73% conversion over 9 h is a reasonable good output for a heterogeneous catalyst. The efficiency could be improved if the product or the water is removed continually so as to shift the equilibrium favourably.

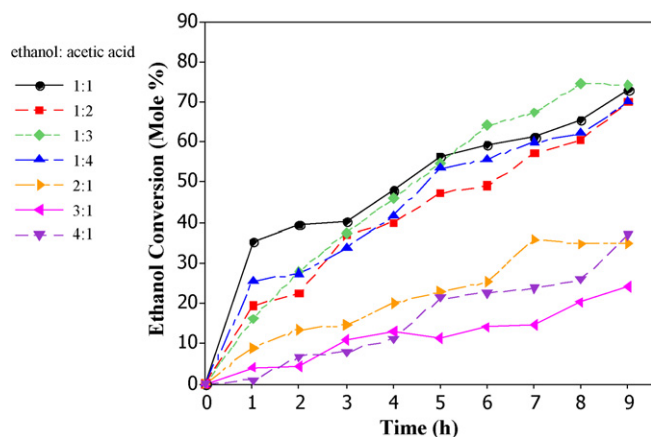
#### 3.8.2. Effect of catalyst mass on the catalytic activity

The esterification was carried out by varying the amount of RHAPrMela between 0.05 and 0.25 g, keeping the alcohol/acid ratio fixed at 1:1 for 9 h at 85 °C. The effect of the amount of catalyst on the alcohol conversion is shown in Table 2. The increase in catalyst mass from 0.05 to 0.10 g increased the conversion of ethyl alcohol from 56 to 73%. Further increase in catalyst mass did not result in any enhancement of conversion. However, a slight decrease in the conversion was observed, probably due to the possible blocking of the active sites. This decrease could also be due to the presence of the reaction equilibrium as shown in the following equation:



(1)

The decrease in the conversion could also arise due to the poisoning of the nitrogen sites responsible for the catalysis by the water molecules via hydrogen bonding.



**Fig. 5.** The conversion of ethyl alcohol in the esterification with acetic acid over RHAPrMela with different molar ratio of acid to alcohol and alcohol to acid. Reaction condition: catalyst 0.10 g, reaction temperature = 85 °C and reaction time = 9 h.

### 3.8.3. Influence of molar ratio of the reactants

The effect of reactant molar ratio on the catalytic activity of RHAPrMela is shown in Fig. 5. When the molar ratio of the reactant was varied from 1:1 to 1:4 with the alcohol kept constant, the conversion of ethyl alcohol was found to be ca. 73%. However, when the molar ratio was varied with the acetic acid held constant, the conversion was only ca. 37%. Since the alcohol is charged into the flask with the catalyst first, it is safe to assume that the catalyst surface will be adsorbed with the alcohol molecules. As the alcohol is increased, the catalyst surface will be saturated with the adsorbed alcohol molecules before the acid was added. On adding the acid, it will have a lower probability to get adsorbed and thus will lead to lower yield. The experimental data suggests that for the catalytic reaction to occur, the acid should be adsorbed on the surface as shown in the mechanism in Scheme 2.

### 3.8.4. Influence of reaction temperature

Table 2 also shows the effect of the reaction temperature on the conversion of ethyl alcohol over RHAPrMela. The conversion increased when the reaction temperature was increased from room temperature (31 °C) to 85 °C, with the conversion reaching nearly 73%. No further increase in temperature was studied as such temperatures would be above the boiling point of ethanol.

### 3.8.5. Catalytic reusability

The catalytic reusability is shown in Table 2. It can be seen that the catalyst is very active and can be used more than four times without loss of activity. The catalyst was regenerated each time by washing with ethanol and drying at 150 °C for 24 h before reuse. It can also be concluded that the catalyst, RHAPrMela, is very stable over a long period of reuse.

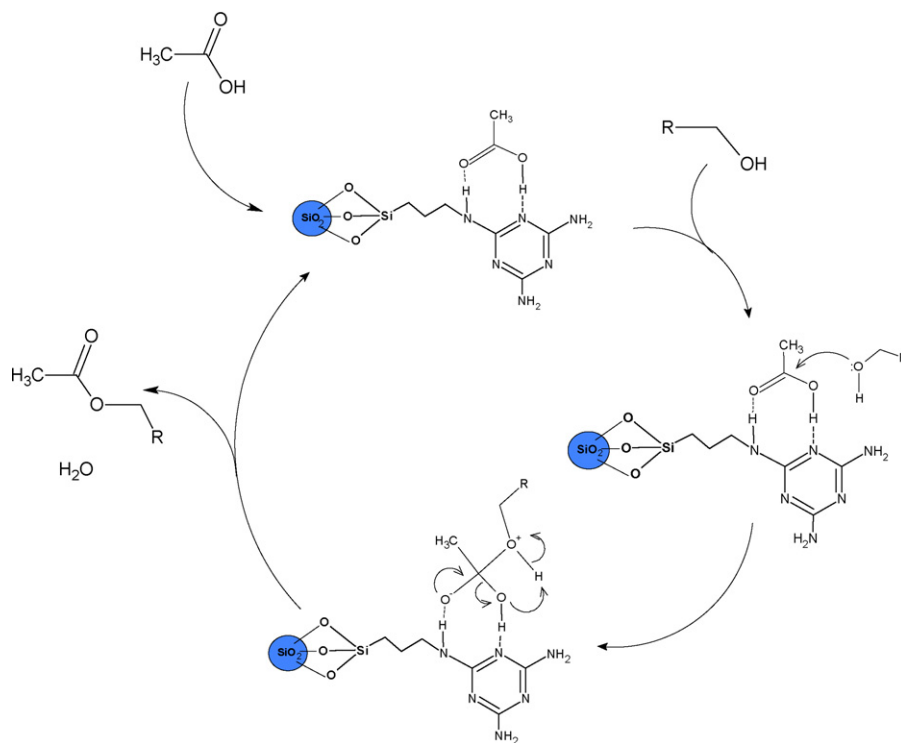
### 3.8.6. The esterification of higher alcohols with acetic acid over RHAPrMela

The esterification of several higher alcohols was also studied over RHAPrMela. The alcohols studied were 1-propanol (conversion = 47%), 1-butanol (conversion = 42%), 2-propanol (conversion = 25%), tert-butanol (conversion = 14%) and benzyl alcohol (conversion = 20%). The conversion generally decreased as the relative molecular mass of the alcohol increased. Primary alcohols also showed a higher conversion rate compared to the 2° or the 3° derivatives as shown for propanol and butanol.

These variations could be due to steric effects as demonstrated for 1-propanol, 2-propanol, tert-butanol and benzyl alcohol. An in-depth study of these higher alcohols will probably help to establish the suggested mechanism in Scheme 2. Such a study is underway in our laboratory.

### 3.9. The proposed mechanism for the esterification over RHAPrMela

The proposed mechanism for the catalytic esterification over RHAPrMela is shown in Scheme 2. In the first step, the acid gets



**Scheme 2.** The involvement of the nitrogen centers on the melamine in the reaction mechanism for the esterification of ethyl alcohol with acetic acid on the surface of RHAPrMela.

adsorbed by the basic nitrogen centers on the catalyst. This results in the formation of a hydrogen bonded stable eight member ring transition state. This is followed by nucleophilic attack by the lone pair electron on the alcohol on the carbonyl carbon of the adsorbed acid. This is followed by the formation of products and 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 melamine. The procedure is simple and environmental friendly. The spectroscopic evidence obtained in this study showed that the melamine molecule had been successfully anchored on the silica. The RHAPrMela showed good catalytic activity towards esterification of ethanol and other heavier alcohols with acetic acid. The RHAPrMela showed 73% conversion of ethanol with 100% selectivity towards ethyl acetate. The catalyst could be reused many times after a simple regeneration procedure. The catalyst is easy to prepare, non-corrosive, environmentally friendly and promotes green chemistry.

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