

## SOLID MELAMINE SULFATE FOR SCHIFF BASE SYNTHESIS

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**Abstract.** Melamine sulfate (Si-MelaSO<sub>4</sub>H) was prepared by treated melamine, which was immobilized onto silica (Si-Mela) with 0.05 M sulfuric acid at room temperature. The TGA confirmed that the thermal stability could reach 473 K. The XRD pattern showed that in some patterns there were sharp peaks and in other pattern a broad band was shown, which indicated that the surface is a mix of crystalline and non-crystalline nature. The Si-MelaSO<sub>4</sub>H was used successfully in the preparation of Schiff bases and its derivatives. The optimum conditions of the Si-MelaSO<sub>4</sub>H were found to be 0.25 g catalyst mass at 343 K for 9 h. The catalyst was reused several times without loss of catalytic activity.

**Keywords:** Schiff base, rice husk ash, melamine, silica.

## 1. Introduction

Melamine (1,3,5-triazine-2,4,6-triamine) is a chemical intermediate originally used to manufacture amino resins and plastics. In our previous study, it was successfully used as a heterogeneous catalyst for esterification reactions [1]. Pyranopyrazole compounds as one of melamine derivatives was synthesized by Davarpanah and Khoram [2] *via* modification of 1,3,5-triazine-2,4,6-triamine and used as a solid catalyst. The target composite was synthesized by the direct incorporation of chloropropyl groups through the condensation of nanosilica, 3-chloropropyltrimethoxysilane and grafting of melamine onto the propyl groups by the simple nucleophilic substitution reaction. The catalytic activity of this solid acid nanocomposite was probed through one-pot synthesis of 1,4-dihydropyrano[2,3-c]pyrazole *via* four-component couplings of aldehydes, hydrazine hydrate, ethyl acetoacetate and malononitrile under solvent-free conditions.

Rice husk (RH) has become an important cheap source for silica [3]. The silica is high content in RH. It is economical important to utilize this free raw material to

extract the silica. The usual method to produce silica from RH is to burn the RH in air, which leads to the formation of rice husk ash (RHA). The RHA contains ca. 95 % silica. However, this method results in environmental pollution. Recently, a new method was reported by Hello *et al.* [4] to produce silica from RH, which reduced the amount of organic pollutants released into the atmosphere when RH is burnt in the furnace. The silica extracted from RH was grafted with organic ligands to form hybridorganic-inorganic catalysts. These catalysts were used successfully for different reactions, *i.e.* esterification [5, 6], acetalization of glycerol with benzaldehyde [7], cellulose hydrolysis [8-10], production of monosaccharide [11], and alkylation [12].

Schiff bases are usually synthesized by the condensation reaction between an aldehyde and a primary amine. This is usually catalyzed by acid with water elimination. The imine groups (C=N) are the main functional groups in a Schiff base. There is an immense interest in Schiff base chemistry due to the wide range of applications as anti-HIV [13], anti-corrosion [14], antibacterial, and anti-fungal agent [15]. It is also widely used in catalysis [16], and as ligands for metal binding [17].

The aim of this study is to immobilize melamine onto silica which extracted from RHA to form heterogeneous catalyst. The resulting heterogeneous catalyst is used in the synthesis of Schiff bases. The catalyst is easy to isolate, stable at high temperature, and was found to be active in different solvents. The catalyst was reused over several cycles without loss of catalytic activity.

## 2. Experimental

### 2.1. Chemicals

The chemicals used in this study were sodium hydroxide (System, 99.0%), 3-chloropropyltrimethoxysilane CPTES (Sigma-Aldrich, 95.0 %), nitric acid (System, 65.0%), aniline (BDH, 99.0%), benzaldehyde (GCC, 99.0 %), butanol (Fluka, 99.5 %), propanol (Fluka, 98.0 %), 4-dimethyl amino benzaldehyde (BDH, 99 %), dimethyl aniline (Fluka, 98.0 %), and *p*-chloroaniline

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(BDH, 99.0 %). The RH was collected from a rice mill in Al-Muthanna Governorate, Iraq. All chemicals were AR grade or of high purity and used directly without further purification.

## 2.2. Sample characterization

The Si-MelaSO<sub>4</sub>H was characterized by powder X-ray diffraction using Siemens diffractometer, D5000, Kristalloflex. The FT-IR spectra were recorded on a Shimadzu 8400S. Thermogravimetric analysis (TGA) was performed using a PerkinElmer TGA-4000. Elemental analysis was obtained using Perkin Elmer-2400.

## 2.3. Sources of silica

The RHA was chosen as the source of amorphous silica as it was available in abundance. The silica was extracted from rice husk and reacted with CPTES according to the method reported in [3]. The product obtained was labeled as RHACCl.

### 2.3.1. Preparation of silica–melamine catalyst

Si-Mela was prepared by adding melamine (2.0 g) to RHACCl (2.0 g) in a mixture of dry toluene (30 ml) and triethylamine (Et<sub>3</sub>N) (2.1 ml). The reaction mixture was refluxed in an oil bath at 383 K for 24 h. The solid product was filtered and then washed with distilled water, flowed with DMF, then dried at 373 K for 24 h. The dry product was ground to produce a fine powder and was labeled as Si-Mela which weighted about 3.875 g.

### 2.3.2. Preparation of Si-MelaSO<sub>4</sub>H

About 1.0 g of Si-Mela was stirred in 25 ml of 0.05 M sulfuric acid at room temperature to obtain Si-MelaSO<sub>4</sub>H catalyst which was filtered and washed with copious amount of distilled water and then with ethanol and dried in an oven at 383 K for 24 h. The resulting compound was labeled as Si-MelaSO<sub>4</sub>H. About 1.015 g was obtained using this method.

## 2.4. Synthesis of Schiff base by using Si-MelaSO<sub>4</sub>H Catalyst

A mixture of aniline (0.93 g, 0.01 mol), benzaldehyde (1.1 g, 0.01 mol), ethanol (10 ml) and Si-MelaSO<sub>4</sub>H (0.25 g) was refluxed at 343 K for 10 h under stirring. The resulted homogenous solution was filtered, and the mixture was cooled in ice bath and filtered to give the products.

Catalytic activity with different masses of catalyst (0.1, 0.15, 0.2 and 0.25 g), different temperatures (313, 333, and 343 K) and different solvents (ethanol, 1-propanol, and 1-butanol) was studied by conducting the experiments as described above.

## 2.5. Reusability of the Catalyst

To confirm the reusability of the catalyst the reaction was running successively with the catalyst under the optimum parameters of the reaction. The reaction was first run with the fresh catalyst to complete the conversion, then the catalysts were filtered and dried at 383 K. After regeneration, by washing with hot ethanol, and drying at 383 K for 24 h before each reuse, the catalyst was reused for catalyzing new reactants under the optimized reaction conditions.

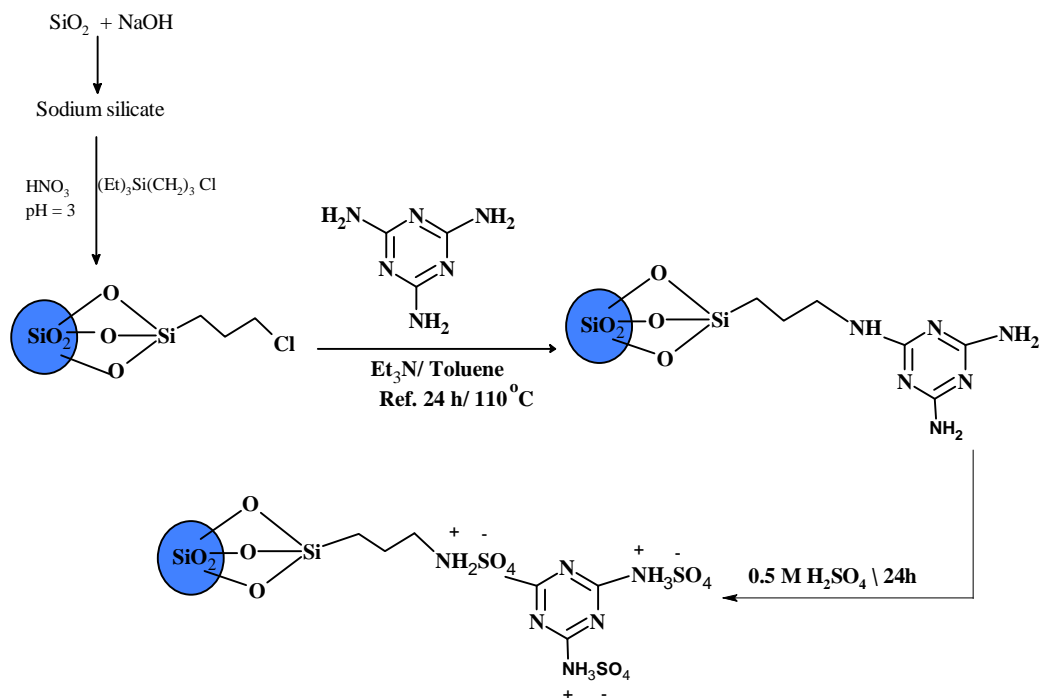
## 3. Results and Discussion

Si-Mela nano solid has been prepared *via* a heterogeneous reaction as in the method described in literature [2]. The reflux was carried out in dry toluene. The amine groups in Si-Mela were sulfonated by simply stirring with dilute sulfuric acid at room temperature to form the melamine sulfate solid catalyst Si-MelaSO<sub>4</sub>H (Scheme 1).

### 3.1. Elemental Analysis

The elemental analysis results of RHA, RHACCl and Si-Mela were reported by our previous study [1]. Both elemental analysis and EDX were used for monitoring the type and percentage of the catalyst. Table 1 shows the elemental analysis of Si-Mela and Si-MelaSO<sub>4</sub>H beside RHA, RHACCl. The percentage of C and H was 13.17 and 1.90 % for Si-Mela while the Si-MelaSO<sub>4</sub>H had 22.87 and 4.09 % of C and H. According to the EDX results the carbon content in Si-MelaSO<sub>4</sub>H was not increased; it clearly decreased from 35.15 % in Si-Mela to 26.82 % in Si-MelaSO<sub>4</sub>H. The decreases in the values of carbon in Si-MelaSO<sub>4</sub>H were due to the presence of new elements, mainly S and O<sub>2</sub>, due to using sulfuric acid.

Both elemental and EDX analysis confirm the presence of nitrogen in Si-Mela and Si-MelaSO<sub>4</sub>H. The percentage of N in EDX was 30.75 % in Si-Mela, and 25.21 % N in Si-MelaSO<sub>4</sub>H, which confirms that the melamine was incorporated successfully in silica. 2.07 % of sulfur was observed in the elemental analysis of Si-MelaSO<sub>4</sub>H, which confirms that the amine groups were sulfated successfully.



**Scheme 1.** The reaction sequence and the possible structures for Si-Mela and Si-MelaSO<sub>4</sub>H. The approximate times taken for the completion of the experimental processes are also shown

Table 1

**Elemental analysis for RHA, RHACCl, Si-Mela and Si-MelaSO<sub>4</sub>H**

Sample	Elemental analysis, %				
	C	H	N	S	Si
RHA [1]	0.84 (6.76)	1.6 –	– –	– –	– (29.09)
RHACCl [3]	11.70 (23.93)	1.98 –	– –	– –	– (23.47)
Si-Mela [1]	13.17 (35.15)	1.88 (6.27)	1.57 (30.75)	– –	– (10.27)
Si-MelaSO <sub>4</sub> H	22.87 (26.82)	4.09 (5.14)	25.76 (25.21)	2.70 (2.9)	– (16.85)

Note: The EDX data in brackets

### 3.2. Thermogravimetric Analysis (TGA)/Differential Thermal Analysis (DTA)

The TGA/DTA of RHACCl and Si-Mela were discussed in our previous study [1, 3]. The TGA/DTA curve of Si-MelaSO<sub>4</sub>H is shown in Fig. 1. About 10.337 mg of Si-MelaSO<sub>4</sub>H was used for the analysis. The TGA/DTA of Si-MelaSO<sub>4</sub>H showed three characteristic decomposition stages. The first mass loss was started from 383 K to 523 K, with the maximum at 383 K which is assigned to water loss (ca. 3.8 %). The second mass loss (ca. 41.3 %) occurred between 575–617 K, with the

maximum at 573 K assigned to the decomposition of *N*-propylmelamine sulfate anchored on the silica. The third continuous mass loss (ca. 24.6 %) occurred between 617–656 K, with the maximum at 623 K and was attributed to the decomposition of the remaining *N*-propylmelamine sulfate. It was also noted that the Si-MelaSO<sub>4</sub>H had high stability reaching 575 K without decomposition.

### 3.3. Fourier Transformed Infrared Spectroscopy Analysis

The FT-IR spectrum in Fig. 2 shows the Si-MelaSO<sub>4</sub>H, while the spectra of RHACCl and Si-Mela were adapted from the literature [1]. The broad band in

the range of  $3520\text{--}3100\text{ cm}^{-1}$  of RHACCl corresponds to the Si-OH groups. The Si-Mela spectra show bands at  $3380\text{--}3150\text{ cm}^{-1}$  corresponding to the free  $\text{NH}_2$  and a weak band at  $2890\text{ cm}^{-1}$  corresponding to the aliphatic C-H stretching of propyl chain. These bands have been changed in the spectrum of Si-Mela $\text{SO}_4\text{H}$ . The Si-Mela $\text{SO}_4\text{H}$  showed band at  $3150\text{ cm}^{-1}$  corresponding to the N-H group. This indicates the successful transformation of  $-\text{NH}_2$  to  $-\text{NH}_3$  group. However, it was also observed that the disappearance of the strong band at

$1378\text{ cm}^{-1}$  (for nitrate ion) may be due to removal of this ion by using aqueous solution of sulfuric acid. This fact was confirmed by appearance of bands at  $1313\text{--}1140\text{ cm}^{-1}$  assigned to the presence of the  $\text{SO}_2$  group, which is the main component of  $\text{SO}_4\text{H}$  group. The band at  $1100\text{ cm}^{-1}$  was related to Si-O-Si, which had clearly seen shifted in all spectra of RHACCl, Si-Mela and Si-Mela $\text{SO}_4\text{H}$ . The presence of this band (Si-O-Si) in FT-IR spectra with the changes of the shape and position of this band indicates that the silica was incorporated with the organic moieties.

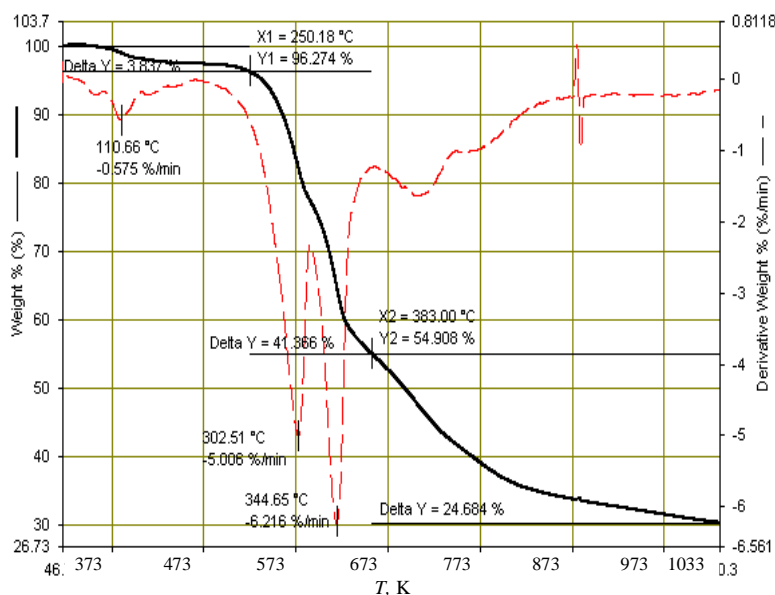


Fig. 1. TGA/DTA data for Si-Mela $\text{SO}_4\text{H}$

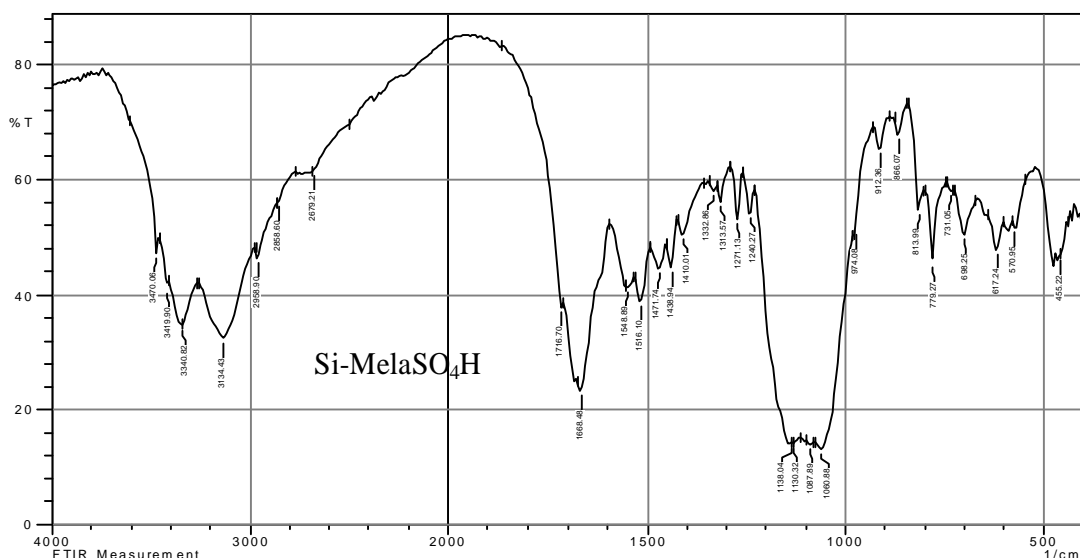


Fig. 2. The FT-IR spectra of Si-Mela $\text{SO}_4\text{H}$

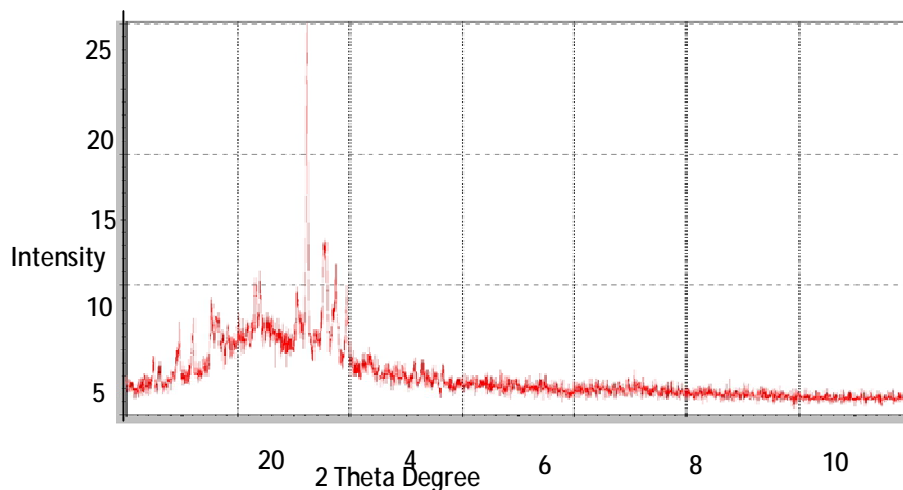


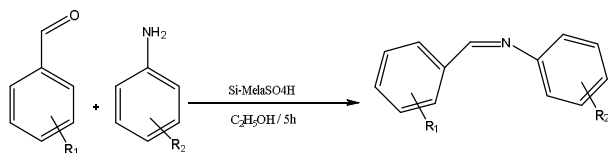
Fig. 3. The X-ray diffraction pattern of Si-MelaSO<sub>4</sub>H

### 3.4. Powder X-Ray Pattern Diffraction (XRD)

The XRD pattern of Si-MelaSO<sub>4</sub>H is shown in Fig. 3. There are two phases clearly seen in the XRD pattern. The broad band at ca. 22° indicated the amorphous nature of surface. The sharp pattern observed in different region indicates that the catalyst has some crystallinity surface. The crystallinity surface could be due to the high content of organic moiety in the sample as shown by elemental analysis and TGA.

### 3.5. Catalytic Study of Si-MelaSO<sub>4</sub>H

One of the aims of the present study is to evaluate the catalytic activity of the heterogeneous catalysts Si-MelaSO<sub>4</sub>H towards the formation of amine bond (C=N-) (Schiff base) by the reaction of different aldehydes with different amines (Scheme 2). Further, various reaction parameters such as effect of the reaction time, the reaction temperature, the solvents type, and the amount of catalyst on the formation of Schiff base were evaluated to optimize the reaction conditions. The usability of the catalyst and the catalyst mechanism were investigated too. The product and rate constants were also calculated as discussed in the sections below.



Scheme 2. The Schiff bases reaction on the surface of Si-MelaSO<sub>4</sub>H.

R<sub>1</sub> = H, R<sub>2</sub> = H; R<sub>1</sub> = *p*-N(CH<sub>3</sub>)<sub>2</sub>,  
R<sub>2</sub> = *p*-Cl; R<sub>1</sub> = *p*-N(CH<sub>3</sub>)<sub>2</sub>, R<sub>2</sub> = 2,5-dimethyl

#### 3.5.1. Influence of reaction time

The effect of the reaction time on the preparation of Schiff base on the surface of Si-MelaSO<sub>4</sub>H is shown in Table 1. The reaction was carried out with 0.1 g of catalyst, at 343 K. The initial product of Schiff base during 1 h was 26 % and then it increased in 9 h to 82 %. However, no change in Schiff base yield was observed with the increase of reaction time for more than 9 h. Therefore, the optimum reaction time of the Schiff base formation was 9 h. The activity of Si-MelaSO<sub>4</sub>H was due to the presence of ammonium sulphate groups as active sites which may play a vital role during the reaction.

#### 3.2.2. Influence of catalyst mass

The formation of Schiff base was carried out by varying the amount of Si-MelaSO<sub>4</sub>H (0.1–0.25 g) while keeping the other parameter fixed (reaction time 9 h and the temperature 343 K). The results are shown in Table 2. When the catalyst mass of Si-MelaSO<sub>4</sub>H increases from 0.1 to 0.25 g, the percentage of Schiff base also increases from 82 to 95 %. Further increase in the catalyst mass has no significant effect. The increased conversion with the catalyst mass could be attributed to the availability of a greater number of catalytically active sites. Therefore, 0.25 g was chosen as the optimum mass of the catalyst.

#### 3.2.3. Influence of temperature

The effect of the reaction temperature on the formation of Schiff base is shown in Table 2. The yield of Schiff base increased from 50 to 94 % when the temperature increased from 313 to 343 K. The temperature increase could lead to the increase of collision between the reactants over the heterogeneous catalyst, which may lead to the increase in product yield

of the Schiff base. No further increase in temperature was studied as it would be above the boiling point of alcohol.

### 3.2.4. Influence of solvent

The effect of the solvents that were used as a medium on the formation of Schiff base is shown in Table 2. Reaction of benzaldehyde with aniline was studied over Si-MelaSO<sub>4</sub>H under optimum conditions. The different solvents (ethanol, propanol, and butanol) were used. It was observed that the increase in the molecular weight of the solvent could reduce the yield of the product in the following order:



### 3.2.5. Catalyst recycling experiments

The catalytic reusability was tested after the catalyst was regenerated. Table 2 shows the reusability of

the Si-MelaSO<sub>4</sub>H. As the TGA shows that the catalyst is stable at the temperatures below 575 K and Schiff base reaction proceeds at 343 K, therefore the recycle experiment could prove these facts due to the activity of the catalyst over the reaction course. It was observed that there is no change of the catalytic activity after the course of the reaction. This indicates that the catalyst was very stable during the reaction.

### 3.2.6. Reaction of different aldehyde and aniline using Si-MelaSO<sub>4</sub>H

The activity of Si-MelaSO<sub>4</sub>H with respect to aldehydes and aniline derivatives was studied and the results are given in Table 2 and Scheme 1. It was shown that the catalyst was active and suitable to be used for the synthesis of Schiff bases derivatives with very good yield. All the tested reactants yielded Schiff bases derivatives with greater than 90 % yield.

Table 2

The effect of different parameters on the Schiff bases yield

Parameters	Variants	Schiff bases yield, %
Catalyst time, h	2	28
	4	30
	6	50
	8	70
	9	82
	10	83
Catalyst mass, g	0.1	82
	0.15	93
	0.2	94
	0.25	95
Solvent	Ethanol	94
	1-Propanol	87
	1-Butanol	82
Reaction temperature, K	313	55
	333	98
	334	99
Amine and aldehyde derivatives	Benzaldehyde + aniline	94
	4-(Dimethylamino)benzaldehyde + <i>p</i> -chloroaniline	89
	4-(Dimethylamino)benzaldehyde + 2,5-dimethylaniline	92
Catalytic cycle	Fresh	95
	Run 1	94
	Run 2	93

## 4. Conclusions

In this study, melamine was successfully immobilized with silica *via* RHACCl to form a catalyst labelled as Si-Mela. The Si-Mela was successfully sulfated to be a solid ammonium sulfate like structure. The free primary amine groups in the melamine were the starting point of the reaction with RHACCl *via* the replacement of chloride end groups onto silica part by

primary amine groups onto melamine side. Then other amine groups were sulfonated by simple reaction with diluted sulfuric acid. The elemental analysis of the catalyst shows that all hydrocarbon elements were found beside the presence of silica. After the sulfonation process the SO<sub>2</sub> functional groups were clearly shown in the FT-IR of the catalyst. The catalyst was stable to 473 K as confirmed by TGA/DTA. This reusable catalyst as proved in the recycle experiment was used successfully in the formation

of imines bonds (Schiff bases). Using of this catalyst for 9 h is enough to give 95 % yield of Schiff bases.

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## ТВЕРДИЙ СУЛЬФАТ МЕЛАМІНУ ДЛЯ СИНТЕЗУ ОСНОВ ШИФФА

**Анотація.** Одержано за кімнатної температури сульфат меламіну (*Si-MelaSO<sub>4</sub>H*) за реакцією меламіну, іммобілізованого на кремнеземі (*Si-Mela*) з 0,05 М сульфатною кислотою. За допомогою ТГА підтверджено, що термостабільність каталізатора може сягати 473 К. Наявність на рентгенограммі гострих піків або широких смуг свідчить про те, що поверхня є сумішшю кристалічної та некристалічної природи. Показано, що *Si-MelaSO<sub>4</sub>H* можна використовувати для синтезу основ Шиффа та його похідних. Встановлено оптимальні умови використання *Si-MelaSO<sub>4</sub>H*: маса каталізатора 0,25 г за 343 К протягом 9 год. Показано, що каталізатор можна повторно використовувати декілька разів без втрати каталітичної активності.

**Ключові слова:** основа Шиффа, зола рисового лушпиння, меламін, кремнезем.