

# Sonochemical Synthesis of Silica and Silica Sulfuric Acid Nanoparticles from Rice Husk Ash: A New and Recyclable Catalyst for the Acetylation of Alcohols and Phenols Under Heterogeneous Conditions

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**Abstract:** Silica nanoparticles were synthesized from rice husk ash at room temperature by sonochemical method. The feeding rate of precipitating agent and time of sonication were investigated. The nanostructure of the synthesized powder was realized by the FE-SEM photomicrograph, FT-IR spectroscopy, XRD and XRF analyses. These analytical observations have revealed that the nano-sized amorphous silica particles are formed and they are spheroidal in shape. The average particle size of the silica powders is found to be around 50 nm. The as-synthesized silica nanoparticles were subsequently modified with chlorosulfonic acid and prepared silica sulfuric acid nanoparticles, which were employed as an efficient catalyst for the acylation of alcohols and phenols with acetic anhydride in excellent yields under solvent-free conditions at room temperature. This reported method is simple, mild, and environmentally viable and catalyst can be simply recovered and reused over 9 times without any significant loss of its catalytic activity.

**Keywords:** Acetylation, rice husk ash, silica sulfuric acid, silica, sonochemical.

## 1. INTRODUCTION

Generally, approximately 600 million tones of rice paddy are produced each year. On average 20% of the rice paddy is husk, giving an annual total production of 120 million tones [1]. In the majority of rice producing countries much of the husk produced from the processing of rice is either burnt or dumped as a waste. The ash is 92 to 95% silica, highly porous and light weight, with a very high external surface area [2]. The silica in the ash undergoes structural transformations depending on the conditions (time, temperature and etc) of combustion. At 550 °C–800 °C amorphous ash is formed and at temperatures greater than this, crystalline ash is obtained [3].

Several methods has been reported for extracted pure silica from rice husk ash (RHA); these method include bubbling fluidized bed [4], high temperature heat treatment [5], chemical pre-and post-treatment with acid and base solutions [6], dry vibratory grinding [7], and alkali-extracted method [8]. Witton *et al.* used rice husk ash as raw material and chitosan as a template to prepare bimodal porous silica [9]. In this paper, we demonstrated that silica nanoparticles could be successfully prepared by a simple sonochemical method from rice husk ash. The sonochemical method, comparing to the other methods which have been used for preparing the silica nanoparticles from RHA, is very fast and it does not need high temperatures during the reactions, using the surfactants is not necessary for this method and the other advantage of using ultrasound radiation is that it yields smaller particles [10].

Silica nanoparticles have attracted intense interest because of their high potential as catalysts or catalytic

supports [11-14]. In this work, we modified the silica nanoparticles with chlorosulfonic acid and prepared silica sulfuric acid nanoparticles. Then this modified silica was employed for the acetylation of alcohols and phenols as heterogeneous catalyst. Acetylation of alcohols and phenols are common transformations in organic chemistry and play an important role in the synthesis of organic molecules such as natural products [15]. Acetylation of alcohols and phenols is usually carried out by using acid anhydrides or acyl chlorides in the presence of various catalysts such as Cu(OTf)<sub>2</sub> [16], I<sub>2</sub> [17], La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O [18], CuSO<sub>4</sub>·5H<sub>2</sub>O [19], cobalt(II) salen [20], phosphomolybdic acid [21], [TMBSA][HSO<sub>4</sub>] ionic liquid [22] and etc. Most of the reported methodologies suffer from various disadvantages, such as highly toxic, use of excess acetylating agent, use of moisture sensitive catalysts and expensive, harsh reaction conditions, poor yields of the desired products and utilization of halogenated volatile organic solvents. Therefore, there is a need to develop a mild, efficient, and environmentally benign acylation reaction.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Rice husk (RH) was collected from a rice mill in Shiraz, Iran. Other materials used in our experiments were of analytical grade and were used as received without further purification. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni filtered Cu K $\alpha$  radiation. FE-SEM images were obtained on HITACHI S-4160. Fourier transform infrared (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. The NMR spectra were recorded on a Bruker avance DPX 250 MHz spectrometer in chloroform (CDCl<sub>3</sub>) using tetramethylsilane (TMS) as an internal reference. All the yields were calculated from isolated products, and GC

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was used to establish their purities. A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 600 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level.

## 2.2. Preparation of Silica Nanoparticles

The rice husk (RH) was washed with water for several time to remove dirt and other contaminants present in it, and dried at 80°C for 12 h. The cleaned pure RH is then burnt inside a muffle furnace and heating at 400°C for 1 hr (labeled as RHA-400) and then held at 700°C for 1 hr (labeled as RHA-700). The white rice husk ash (RHA) obtained was used for silica extraction and preparation of silica nanoparticles.

For extraction of silica from RHA, 5.0 g of the RHA was added to 250 mL of 1.0 M HNO<sub>3</sub> solution and stirred for about 18 h at room temperature to remove the metal oxide (CaO, Fe<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, MnO, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and K<sub>2</sub>O) from RHA and extract the silica. The resulting white powder was filtered and washed three times with ethanol and distilled water. The washed powder was dried at 80°C for 3 h under vacuum and labeled as SiO<sub>2</sub> extracted. For further purification of silica, 5.0 g of the SiO<sub>2</sub> extracted mixed with 2.0 g of the NaOH and heated at 600°C for 1h. The resulting powder dissolved in 50.0 ml distilled water and the solution was filtered and the residue was washed with 20 ml boiling water. The filter solution is sodium silicate. For preparation of silica nanoparticles, While 10 ml of sodium silicate solution (1.0 M) was irradiated with high-intensity ultrasound simultaneously, a solution of HCl (1.0 M) was added dropwise to the Na<sub>2</sub>SiO<sub>3</sub> solution. The resulting white powder was filtered and washed three times with ethanol and distilled water. The washed powder was dried at 80°C for 3 h under vacuum. Dried powder was calcined in air at 750°C for 2 h. The time of sonication and volume of HCl solution were changed for more investigation. The feeding rate for sample no. 1 to 4 is indicated by divided of volume of HCl per time of sonication. For example: the feeding rate of sample no.1 is 4 ml per 10 min or 0.40 (ml/min). Table 1, shows the conditions of reactions in detail.

## 2.3. Preparation of Silica Sulfuric Acid Nanoparticles

To a mixture of silica nanoparticles (2 g) in chloroform (15 mL), chlorosulfonic acid (1.65 mL) was added dropwise

at 0 °C during 2 h. After addition was complete, the mixture was stirred for 2 h until HCl gas evolution was stopped. The resulting white powder was filtered and washed three times with ethanol and distilled water. The washed powder was dried at room temperature to obtain silica sulfuric acid nanoparticles. A flow diagram of the above procedure for synthesis of silica and silica sulfuric acid nanoparticles from rice husk is shown in Fig. (1).

**Table 1. Experimental Condition for the Preparation of Silica Nanoparticles**

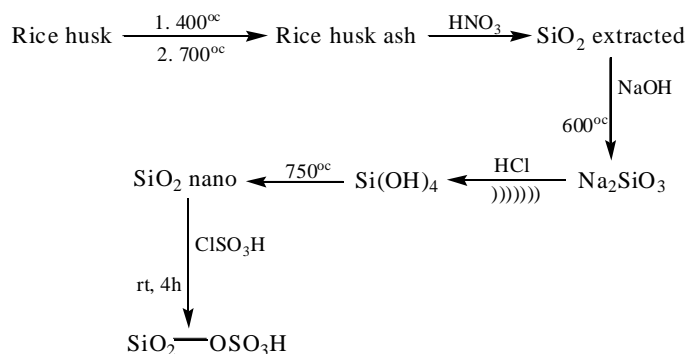
Sample	HCl (ml)	Time of Sonication (min)	Feeding Rate (ml/min)
1	4	10	0.4
2	5	10	0.5
3	7	10	0.7
4	10	10	1.0
5	7	15	0.7
6	7	20	0.7
7	7	30	0.7
8	7	without sonication	0.7

## 2.4. General Procedure for Acetylation of Alcohols and Phenols with Acetic Anhydride

To a mixture of alcohol or phenol (1.00 mmol) and acetic anhydride (1.20 mmol), silica sulfonic acid (0.015 mmol) was added and the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC or GC. When the reaction was complete, 10.0 mL CH<sub>2</sub>Cl<sub>2</sub> was added and the mixture filtered. The recovered catalyst was washed with CH<sub>2</sub>Cl<sub>2</sub> (3×5 mL). The organic layer was washed with 10% solution of saturated NaHCO<sub>3</sub> (2×5 mL) and 10 mL H<sub>2</sub>O and dried over Na<sub>2</sub>SO<sub>4</sub>. If needed, further purification was performed by column chromatography on silica gel afforded the pure acetate.

## 3. RESULTS AND DISCUSSION

Quantitative chemical analyses of RH, RHA-400, RHA-700 and SiO<sub>2</sub>-extracted were accomplished by X-ray fluorescence and shown in Table 2. This analysis showed that inorganic content of rice ash has a high amount of silica (98.30 %) and a few impurities. With increase in temperature



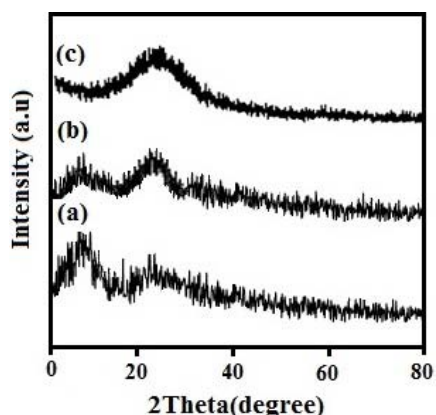
**Fig. (1).** A flow diagram for synthesis of silica and silica sulfuric acid nanoparticles from rice husk.

the relative contents of other elements increased in general. Small divergences of this rule are probably caused by inherent uncertainty of measurements. The percentage of loss on ignition decreased after heat treatment. These results are in agreement with previous reports [23-25] and differences in composition are due to geographical factors, year of harvest, sample preparation and analysis methods.

**Table 2. Chemical Composition of RH, RHA-400, RHA-700 and SiO<sub>2</sub>-Extracted**

Component	RH	RHA-400	RHA-700	SiO <sub>2</sub> Extracted
SiO <sub>2</sub>	64.60	73.30	93.88	98.30
Al <sub>2</sub> O <sub>3</sub>	0.12	0.25	0.34	-
Fe <sub>2</sub> O <sub>3</sub>	0.06	0.10	0.22	-
CaO	0.18	0.32	0.43	-
Na <sub>2</sub> O	0.20	0.47	0.23	-
MgO	0.25	0.60	0.8	-
K <sub>2</sub> O	0.31	0.67	0.85	-
MnO	0.09	0.20	0.22	-
TiO <sub>2</sub>	0.03	0.08	0.04	-
P <sub>2</sub> O <sub>5</sub>	0.01	0.06	0.72	-
Loss of Ignition	-	22.50	2.27	-

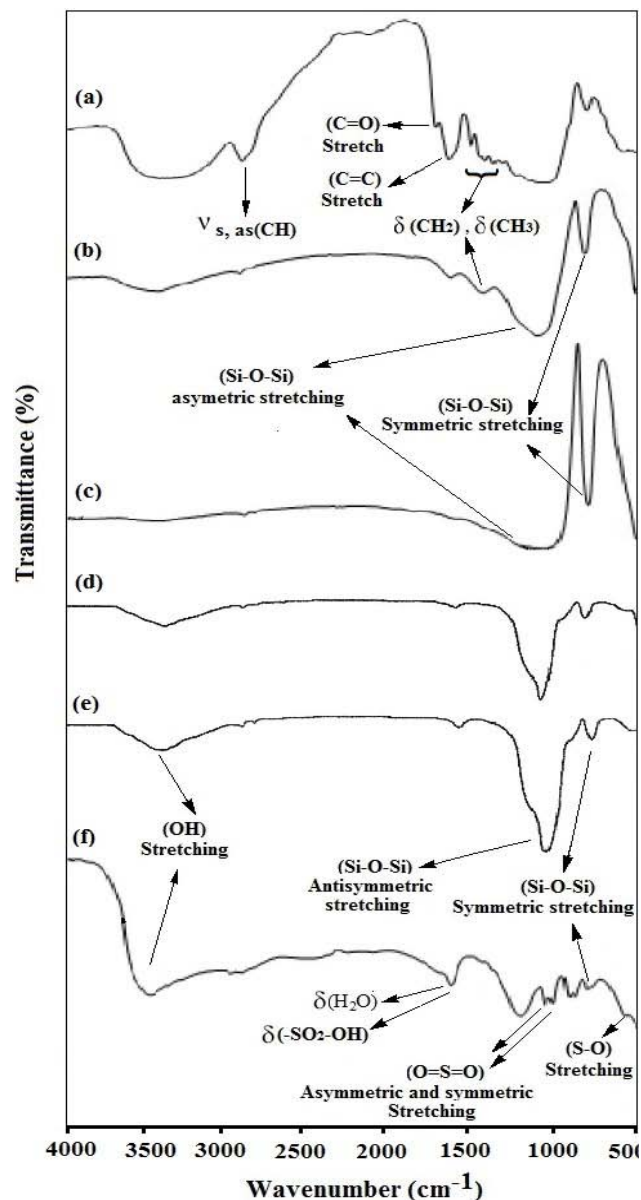
XRD analysis was employed to investigate the crystalline properties of the prepared sample, and results were shown in Fig. (2). The presence of crystalline or amorphous silica, or both, in RHA depends on the burning temperature achieved in the ash production [26]. In Fig. (2a) and b X-ray diffraction patterns of RHA-400 and RHA-700 are shown respectively. With increased in temperature, as remove impurities the content of silica in RHA become major and the strong broad peak of a characteristic of amorphous SiO<sub>2</sub> is explicit. The type of silica phases of the rice husk ash depends on the combustion temperature. Amorphous rice husk ash was formed when the rice husk was burnt below 800°C for 10 hours whereas crystalline rice husk ash of  $\alpha$ -cristobalite and tridymite were formed when the combustion temperature was higher than 800°C



**Fig. (2).** XRD pattern of RHA-400 (a), RHA-700 (b) and silica nanoparticles (c).

[3]. X-ray diffraction pattern of silica nanoparticles is shown in Fig. (2c). It can be seen that broad peaks at  $2\theta = 22.14$  degrees confirming the formation of amorphous silica.

Results obtained from the FT-IR spectroscopy of RH, RHA-400 and RHA-700 are shown in Fig. (3a-c) respectively. As seen in Fig. (3a), RH contains several absorption bands, which have been assigned to individual structural units of carbon compounds. Heat treatment of RH at 400°C and 700°C caused to organic compounds were decomposed and intensity of absorption peaks at 2870-2975 cm<sup>-1</sup> (C-H), 1200-1500 cm<sup>-1</sup> (CH<sub>3</sub> and CH<sub>2</sub>), 1627 cm<sup>-1</sup> (C=C) and 1720 cm<sup>-1</sup> (C=O) was diminished. (Fig. 3d, e)



**Fig. (3).** IR pattern of RH (a), RHA-400 (b), RHA-700 (c) and silica-extracted (d), silica nanoparticles (e) and silica sulfuric acid nanoparticles (f).

are show FT- IR spectroscopy of SiO<sub>2</sub>-extracted and silica nanoparticles. The absorption bands at 3300-3500, (850-900 and 1000-1300) and 900 cm<sup>-1</sup> corresponded to silanol OH

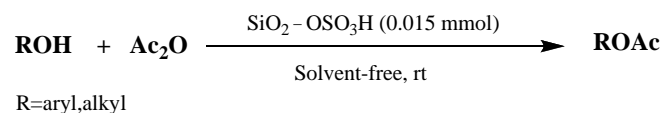
groups, Si–O–Si and Si–OH stretching respectively. For silica sulfuric acid nanoparticles, the absorption peak at 1020 and 1080  $\text{cm}^{-1}$  in Fig. (3f) were attributed the symmetric and asymmetric stretching modes of the O=S=O group respectively. The S–O stretching mode lies around 571  $\text{cm}^{-1}$ . FT-IR spectrum shows the overlap asymmetric and symmetric stretching bands of  $\text{SO}_2$  with Si–O–Si stretching bands in the silica functionalized alkyl-sulfuric acid. The spectrum also shows a broad OH stretching absorption around 3000–3600  $\text{cm}^{-1}$ .

The effect of feeding rate on the morphology and particle size of the products was investigated. FE-SEM images of the formed nanoparticles (Sample no. 1 to 4) are shown in Fig. (4). As shown, with the decrease of feeding rate, the size of nanoparticles became smaller because the rate of nucleation is higher than the rate of growth. On the other hand at the same time, the mechanical influence produced by ultrasonic cavities was increased with prolonging of feeding rate. Thus, it could prevent the nanoparticle growing and aggregating [10]. Sample no. 3 (Fig. 4c) has the smallest particle size and the feeding rate equal with 0.70 ml/min is optimum condition.

For investigating the effect of sonication time on the morphology of the products, the reaction carried out in 10, 15, 20, and 30 min at the feeding rate 0.70 ml/min and FE-SEM images of the resulted nanoparticles (Sample no. 3, 5, 6 and 7) are shown in Fig. (5). In Fig. (5a) FE-SEM image of the sample no. 3 (optimum condition) was shown. With the increase of the sonication time from 10 min. to 20 min., the particle size of the formed nanoparticles become smaller (Fig. 5b) (sample no. 5). Further increase in the sonication time, due to the effect of the mechanical stress which produced by

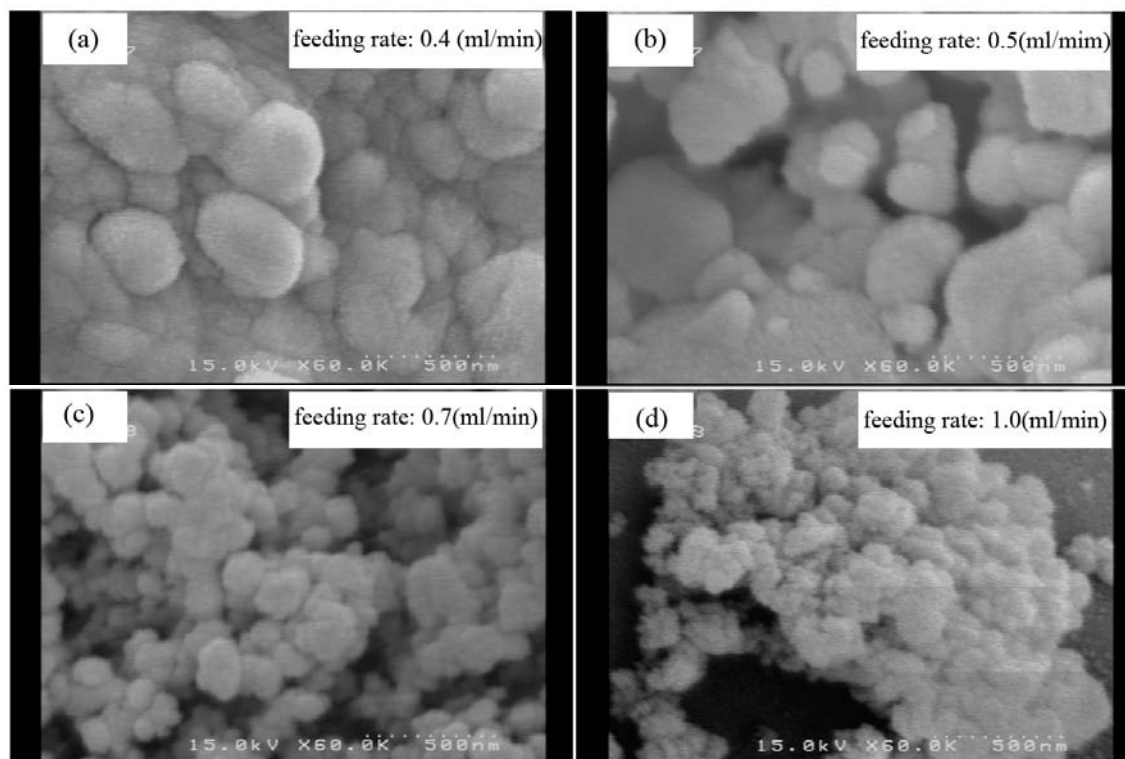
ultrasonic cavities, caused the nanoparticle growing [10]. At the same time, the mechanical influence produced by ultrasonic cavities was increased with prolonging of ultrasonic time. Thus, it could prevent the nanoparticle growing and aggregating. The mechanical influence produced by ultrasonic activate such as emulsification, stir, and others, could prevent the crystal growth and aggregation. But when the ultrasonic time was too long, shock wave with high pressure, micro-emission fluid and “Brown phenomenon” of nano-particle itself could make nano-particles aggregated. For investigating the effect of sonication on the morphology and particle size of the products, the reaction carried out in the absence of sonication (Fig. 5e). In the absence of sonication, when HCl solution was added the milky color of the samples suspension are formed, indicating that the  $\text{Si}(\text{OH})_4$  was formed, but the particle size of obtained product is large and these aggregated.

The application of silica sulfuric acid as a mild heterogeneous catalyst to acetylation of alcohols and phenols with acetic anhydride at room temperature under solvent-free conditions was investigated Scheme (1).

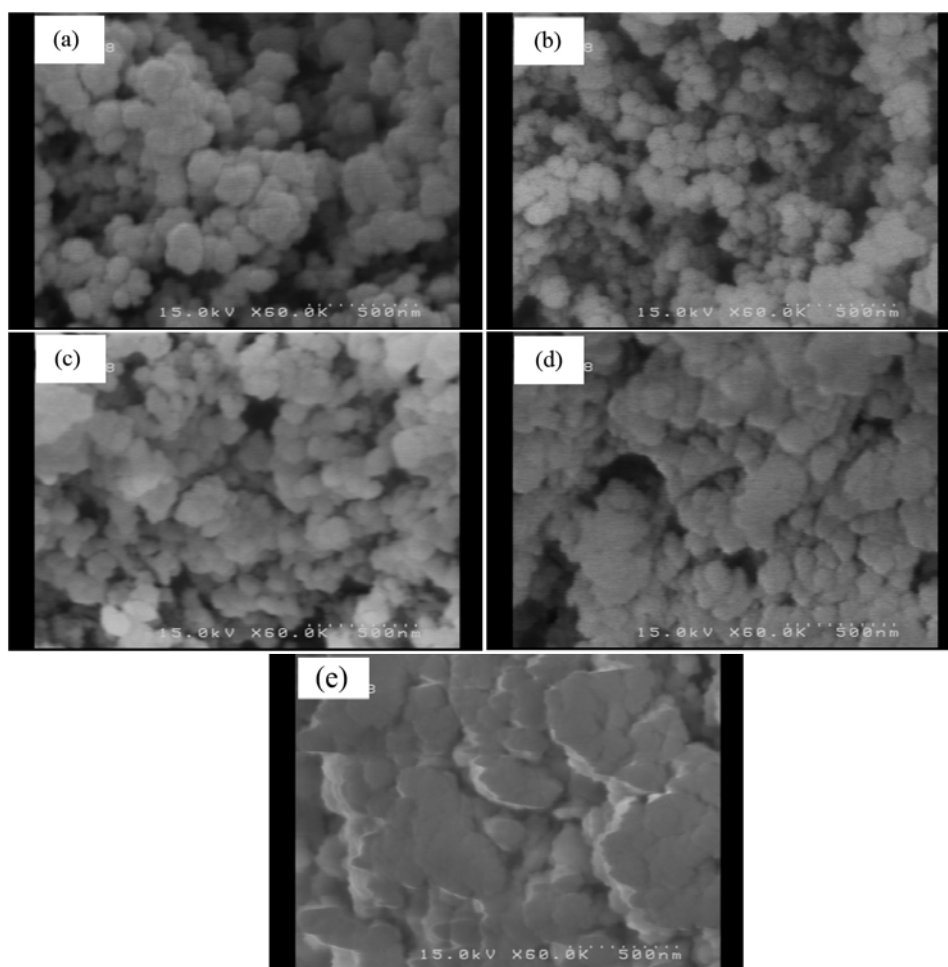


#### Scheme 1.

First, the reaction conditions for acetylation of alcohols and phenols in acetic anhydride were optimized. The acetylation of benzyl alcohol (1.00 mmol) with acetic anhydride (1.20 mmol) in the presence of 0.005, 0.010, 0.015, 0.020, 0.025 and 0.030 mmol of  $\text{SiO}_2\text{-OSO}_3\text{H}$  nano catalyst at room temperature was investigated. When the



**Fig. (4).** The effect of feeding rate on the morphology and particle size of (a) sample no. 1, (b) sample no. 2, (c) sample no. 3, (d) sample no. 4.



**Fig. (5).** The effect of sonication time on the morphology and particle size of (a) sample no. 3, (b) sample no. 5, (c) sample no. 6, (d) sample no. 7 and (e) sample no 8.

catalyst was used in amount of 0.015 mmol, the reactions were completed in shorter time and 97% isolated yield. In the absence of the catalyst, at the same reaction conditions, benzyl acetate was obtained in low yield (4%) even after a prolonged reaction time. When the reaction was carried out under solvent free condition, the best rate of acetylation was observed.

To show the generality and scope of this procedure, a wide range of alcohols and phenols containing various electron-donating and -withdrawing groups were treated with acetic anhydride Table 3. The rate of acetylation is also influenced by the steric and electronic factors associated with substrates (Table 3, entry 20, 3-6, 12-18).

As shown in Table 3, both primary and secondary alcohols reacted very well and 1-phenyl-2-methyl-2-propanol was also acetylated smoothly without any side reactions. The applicability of this method to various alcohols and phenols was evaluated by electron-withdrawing (Table 3, entry 4-6, 13-16) and electron-releasing alcohols and phenols (Table 3, entry 3, 8-10,18) at the same conditions. In all cases, rapid acetylation was observed in excellent yields. Optically active substrates are efficiently acetylated without any detrimental effect on the optical purity (Table 3, entry 19).

It should be noted that the catalyst is reusable for nine cycles without significant loss of its efficacy, as shown in Table 4.

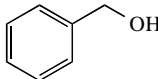
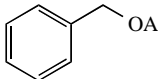
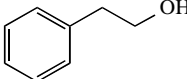
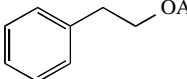
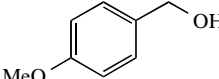
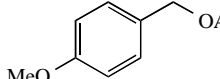
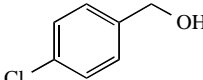
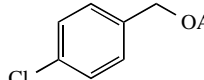
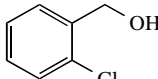
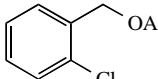
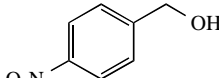
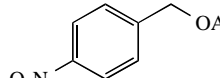
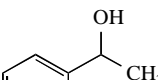
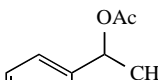
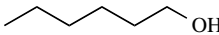
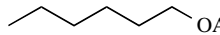
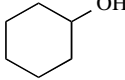
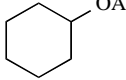


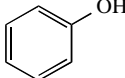
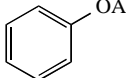
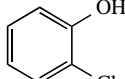
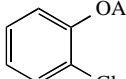
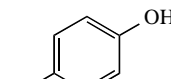
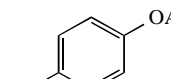
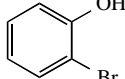
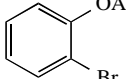
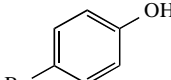
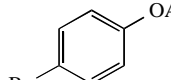
**Table 4. Reuse of the Catalyst for Acetylation of Benzyl Alcohol**

Cycle	0	1	2	3	4	5	6	7	8	9
Yield	97	96	96	94	92	92	87	87	87	87

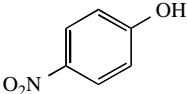
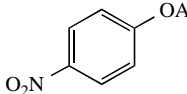
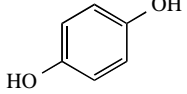
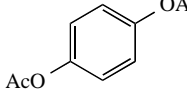
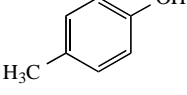
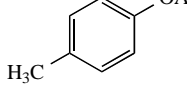
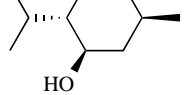
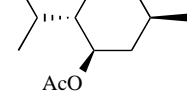
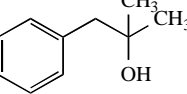
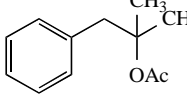
## CONCLUSION

A novel method for the synthesis of silica nanoparticles from rice husk ash by sonochemical method was developed. The effect of some parameters such as, feeding rate of percipitating agent and time of sonication on the size and morphology of the obtained products were investigated by FE-SEM. The silica nanoparticle had a uniform spherical structure with a diameter of 45–55 nm. The as-synthesized silica nanoparticles were subsequently modified with chlorosulfonic acid and prepared silica sulfuric acid nanoparticles, were employed as an efficient catalyst for the acylation of alcohols and phenols. We described for the first

**Table 3. Acetylation of Alcohols and Phenols Catalyzed by Silica Sulfuric Acid<sup>a</sup>**

Entry	Substrates	Products	Time(min)	Yield <sup>b</sup> (%)
1			5	97
2			5	97
3			5	96
4			8	95
5			10	94
6			10	93
7			7	96
8			6	95
9			8	95
10			7	94
11			10	95
12			15	93
13			15	94
14			10	93
15			10	95

(Table 3) contd.....

Entry	Substrates	Products	Time(min)	Yield <sup>b</sup> (%)
16			15	91
17 <sup>c</sup>			10	95
18			10	95
19			15	93
20			30	92

<sup>a</sup> Reaction conditions: Alcohol or Phenol (1.0 mmol); Catalyst (0.015 mmol); Ac<sub>2</sub>O (1.2 mmol); Solvent free; rt.

<sup>b</sup> Isolated yields.

<sup>c</sup> Ac<sub>2</sub>O (2.4 mmol); Catalyst (0.03 mmol); Solvent free; rt.

time a simple, clean, and efficient method for the acetylation of alcohols and phenols under solvent free condition. The features of this procedure are reusable catalyst, excellent yields, and enhanced reaction rates, a very small amount of acetic anhydride usage, retention of chirality and simplicity of manipulation.

## CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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