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## Research article

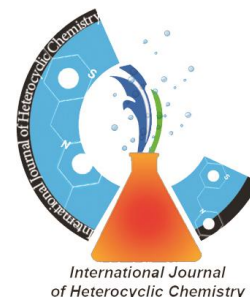
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## **nanosilica extracted from rice husk in Polyhydroquinillion Synthesis**

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### **Abstract:**

Phosphosulfonic acid as a multi solid site was easily prepared from the reaction of ammonium dihydrogen phosphate with chlorosulfonic acid in  $CCl_4$  and for improved its catalytic activity was supported nano Silica was extracted from husk rice contains about 95% of Silica the size of extracted nano silica was determined by SEM efficiency of this solid acid in four component condensation reaction of aromatic aldehydes, dimidone, diketone, an ammonium acetate was investigated the results were clearly shown that aldehydes having electron withdrawing and electron donating groups were efficiently converted to the corresponding Polyhydroquinillion the high yields and short time products were produced at 110 °C under solvent free conditions.

**Keywords:** Nanosilica, Phosphosulfonic, Polyhydroquinolin, Hantzsh condensation

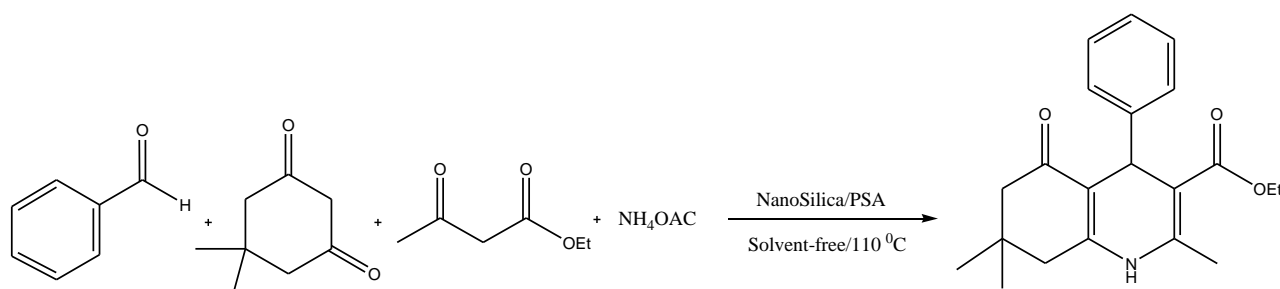
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### **Introduction**

Rice husk (RH) are the natural sheaths that form on rice grains during their growth and removed as waste during the processing of rice in the mills. This husk has no commercial value, and normally, it will end up being burned openly which eventually will cause environmental pollution. Rice husk is composed of about 20% ash and the rest are organic components [1] The Silica,  $SiO_2$  content of ash is more than 94% . Sodium

silicate, the precursor for silica production is currently manufactured by smelting quartz sand With sodium carbonate at 1300 °C. The amorphous nature of rice husk ash (RHA) silica makes it extractable at lower temperature, and hence provides a low energy method as an alternative to the current high energy method used to obtain silica.[2]

1,4-dihydropyridines (1,4- In recent years, much attention has been devoted to the synthesis of polyhydroquinoline compounds due to their diverse therapeutic and pharmacological properties, such as vasodilator, antitumor, bronchodilator, anti artherosclerotic, geroprotective and hepatoprotective activity [3] and [4]. Particularly, 4-substituted DHPs) are well known as Ca<sup>2+</sup> channel blockers and have emerged as one of the most important class of drugs for the treatment of cardiovascular diseases. Despite their importance from a pharmacological, industrial and synthetic point of view, comparatively very few methods for their preparation have been reported. Generally, 1,4-DHPs are synthesized by the Hantzsch condensation method, which involves cyclocondensation of aldehyde, β-ketoester and ammonia either in acetic acid at room temperature or refluxing in alcohol for a long time [5]. However, this method involves long reaction times, harsh reaction conditions and generally gives low yields of the products. Recently much effort has been expended to develop more efficient methods for the preparation of polyhydroquinoline derivatives such as using solar thermal energy [6], ionic liquid [5], TMSCl–NaI[6], montmorillonite K-10 [7], HClO<sub>4</sub>–SiO<sub>2</sub>[8], molecular iodine [9], PTSA [10], L-proline and derivatives [11], nickel nano particle [12], Palladium(0) nanoparticle [13], Mn(III) complex[14], PPA-SiO<sub>2</sub>[15], Proticpyridinium ionic liquid [16], Recently, solid-supported reagents, such as silica gel-supported acids, have gained considerable interest in organic synthesis because of their unique properties of the reagents such as high efficiency due to more surface area, more stability and reusability, low toxicity, greater selectivity and ease of handling . For these reasons, in the present study, nanosilica-supported phosphosulfonicacid (PSA-nanoSiO<sub>2</sub>) was introduced as a heterogeneous and reusable catalyst for synthesis of the polyhydroquinoline derivatives by one-pot four-component Hantzsch condensation reaction of aryl aldehydes, dimedone, ethyl acetoacetate and ammonium acetate .



**Scheme 1:** Synthesis of polyhydroquinoline

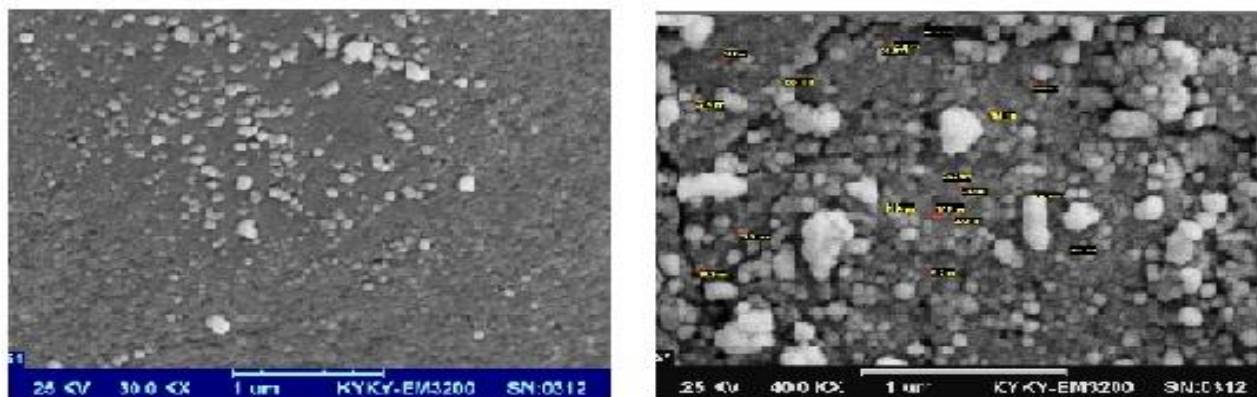
## Extraction and modification of silica from RHA

### Washing and treatment of RH

The rice husk (RH) was washed with water and rinsed with distilled water, and dried at room temperature for 24h. It was thoroughly washed with distilled water until the pH of the rinse became constant. The wet RH was subsequently dried in an oven at 100 °C for 24h. The acid-leached RH was burned in a furnace at 800 °C for complete combustion. The white rice husk ash (RHA) obtained was used for silica extraction and modification.

### Preparation of silica

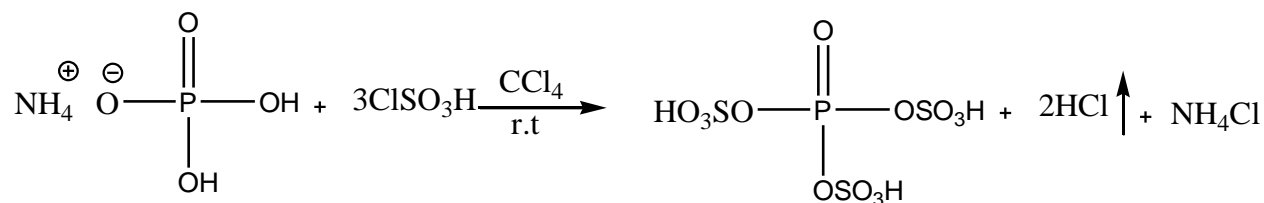
5.0g of the RHA sample was added to 250mL of 1.0 M NaOH in a plastic container and stirred for about 18 h at room temperature to extract the silica as sodium silicate. The solution was filtered through Whatman No. The extracted sodium silicate was titrated with 3.0M HNO<sub>3</sub>. The acid solution was added at a slow rate of ca. 1.0mL min<sup>-1</sup> with constant stirring. Silica gel started to precipitate when the pH decreased to less than 10. The titration was continued until the solution pH reached 5.0. The silica gel/precipitate was filtered, washed thoroughly with distilled water and dried at 100 °C for 18h. The silica xerogel was ground to powder and washed again with distilled water several times then filtered and dried at 100 °C for 18h. This extra washing enabled the nitrate ions present to be washed off completely. The silica obtained was labeled as RHA-SiO<sub>2</sub> (1M). Scheme 1 shows the SEM images of RHA-SiO<sub>2</sub> (1M)



**Scheme 1:** The SEM Micrographs of RHA-SiO<sub>2</sub>(1M)

### Preparation of the catalyst

The phospho sulfonic acid has not been exploited so much to carry out organic reactions unlike other heterogeneous catalysts. This is a mild, worthwhile heterogeneous catalyst, and the catalyst was recovered, activated, and reused for two consecutive times with only slight variation in the yields of the products. Phospho sulfonic acid was easily prepared by simple mixing of ammonium dihydrogen phosphate and chlorosulfonic acid in CCl<sub>4</sub> at room temperature (Scheme 2).



**Scheme 2:** Preparation of the Phosphosulfonic acid

### Optimum conditions for the condensation reaction

In order to carry out the synthesis of polyhydroquinoline under environmentally benign conditions, Initially, the synthesis of Ethyl-1,4,6,8-tetrahydro-2,7,7-trimethyl -4-(phenyl)-5(6H)-oxoquinolin-3- carboxylate was selected as a model reaction to optimize the reaction conditions. The reaction was carried out by heating a mixture of benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol) and ammonium acetate (1.5 mmol) in the presence of various amount of nano silica/PSA at different temperatures under solvent free conditions. As can be seen from Table 1, the shortest time and best yield were achieved in the presence of 0.02 gr of catalyst at 110°C .

**TABLE 2:**SYNTHESIS OF POLYHYDROQUINOLINE BY CONDENSATION OF ALDEHYDES, 1,3-DIKETONE, ETHYL ACETOACETATE AND AMMONIUM ACETATE USING PSA (0.02 GR) AS CATALYST UNDER SOLVENT FREE CONDITIONS

ENTRY	R	PRODUCT	TIME (MIN)	YEILD (%)	M.P. (°C)	M.P. (°C)
1	C <sub>6</sub> H <sub>5</sub>	2A	15	75	204-205	202-204[20]
2	4-CL C <sub>6</sub> H <sub>4</sub>	2B	15	84	244-245	244-246[20]
3	4-OH C <sub>6</sub> H <sub>4</sub>	2C	10	89	237-239	230-232[20]
4	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2D	10	80	258-261	260-263[20]
5	4-OMEC <sub>6</sub> H <sub>4</sub>	2F	20	87	251-256	255-258[21]
6	3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2G	15	91	179-181	176-178[20]
7	3-BRC <sub>6</sub> H <sub>4</sub>	2H	10	66	183-189	-
8	2,4CLC <sub>6</sub> H <sub>3</sub>	2I	10	73	235-237	241-243[22]
9	4-BR C <sub>6</sub> H <sub>4</sub>	2	15	78	251-253	252-254[20]
10	4-CNC <sub>6</sub> H <sub>4</sub>	2	8	95	139-141	140-142[21]
11	2,4OCH <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	2	10	74	197-201	198-199
12	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	2	5	96	238-242	244-246[20]

## Experimental

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka Chemical Companies. All yields refer to isolated products. The products were characterized by comparing of their physical data with those of known samples or by their spectral data. IR spectra were recorded on a4300 Shimadzu spectrophotometer as KBr disks. Melting points were recorded on an electrothermal type 9100 melting point apparatus.  $^1\text{H}$  NMR spectra were recorded on a Bruker DRX500 300-MHz spectrometer in  $\text{CDCl}_3$  as the solvent relative to TMS.

Preparation of phospho sulfonic acid Suspension was prepared by the mixture of (6.6 g, 15 mmol) diammonium hydrogen phosphate and 20 mL dried  $\text{CCl}_4$ . (10mL, 3 mmol) chlorosulfonic acid solved in 30 ML  $\text{CH}_2\text{Cl}_2$  was added dropwise the produced mixture by means of the dropping funnel over a period of 30 min at room temperatur. Durig the whole process of addition, the reaction is under the  $\text{N}_2$  gas. After completion of the addition, the mixture was shaken for 1.30 h, while the residual HCl was eliminated by suction. Then the mixture was washed with excess dried  $\text{CCl}_4$ .

### General procedure to synthesis of polyhydroquinoline derivatives using PSA-nanoSiO<sub>2</sub> as catalystA

mixture of ethyl acetoacetate (1 mmol), aromatic aldehyde (1 mmol), dimedone (1 mmol), ammonium acetate (1 mmol) and PSA-nanoSiO<sub>2</sub> (0.02 g) was heated on the oil bath at 110 °C for 5–15 min. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature and hot ethanol was added. The solid residue was dissolved in hot ethanol and the reaction mixture was washed with ice cold filtered off and recrystallized from ethanol and water. followed by water and brine solution and dried with  $\text{Na}_2\text{CO}_3$  to give compounds in high yields. All of the polyhydroquinoline . The reactions of various aldehydes possessing either electron donating or electron withdrawing substituents with ethyl acetoacetate and ammonium acetate in the presence of a catalytic amount (0.02 gr) of Phospho sulfonic acid supported on nanosilica afforded high yields of the corresponding polyhydroquinoline (87–95%) in short times. The results are presented in Table 2.

2,7,7-Trimethyl-5-oxo-4-(2,4methylphenyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylic acid ethyl ester (compound 2b):

IR (KBr): 3290, 3220, 3082 , 1699, 1643, 1280, 1213,  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300MHz),  $\delta$  = 0.9 (s, 3H,  $\text{CH}_3$ ), 1.02 (s, 3H,  $\text{CH}_3$ ), 1.19 (t,  $J$  = 6.9 Hz, 3H,  $\text{CH}_3$ ), 2.04–2.18 (m, 4H, 2 $\text{CH}_2$ ), 2.25 (s, 3H,  $\text{CH}_3$ ), 3.73 (s, 3H,  $\text{OCH}_3$ ), 3.75 (s, 3H,  $\text{OCH}_3$ ), 4.01 (q,  $J$  = 6.9 Hz, 2H,  $\text{OCH}_2$ ), 5.16 (s, 1H, CH), 6.89 (s, 1H, NH), 6.32-6.35 (m, 2H, ArH), 7.17-7.20 (1H,  $m$ , ArH)

## Conclusion

In Conclusion, we have reported an efficient procedure for the synthesis of polyhydroquinoline derivatives using PSA/nanosilica as heterogeneous catalyst, reaction, high yields of products, short reaction times and use of various substrates, which makes it a useful and attractive strategy for the synthesis of polyhydroquinoline derivatives.

## Acknowledgment

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