Nano Silica with High Surface Area from Rice Husk as a Support for 12-Tungstophosphoric Acid: An Efficient Nano Catalyst in Some Organic Reactions

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Abstract: Nano silica was prepared from rice husk with high surface area. X-ray diffraction (XRD) pattern showed that the amorphous form of silica was produced. Chemical composition of the nano silica was estimated by X-ray fluorescence spectroscopy and CHN analysis. The nano silica was used as a support for $H_3PW_{12}O_{40}$. The nano silica and nano silica supported $H_3PW_{12}O_{40}$ were characterized by inductively coupled plasma, XRD, transmission electron microscopy (TEM), N_2 adsorption-desorption, and Fourier transform infrared spectroscopy. TEM images of nano silica as well as the supported catalyst displayed average size of 6 and 7 nm, respectively. The catalyst showed excellent activity in some important organic reactions including Biginelli, Hantzsch, Mannich, and Claisen-Schmidt reactions with good reusability. Catalytic activity of this nano catalyst is an improvement over the commercially available silica that is used to support $H_3PW_{12}O_{40}$.

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Heterogeneous solid acids are preferred over conventional homogeneous because the former can easily be recovered from the reaction mixture, thereby eliminating the need for separation through distillation or extraction. In many cases, they can be reused without significant changes in activity and selectivity [1]. Among them, heteropolyacids (HPAs) with Keggin structure have received the most attention due to their unique structure and stronger acidity [2]. The flexibility in their acid strength, low toxicity, and fairly high thermal stability make them excellent and versatile catalysts for a wide variety of acid catalyzed reactions in homogeneous and heterogeneous media [3,4]. Usually, $H_3PW_{12}O_{40}$ (PW) is preferred over other HPAs because of their stronger acidity, higher thermal stability, and low reducibility [5]. Heterogeneous phase reactions are often preferred and therefore immobilizing HPAs on an insoluble, easily separable, and high surface area solid are desirable [6]. For heterogeneous systems, it is possible to increase the accessibility to the acid sites and control solid acid strength by supporting HPA on different carriers [7]. Furthermore, there are no waste products, which is an added advantage to clean technologies.

Rice husks (RHs) are the natural sheaths that form on rice grains during their growth and are removed as waste during processing the grains. Husks have no commercial value and

are normally combusted openly, thereby causing environmental pollution and disposal problems. Recently, efforts are being put into not only overcoming the pollution issues but also finding value addition to these wastes by using them as secondary resource materials. 15% to 30% of the inorganic constituents in dry husks contain silica and the utilization of RHs as source of silica requires the removal of impurities. Therefore, it is preferable to treat RHs with an acidic solution to remove the impurities. The major constituents of RHs are organic volatiles as found in most biomass materials. Approximately one-fifth of the ash is obtained on burning RHs in programmable furnace at controlled conditions. The rice husk ash (RHA) contains over 90% silica by mass with a small proportion of metallic elements and is considered to be the most economical source of silica. At present, nanoscale silica materials are prepared using several methods, including vapor-phase reaction, sol-gel, and thermal decomposition techniques [8–10]. However, due to their high cost of preparation they have limited wider applications. Because the silicon atoms in the RHs are often naturally uniformly dispersed by molecular units, very fine particle size with high purity and surface area silica powder can easily be prepared under controlled conditions. When RHA is produced by uncontrolled combustion, the ash is generally crystalline and exhibits poor

reactive properties.

Large amounts of silica freely obtained from RHA provide an abundant and cheap alternative source of silica which is useful for many applications particularly as a support for heterogeneous catalysis. Supported PW have been recently introduced to heterogeneous catalytic researches which include esterification, synthesis of imidazole derivatives, and enamines, just to mention a few [11–14]. Among these fine chemical reactions, Biginelli, Claisen-Schmidt, Mannich, and Hantzsch attract much attention since 3,4-dihydropyrimidin-2(1*H*)-ones, named Biginelli compounds, are known to exhibit a wide range of biological activities such as antiviral, antitumor, antibacterial, anti-inflammatory actions, calcium channel blockers, and antihypertensive agents [15–19]. Also, β -amino carbonyl compounds are important intermediates for various pharmaceutical and natural product syntheses including β -amino alcohols, β -amino acids, and lactams [20–22]. Among the various methods for the synthesis of these compounds, Mannich-type reaction constitutes a preferred choice due to its versatility [23]. Hantzsch reaction generates multi functionalized products including 1,4-dihydropyridines, polyhydroquinoline derivatives, and other related heterocyclic compounds [24]. These compounds exhibit various medicinal functions such as neuroprotectant, platelet anti-aggregator activity, chemosensitizer in tumor therapy, and cerebral antiischemic activity in the treatment of Alzheimer's disease [25–27]. Moreover, they serve as key intermediates in biogenesis of indol alkaloids [28]. In addition, chalcones form the central core for a variety of important biological compounds. They show antimalarial [29], anti-inflammatory [30], antileishmanial [31], and anticancer [32] properties. Some chalcones also demonstrate the ability to block the voltage-dependent potassium channels [33]. They are known as important intermediates in the biosynthesis of flavonoids [34] and flavones [35], which are present in the human diet in soy beans and soy derived products [36]. The chalcones have been synthesized via Claisen-Schmidt condensation.

The present work deals with preparation and characterization of nano silica from RHs and using this nano particle as a support for PW. Then, the activity of the catalyst was investigated in some valuable organic reactions. Though researches have been carried out on the preparation, properties, and application of RHA during the last three decades [37–41], to the best of our knowledge, this is the first attempt using this nano silica as support for PW.

1 Experimental

1.1 Preparation of nano silica

RHs (from a rice mill in Northern Iran) were washed thoroughly with water to remove the soluble particles and dust or other contaminants such as heavy impurities. They were then dried in an air oven at about 110 °C for 24 h. The dried RHs were refluxed with an acidic solution (0.1 mol/L HCl) for nearly 90 min with frequent stirring. The solid was cooled and kept intact for about 20 h. Then it was decanted and thoroughly washed with warm distilled water until the rinse became free from acid. The wet solid was subsequently dried in an oven at 110 °C for 24 h. The obtained white powder (hereafter RH') was burned inside a programmable furnace (Model Nobertherm controller B 170) at 700 °C at the rate of 10 °C/min with 2 h soaking time. The obtained powder was designated as RHA.

RHA sample (20 g) was stirred in 160 ml sodium hydroxide solution (2.5 mol/L). The solution was heated in a covered beaker for 3 h with constant stirring. It was filtered and the residue was washed with 40 ml boiling distilled water. The obtained viscous, transparent, and colourless solution was allowed to cool down to room temperature. Then H₂SO₄ (5.0 mol/L) was added under constant stirring at controlled condition until pH = 2 and then NH₄OH was added until pH = 8.5, and allowed to sit at room temperature for 3 h. Nano silica was prepared by refluxing of extracted silica with HCl (6.0 mol/L) for 4 h and then washed repeatedly using deionised water to make it acid free. It was then dissolved in sodium hydroxide (2.5 mol/L) with stirring. H₂SO₄ was added until pH = 8. The precipitate silica was washed repeatedly with warm deionised water to make it alkali free and dried at 50 °C for 48 h in the oven.

1.2 Preparation of nano silica supported PW

For the preparation of 40% PW/N-SiO₂ catalyst defined as 40 wt% loading of PW supported on nano silica, 2.0 g of PW (Aldrich) was dissolved in 40 ml of water and used for impregnating 3.0 g of nano silica. The mixture was stirred overnight at room temperature and sonicated for 2 h. The solvent was removed by using rotary evaporator followed by calcination at 150 °C for 2 h. Similar procedures were used for the preparation of 20 and 60 wt% of PW/N-SiO₂ samples.

1.3 Characterization methods

The silica content and the amount of metallic impurities in the sample were estimated by X-ray fluorescence (XRF) Philips X-ray spectrometer (model PW 2404). CHN composition was measured by Hekatech elemental analysis model Euro EA 3000. Fourier transform infrared spectra (FTIR) were recorded with KBr pellets using a WQF-510 FTIR

Rayleigh. The X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X'Pert (40 kV, 30 mA) X-ray diffractometer. Scans were taken with a 2θ and a counting time of 1.0 s using a Cu K_α radiation source ($\lambda = 0.1542$ nm) and a nickel filter. Surface areas were calculated from the linear part of the BET plot. Low temperature nitrogen adsorption experiments were performed using a Quantachrome instrument (model Nova 2000) for measuring surface area and pore volume. Transmission electron microscopy (TEM) examination was performed with a TEM microscope Philips CM 120 KV Netherland. NMR spectra were recorded on a Bruker Avance 200 MHz NMR spectrometer with CDCl_3 as the solvent and TMS as the internal standard. Tungsten content in the catalyst was measured by inductively coupled plasma (ICP) atomic emission spectroscopy on a Spectro Ciros CCD spectrometer.

The acidity of the samples was measured by the potentiometric titration method. The solid (0.05 g) was preheated and suspended in acetonitrile (90 ml) and stirred for 3 h. The suspension was titrated with a 0.05 mol/L solution of *n*-butylamine in acetonitrile. The potential variation was measured with a Hanna 302 pH meter using a double junction electrode.

1.4 Catalytic reactions

1.4.1 Biginelli reaction

A mixture containing an appropriate acetylacetone (2 mmol), benzaldehyde (2 mmol), urea (3 mmol), and catalyst (0.2 g) were crushed at 80 °C for appropriate time (completion of the reaction was monitored by TLC). The reaction mixture was diluted with acetonitrile then filtered to remove the catalyst for reuse, and the filtrate was poured into crushed ice and stirred for several minutes. The solid product was filtered off, washed with cold water (30 ml $\times$ 2), and recrystallized from ethyl acetate/*n*-hexane to generate the pure product. The wet catalyst was washed with ether, dried, and recycled to check the reusability of the catalyst.

1.4.2 Hantzsch reaction

A mixture of benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), amine (1 mmol), and catalyst (0.2 g) were crushed at ambient temperature. Progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was treated with acetonitrile (5 ml $\times$ 2) and filtered to recover the catalyst. Filtrate was concentrated in vacuum to afford the crude product. The pure product was obtained as a yellow solid by further recrystallization in ethanol. The wet catalyst was washed with ether, dried, and recycled to check the reusability.

1.4.3 Mannich reaction

Typically, 0.04 g catalyst was added to a mixture of benzaldehyde (1 mmol), aniline (1 mmol), cyclohexanone (2 mmol), and H_2O (5 ml). The reaction mixture was vigorously stirred. Progress of the reaction was monitored by TLC. The resulting solid substance was filtered off and diethyl ether was added to dissolve the target product. The filtrate was concentrated at room temperature to generate the crude product. The crude product was purified by column chromatography on silica-gel using ethyl acetate/hexane as eluent.

To exam the reusability of the catalyst, 0.4 g of catalyst was added to a mixture of benzaldehyde (10 mmol), aniline (10 mmol), and cyclohexanone (20 mmol) in water. Then the mixture was stirred. After 30 min, water was removed from the mixture to leave residue. Then, the residue was dissolved in 30 ml diethyl ether to isolate the catalyst via centrifugation. The isolated catalyst was washed with diethyl ether and used for catalyzing the next reaction cycle.

1.4.4 Claisen-Schmidt condensation reaction

A mixture of benzaldehyde (2 mmol) and cyclohexanone (1 mmol) were crushed in the presence of 0.2 g of catalyst at room temperature. Progress of the reaction was followed by TLC. After completion of the reaction, CH_2Cl_2 was added to the mixture and filtered off to recover the catalyst. The solvent of the filtrate was then evaporated and the crude product was crystallized from ethanol. Also, the wet catalyst was washed with ether, dried, and recycled to check the reusability of the catalyst.

The products of all the reactions were identified by comparing their spectral data with those of the authentic samples [42–45].

2 Results and discussion

Metallic ingredients play significant role on the quality of silica from RHs and therefore, it is preferable to treat RHs with an acidic solution. This treatment effectively eliminates impurities to obtain highly pure silica powder. These impurities are decreased mainly because of the chemical reaction between the acid and metals. The reacted metals are leached from the acidic solution during filtration. The change in color during digestion is also remarkable as the original RHs color changes from brown to light yellow on increasing the time of digestion as displayed in Fig. 1(a, b). The metals are also probably carried out from the volatiles during thermal decomposition as burning RH' generates ash. However, if RH' is burnt under controlled conditions, amorphous silica is produced which is highly reactive in nature. Quality of

Fig. 1. Pictures of RH (a), RHA (b), and nano silica (c).

the RHA (such as surface area, pore volume, particle size, percent of amorphous form, etc.) is dependent on various factors such as temperature and time of burning, rate of heating, and soaking time. Treatment with HCl (0.1 mol/L) and combustion at 700 °C at a rate of 10 °C/min and 2 h soaking time in a programmable furnace is suitable for the preparation of highly pure amorphous RHA. This white RHA was used for preparation of nano silica as shown in Fig. 1(c).

The nano silica prepared above was used as support for PW. Of note, PW with Keggin structure is the most studied in the HPAs because it possesses relatively high thermal stability and high intrinsic acidity [7,46]. Since the PW has low specific surface area (1–10 m²/g), it is important to increase the surface area or even better to increase the number of accessible acid sites of the PW. This can be achieved by dispersing the PW on nano silica with high surface area. Surface area enhancement, higher dispersion of acidic protons, heterogenization, and the control of acid strength are some of the strategies used to generate this supported catalyst. According to recommended cases in our previous publications [11–14], we have chosen 40% PW/N-SiO₂ as the best mass percent, and full characterization of this sample has been reported in the following section. However, for comparison purpose, 20% and 60% PW/N-SiO₂ samples have also been prepared and their acidities and catalytic activities have been included in this reported.

2.1 Characterization results

After acid treatment and controlled combustion of RHs, 22.5% of RHA was produced. Percent of silica in the prepared RHA and nano silica are 90.469% and 98.801%, respectively (Table 1). It is interesting to note that only MgO was detected in the nano silica. Other impurities can also be detected below the limit of quantification < 0.01% (or 0.1 mg/g). The color of nano silica was white.

As shown in Fig. 2, the FTIR spectra of nano silica, PW,

Fig. 2. FTIR spectra of bulk PW, 40% PW/N-SiO₂, and nano silica.

and 40% PW/N-SiO₂ generate two peaks at 1101 and 804 cm⁻¹ due to Si–O–Si asymmetric and symmetric stretching modes, respectively. The band centered at 469 cm⁻¹ is due to the bending frequency of Si–O–Si. A large broad band around 3429 cm⁻¹ is attributed to the presence of the O–H stretching frequency for the silanol group and the remaining adsorbed water. A band around 1630 cm⁻¹ is assigned to the bending vibration of water molecules bound to the silica matrix. There is no peak at about 2800–3000 cm⁻¹, which means there are no organic compounds in the silica after combustion. This result corresponds well to the carbon measurement by CHN analysis reported in Table 1. The primary structure of PW can be identified with four characteristic FTIR bands at the 700–1200 cm⁻¹ range. Characteristic bands of the bulk PW appears at 1080 (P–O), 985 (W=O), 890 and 814 cm⁻¹ (W–O–W). In 40% PW/N-SiO₂, the PW band placed at 1080 cm⁻¹ is masked by the Si–O–Si absorption band. Regardless, information can still be obtained from the less affected regions, which shows an increase in intensity of the band placed at 814 cm⁻¹ and non-overlapped bands at 890 and 985 cm⁻¹ that confirm the existence of PW on support in the Keggin structure.

Silica with high surface area is a good compound as an adsorbent or support for catalyst. Also, the activity of silica is directly related to its surface area. BET specific surface area and pore volume of the nano silica and 40% PW/N-SiO₂ are given in Table 2. Nano silica shows a higher surface area than commercial silica (about 90–400 m²/g). A major contribution for this high surface area is that the organic matter has been broken up during the thermal de-

Table 1 Chemical and elemental composition of RHA and nano silica

Sample	Color	Chemical composition (%)								LOI ^b (%)	Elemental composition ^c (%)		
		SiO ₂	Na ₂ O	K ₂ O	MgO	CaO	Fe ₂ O ₃	Al ₂ O ₃	SO ₃		C	H	N
RHA ^a	white	90.469	0.630	trace	0.050	trace	trace	0.097	0.153	8.600	25.313	3.952	0.551
Nano silica	white	98.801	trace	trace	0.020	trace	trace	trace	trace	1.179	0.119	0.113	0.000

^aP, Cl, Ni, Cu, Zn, Pd, W, and Bi are as trace in RHA. ^bLoss-on-ignition. ^cObtained by CHN analyses.

Table 2 Properties of nano silica and 40% PW/N-SiO₂

	$S_{\text{BET}}/(\text{m}^2/\text{g})$	Pore volume (cm^3/g)	Particle size (nm)
Nano silica	623	0.0241	6
40% PW/N-SiO ₂	275	0.0082	7

composition of RH', thus leaving a highly porous structure. The surface area of 40% PW/N-SiO₂ decreases remarkably compared to their parent support, but still shows very high value in comparison with PW/commercial SiO₂ [11]. The reduction in the surface area of supported catalyst may be due to the blockage of smaller pores by active species.

Evaluation of the amount of amorphous silica is very important because the crystalline form exhibits poor reactive properties. For this purpose, there are some specific methods in the literature to estimate the percent of amorphous form [47,48]. One of them establishes that the degree of amorphous form of silica is estimated by the "silica activity index", which is determined by calculating the percentage of valuable silica that is dissolved in an excess of boiling KOH (4 mol/L) in 3 min extraction period [47]. This method has been investigated for nano silica and shows 99.8% of the amorphous form as confirmed by XRD techniques. In Fig. 3 the nano silica presents a broad peak at around $2\theta = 22^\circ$ associated with amorphous silica. The lack of sharp peaks indicates the absence of any ordered crystalline structure, confirming the results from silica activity index and the lack of crystalline phase. Also, there are no peaks from carbon in the XRD pattern. It was previously reported that porous or activated carbon can be produced by heating RHs at relatively lower temperatures [40]. However, acid treatment of the husk removes most of the potassium and the ash becomes free of fixed carbon. This is in accordance with CHN results (Table 1). The size of the particles is estimated by the half width, β , of peak using the Scherrer formula: $D = K\lambda/\beta\cos\theta$, where K is a constant with a value of 0.9 nm, λ is the wavelength of Cu K_α with the value of 0.1542 nm, and β is in radian. By manual evaluation of

Fig. 3. XRD patterns of nano silica, 40% PW/N-SiO₂, and bulk PW.

XRD charts, particle size of nano silica of about 7 nm is found. The XRD pattern of 40% PW/N-SiO₂ shows characteristic peaks of Keggin type PW, thus, PW with undegraded structure is present on the silica (Fig. 3).

Figure 4 shows the TEM images of the nano silica and 40% PW/N-SiO₂. The shape of the silica and PW supported silica grains are spherical with an average particle size of 6 and 7 nm, respectively. This is in agreement with the size estimated by the Scherrer formula for nano silica.

Fig. 4. TEM images of nano silica (a) and 40% PW/N-SiO₂ (b).

Figure 5 shows the size distributions of nano silica and 40% PW/N-SiO₂ derived from results of TEM. It is worth noting that PW content in 40% PW/N-SiO₂ has been measured by ICP and it is 34 wt% of PW to nano silica (this measurement for 20% PW/N-SiO₂ and 60% PW/N-SiO₂ are 14 and 51 wt%, respectively). Typically, the PW content from ICP was slightly lower than expected from the preparation stoichiometry.

Fig. 5. Size distributions of nano silica and 40% PW/N-SiO₂.

The acidity measurement of catalyst by means of potentiometric titration with *n*-butylamine is used to estimate its relative acid strength according to the two values: E_i as initial potential and number of acid sites (Fig. 6). The initial electrode potential E_i indicates the maximum strength of the acid sites and the value from which the plateau is reached indicates the total number of acid sites that are present in the titrated solid [49]. The acidic strength of the solids can be classified according to the following range: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 <$

Fig. 6. Potentiometric titration curves of nano silica, bulk PW, and PW/N-SiO₂.

$E_i < 0$ mV (weak sites), and $E_i < -100$ mV (very weak sites). The PW ion is strongly interacting with the surface hydroxyl groups of silica leading to the formation of $\text{SiH}_2\text{PW}_{12}\text{O}_{40}$ and/or $(\text{SiOH}_2^+)(\text{H}_2\text{PW}_{12}\text{O}_{40}^-)$ species [50]. Therefore, the addition of PW to nano silica surface should decrease the strength of the acid sites of PW molecules. This effect depends on the extent of interaction of PW with the support. According to the potentiometric titration curves (Fig. 6), PW presents very strong acidic sites ($E_i = 650$ mV). 40% PW/N-SiO₂ sample shows acidic sites with essentially the same maximum strength, which may be an indication of low interaction level, and the formation of predominantly

less dispersed intact PW anions on the silica support. Potentiometric titration results of PW/N-SiO₂ samples show the lower E_i values compared to PW and 40% PW/SiO₂ samples. This behavior is related to the textural properties of nano silica, mainly to its surface area. Nano silica has higher surface area and more surface hydroxyl groups compared to commercial silica, increasing the PW-silica interaction and leading to well-dispersed PW phase. This increase leads to a decrease of the acidic strength in PW/N-SiO₂ samples. In 20% PW/N-SiO₂ the lower E_i value may be a consequence of a higher interaction of PW with the surface groups of the supports, which will be more dispersed in the low concentration sample. Addition of PW is accompanied by a gradual increase in both surface acidity and acid strength up to 40% PW/N-SiO₂, and then followed by a decrease at 60% PW/N-SiO₂. These results indicate that 40% PW/N-SiO₂ contains the strongest acid sites. The increases in the surface area enhance the dispersion of acidic protons up to monolayer coverage at 40% PW/N-SiO₂. The further increase in PW content above monolayer leads to the aggregation of PW on the support surface and results in decrease in the surface acidity.

2.2 Catalytic activity

Some valuable organic reactions have been employed in this work for catalytic activity measurement and yields of the corresponding products are listed in Table 3. Effect of

Table 3 Catalytic activity of nano silica and PW/N-SiO₂ in some organic reactions

Reaction ^a	Catalyst	Time (min)	Yield ^b (%)
Claisen-Schmidt	nano silica	30	0 ^c
	20% PW/N-SiO ₂	30	20
	40% PW/N-SiO ₂	20	98
	60% PW/N-SiO ₂	70(60 ^c)	95(88 ^c)
Biginelli	nano silica	30	58
	40% PW/N-SiO ₂	5(120)	95(89)
Hantzsch	nano silica	60	51
	40% PW/N-SiO ₂	5(5)	90(90)
Mannich	nano silica	120	0
	40% PW/N-SiO ₂	25(10)	93(65)

^aAll products are known and identified by comparing of their spectral data with those of the authentic samples [47–49].

^bIsolated yield and all products were obtained with 100% selectivity.

^cReaction temperature was 50 °C.

Results in parentheses are for PW/commercial SiO₂ catalyst.

PW loading and bulk nano silica was investigated in Claisen-Schmidt condensation (Table 3). The results show that 40% PW/N-SiO₂ is the best catalyst since the maximum yield of the product was obtained in a short reaction time. This result indicates that the catalytic activity is directly proportional to the number of the surface acid sites which are the ones accessible to the reactants. Thus, 40% PW/N-SiO₂ is used as the best catalyst in other organic reactions. It is very obvious from the results that PW/N-SiO₂ exhibits excellent activity in all selected catalytic reactions in a very short reaction time. The products were obtained with excellent selectivity in the presence of a low amount of catalyst in all the reactions. Catalytic performances of bulk PW and PW/commercial SiO₂ in these organic reactions are previously reported in literatures [51–53]. 40% PW/N-SiO₂ showed higher catalytic activity in comparison with PW/commercial SiO₂ due to its higher surface area and higher dispersion of acidic protons. The present investigation has therefore developed a low-cost methodology with a very cheap support material.

2.3 Recyclability

One of the advantages of using heterogeneous catalyst is the possibility of their reusability and/or regeneration to reduce waste. The stability of the supported catalyst has been studied by running the reaction successively with the same catalyst in the same reaction. Figure 7 shows the results of this study. It is interesting to note that the catalyst could be used several times in one reaction without any significant change in its percentage yield.

Fig. 7. Reusability of 40% PW/N-SiO₂ in the selected organic reactions (after 30 min).

To check the leaching of PW into the reaction mixture, the selected organic reactions (Table 3) were carried out for appropriate time in each case under selected reaction conditions. Then, the reactions were stopped. Catalysts were recovered according to the procedures and separated by cen-

trifugation, and the filtrate were added to a mixture of reactants (in each case) as model substrates and stirred again for appropriate time. 9%, 11%, 14%, and 17% of the corresponding products were obtained in Claisen-Schmidt, Biginelli, Hantzsch and Mannich reaction, respectively, which indicate a small amount of PW leaching into the reaction mixtures. In addition, the content of PW in filtrates was evaluated quantitatively by ICP-AES. The results showed that 10%, 10.8%, 9.2%, and 12.2% of the initial content were leached into the reaction mixtures in the four reactions, respectively. These observations confirmed that the reactions were catalyzed heterogeneously.

3 Conclusions

Acid treatment followed by thermal combustion of RH from Northern Iran under controlled conditions gave 22.5% ash. At the appropriate conditions, highly pure amorphous silica of 98.8% was produced, which is nano-size with high surface area, high activity, and in 99.9% amorphous form. PW was supported on this nano silica easily by impregnation method. Also, no complicated procedures or additional chemicals or surfactant were required for the preparation of the catalyst. Keggin structure of PW was preserved after catalyst preparation. The average size of the 40% PW/N-SiO₂ catalyst was 7 nm and PW content in the supported catalyst was 34 wt% measured by ICP. 40% PW/N-SiO₂ was found to be active as heterogeneous catalyst and showed high activity and reusability in some important organic synthesis including Biginelli, Hantzsch, Mannich, and Claisen-Schmidt reactions. Acidity measurement and activity of the catalyst showed a good correlation.

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