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Research Article

Synthesis of Ibuprofen Using Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) as an Eco-Friendly, Inexpensive, and Efficient Catalyst

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This paper describes an alternative and simple procedure for the synthesis of Ibuprofen using Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs), as an eco-friendly, inexpensive, and efficient catalyst. High yields, simplicity of operation, and easy work-up procedure are some advantages of this protocol. Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) offer the advantages of a higher hydrolytic and thermal stability. The salient features of Preyssler's anion are availability, nontoxicity and reusability. We believe this methodology can find usefulness in organic synthesis.

1. Introduction

Ibuprofen was developed by the Boots Pure Chemical Company and then patented in 1961. It is a nonsteroidal anti-inflammatory drug (NSAID) and is marketed under a wide variety of trade names including Advil and Motrin. Ibuprofen is one of several 2-aryl propanoic acids that are currently on the market. Others include ketoprofen, flurbiprofen, and naproxen.

The name "ibuprofen" originally came from the name isobutylpropanoicphenolic acid, but this nomenclature has not been used for many years and, in fact, virtually all chemists today are unfamiliar with it. Fortunately, however, the name is still a reasonably good match for the currently accepted name 2-(4-isobutylphenyl)propanoic acid. Ibuprofen ((+/−)2-(4-isobutylphenyl)propionic acid, Figure 1(a)) is one of the most commonly used anti-inflammatory agents. It is considered to be the prototype for the family of synthetic 2-arylpropionic acids, profens, a subclass of the nonsteroidal anti-inflammatory drugs (NSAIDs). In recent years, the profens have come to dominate this therapeutic class. Ibuprofen, for example, is used to treat arthritis, muscular strain, cephalalgia, and so forth.

The profens have an asymmetric carbon centre which is attached to a carboxylic acid, a methyl, and an aryl group of varying structures. Some of the available profen drugs are depicted in Figure 1: ibuprofen (a), naproxen (b), ketoprofen (c), and flurbiprofen (d). Ibuprofen is distributed over the counter and naproxen belongs to the top ten of drugs marketed worldwide in 1989 [1]. Ibuprofen is used to relieve the symptoms of a wide range of illnesses including headaches, backache, period pain, dental pain, neuralgia, rheumatic pain, muscular pain, migraine, cold and flu symptoms, and arthritis. NSAIDs exert their pharmacological and toxicological effects primarily by specifically inhibiting the binding of arachidonic acid to the cyclooxygenase subunit of prostaglandin synthetase, thereby preventing the formation of various prostaglandins [2]. In the last two decades, heteropolyacids (HPAs) have found numerous applications as useful and versatile acid catalysts for a range of acid-catalyzed reactions. Heteropolyacids are several times more active than inorganic and organic acids and their molar

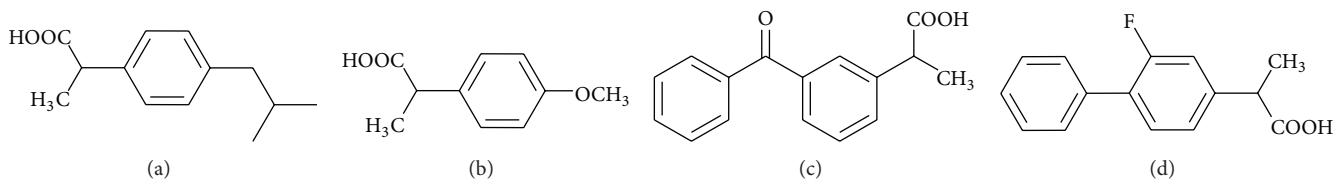


Figure 1

catalytic activity is 100–1000 times more active than H_2SO_4. They can also be used in low concentrations [3]. The synthesis and characterization of catalysts with lower dimensions have become the most interesting topic of research. We know that as the particle size decreases, the relative number of surface atoms increases and thus the activity increases. Moreover, due to quantum size effects, nanometer-sized particles may exhibit unique properties for a wide range of applications [4]. A Preyssler acid is a highly acidic catalyst from the heteropolyacid family with excellent catalytic activity in a variety of acid-catalyzed reactions [5]. Therefore, we hoped to further improve this catalyst by using it in the form of nanoparticles in organic reactions and synthesizes. Catalysts based on heteropolyacids have many advantages over liquid acid catalysts. They are not corrosive, environmentally benign, presenting fewer disposal problems. Solid heteropolyacids have attracted much attention in organic synthesis owing to easy work-up procedures, easy filtration, and minimization of cost and waste generation due to reuse and recycling of the catalysts [6]. There have been many attempts to optimize these catalysts. Recently, Keggin nanocatalysts have been synthesized [7]. In our attempt to use heteropolyacids as catalysts in organic reactions, we reported that nano-SiO_2-supported Preyssler heteropolyacid (HPA) and Preyssler type heteropolyacids, $H_{14}[NaP_5W_{30}O_{110}]$, show strong catalytic action [8, 9]. We also have demonstrated an alternative and simple procedure for the synthesis of (*S*)-Naproxen using Preyssler catalyst, $H_{14}[NaP_5W_{30}O_{110}]$, as an eco-friendly, environment friendly, reusable, inexpensive, noncorrosive, and efficient catalyst [8].

2. Experimental

2.1. Chemicals. All the chemicals were obtained from Merck (Darmstadt, Germany) and used as received. All solvents were purchased from commercial sources.

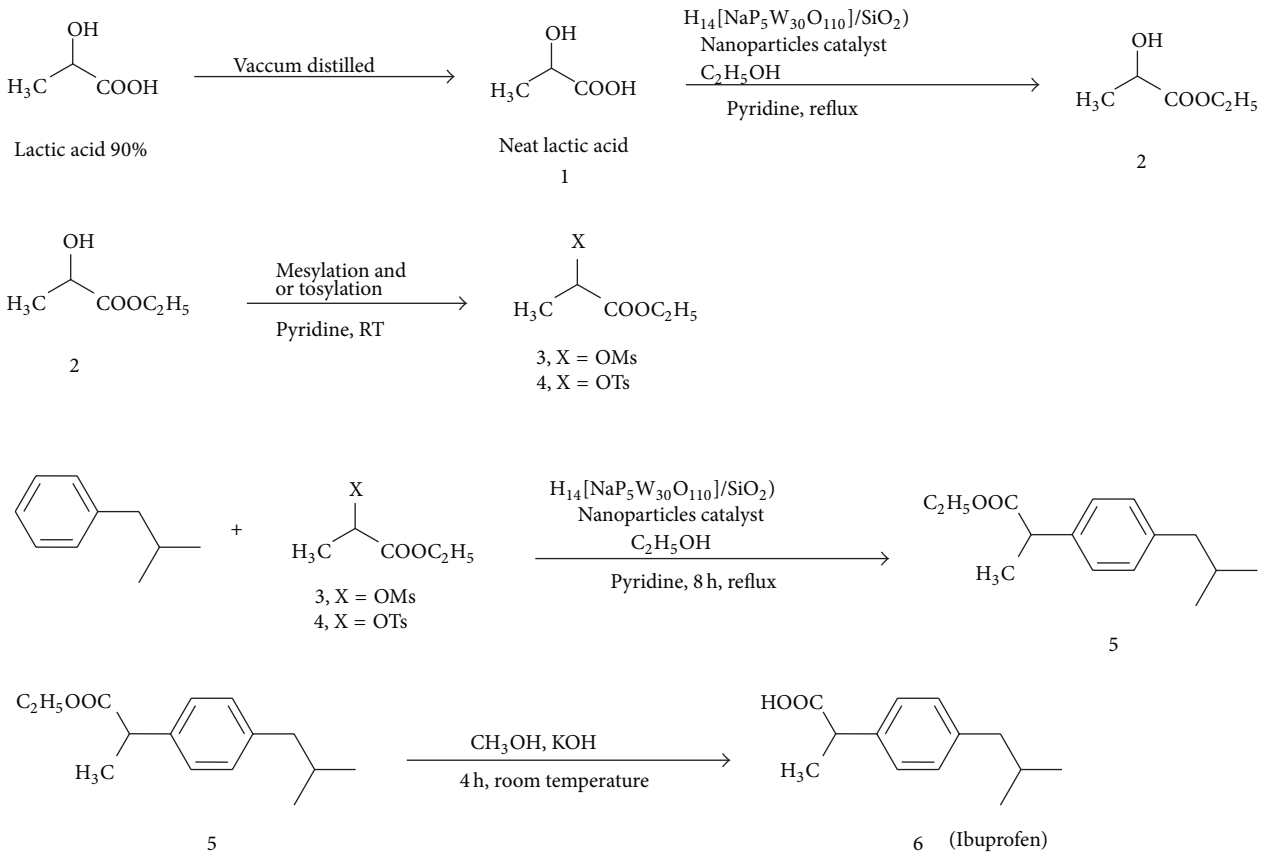
2.2. Instruments. Melting points (uncorrected) were measured using Electrothermal IA 9100 digital melting point apparatus. Yields are based on GC/mass analysis using an Agilent (Denver, CO, USA) 6890 GC system Hp-5 capillary 30 m × 530 μm × 1.5 μm nominal. The IR spectra were recorded on a Shimadzu model impact 400D FT-IR spectrophotometer using KBr pellets. ^{1}H NMR were recorded on a Bruker AC-300F 400 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard with ^{1}H resonant frequency of 400 MHz. Optical rotation values were considered on Bellingham Stanly polarimeter.

2.3. Catalyst Synthesis Procedure. Silica-Supported Preyssler Nanoparticles (SPNPs) catalyst was synthesized according to the literature [10]. Thus a solution of surfactant, sodium bis(2-ethylhexyl) sulphosuccinate, in cyclohexane (0.2 M), was treated with a solution of Preyssler acid in a specified amount of water was added. The molar ratio of water to surfactant selected was 3, 5, and 7. Tetraethoxysilane was then added into the microemulsion phase. After mixing for various times (8, 12, 18, 25, and 30 h) at room temperature, dispersed Preyssler acid/SiO_2 nanostructures were centrifuged (1500 rpm) and the particles were rinsed with acetone (4 times) and dried in a vacuum oven. The optimum ratio of water to surfactant was 3 : 1 and the optimum time was 30 h.

*2.4. Synthesis of Ethyl Lactate **(2)**.* Lactic acid (10 mL) was dehydrated by vacuum distillation and then refluxed for 3 h in presence of Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) (0.05 g), ethanol (12 mL), and pyridine (20 mL). The reaction progress was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and solidified within an hour. The reaction mixture was filtered to separate out the catalyst, and, following evaporation of the solvent under reduced pressure, a crude product was obtained, which was purified by recrystallization.

*2.5. Synthesis of Ethyl-2-(methylsulphonyloxy) Propanoate **(3)**.* To a solution of ethyl lactate (1 g, 8.47 mmol) and triethylamine (1.77 mL, 12.71 mmol) in 15 mL of dry pyridine was added portionwise MsCl (0.7723 mL, 9.32 mmol) at 0°C. The resultant mixture was stirred at 0°C for 1 h and then at room temperature for 2 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethyl acetate. The organic layer was washed with H_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude compound. Purification of the crude compound by column chromatography over silica gel (100–200 mesh) using hexane as an eluent yielded the pure product ethyl-2-(methylsulphonyloxy) propanoate **3**. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.15 (q, J = 7 Hz, 1H), 4.33 (q, J = 7.5 Hz, 2H), 3.15 (s, 3H), 1.62 (d, J = 7 Hz, 3H), 1.35 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c 37.90, 61.60, 70.22, 170.83.

*2.6. Synthesis of Ethyl-2-(tosyloxy) Propanoate **(4)**.* To a solution of ethyl lactate (1 g, 8.47 mmol) in 15 mL of dry pyridine was added portionwise TsCl (1.77 g, 9.32 mmol) at 0°C. The resultant mixture was stirred at 0°C for 1 h and then at room



Scheme 1: Synthesis of ibuprofen using Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) using ethanol and pyridine in their reactions.

temperature for 2 h. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with C_2H_5OAc. The organic layer was washed with H_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude compound. Purification of the crude compound by column chromatography over silica gel (100–200 mesh) using hexane as an eluent yielded the pure product **4** ethyl-2-(tosyloxy) propanoate **4**. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.78 (d, 2H), 7.30 (d, 2H), 4.10 (q, 2H), 2.46 (s, 3H), 1.50 (d, 3H), 1.21 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c 21.31, 61.62, 70.44, 128.30, 130.50, 140.33, 144.41.

2.7. Synthesis of Ethyl-2-(4-isobutylphenyl) Propanoate ***(5)***. ($H_{14}[NaP_5W_{30}O_{110}]$)/$SiO_2$ nanoparticles (SPNPs) (0.05 g) were added to pyridine (15 mL) and isobutylbenzene (2.73 g, 20.41 mmol) at 0°C. Ethyl-2-(methylsulphonyloxy) propanoate was added to the cold solution portionwise and the mixture was warmed to room temperature. This was then heated to 80°C for 8 h (the solution was reflux for 8 h) and then cooled to room temperature. The reaction mixture was quenched with dil. HCl at 0°C and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give crude compound. Purification of the crude compound by column chromatography over silica gel using hexane as an eluent yielded the pure product **5.** ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.12-7.63 (m, 4H), 4.23 (m, 2H), 3.66 (m, 1H), 2.64 (d, J = 8 Hz, 2H), 2.41 (m, 1H), 1.54 (m, 3H), 1.13 (m, 3H), 0.91 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c 22.81, 29.05, 40.44, 44.50, 44.51, 61.62, 128.80, 128.91, 132.22, 140.23.

2.8. Synthesis of Ibuprofen ***(6)***. To a solution of ethyl-2-(4-isobutylphenyl) propanoate (1 g, 4.27 mmol) in 6 mL of CH_3OH a solution of KOH was added (479 mg, 8.55 mmol) in 5 mL of H_2O. The resultant solution was stirred at room temperature for 4 h. Methanol was removed under reduced pressure and the resulting solution was extracted with ethyl acetate and the organic extracts were washed with H_2O, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give compound **6**. M.P (°C) 130-133, IR (KBr, cm^{-1}): 3100, 2920, 2870, 1716, 1408, 1419, 1321, 1230, 1184, 935, 779, 668, 583. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.15 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 3.64 (q, J = 7.2 Hz, 1H), 2.37 (d, J = 7.1 Hz, 2H), 1.75 (m, 1H), 1.43 (d, J = 7.1 Hz, 3H), 0.82 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c 22.81, 22.82, 29.07, 42.64, 44.50, 128.80, 128.93, 128.95, 132.22, 140.23, 181.26. Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80%. Found: C, 75.61; H, 8.70%. HRMS (EI) Calcd. for $C_{26}H_{25}FN_4O_6$ $[M]^+$, 206.1600, Found 206.1009.

3. Results and Discussion

This experiment was carried out for the first time by inexpensive, recyclable Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) nanocatalyst. We used Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) heteropolyacid for the synthesis of Ibuprofen. Friedel-Crafts type alkylation of isobutylbenzene with various lactic acid derivatives was explored for the synthesis of Ibuprofen. Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) were employed as catalysts for Friedel-Crafts alkylation. Mesylate and tosylate of ethyl lactate were the lactic acid derivatives used for the reaction. The scheme for the synthesis of Ibuprofen employing lactic acid derivatives is shown below (Scheme 1).

Lactic acid (90%) was dehydrated by vacuum distillation and immediately refluxed with ethanol in presence of Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) and with azeotropic removal of water to afford ethyl lactate **(2)** in 82 % yield, (Scheme 1). Mesylation and tosylation of ethyl lactate in the presence of triethylamine or pyridine at room temperature afforded the corresponding ethyl-2-(methylsulphonyloxy) propanoate **(3)** and ethyl-2-(tosyloxy) propanoate **(4)**. Friedel-Crafts alkylation of mesylate or tosylate with isobutylbenzene for single step synthesis of ethyl-2-(4-isobutylphenyl) propanoate was carried out by heating with Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) under neat reaction conditions. Ethyl-2-(4-isobutylphenyl) propanoate **(5)** formed in 65% yield was hydrolysed with KOH in methanol to afford the racemic Ibuprofen **(6)** in 97% yield. The nanocatalyst was found to be ineffective for the Friedel-Crafts alkylation using mesylates and tosylates with isobutylbenzene.

The yields of the synthesis of Ibuprofen ethyl ester with Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) and other acid catalysts are given (Scheme 1, Table 1). The result shows that the Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) catalyst has higher activity and performance in Ibuprofen synthesis compared with other heteropolyacids such as Keggin as well as the standard method using H_2SO_4(Table 1). The best yield of Ibuprofen (97%) with good selectivity was attained with $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ (SPNPs) nanocatalyst after 4 h at room temperature (Table 1, entry **1**). Keggin ($H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$) heteropolyacid has also lower activity than $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(SPNPs) nanocatalyst. They lead to order 97, 91, 88, 86% Ibuprofen with good selectivity after 4 h of reaction at room temperature (Table 1, entries **1**, **2**, **5**, **10**).

3.1. Effect of the Catalyst Type. Initially, we compared the catalytic performance of Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) catalyst, Keggin, $H_3[PW_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiMo_{12}O_{40}]$, $H_{14}[NaP_5W_{29}MoO_{110}]$, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(50%), $H_3[PW_{12}O_{40}]/SiO_2$(50%), H_2SO_4, and without catalyst in the synthesis of Ibuprofen. The results are shown in Table 1.

Table 1: Synthesis of Ibuprofen (**6**) in the presence of various heteropolyacids catalysts at room temperature conditions.

Entry	Catalyst	[a]Yield (%)
1	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, (SPNPs)	97
2	$H_{14}[NaP_5W_{30}O_{110}]$	91
3	$H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ (50%)	81
4	$H_3[PW_{12}O_{40}]/SiO_2$ (50%)	67
5	$H_{14}[NaP_5W_{29}MoO_{110}]$	88
6	$H_3[PMo_{12}O_{40}]$	62
7	$H_3[PW_{12}O_{40}]$	72.5
8	$H_4[SiW_{12}O_{40}]$	64
9	$H_4[SiMo_{12}O_{40}]$	51
10	$H_6[P_2W_{18}O_{62}]$	86
11	H_2SO_4	59
12	Free	9
13	*p*-TSA	63
14	Zeolite	68

[a]Isolated yield and were analyzed by GC.

The Yield of Product Decreases in the Following Order. Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) nanocatalyst > $H_{14}[NaP_5W_{30}O_{110}]$ > $H_{14}[NaP_5W_{29}MoO_{110}]$ > $H_6[P_2W_{18}O_{62}]$ > $H_3[PW_{12}O_{40}]$ > Zeolite > $H_3[PW_{12}O_{40}]/SiO_2$(50%) > $H_4[SiW_{12}O_{40}]$ > *p*-TSA > $H_3[PMo_{12}O_{40}]$ > H_2SO_4 > $H_4[SiMo_{12}O_{40}]$ catalyst > free catalyst. The results are summarized in Table 1.

As could be seen 30-tungstophosphoric acid, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$ nanocatalyst, is more effective than the other heteropolyanions and in the presence of this catalyst the highest yields of products are obtained. The interesting feature of this polyanion compared the other heteropolyacids is its hydrolytic stability (pH 0–12), which is very important in catalytic processes. It is clear from these reactions that the efficiency of $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$(SPNPs) nanocatalyst is higher than these of Keggin heteropolyacids. The reason is likely to be due to higher surface area available. Also, as the particle size of nanomaterial decreases, the relative number of surface atoms will be increased and thus the catalyst activity will be enhanced. Silica-Supported Preyssler Nanoparticles, $H_{14}[NaP_5W_{30}O_{110}]/SiO_2$, (SPNPs) were found to be the best catalyst in terms of reaction time, yield, and recyclability. Silica-Supported Preyssler Nanostructures were obtained through a microemulsion method. A shape change of the particles has been observed in other synthetic methods of nanoparticle preparation [11]. The reason for this can be attributed to metastable states, which can spontaneously change under equilibrium reaction conditions, which is in agreement with previous observations [11]. Silica nanostructures were obtained through a sol-gel method. All of the conditions are shown in Experimental section. The BET surface area, pore volume, and average pore size of nanosized SiO_2 were obtained as 287 m^2/g, 0.28 cm^3/g, and 0.25 nm, respectively. After the

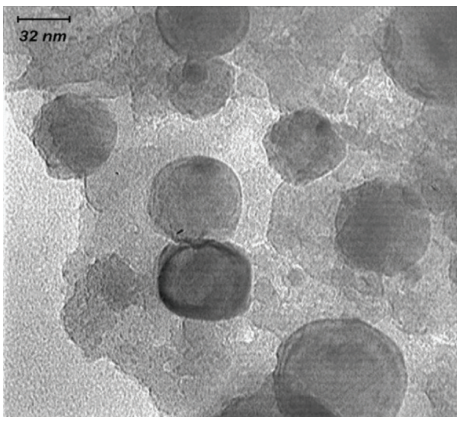


Figure 2: TEM image of the synthesized nano-SiO_2(SPNPs).

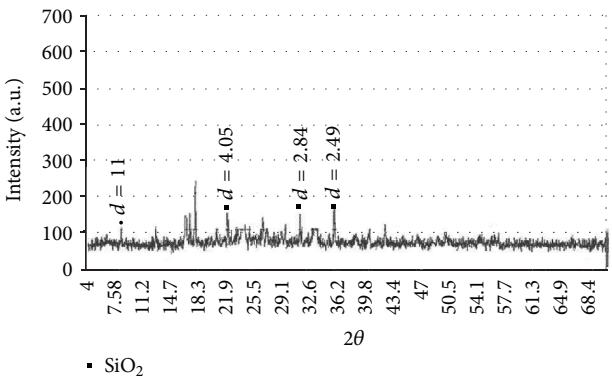


Figure 3: X-ray diffraction (XRD) pattern.

impregnation of HPA (with 30% being the best loading), the BET surface area, pore volume, and average pore size were obtained as 201 m^2/g, 0.10 cm^3/g, and 0.21 nm, respectively. The BET surface area and pore volume decreased, indicating that the pores of nanosized silica are being filled and the supported HPA blocked some pores of the support. Scanning electron microscopy (SEM) pictures of samples and X-ray diffraction (XRD) patterns of the synthesized samples were taken. The obtained nanostructures were characterized by TEM as shown in Figure 2. This figure shows 40 nm spheres (Figure 2) [9].

Figure 3 shows powder X-ray diffraction (XRD) patterns of the synthesized samples. The patterns of the spherical products confirm the SiO_2 structure. The XRD pattern of nano-SiO_2 with sharp peaks in the 2θ range from 7° to 36° confirmed the crystalline nature of SiO_2. In addition, the lack of an XRD peak centered at 2θ angle 22° (typical for amorphous SiO_2) supports the crystallinity. The patterns of the spherical products confirm the SiO_2 structure [9].

Analogous diffraction patterns have been observed for other synthesized samples. The heteropolyacid ($H_{14}[NaP_5W_{30}O_{110}]$) on SiO_2 nanoparticles (SPNPs) was characterised by infrared (IR) spectroscopy (Figure 4) [9]. IR spectroscopy demonstrates that ($H_{14}[NaP_5W_{30}O_{110}]$) is preserved in the HPA/SiO_2 nanoparticles. The antisymmetric

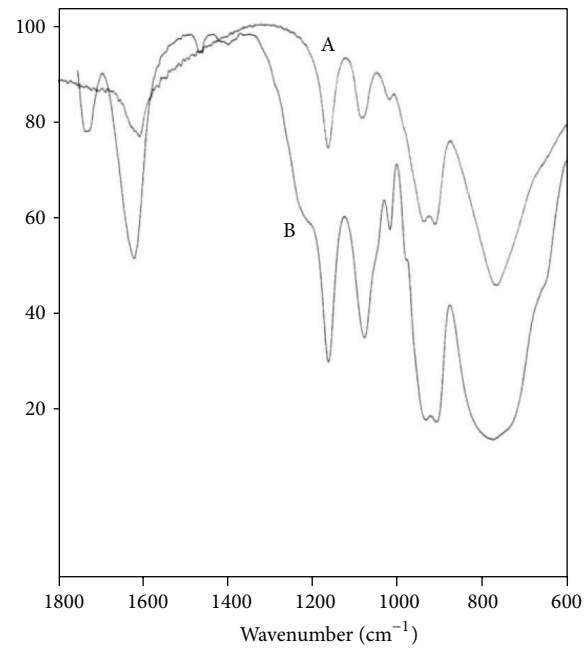


Figure 4: IR spectra of Preyssler heteropolyacid in bulk form (1) and nano form (2).

stretching wavenumber of the terminal oxygen-containing group is observed at 960 cm^{-1} and the antisymmetric P-O stretching wavenumber is noted at 1080 and 1165 cm^{-1}. The prominent P-O bands at 960, 1080, and 1165 cm^{-1} are consistent with a C_{5v} symmetry anion [9]. It could therefore be concluded that the heteropolyacid ($H_{14}[NaP_5W_{30}O_{110}]$) was successfully immobilized onto the SiO_2 nanoparticles. TEM and IR studies showed that the heteropolyacid stayed intact on the nanoparticles after it was recycled several times in the reaction reported below. Bleeding of the heteropolyacid was found to be negligible by weighing the catalyst again after it was recycled five times.

It is clear that in the synthesis of Ibuprofen the efficiency of ($H_{14}[NaP_5W_{30}O_{110}]$)/$SiO_2$ is slightly higher than that of the conventional Preyssler catalyst. Infrared spectroscopy shows that in ($H_{14}[NaP_5W_{30}O_{110}]$)/$SiO_2$ nanoparticles (SPNPs) the heteropolyacid structure ($H_{14}[NaP_5W_{30}O_{110}]$) is preserved (Figure 4). It is therefore expected that ($H_{14}[NaP_5W_{30}O_{110}]$)/$SiO_2$ nanoparticles (SPNPs) will exhibit the same catalytic characteristics of classical Preyssler catalysts. As the particle size of the nanomaterial decreases, the relative number of surface atoms increases, and thus activity increases. Moreover, due to quantum size effects, nanometre-sized particles can exhibit unique properties.

3.2. Reusability of the Catalyst. The catalyst was recovered after the reaction and reused as a catalyst in the synthesis of Ibuprofen. Several recycling of the catalyst had only slightly decreased the catalytic activity, demonstrating the stability and retention capability of this useful polyanion. Recycling of the catalyst at the end of the reaction involved filtering the catalyst, washing with diethyl ether, and drying at 130°C for

Table 2: Reuse of the Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) catalyst for the synthesis of Ibuprofen.

Entry	Run	[a]Yield (%)
1	1	97
2	2	97
3	3	96
4	4	96
5	5	95

[a]Isolated yields.

1 h. The recycled catalyst was used for three reactions without observation of appreciable loss in its catalytic activities. In Table 2, the comparison of efficiency of Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) catalyst in the synthesis of Ibuprofen after five times is reported. As it is shown in Table 2 the first, second, third, fourth, and fifth reactions using recovered Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) afforded similar yields. The reusability of the catalyst was also investigated. At the end of the reaction, the catalyst was recovered by a simple filtration. The recovered catalyst was reused successfully.

4. Conclusions

In conclusion, we have reported a new catalytic method for the synthesis of Ibuprofen using Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) as an efficient, reusable, and eco-friendly heterogeneous inorganic catalyst. The advantages of this method are reusability of the catalyst, easy work-up procedure, and high yields. The Ibuprofen synthesis is carried out in three steps with usual reagents. However, the results show that Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) catalyst gives the highest yield. Compared with mineral acids, such as H_2SO_4, Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) catalyst is more active and shows a higher selectivity and minimized side reactions. Important features of this polyanion are high thermal and hydrolytic stability throughout a wide pH range. Eco-friendly, recyclable, and easily prepared Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) catalyst is an efficient solid acid catalyst for highly selective synthesis of Ibuprofen. In the Silica-Supported Preyssler Nanoparticles ($H_{14}[NaP_5W_{30}O_{110}]/SiO_2$) (SPNPs) catalyst in both heterogeneous conditions can easily be recovered and reused without loss of structure and activity. The SPNPs catalyst was prepared in the nanoscale and used as a heterogeneous catalyst for the synthesis of Ibuprofen.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

[1] S. G. Nerurkar, S. V. Dighe, and R. L. Williams, "Bioequivalence of racemic drugs," *Journal of Clinical Pharmacology*, vol. 32, no. 10, pp. 935–943, 1992.

[2] S. H. Ferreira and J. R. Vane, Eds., *Anti-Inflammatory Drugs*, vol. 50/2 of *Handbook of Experimental Pharmacology*, Springer, Berlin, Germany, 1979.

[3] P. Biginelli, "The first synthesis of dihydropyrimidinone by refluxing a mixture of an aldehyde, a β-ketoester, and urea under strongly acidic condition," *Gazzetta Chimica Italiana*, vol. 23, pp. 360–413, 1893.

[4] F. F. Bamoharram, M. M. Heravi, J. Ebrahimi, A. Ahmadpour, and M. Zebarjad, "Catalytic performance of nano-SiO_2-supported Preyssler heteropolyacid in esterification of salicylic acid with aliphatic and benzylic alcohols," *Chinese Journal of Catalysis*, vol. 32, no. 5, pp. 782–788, 2011.

[5] F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Jahangir, and A. Gharib, "Preyssler catalyst, $[NaP_5W_{30}O_{110}]^{14-}$: a green, efficient and reusable catalyst for esterification of salicylic acid with aliphatic and benzylic alcohols," *Applied Catalysis A: General*, vol. 302, no. 1, pp. 42–47, 2006.

[6] M. A. Schwegler, P. Vinke, M. van der Eijk, and H. van Bekkum, "Activated carbon as a support for heteropolyanion catalysts," *Applied Catalysis A: General*, vol. 80, no. 1, pp. 41–57, 1992.

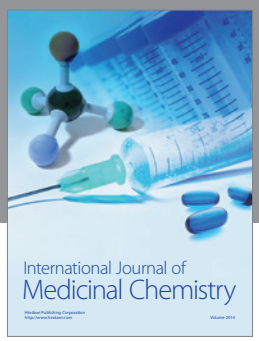
[7] D. P. Sawant, A. Vinu, N. E. Jacob, F. Lefebvre, and S. B. Halligudi, "Formation of nanosized zirconia-supported 12-tungstophosphoric acid in mesoporous silica SBA-15: a stable and versatile solid acid catalyst for benzylation of phenol," *Journal of Catalysis*, vol. 235, no. 2, pp. 341–352, 2005.

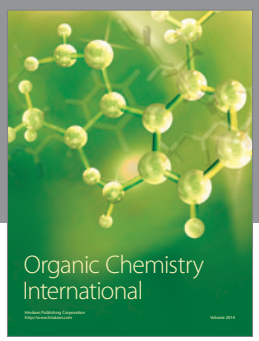
[8] A. Gharib, M. Daneshtalab, J. Scheeren, F. Bamoharram, M. Roshani, and M. Jahangir, "One-pot synthesis of (*S*)-2-(6-methoxynaphtalen-2-yl)propanoic acid, (*S*)-Naproxen using Preyssler and Keggin-type heteropolyacids as green and reusable catalysts," *Polish Journal of Chemical Technology*, vol. 11, no. 3, pp. 8–14, 2009.

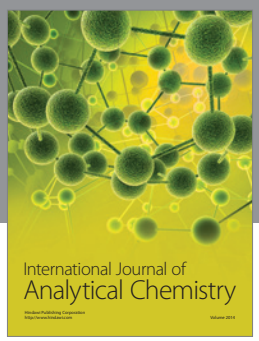
[9] A. Gharib, B. R. Hashemipour Khorasani, M. Jahangir et al., "Synthesis of bis-2,3-dihydroquinazolin-4(1*H*)-ones and 2,3-dihydroquinazolin-4(1*H*)-ones derivatives with the aid of silica-supported Preyssler nanoparticles," *Organic Chemistry International*, vol. 2013, Article ID 848237, 14 pages, 2013.

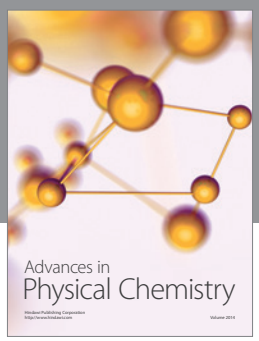
[10] M. M. Heravi, S. Sadjadi, S. Sadjadi, H. A. Oskooie, R. H. Shoar, and F. F. Bamoharram, "Silica-supported preyssler nanoparticles as new catalysts in the synthesis of 4(3*H*)-quinazolinones," *South African Journal of Chemistry*, vol. 62, pp. 1–4, 2009.

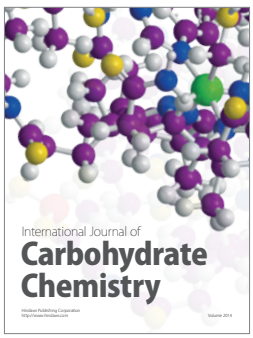
[11] B. K. Bartsch and A. Leonhardt, "An approach to the structural diversity of aligned grown multi-walled carbon nanotubes on catalyst layers," *Carbon*, vol. 42, no. 8-9, pp. 1731–1736, 2004.











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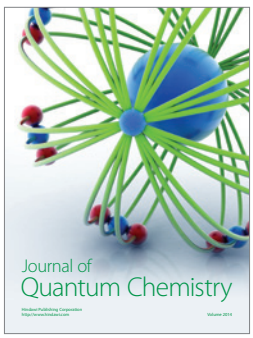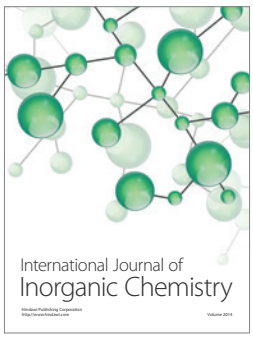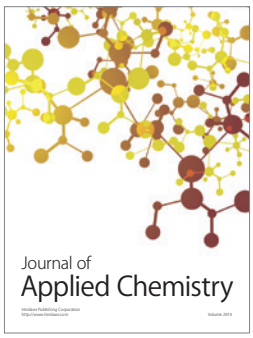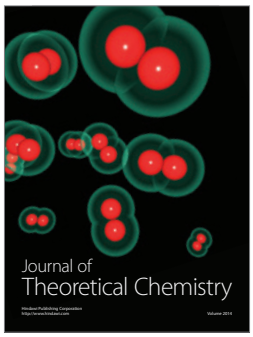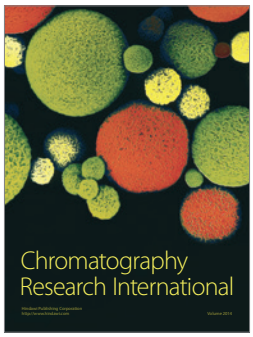
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