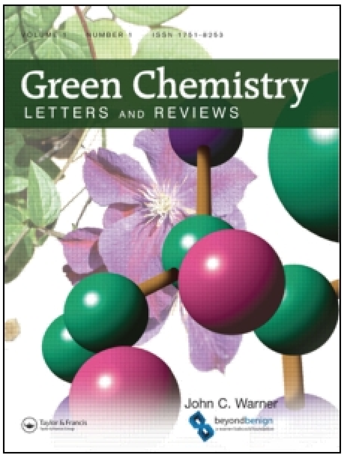

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Silica-supported Preyssler nano particles: a green, reusable and highly efficient heterogeneous catalyst for the synthesis of carbamatoalkyl naphthols

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RESEARCH LETTER

Silica-supported Preyssler nano particles: a green, reusable and highly efficient heterogeneous catalyst for the synthesis of carbamatoalkyl naphthols

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An efficient and green procedure has been developed for the preparation of carbamatoalkyl naphthols by the one-pot condensation of aryl aldehydes, β-naphthol, and methyl carbamate in the presence of silica-supported Preyssler nano particles as a heterogeneous catalyst under solvent-free conditions. The present methodology offers several advantages such as excellent yields, simple procedure, easy work-up, and eco-friendly reaction conditions. The catalyst is easily prepared, stable, reusable, and efficient under the reaction conditions.

Keywords: silica-supported Preyssler nano particles; carbamatoalkyl naphthols; heterogeneous catalyst; multicomponent reactions

Introduction

Green chemistry is an approach to the synthesis, processing, and use of chemicals that reduces risks to humans and the environment. Much innovative chemistry has been developed over the past several years that are effective, efficient, and more environmentally benign. These approaches include new syntheses and processes as well as new tools for instructing aspiring chemists how to do chemistry in a more environmentally benign manner. Thus, the development and using of solid and green catalysts are very important in organic syntheses. The development of methods using heteropolyacids (HPAs) as solid and green catalysts for fine organic synthetic processes related to fine chemicals, such as flavors, pharmaceuticals, and food industries have been under attention (*1*). They are good acid catalysts in homogeneous and heterogeneous medium (*2*). These catalysts have many advantages over liquid acid catalysts. They are not corrosive and are environmentally benign, presenting fewer disposal problems. Solid HPAs 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 (*3*). There have been many attempts to optimize these catalysts.

Recently, because of the unique properties of nano particles (*4–6*) the applications of them as catalysts has attracted much attention. As the particle size decreases, the relative number of surface atoms increases, and thus the activity increases. In addition, nanometer-sized particles may show unique properties for several applications (*7–9*). In recent years, interest has focused mainly on the synthesis of nano catalysts such as the Keggin nano catalysts (*10,11*). In our attempt to use HPAs as catalysts in organic reactions, we reported that Preyssler type of HPAs, $H_{14}[NaP_5W_{30}O_{110}]$, shows strong catalytic characterization (*12–16*). Due to the novel properties of nano particles and potential applications in different fields (*17*), recently, we immobilized $H_{14}[NaP_5W_{30}O_{110}]$ into the SiO_2 nano particles (*18*) and we wish to investigate the catalytic behavior of this new catalyst in organic synthesis.

Multicomponent reactions (MCRs) have attracted considerable attention since they are performed without the need to isolate any intermediate during their processes. This reduces time and saves both energy and raw materials (*19–22*). They have merits over two-component reactions in several aspects including the simplicity of a one-pot procedure, possible structural variations, and building up complex molecules. Bigenilli (*23–25*), Ugi (*26–28*), Passerini (*29,30*), and Mannich (*31–33*) reactions are some examples of MCRs. To the best of our knowledge, the synthesis of carbamatoalkyl naphthols have been largely overlooked and there is only one reference about the synthesis of these compounds

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using silica-supported sodium hydrogen sulfate as heterogeneous catalyst (*34*). Therefore, herein we wish to report a simple and efficient use of silica-supported Preyssler nano particles as a catalyst in the synthesis of carbamatoalkyl naphthols via a three-component condensation reaction between aryl aldehydes, β-naphthol, and methyl carbamate under thermal and solvent-free conditions (Scheme 1).

Results and discussion

Silica-supported Preyssler nanostructures were obtained through a microemulsion method. Although some authors have used this procedure, this method has never been reported for the synthesis of Preyssler nanostructures with different morphologies. In addition, in the same reactions, only spherical nanoparticles have been obtained. The samples were analyzed by tunneling electron microscopy (TEM). A mixture of nano wire (tubular shape) and nano spherical structures was obtained at ratio 3:1 after 12 h. The fraction of tubular shapes increased up to about 18 h (*18*). Scanning electron microscopy (SEM) pictures of samples and X-ray diffraction (XRD) patterns of the synthesized samples were taken. The patterns of the spherical synthesized products contain a broad peak centered at 52A°. Analogous diffraction patterns have been observed for other synthesized samples. The HPA ($H_{14}[NaP_5W_{30}O_{110}]$) on the SiO_2 nano particles was confirmed by infrared (IR) spectroscopy. IR spectroscopy demonstrates that ($H_{14}[NaP_5W_{30}O_{110}]$) is preserved in the HPA/SiO_2 nano particles. The anti-symmetric stretching wave number of the terminal oxygen-containing group is observed at 960 cm^{-1} and the anti-symmetric P–O stretching wave number 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. It could therefore be confirmed that the HPA ($H_{14}[NaP_5W_{30}O_{110}]$) was successfully immobilized onto the SiO_2 nano particles. TEM and IR studies showed that the HPA stayed intact on the nano particles after it was recycled several times in the reaction (*18*).

To investigate the efficiency of this catalyst in organic reactions, the three-component reaction of an aryl aldehyde, β-naphthol, and methyl carbamate was performed in the presence of silica-supported Preyssler nano particles as catalyst.

Table 1. Synthesis of methyl [(2-hydroxynaphthalen-1-yl)(phenyl)methyl] carbamate **4a** in the presence of Silica-supported Preyssler nano particles at different temperatures in solvent-free conditions.

Entry	Temperature (°C)	Time (min)	Yield (%)[a]
1	25	30	20
2	50	20	35
3	70	8	54
4	90	3	84
5	120	3	87

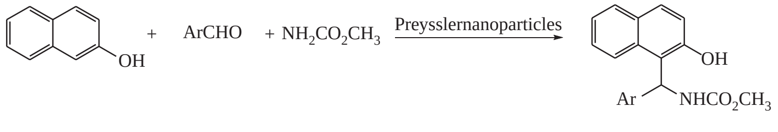
[a]Isolated yields.

In order to determine the most appropriate reaction conditions and evaluate the catalytic efficiency of the catalyst, initially a model study was carried out on the synthesis of **4a**. Among the tested solvents such as methanol, ethanol, DMF, CH_3CN, chloroform, 1,2-dichloroethane, and solvent-free system, the reaction between benzaldehyde, β-naphthol, and methyl carbamate was more facile and proceeded to give the highest yield, under solvent-free conditions.

The effect of temperature was also studied by carrying out the same model reaction in the presence of the catalyst and at different temperatures in solvent-free conditions. It was observed that yield is a function of temperature, therefore the yield increased as the reaction temperature was raised and at 90°C the product **4a** was obtained in high yield (Table 1).

The efficiency of the reaction is mainly affected by the presence of the catalyst because no product could be detected in the absence of this catalyst at 90°C after 20 min. Preparation of compound **4a** in the presence of non-supported Preyssler was also investigated. Therefore, a mixture of benzaldehyde, β-naphthol, and methyl carbamate in the presence of non-supported preyssler was heated at 90°C for 10 min to give compound **4a** in 67% yield. It can be concluded that the silica-supported Preyssler nano particles act as catalyst better than non-supported one.

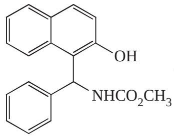
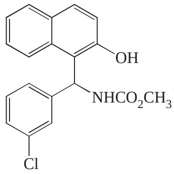
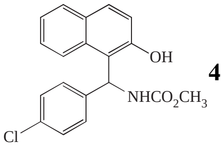
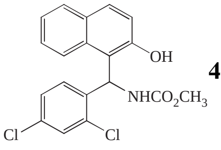
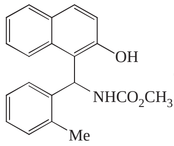
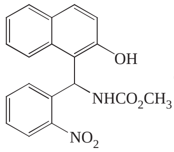
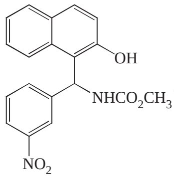
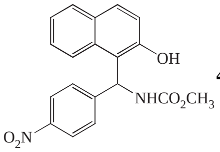
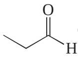
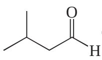
To show the generality of this method, using these optimized reaction conditions, the scope and efficiency of the reaction were explored for the synthesis



1 **2** **3** **4a-j**

Scheme 1.

Table 2. Silica-supported Preyssler nano particles catalyzed synthesis of carbamatoalkyl naphthols.

				M.P. (°C)	
Entry	Products[a]	Time (min)	Yield (%)[b]	Found	Reported
1	 **4a**	3	84	222–224	217–218
2	 **4b**	2	87	201–203	196–198
3	 **4c**	2	88	203–205	198–200
4	 **4d**	3	83	194–196	192 (dec)
5	 **4e**	3	82	230–232	–
6	 **4f**	3	86	241–242	–
7	 **4g**	2	90	253–255	252 (dec)
8	 **4h**	2	91	200–202	205–207
9	 **4i**	20	–	–	–
10	 **4j**	20	–	–	–

[a] New products (**4e** and **4f**) were characterized by IR, ^{1}H NMR, ^{13}C NMR and MASS spectra and known products were characterized by IR and ^{1}H NMR and comparison of their melting points with those of authentic samples (*34*).

[b] Isolated yields.

of a wide variety of substituted carbamatoalkyl naphthols using various aryl aldehydes. The results are summarized in Table 2. As shown, the direct three-component reactions worked well with a variety of aryl aldehydes including those bearing electron-withdrawing and electron-donating groups such as Me, Cl, and NO_2, and the desired compounds were obtained in high yields. Under the same conditions, this reaction did not proceed when aliphatic aldehydes such as propionaldehyde or isobutyraldehyde (Table 2, entries 9 and 10) were used as the starting material.

Reusability of the catalyst was also investigated. For this purpose, the model reaction was again studied in the optimized conditions. After the completion of the reaction, the catalyst was recovered (Experimental section) and reused for the similar reaction. This process was carried out over three runs without appreciable reduction in the catalytic activity of the catalyst (Table 3).

Experimental

Some of the compounds were new, and some of them were known and their physical and spectroscopic data were compared with those of authentic samples and found to be identical. Melting points were recorded on an electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrophotometer as KBr disks. The ^{1}H NMR (500 MHz) spectra were recorded on Bruker DRX500 spectrometer. The ^{13}C NMR (125 MHz) spectra were recorded on Bruker DRX500 spectrometer. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV.

General procedure for the preparation of carbamatoalkyl naphthols

A mixture of β-naphthol (1 mmol), aldehyde (1 mmol), and methyl carbamate (1.2 mmol), in the presence of silica-supported Preyssler nano particles (0.03 mmol) was heated at 90°C for the indicated time (Table 2). After completion of the reaction, the mixture was cooled to room temperature, and then hot ethanol was added to dissolve the precipitated product. The catalyst was filtered and the filtrate evaporated. Then, the solid product was purified by recrystallization from aqueous EtOH.

Table 3. The comparison of efficiency of Preyssler nano particles in the synthesis of carbamatoalkyl naphthols after three times.

		Yield%[a]/run		
Entry	Ar	First	Second	Third
4a	C_6H_5	84	82	79
4c	4-ClC_6H_4	88	85	84
4h	4-$O_2NC_6H_4$	91	87	85

[a]Isolated yields.

Recycling of the catalyst

The catalyst was recovered by filtration, was dried and reused for three times in reactions. The obtained results are summarized in Table 3. As it is shown in this table there is not any significant loss of activity in using recycled catalyst in this reaction.

Spectral data for new compounds

Methyl [(2-hydroxynaphthalen-1-yl)(2-methylphenyl) methyl]carbamate ***4e***. ^{1}H NMR (DMSO-d_6, δppm): 2.21 (s, 3H, CH_3), 3.51 (s, 3H, OCH_3), 6.79 (d, 1H, $J=8.5$ Hz, CH), 7.05 (t, 1H, $J=6.5$ Hz, arom-H), 7.08–7.21 (m, 4H, arom-H), 7.25 (t, 1H, $J=7.5$ Hz, arom-H), 7.34 (t, 1H, $J=7.6$ Hz, arom-H), 7.67 (br, 1H, NH), 7.75 (d, 1H, $J=8.8$ Hz, arom-H), 7.79 (d, 1H, $J=8.0$ Hz, arom-H), 7.92 (d, 1H, $J=8.6$ Hz, arom-H), 9.95 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, δppm): 154.8, 153.4, 146.5, 136.2, 133.1, 131.8, 131.2, 128.8, 128.3, 127.4, 126.6, 126.2, 124.8, 122.3, 121.7, 117.9, 117.2, 52.4, 44.6, 23.6; IR (KBr disc): υ 3427 (NH), 3226 (OH), 1686 cm^{-1} (C=O); MS, *m/z*: 321 (M^+).

Methyl [(2-hydroxynaphthalen-1-yl)(2-nitrophenyl)methyl]carbamate ***4f***. ^{1}H NMR (DMSO-d_6, δppm): 3.56 (s, 3H, OCH_3), 7.05 (d, 1H, $J=8.8$ Hz, CH), 7.23–7.30 (m, 2H, arom-H), 7.42 (t, 1H, $J=7.8$ Hz, arom-H), 7.47 (t, 1H, $J=7.5$ Hz, arom-H), 7.58 (d, 1H, $J=7.6$ Hz, arom-H), 7.63 (t, 1H, $J=7.5$ Hz, arom-H), 7.74 (t, 2H, $J=8.6$ Hz, arom-H), 7.79 (d, 1H, $J=8.0$ Hz, arom-H), 7.87–7.95 (m, 2H, arom-H & NH), 9.80 (s, 1H, OH); ^{13}C NMR (DMSO-d_6, δppm): 157.3, 154.5, 149.5, 137.3, 133.7, 133.0, 130.8, 129.9, 129.3, 129.0, 128.6, 127.5, 124.9, 123.4, 123.3, 119.3, 116.9, 52.5, 48.7; IR (KBr disc): υ 3416 (NH), 3271 (OH), 1684 cm^{-1} (C=O), 1522 & 1341 (NO_2); MS, *m/z*: 352 (M^+).

Conclusion

In conclusion, we have reported a new catalytic method for the synthesis of carbamatoalkyl naphthols with aromatic aldehydes, β-naphthol, and methyl carbamate in the presence of silica-supported Preyssler nano particles as efficient, reusable, and eco-friendly heterogeneous catalyst. The catalyst can be reused after a simple work-up, with a gradual decline of their activity being observed. High yields, short reaction times, simplicity of operation, and easy work-up are some advantages of this protocol.

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