Sodium 30-tungstopentaphosphate as a green and novel nanocatalyst: synthesis and study of application

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Abstract: Encouraged by our recent success in work with POMs as green catalysts, we have developed our research in field of nanotechnology. Sodium 30-tungstopentaphosphate, so called Preyssler anion, nanoparticles were synthesized and the morphology and size of these nanoparticles were characterized using, transmission electron microscopy (TEM), scanning electron microscopy(SEM), X-ray diffraction(XRD) and IR spectroscopy. The photodegradation of methyl orange, synthesis of 4(3H)-quinazolinones, synthesis of isobenzofuran-1(3H)-ones , rapid and efficient synthesis of 4(3H)-quinazolinones under ultrasonic irradiation, synthesis of bis(indoly)alkanes under ultrasonic irradiation and synthesis of 1,3-diaryl-5-spirohexahydropyrimidines were selected to estimate the catalytic activity of the synthesized nanoparticles and found to be excellent.

Key-Words: Nanocatalyst, Nanoparticle, Silica-supported, Heteropolyacid, Polyoxometalate, Preyssler.

1 Introduction

Over the last decade, due to the unique properties of nanoparticles along with their novel properties and potential applications in different fields [1] the synthesis and characterization of catalysts with lower dimension has become an active topic of research. As the particle size decreases, the relative number of surface atoms increases, and thus activity increases. Moreover, due to quantum size effects, nanometer-sized particles may exhibit unique properties for a wide range of applications[2]. Along this line, polyoxometalates (POMs) are attracting much attention as building blocks for functional composite materials because of their interesting nanosized structures[3].They are ideal models for the construction of hybrid systems, so they are regarded as the potential candidates to be transformed into nanometer-sized materials. In recent years, considerable effort has been devoted to the design and controlled fabrication of nanostructured POMs for using in green reactions. This interest has resulted in the development of numerous protocols for the synthesis of nanostructured materials over a range of sizes. Therefore the field of nano POMs and their applications continue to attract significant attention, so the number of publications and patents continue to grow, and new researchers are entering the field. Thus, plenty of room exists for expanding the exploration of the opportunities for these materials and further exploring, so developing new POMs is still a challenge for POM chemistry.

However, in spite of extensive investigations on synthesis and characterization of Keggin-type nanocatalysts[4,5], the synthesis of sodium 30-tungstopentaphosphate nanocatalysts has been largely overlooked. Recently we have explored the application of Preyssler catalyst in various organic reactions. In our attempt to use POMs as catalysts in organic reactions, we reported that Preyssler-type heteropolyacid [NaP5W30O110]14-, shows good catalytic reactivity[6-12]. Encouraged by our recent success in work with POMs as green catalysts, we have developed our research in field of nanotechnology [13,14].

Considering many reports on the modification of heteropolyacids by supporting them on silicagel[15], and due to the unique properties of nanoparticles along with their novel properties and potential applications in different fields[1], we decided to synthesis of silica-supported Pyressler nanoparticles. It was hoped that
this would modify the catalytic activity of the Preyssler-type heteropolyacid. This would hopefully enable us to investigate the catalytic behavior of this proposed new nanocatalyst in the different reactions. In this present work we were studied synthesis and characterization of silica-supported Preyssler nanoparticles and its catalytic activity for photodegradation of methyl orange, synthesis of 4(3H)-quinazolinones, synthesis of isobenzofuran-1(3H)-ones, rapid and efficient synthesis of 4(3H)-quinazolinones under ultrasonic irradiation, synthesis of 1,3-diaryl-5-spirohexahydropyrimidines and synthesis of bis(indolyl)alkanes under ultrasonic irradiation.

2 Results and Discussions

2.1 Synthesis and characterization of silica-supported Preyssler nano particles

A Pryessler acid is a highly acidic catalyst with excellent catalytic activity in a variety of acid catalyzed reactions [6-12]. The catalyst consists of an anion with a formula of \([\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}\) which has an unusual five-fold symmetry achieved by fusion of five \(\{\text{PW}_{6}\text{O}_{22}\}\) groups. The central sodium ion lies not on the equator of the anion but in a plane roughly defined by oxygen atoms of the phosphate groups. The presence of the sodium cation reduces the overall anion symmetry from \(\text{D}_{3h}\) to \(\text{C}_{5v}\) [16].

Silica-supported Preyssler nano structures were obtained through a micro emulsion method. Although this procedure has been reported previously, this method has never been reported for the synthesis of Preyssler nano structures with different morphologies. The morphology of the product was found to be strongly dependent on the reaction conditions such as concentration and reaction time. In addition, in the same reactions under specific reaction conditions, only spherical nano particles could be obtained. The sizes and morphology of products were controlled by changing the water to surfactant, sodium bis (2-ethylhexyl) sulfosuccinate molar ratio (S) and reaction time. For a short time, the tubular structure prevails, whereas the spherical shapes dominate at longer times. When the concentration was kept at \(S=3\) and reaction time was raised to 30 h, the spherical structures only were obtained (Fig. 1). A mixture of nano wire and nano spherical structures were obtained at \(S=3\) and 12 h (Fig. 2).
The reason is not clear for us now, but can be attributed to the particular conditions and time. When the reaction time was 18 h (S=3), the fraction of nano wire increased evidently, so the nano wires with diameter of about 100 nm were only obtained (Fig. 3).

Fig.3: TEM images of the synthesized nano structures S=3, time = 18 h.

One explanation for the shape changes can be attributed to the meta stable states, which could spontaneously change into an equilibrium state under reaction conditions, which is in agreement with the observations [17]. The heteropolyacid H14[NaP3W30O110] in the SiO2 nano particles was confirmed by infrared spectroscopy as shown in Fig. 4.

Fig. 4: Infrared spectroscopy of Preyssler heteropolyacid in nano form (A) and bulk form (B).

2.2 Catalytic performance of silica–supported Preyssler nanoparticles

A literature survey shows that the synthesis and catalytic activity of the Preyssler nanocatalyst has not been studied extensively, and has been largely overlooked. In continuation of our works with Preyssler catalyst, it was of great interest to synthesize a nano Preyssler structure and use this nanocatalyst in different reactions. We report in this section, for the first time, the catalytic performance of nano structured Preyssler catalysts supported on silica in some of organic reactions.

2.2.1 Photodegradation of methyl orange

The photodegradation of methyl orange, in a designed photo reactor by research team was performed as a test reaction to estimate the catalytic activity of these nano structures. We designed a photo reactor and checked the intensity changes of UV band in methyl orange in a photocatalytic reaction. The degree of methyl orange decolorization was used as a measurement for photocatalytic activity.

The photodegradation of methyl orange solution with various amounts of nano catalyst were analyzed including: 5 × 10^{-6}, 1 × 10^{-5}, 1.5 × 10^{-5} and 3 × 10^{-5} moles. The first-order constants are listed in Table 1.

<table>
<thead>
<tr>
<th>Moles of the catalyst</th>
<th>5×10^{-6}</th>
<th>1×10^{-5}</th>
<th>1.5×10^{-5}</th>
<th>3×10^{-5}</th>
</tr>
</thead>
<tbody>
<tr>
<td>k×10^{-2}(s^{-1})</td>
<td>3.75</td>
<td>3.80</td>
<td>5.29</td>
<td>6</td>
</tr>
</tbody>
</table>

It is inferred from this study that the rate increases with an increase in the amount of catalyst, obviously due to the higher number of photocatalytically active sites. The UV results for under optimum conditions are shown in Fig. 5. This figure shows that methyl orange solution can be degraded under UV light in the presence of Preyssler nano catalyst. After 40 minutes, the total absorption of methyl orange decreased and 95% decolorization was obtained.
We observed that all of the synthesized nano structures exhibit excellent photo catalytic activity when exposed in UV irradiation. The remarkable degradation of methyl orange in the presence of this nano catalyst indicates that the treatments of other organic pollutants could be performed in the presence of this catalyst, in order to obtain a perfect photodegradation degree. This catalytic activity can also be extended to the other catalytic reactions.

2.2.2. Synthesis of 4(3H)-quinazolinones

The quinazolinone core and its derivatives form an important class of bioactive molecules, with useful therapeutic and pharmacological properties, such as anti-inflammatory, anticonvulsant, antihypertensive and antimalarial activity [18]. Several bio-active natural products including febrifugine and isofebrifugine contain a quinazolinone moiety and possess antimalarial activity [19].

![Scheme 1](image)

The results of the synthesis of 4(3H)-quinazolinones in the presence of silica-supported Preyssler nanoparticles (scheme 1) are reported in Table 2.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R'</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>m.p. (°C)</th>
<th>Lit. m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>C₂H₅</td>
<td>15</td>
<td>98</td>
<td>138</td>
<td>139</td>
</tr>
<tr>
<td>2</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>15</td>
<td>98</td>
<td>147</td>
<td>147</td>
</tr>
<tr>
<td>3</td>
<td>4-Cl</td>
<td>C₂H₅</td>
<td>25</td>
<td>94</td>
<td>181</td>
<td>182</td>
</tr>
<tr>
<td>4</td>
<td>4-Br</td>
<td>C₂H₅</td>
<td>25</td>
<td>91</td>
<td>185</td>
<td>186</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>CH₃</td>
<td>25</td>
<td>96</td>
<td>139</td>
<td>139</td>
</tr>
<tr>
<td>6</td>
<td>CH₃</td>
<td>CH₃</td>
<td>25</td>
<td>97</td>
<td>147</td>
<td>147</td>
</tr>
<tr>
<td>7</td>
<td>4-Cl</td>
<td>CH₃</td>
<td>35</td>
<td>92</td>
<td>182</td>
<td>182</td>
</tr>
<tr>
<td>8</td>
<td>4-Br</td>
<td>CH₃</td>
<td>35</td>
<td>90</td>
<td>186</td>
<td>186</td>
</tr>
</tbody>
</table>

Yields refer to isolated products.

Lower yields and longer reaction times were obtained for anilines with electron-withdrawing groups, namely 4-bromo-aniline and 4-chloro-aniline. It is presumed that the electron-withdrawing groups on aniline may reduce the nucleophilicity of aniline.

Combining the advantages of ultra sonic irradiation and nanotechnology, we design a new method for synthesis of 4(3H)-quinazolinone derivatives using silica-supported Preyssler nano particles under ultra sonic irradiation. We were studied a simple method for synthesis of 4(3H)-quinazolinone from reaction of 2-amino-benzamide, acylchlorides in the presence of catalytic amounts of $\text{H}_{14}\text{NaP}_{5}\text{W}_{30}\text{O}_{110}/\text{SiO}_2$ under ultra sonic irradiation (Scheme 2).

![Scheme 2](image)

The results are summarized in Table 3. As it is shown in this table, both aliphatic and aromatic acyl chlorides led to desired 4(3H)- quinazolinone under ultra sonic irradiation. Benzy1 chlorides with electron withdrawing and electron donating groups gave 4(3H)- quinazolinones in high yields.
Table 3: Synthesis of 4(3H)-quinazolinones using H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]/SiO$_2$ under ultra sonic irradiation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Time (min)</th>
<th>Yield%$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>Ph</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>4-MePh</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>4-ClPh</td>
<td>7</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td>4-NO$_2$</td>
<td>10</td>
<td>88</td>
</tr>
</tbody>
</table>

$^a$ Yields refer to isolated products.

2.2.3 Synthesis of bis(indolyl)alkanes

The development of bis(indolyl)alkane synthesis has been of considerable interest in organic synthesis because of their wide occurrence in various natural products possessing biological activity and usefulness for drug design [20]. Bis(indolyl)alkane is known to promote estrogen metabolism in both women and men is expected to have an application in the prevention of breast cancer [21]. Several catalysts have been used for the preparation of these compounds such as lanthanide triflate [22], FeCl$_3$ [23], HOAc [24], molecular iodine [25], indiumtrichloride [26], trifluoroacetic acid [27], copper(II) bromide [28], and trichloro-1,3,5-triazine [29].

To develop the application of nano POMs in organic reactions we were studied the synthesis of bis(indolyl)alkanes from the reaction of indoles with aldehydes in the presence of a catalytic amount of silica-supported Preyssler nanoparticles under ultra sonic irradiation (Scheme 3).

The results are summarized in Table 4.

Table 4: Synthesis of bis(indolyl)alkanes derivatives catalyzed by (H$_{14}$ [NaP$_5$W$_{30}$O$_{110}$])/SiO$_2$ under ultra sonic condition.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>R’</th>
<th>R&quot;</th>
<th>Time (min)</th>
<th>Yield%$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>5</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>H</td>
<td>4-OH</td>
<td>15</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>H</td>
<td>4-Cl</td>
<td>5</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>H</td>
<td>3-NO$_2$</td>
<td>3</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>H</td>
<td>4-Me</td>
<td>7</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>Me</td>
<td>H</td>
<td>4-OMe</td>
<td>15</td>
<td>88</td>
</tr>
<tr>
<td>7</td>
<td>Me</td>
<td>H</td>
<td>3-NO$_2$</td>
<td>15</td>
<td>89</td>
</tr>
</tbody>
</table>

$^a$ Yields refer to isolated products.

As it is shown in this table for both aldehydes with electron donating and electron withdrawing groups the yields are high. For comparison, this reaction was carried out under stirring condition in ethanol at room temperature. In the same conditions, ultra sonic irradiation led to relatively higher yields and shorter reaction times. It is presumed that the efficiency using ultra sound irradiation is due to the cavitations phenomena, the energy being more efficiently transmitted to the substrates compared to the reactions performed under silent condition at room temperature. On the other word, the cavitation mediated by ultra sonic irradiation can cause extension of the surface area available for reaction.

2.2.4 Synthesis of 1,3-Diaryl-5-spirohexahydropyrimidines

Various natural products and pharmaceutical agents containing the hexahydropyrimidine moiety exhibit a broad range of biological activities[30]. N-Substituted hexahydropyrimidines are synthetic intermediates for spermidinenitroimidazole drugs for the treatment of A549 lung carcinoma [31] and structural units in new trypanothione reductase inhibiting ligands for the regulation of oxidative stress in parasite cells [32].

We were used silica-supported Preyssler nanoparticles H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]/SiO$_2$ as a new and recyclable catalyst for the preparation of 1,3-diaryl-5-spirohexahydropyrimidines via a one-pot condensation of anilines, formaldehyde, and cyclohexanone(scheme 4).
Table 5: Synthesis of 1,3-diaryl-5-spirohexahydropyrimidines

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Amine</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>Aniline</td>
<td>60</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>4-Methylaniline</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>3,4-Dimethylaniline</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>3-Chloroaniline</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>H</td>
<td>4-Bromoaniline</td>
<td>51</td>
</tr>
<tr>
<td>6</td>
<td>CH3</td>
<td>4-Methylaniline</td>
<td>73</td>
</tr>
<tr>
<td>7</td>
<td>CH3</td>
<td>3,4-Dimethylaniline</td>
<td>75</td>
</tr>
</tbody>
</table>

*Yields refer to isolated products.*

To obtain the optimum amount of catalyst for this reaction, various amounts of catalysts were used. Using 0.1 mol% of catalyst led to longer reaction times and slightly lower yields. Catalyst of more than 0.3 mol% did not change the yields and reaction times, so the 0.3 mol% was selected as the optimum amount of catalyst.

3 Reusability of Catalyst

At the end of the reaction, the catalyst could be recovered by a simple filtration. The recycled catalyst could be washed and subjected to a second run of the reaction process. The yields of reactions after using this catalyst for five times show a slight reduction.

4 Conclusions

In this research, for the first time, the synthesis of sodium 30-tungstophosphate nanoparticles has been carried out using a simple method. The synthesized nanoparticles have shown an excellent catalytic activity for different organic reactions. This catalytic activity can also be extended to the other catalytic reactions. Some advantages of these reactions are: high yield, short reaction times, reusability of catalyst and easy work up procedure. The advantages of this method are reusability of catalyst, easy work up procedure and high yields.

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