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Preyssler Heteropolyacid Supported on Nano-SiO₂: A Green and Reusable Catalyst in Selective Oxidation of Benzyl Alcohols to Benzaldehydes

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Preyssler Heteropolyacid Supported on Nano-SiO$_2$: A Green and Reusable Catalyst in Selective Oxidation of Benzyl Alcohols to Benzaldehydes

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An efficient, improved, and environmentally benign procedure for catalytic oxidation of benzyl alcohols to the corresponding benzoaldehydes was developed in the presence of nano-SiO$_2$-supported Preyssler heteropolyacid (HPA), both in thermal conditions and under microwave irradiation. Silica nanostructures were obtained through a sol–gel method and were characterized by transmission electron microscopy and powder X-ray diffraction. Nano-SiO$_2$-supported Preyssler HPA was synthesized by an impregnation method and confirmed by infrared spectroscopy. In catalytic reactions, the effects of various parameters such as catalyst loading, catalyst amount, temperature, and reaction time were studied and the optimum conditions were obtained.

Keywords: benzyl alcohols, catalyst, heteropolyacid, nano-SiO$_2$-supported, Preyssler

INTRODUCTION

The recent advances in nanotechnology, particularly when coupled with modifying of organic reactions, have opened new avenues for catalytic technology. As an example to explain its potential significance, heterogeneous catalysis was cited as a successful application that has great benefits for society. Thus, it is reasonable to expect that the explosion in new developments in nanoscience and nanotechnology would have an important effect in nanocatalysis field. Therefore, it is necessary to develop new catalysts. The current push to develop environmentally benign nanocatalysts has led to much research in the area of solid acids.[11]

Solid heteropolyacids (HPAs) and their derivatives have been intensively studied because they can be used as excellent acidic, redoxidation, and bifunctional catalysts in catalytic reactions.[2–4] In this area, increasing attention has been paid to searching for preparing supported HPA catalysts. Efforts have also been made to study the support of HPAs on suitable nano supports.[5,6] The use of supported HPAs increases the specific surface area of the catalysts and modifies their catalytic properties. Catalytic properties can increase using nano supports. Thus, immobilization of HPAs on a number of supports was extensively studied. Silica, alumina, and active carbon were the most investigated systems.[7–11] It has been found that HPAs supported on SiO$_2$ are most stable. This is due to their high thermal stability, unique pore system, and numerous possibilities for modifying their composition, morphology, and sorption properties.

The objective of this study is to improve and modify the catalytic properties of Preyssler catalyst, with formula of H$_{14}$[NaP$_5$W$_{30}$O$_{110}$], via supporting on nano-SiO$_2$ in oxidation of benzylic alcohols. The structure of the anion [NaP$_5$W$_{30}$O$_{110}$]$^{14-}$ is a cyclic assembly of five {PW$_6$O$_{22}$} groups. The unusual fivelfold symmetry of this anion is achieved by fusion of five {PW$_6$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.[12] Catalysis using Preyssler HPA has been widely developed in a broad range of organic synthesis and environmentally benign catalysis during the past few years, by our research group.[13–22] Good yields, high selectivity, economic convenience, ease of work-up, high hydrolytic and thermal stability, and high catalytic activity of Preyssler HPA have motivated increasing potential for nanocatalysis in organic synthesis and environmentally benign catalysis.[23–29]

Recently, we developed an efficient method for the oxidation of benzyl alcohols to corresponding carbonyl compounds using...
Preyssler catalyst in the bulk form. We studied these reactions in both thermal and photochemical conditions.[20,30] In all cases benzaldehydes were the major and benzoic acids were the minor reaction products. Thus, we were inspired to access the major product without any by product, using other forms of Preyssler catalyst.

The oxidation of alcohols to aldehydes is a frequently used transformation for the synthesis of pharmaceuticals, flavors and fragrances. Thus, high selectivity and pure products are very important prerequisites for ease of product work-up and lower cost.[31]

Therefore, in recent years, various improved methodologies using different oxidants and catalysts have been reported in the literature.[32,33] However, these methods are associated with drawbacks such as the use of strong acidic/basic conditions, use of toxic and heavy metals, high cost, large excess of oxidants, and lower yields of the benzaldehydes because of benzoic acids formation. To the best of our knowledge there is no literature report on the use of nano-silica-supported Preyssler HPA as catalyst in oxidation of benzyl alcohols to benzaldehydes as the major product.

We were particularly interested to evaluate the condition favoring oxidation of different benzyl alcohols to benzaldehydes as the major product using the Preyssler HPA over nano-SiO2. Interestingly, in contrast to the earlier reported procedures for the oxidation of benzyl alcohols using Preyssler catalyst in the bulk form,[20,30] we obtained benzaldehydes as the major products in higher yields and shorter times, when used nano-SiO2-supported Preyssler HPA.

We carried out the successful oxidation of benzyl alcohols both in thermal conditions and under microwave irradiation using different loading of nano-SiO2 and SiO2-supported Preyssler catalyst.

### EXPERIMENTAL

#### Chemicals and Instruments

All of the chemicals were commercially available. A Milestone APC-55E microwave was used for all of the experiments. Infrared (IR) spectra were recorded on a Buck 500 scientific spectrometer (KBr pellets).

The particle size and shape of nanostructures of SiO2 were observed by transmission electron microscopy (TEM; LEO 912 AB). The x-ray diffraction (XRD) profiles of the samples were obtained using a PW 3710-Philips powder diffractometer (Cu Kα irradiation). Gas–liquid chromatography (GLC) analysis was performed on a Pu 4500 gas chromatograph with flame ionization detector (FID).

##### Synthesis of SiO2 Nanoparticles

The materials used in this work include tetraethyl orthosilicate (TEOS) (Merck, 98%) as the SiO2 precursor. Besides the main precursor, nitric acid (Arman Sina, 65%) and double-distilled water were used for peptization and solvent, respectively.

The sol–gel precursor solution was obtained by mixing tetraethyl orthosilicate (TEOS) and ethanol with specific molar ratios of ethanol to TEOS. The mixture was stirred using magnetic stirring. The certain pH value (as mentioned in Table 1) forms a clear solution. The molar ratio water to TEOS was chosen according to the Table 1. After the specified solution was obtained, it was poured in a clean container and left in ambient temperature for gelation. After the gel was formed, the gelation time was calculated for the sample. The final step in the process consisted of drying the sample (as shown in Table 1).

#### Catalyst Preparation

$H_{14}[NaP_{5}W_{30}O_{110}]$ was prepared according to our earlier work.[13] For the preparation of supported catalyst, 2.5 g of the synthesized nanosilica was suspended in 20 mL of water and then to this suspension the heteropolyacid in different loadings of tungsten was added. After stirring the heterogeneous solution–support mixture, the solvent was evaporated, samples were dried at 120°C, and the catalysts were calcined at 250°C in a furnace prior to use.

##### General Procedure

All reaction mixtures were refluxed in a 10-mL two-necked round-bottom flask equipped with magnetic stirrer, reflux condenser, and thermometer. In all cases, catalyst was added to the mixed solvent (acetonitrile on water) and benzyl alcohol ($10^{-3}$ mol). The reaction mixture was stirred and refluxed for mentioned times and temperatures. At equal intervals, 30% hydrogen peroxide (0.211 mol) was added to the final mixture. After cooling to room temperature, the mixture was filtered and analyzed by gas chromatography (GC).

Under microwave irradiation, benzyl alcohol ($10^{-3}$ mol), catalyst (0.03 g), and hydrogen peroxide (6 mL) were mixed thoroughly in a small beaker. The reaction mixture was placed in a microwave oven and irradiated for 3 min. After cooling to room temperature and filtering of the mixture, the procedure was the same as above.

### RESULTS AND DISCUSSION

Silica nanostructures were obtained through a sol–gel method. In this study, the gelation time is defined as the time...
between pouring the solution in the container and the time at which the solution ceases to discernibly flow under the influence of gravity. The conditions used were shown in Table 1 (Experimental section). The obtained nanostructures were characterized by TEM as shown in Figure 1. This figure shows 40-nm spheres.

Figure 2 shows powder x-ray diffraction (XRD) patterns of the synthesized samples. The patterns of the spherical products confirm the SiO$_2$ structure.

The heteropolyacid $\text{H}_{14}[\text{NaP}_3\text{W}_{30}\text{O}_{110}]$ in the SiO$_2$ nanoparticle was confirmed by infrared spectroscopy as shown in Figure 3. The asymmetric stretching frequency of the terminal oxygen is observed at 960 cm$^{-1}$ and the P–O asymmetric stretching frequency 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. These bands demonstrate that $\text{H}_{14}[\text{NaP}_3\text{W}_{30}\text{O}_{110}]$ is preserved in the HPA/SiO$_2$ nanoparticles. In addition, the protonated water of $\text{H}_{14}[\text{NaP}_3\text{W}_{30}\text{O}_{110}]$ also remained in the nanoparticles at 1730 cm$^{-1}$. It could be confirmed that the heteropolyacid $\text{H}_{14}[\text{NaP}_3\text{W}_{30}\text{O}_{110}]$ was successfully
immobilized into the SiO$_2$ nanoparticles since the heteropoly-acid does not react with SiO$_2$ or with water, but it can remain in the silica nanoparticles without appreciable change of the structures.

In order to evaluate the catalytic activities of nano-SiO$_2$-supported Preyssler (H$_{14}$P$_5$/SiO$_2$), for the oxidation of alcohols, the reaction were optimized according to the oxidation of 4-Br benzyl alcohol through the investigation of the important factors, such as loading effect, amount of the catalyst, the temperature, and the reaction time.

First, we investigated for the optimum ratio of alcohol to hydrogen peroxide 30% in CH$_3$CN and H$_2$O as solvent. The results showed that 0.211 mol of H$_2$O$_2$ is the best in 6 h at reflux conditions. It was also observed that the addition of hydrogen peroxide in one portion gave poor yield of the desired product, while its step-by-step addition gave maximum yield.

In order to examine the effect of catalyst loading, the catalyst with different initial Preyssler HPA loadings on nano-silica (10–50%) was prepared. As a model reaction and for obtaining the optimum loading percentage, we selected 4-Br benzyl alcohol. The results are shown in Figure 4.

The results show that the higher yield can be achieved with 30% loading. The yield increases with an increase in catalyst

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**FIG. 4.** Effect of loading percentage on percent yield of benzaldehydes (color figure available online).

**FIG. 5.** Relation of catalyst amount with percent yield of benzaldehydes (color figure available online).
loading from 10% to 30%. This is attributed to the increase in the total number of available active catalytic sites for the reaction.

Higher catalyst loadings (>30%) affected yields and gave lower yield of benzaldehydes, which was attributed to likely further oxidation of alcohol into acid catalyzed by the excess amount of acidic sites. Thus, 30% loading is the optimum condition for this transformation.

After optimizing the percentage loading, we endeavored to optimize the amount of the catalyst. The observations are presented in Figure 5.

Decrease of yields with increase of catalyst amount can be attributed to further oxidation of benzyl alcohols. For further studies, we have examined the catalytic reactions with different loadings for the other benzyl alcohols. The results are shown in Figure 6.

TABLE 2
Comparison between SiO2-supported Preyssler HPA and nano-SiO2-supported Preyssler HPA in catalytic oxidation of benzyl alcohols (under optimum conditions)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alcohol</th>
<th>SiO2-supported Preyssler HPA</th>
<th>Nano-SiO2-supported Preyssler HPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-Br</td>
<td>40</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>4-Cl</td>
<td>31</td>
<td>63</td>
</tr>
<tr>
<td>3</td>
<td>2-Cl</td>
<td>20</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>4-Nitro</td>
<td>19</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>2-Nitro</td>
<td>16</td>
<td>23</td>
</tr>
</tbody>
</table>

FIG. 6. Percent yield of benzaldehydes with different loading of catalyst (color figure available online).

FIG. 7. Yields of benzaldehydes with different amount of the catalyst (color figure available online).
We have also studied the effect of catalyst amount for the mentioned alcohols (Figure 7). Interestingly, in all cases the observed yields were higher with 30% loading and 0.03 g.

A comparison between obtained yields with commercial SiO₂ and nano-SiO₂ as support shows that yields are lower with commercial SiO₂. The results are shown in Table 2.

As the particle size decreases, the relative numbers of surface atoms increases, and thus the activity increases. In optimum conditions (30% loading and 0.03 g catalyst) the effect of the time was studied in the time range of 6–10 h and the results are presented in Figure 8.

Alcohol conversion increases with increases in the reaction time from 1 to 6 h and it decreases thereafter. This may be due to the nonavailability of enough oxidant in the reaction mixture after 6 h. This is confirmed by the determination of unreacted hydrogen peroxide by titration method, which shows little oxidant left in the mixture after 6 h.

The effect of temperature on the reaction showed a maximum yield at 80°C (Figure 9).

Higher temperature results in a decrease in the yield. This can be related to the hydrogen peroxide decomposition and further oxidation of benzyl alcohols.

To evaluate that effect of catalyst, the blank oxidation of alcohols was carried out with hydrogen peroxide alone under similar reaction conditions without using catalyst. The oxidation was found to be very slow and gave very poor yield.

**Microwave Irradiation**

In general, most organic reactions have been heated using traditional heat transfer equipment such as oil baths, sand baths, and heating jackets. These heating techniques are, however, rather slow and a temperature gradient can develop within the sample. In addition, local overheating can lead to product, substrate, and reagent decomposition. In contrast, in microwave dielectric heating, the microwave energy is introduced into the
chemical reactor remotely and direct access by the energy source to the reaction vessel is obtained.

To determine the scope of this new catalytic system, all of the alcohols were oxidized under the optimized conditions in solvent-free conditions under microwave irradiation. The results are summarized in Figure 10. It is clear that all of the alcohols were easily oxidized to the corresponding aldehydes in short times (2–3 min).

Besides the efficient energy input that microwaves can provide to the reaction mixtures, a chemical activation effect cannot be discounted. During the irradiation, there is a total or partial alignment of dipolar molecules and/or ionic species with the direction of the electrical field. Such an alignment may then favor interactions between reactants and may lead to shorter and more efficient reactions.

Reusability of the Catalyst

The recycling of the catalyst is very important for industrial applications.

In order to further evaluate performance of the catalyst, reused the experiments were repeated. The catalyst was filtered at the end of the reaction. The obtained precipitate was washed with water and dried. The catalyst was reused for the next run under the same conditions. The results indicated that the activity of the catalyst was not affected even at the third run with the reused catalyst. This phenomenon implied that the catalyst can be efficiently recovered and recycled. By this token, the catalyst possesses potential application value in industry.

CONCLUSIONS

Nano-SiO₂-supported Preyssler catalyst produced by an impregnation method has been found to be highly efficient for selective oxidation of benzyl alcohols to benzaldehydes with H₂O₂ as oxidant both at reflux conditions and under microwave irradiation. This material catalyzes the oxidation of benzyl alcohols to benzaldehydes as the main product. The loading percentage and catalyst amount as well as the reaction time and temperature are important factors. This method is not only economically viable but will also be environmentally friendly in commercial applications. This catalyst is easily recycled and reused, that shows its highly potential application value in industry.

REFERENCES