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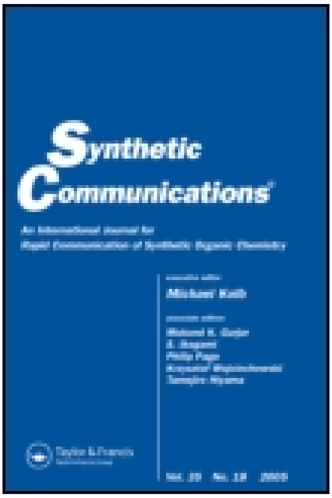

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# Green and Reusable Synthetic Procedure for Pyridine N-Oxides Catalyzed by a Lacunary Polyoxometalate

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# GREEN AND REUSABLE SYNTHETIC PROCEDURE FOR PYRIDINE N-OXIDES CATALYZED BY A LACUNARY POLYOXOMETALATE

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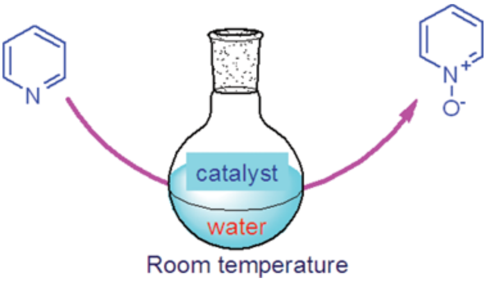
## GRAPHICAL ABSTRACT



**Abstract** *A lacunary Keggin polyoxometalate of* $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ *was used as an effective and reusable catalyst for pyridine oxidation. Good yields of pyridine N-oxides were obtained in this catalytic system with hydrogen peroxide in water under mild conditions.*

*[Supplementary materials are available for this article. Go to the publisher's online edition of* Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

**Keywords** Catalysis; green; polyoxometalate; pyridine-N-oxide; reusable

## INTRODUCTION

Pyridine N-oxides are important and versatile synthetic intermediates, which are used widely in fields of chemistry and biology. They can be used as protecting groups, auxiliary agents, oxidants, catalysts, surrogates for heterocyclic boronic acids, and ligands in metal complexes.[1–5] In addition, pyridine N-oxide derivatives have been reported to represent a new class of anti-HIV compounds.[6] In the past, pyridine N-oxides were usually prepared by noncatalytic oxidation of pyridines using strong oxidants.[7–9] The oxidation of pyridines was also represented high

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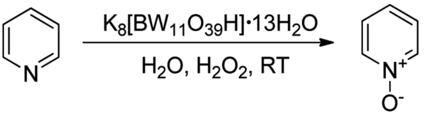


**Scheme 1.** Process of pyridine oxidation in water catalyzed by $K_8[BW_{11}O_{39}H]\cdot 13H_2O$.

activity in the presence of peracetic acid or acetic acid.[10,11] However, the by-product for pyridine oxidation in the presence of acetic acid or peracetic acid is acetic acid, which is corrosive for the equipment and environment. Besides, peracetic acid used as oxidant is also dangerous during the reaction because of risk of explosion. For green chemistry, hydrogen peroxide as a mild oxidant is used widely in catalytic oxidations. Catalytic oxidation using homogeneous catalysts with hydrogen peroxide of pyridines to N-oxides has received much attention in recent years. Such catalysts include AcOH/$H_2O_2$,[12] $MeReO_3/H_2O_2$,[13] trifluoroacetic anhydride (TFAA)/$H_2O_2$,[14] and $Tf_2O/Na_2CO_3\cdot 1.5H_2O_2$.[15] To overcome the difficulties of the catalyst recycling, several heterogeneous catalysts including perfluoroketone-silicate,[16] TS-1,[17] and $V_xSi_{4x}O_{6.4x}$[18] were also demonstrated for the oxidation of pyridines. However, in these recovered catalytic systems, high reaction temperature and poisonous organic solvents are usually required, so the design of a new recyclable, effective, and mild catalytic system for the oxidation of pyridine is necessary.

Polyoxometalates (POMs) have been used widely as effective catalysts for liquid oxidations with hydrogen peroxide, such as olefin epoxidation, alcohol oxidation, and so on.[19–30] Reports about oxidation of pyridines using POMs with hydrogen peroxide are less,[5,31,32] and high reaction temperatures or poisonous organic solvents were necessary in these procedures. Recently, a vanadium-substituted POM, $K_6[PW_9V_3O_{40}]\cdot 4H_2O$, was used as a recyclable and effective catalyst for the oxidation of pyridines.[33] The reactions were successfully conducted in water under mild conditions. However, the substituted metal of vanadium was necessary in the POM catalyst. To expand the applications of POMs in water for oxidation of pyridines under mild temperature, here we report a nonsubstituted lacunary POM ($K_8[BW_{11}O_{39}H]\cdot 13H_2O$) as an effective catalyst for the oxidation of pyridines. The oxidation was carried out in water under room temperature, and good yields of N-oxides were obtained. Recently, some significant progress has been achieved, ranging from oxidation of organic compounds, which is environmentally benign, or green catalytic oxidation using the big class of POMs as catalysts, especially for detoxification of toxic industrial chemicals[34] and photocatalytic water oxidation.[35] The system in this article is consistent with green environmental science; the solvent of water and the mild reaction temperature (room temperature) is green and environmentally benign. The process is outlined in Scheme 1. The catalyst can be reused several cycles without obvious loss in activity.

## RESULTS AND DISCUSSION

The catalytic oxidations of 4-picoline using different catalysts in water are shown in Table 1. The reaction proceeded very well in water in the presence of a catalytic amount of $K_8[BW_{11}O_{39}H]\cdot 13H_2O$ at room temperature. An excellent yield

**Table 1.** Oxidation of 4-picoline using different catalysts in water[a]

| Entry | Catalyst | Time (h) | Yield[b] (%) |
|---|---|---|---|
| 1 | no | 24 | 5 |
| 2 | $H_3BO_3$ | 24 | 8 |
| 3 | $Na_2WO_4 \cdot 2H_2O$ | 24 | 68 |
| 4 | $H_3BO_3 + Na_2WO_4 \cdot 2H_2O$ | 24 | 65 |
| 5[c] | $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ | 16 | 0 |
| 6 | $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ | 16 | 92 |
| 7 | $K_7PW_{11}O_{39} \cdot 12H_2O$ | 24 | 87 |
| 8 | $K_8[\beta\text{-}SiW_{11}O_{39}] \cdot 14H_2O$ | 24 | 82 |

[a] Reaction conditions: 0.03 mmol catalyst; 3 ml water; 4 mmol substrate; 20 mmol (30% aq.) $H_2O_2$; reaction temperature: room temperature. Assignments of products were analyzed by $^1$H NMR and $^{13}$C NMR.

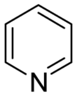
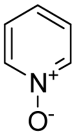
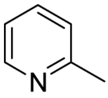
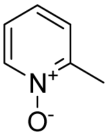
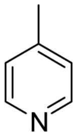
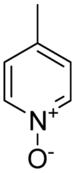
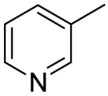
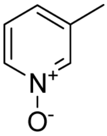
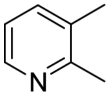
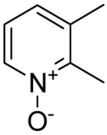
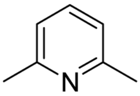
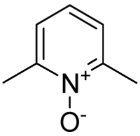
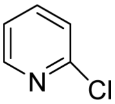
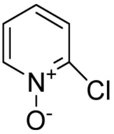
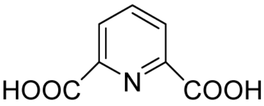
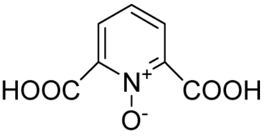
[b] Isolated yields.

[c] Without $H_2O_2$.

of 4-picoline-N-oxide (92%) was obtained with an exclusive selectivity (Table 1, entry 6). Some control experiments were also conducted in water with $H_2O_2$ at room temperature for the oxidation of 4-picoline. Only 5% yield was observed in the absence of catalyst (entry 1), and the reaction was hardly processed without hydrogen peroxide (entry 5). The oxidation proceeded sluggishly using $H_3BO_3$, $Na_2WO_4 \cdot 2H_2O$, or the simple mixture of $H_3BO_3$ and $Na_2WO_4 \cdot 2H_2O$. In addition, some keggin-type POMs (entries 7, 8) were also used, and it was found that they exhibited less activity than $K_8[BW_{11}O_{39}H] \cdot 13H_2O$, indicating the special activity of this lacunary POM.

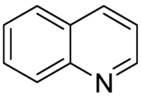
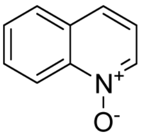
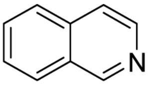
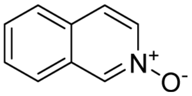
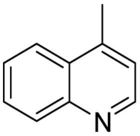
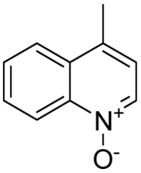
Having obtained these results, we extended this catalytic system to the oxidation of other pyridine derivatives. The results are listed in Table 2. Most of the substrates were successfully oxidized to the corresponding N-oxides in good yields at room temperature. Selectivities to the N-oxides were $\geq$99%. For pyridine, a yield of 95% was obtained within 16 h catalyzed by $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ in water at room temperature (Table 2, entry 1). The substrates of picolines were also examined. It was found that 2-picoline, 3-picoline, and 4-picoline were converted to the corresponding N-oxides in excellent yields with an appropriate reaction time (entries 2–4). Disubstituted pyridine derivatives were also examined in this catalytic system. 2,6-Lutidine and 2,3-lutidine were more difficult to oxidize than monosubstituted pyridines, and the results might be attributed to their comparative hydrophobicity compared with monosubstituted pyridines. We are able to obtain the corresponding N-oxides in excellent yields within 24 h by using $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ as catalyst (entries 5 and 6). The electron-deficient substrate 2-chloropyridine was less reactive, as expected (entry 7). Even if the reaction temperature elevated to 65 °C, 2,6-pyridinedicarboxylic acid was hardly reactive because of its electron-deficient property and the hydrophobic of the substrate (entry 8). The oxidation of quinoline was also determined in water. A poor yield of quinoline-N-oxide was obtained after 24 h of reaction at room temperature in water (not listed here). However, when the reaction temperature increased to 65 °C, quinoline was successfully converted to the N-oxide with an excellent conversion within 7 h (entry 9). This improvement might be partially attributed to the effect of the hydrophobicity of the substrate. The poor solubility of quinoline in

**Table 2.** Oxidation of pyridine derivatives with $H_2O_2$ catalyzed by $K_8[BW_{11}O_{39}H] \cdot 13H_2O$[a]

| Entry | Substrate | Product | Reaction temperature (°C) | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 |  |  | 25 | 16 | 95 |
| 2 |  |  | 25 | 16 | 90 |
| 3 |  |  | 25 | 16 | 92 |
| 4 |  |  | 25 | 24 | 94 |
| 5 |  |  | 25 | 24 | 90 |
| 6 |  |  | 25 | 24 | 93 |
| 7 |  |  | 65 | 6 | 38 |
| 8 |  |  | 65 | 6 | <5 |

(*Continued*)

**Table 2.** Continued

| Entry | Substrate | Product | Reaction temperature (°C) | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| 9 |  |  | 65 | 6 | 90 |
| 10 |  |  | 65 | 6 | 88 |
| 11 |  |  | 65 | 6 | 87 |

[a]Reaction conditions: 0.03 mmol $K_8[BW_{11}O_{39}H] \cdot 13H_2O$; 3 ml water; 4 mmol substrate; 20 mmol (30% aq.) $H_2O_2$; reaction temperature: room temperature. Assignments of products were analyzed by $^1H$ NMR and $^{13}C$ NMR.

[b]Isolated yields.

water at room temperature resulted in an unsuccessful contact between the substrate and the catalyst, but the mass transfer could be significantly improved by elevating the reaction temperature to 65 °C, and thus the performance of the catalyst was improved. This phenomenon was also observed in the oxidation of other quinoline derivatives. Isoquinoline and 4-methyl-quinoline were also oxidized to the corresponding N-oxides with good yields (entries 10 and 11) at 65 °C during 6 h.

To show the efficiency and applicability of this method, our results have been compared with some of the recently reported methods on the oxidation of 4-picoline, which is carried out in water catalyzed by polyoxometalates. As shown in Table 3, some Keggin-type polyoxometalates (entries 1–3) were also used as catalysts for oxidation of 4-picoline, indicating the greater catalytic activity of $K_8[BW_{11}O_{39}H] \cdot 13H_2O$.

**Table 3.** Comparison of results for oxidation of 4-picoline catalyzed by different catalysts

| Catalyst | Reaction temperature (°C) | Reaction time (h) | Yield (%) | Remark |
|---|---|---|---|---|
| $Na_2HPW_{12}O_{40} \cdot xH_2O$ | 25 | 24 | 82 | — |
| $H_4SiW_{12}O_{40} \cdot xH_2O$ | 25 | 24 | 78 | — |
| $K_6H[SiW_9V_3O_{40}] \cdot 3H_2O$ | 25 | 24 | 60 | — |
| $Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$ | 75 | 7 | 43 | Ref. [31], zinc-substituted |
| $K_6[PW_9V_3O_{40}] \cdot 4H_2O$ | 25 | 16 | 92 | Ref. [33], vanadium-substituted |
| $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ | 25 | 16 | 92 | This work, nonsubstituted lacunary |

**Table 4.** Oxidation of 4-picoline using $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ under different solvents[a]

| Entry | Solvent | Yield[b] (%) |
|---|---|---|
| 1 | Ethanol | 47 |
| 2 | Acetonitrile | 40 |
| 3 | Chloroform | 48 |
| 4 | Ethyl acetate | 82 |
| 5 | Water | 92 |

[a] Reaction conditions: 0.03 mmol $K_8[BW_{11}O_{39}H] \cdot 13H_2O$; 3 ml solvent; 4 mmol substrate; 20 mmol (30% aq.) $H_2O_2$; reaction temperature: room temperature. Assignments of products were analyzed by $^1H$ NMR and $^{13}C$ NMR.

[b] Isolated yields.

Compared with the reported water-soluble polyoxometalate catalytic systems, our method is superior to the most of the previously reported methods (entries 4–6).

Table 4 shows the solvent effect of oxidation of 4-picoline using $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ at room temperature. It was found that water was proven to be the best solvent for the oxidation. A 92% yield of 4-picoline-N-oxide was obtained catalyzed by $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ in water. The catalytic results were not satisfied in other organic solvents. These results should be attributed to the solubility of the catalyst in these solvents. The catalyst was insoluble in all of the organic solvents because of the components of the catalyst. The catalyst precipitated from water with potassium cation by addition of the potassium chloride, so the catalyst was a "water-soluble" catalyst: It can be dissolved in water but is insoluble in organic solvents. It is noteworthy that this catalytic system based on $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ in water is more effective than other systems.

The catalyst could be reused in this catalytic system. After the reaction, the system was concentrated by evaporation and then the catalyst was recovered from the mixture by the addition of anhydrous ethyl alcohol. The recovered catalyst was washed with anhydrous ethyl alcohol and $Et_2O$ and then used for the next oxidation. The performance of $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ in the oxidation of pyridine is shown in Table 5. After three consecutive reuses, the yield of pyridine-N-oxide obtained with the recovered catalyst was nearly the same as that of the first reaction (95%), indicating that $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ is a reusable catalyst in the oxidation system.

The fresh catalyst of $K_8[BW_{11}O_{39}H] \cdot 13H_2O$, the used catalyst of cycle 1, the used catalyst of cycle 3, and the catalyst treated with hydrogen peroxide were

**Table 5.** Recycling of the catalytic system for the oxidation of 4-picoline[a]

| Entry | Cycle | Selectivity (%) | Yield (%) |
|---|---|---|---|
| 1 | 1 | 99 | 95 |
| 2 | 2 | 99 | 96 |
| 3 | 3 | 99 | 95 |

[a] Reaction conditions: 0.12 mmol $K_8[BW_{11}O_{39}H] \cdot 13H_2O$; 8 ml water; 16 mmol substrate; 80 mmol (30% aq.) $H_2O_2$; reaction temperature: room temperature; reaction time: 16 h.

characterized with Fourier transform–infrared (FT-IR) spectra (the spectrum of the used catalyst of cycle 2 is nearly the same as that of cycle 3). As shown in Fig. 1, there existed differences in IR spectrum between the fresh catalyst and used one, indicating that the structure of the fresh catalyst has been changed during the oxidation. The relative instability of polyoxotungstate anion of $[BW_{11}O_{39}H]^{8-}$ has been reported.[36] The conversions between the species of $[BW_{11}O_{39}H]^{8-}$, $[BW_{13}O_{46}H_3]^{8-}$, and $[B_3W_{39}O_{132}]^{21-}$ are rapid and reversible. The formation of the other heteropolyanions could be observed by treatment of the $[BW_{11}O_{39}H]^{8-}$ aqueous solution. The recovered catalyst after first oxidation is a mixture of several heteropolyanions, so the IR spectrum of it is different from the pure $K_8[BW_{11}O_{39}H] \cdot 13H_2O$. By comparing the spectra of the used catalyst of cycle 1 with the used catalyst of cycle 3, it can be found that their structures were similar, indicating that there were no obvious changes from the first cycle (the spectrum of the used catalyst of cycle 2 is nearly the same as that of cycle 3). An obvious peak at 840 $cm^{-1}$ was appeared in the spectrum of the catalyst treated with hydrogen peroxide (Fig. 1b), which was attributed to $\nu$ (O-O).[19] The characterization of the ultraviolet–visible technique was taken for the structures (shown in the Supporting Information). The spectrum of the first recycled catalyst was obviously different from that of the fresh one, and similar spectra of the used catalyst of cycle 1 and the used catalyst of cycle 3 were obtained. The results were consisted with FT-IR spectra.

There have been many similar cases for the structure changes of POMs during the oxidation with hydrogen peroxide.[32,33] They all have similar procedures, which have been proved by several characterization methods. According to the characterizations and the previous report, we proposed a possible mechanism for oxidation of pyridines catalyzed by $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ in water with hydrogen peroxide (shown in Fig. 2). During the reaction, the catalyst of $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ was treated with hydrogen peroxide in water. The heteropolyanion of $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ became a mixture of

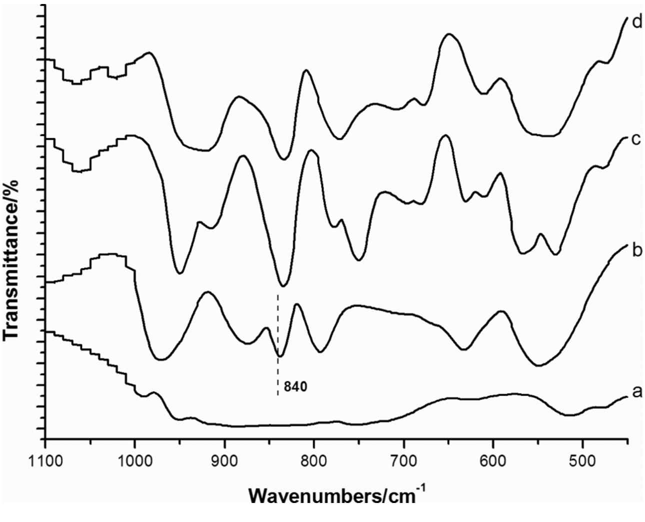


Figure 1. IR spectra of the catalyst before and after oxidation reaction: (a) the freshly prepared catalyst; (b) the catalyst treated with $H_2O_2$; (c) the catalyst of cycle 1; and (d) the catalyst of cycle 3.

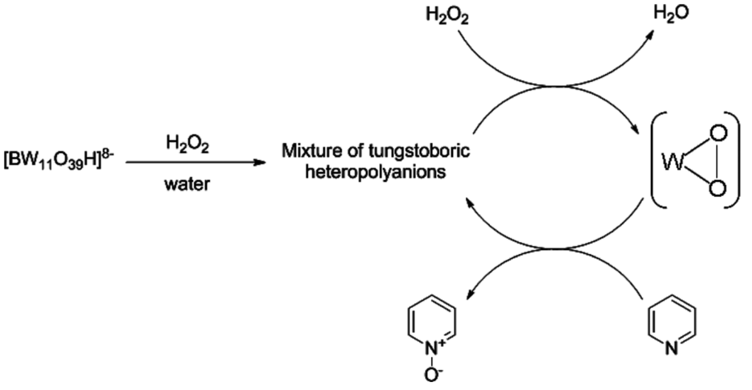


Figure 2. Possible mechanism for oxidation of pyridines catalyzed by $K_8[BW_{11}O_{39}H] \cdot 13H_2O$ in water.

heteropolyanions. Then, the hydrogen peroxide promoted the mixture of heteropolyanions formed the tungsten-peroxo intermediate. The active intermediate is quite active and might be responsible for the oxidation of pyridines to the corresponding N-oxides. Then, the intermediate delivers active oxygen to the substrates and oxidizes pyridines to the corresponding heterocyclic N-oxides. Simultaneously, the mixture of heteropolyanions after losing their active oxygen oxidation was regenerated.

In summary, a green catalytic system for the synthesis of pyridines N-oxides has been developed in water with hydrogen peroxide under room temperature based on a nonsubstituted lacunary polyoxometalate ($K_8[BW_{11}O_{39}H] \cdot 13H_2O$). Pyridine and pyridine derivatives were efficiently oxidized to the corresponding N-oxides in good yields under mild conditions. The catalyst was reused several times without obvious loss in activity. This system is an environmentally friendly and reusable oxidation system for pyridine oxidation.

## EXPERIMENTAL

$K_8[BW_{11}O_{39}H] \cdot 13H_2O$ was synthesized by the procedure reported in Ref.[36] Catalyst (0.03 mmol), $H_2O$ (3 ml), substrate (4 mmol), and $H_2O_2$ (20 mmol, 30% aq.) were charged in the reaction flask, which was first bathed in cold water (about 283 K). The mixture was then stirred at room temperature for 16–24 h. The reaction was detected by thin-layer chromatography (TLC). After the reaction, the system was concentrated by evaporation, and the catalyst precipitated from the mixture after the addition of anhydrous ethyl alcohol. The recovered catalyst, obtained by filtration, was washed with anhydrous ethyl alcohol and diethyl ether and then used for the next oxidation after drying. The filtrate was extracted with dichloromethane. The combined organic layers were dried over anhydrous $Na_2SO_4$, and the pure products were obtained by evaporation or column chromatography. The products were analyzed by $^1H$ NMR and $^{13}C$ NMR.

## SUPPORTING INFORMATION

Full experimental detail and $^1H$ and $^{13}C$ NMR spectra of pyridine-N-oxides can be found via the Supplementary Content section of this article's Web page.

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