

RAPID COMMUNICATION

Aerobic Oxidation of Alcohols to Carbonyl Compounds Catalyzed by N-Hydroxyphthalimide (NHPI) Combined with CoTPP-Zn₂Al-LDH

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Abstract. A catalytic system for the aerobic oxidation of alcohols by N-hydroxyphthalimide (NHPI) combined with cobalt porphyrin intercalated heterogeneous hybrid catalyst (CoTPP-Zn₂Al-LDH) has been developed. The results showed that this catalytic system can effectively catalyze the oxidation of alcohols to the corresponding carbonyl compounds. And the hybrid catalyst can be reused for five times with no appreciable reduction of activity.

Keywords. Hydrotalcite-like compounds; cobalt porphyrin; alcohol oxidation; N-hydroxyphthalimide.

1. Introduction

The selective oxidation of alcohols to the corresponding carbonyl compounds is one of the most important reactions in organic synthesis and fine chemical industries.¹ Numerous methods have been developed for the transformation using varied oxidants, such as KMnO₄, H₂O₂, *t*-butylhydroperoxide, *m*-chloroperbenzoic acid, *etc.* From the sustainable and environmental viewpoints, development of efficient methodology for the oxidation using molecular oxygen as the terminal oxidant without a stoichiometric amount of additives is very attractive.

Since Ishii *et al.*, first found that NHPI could efficiently catalyze the aerobic oxidation of various organic substrates to oxygen containing compounds,² an efficient catalytic method for the low temperature oxygenation of alcohol with dioxygen was developed by using NHPI as a catalyst and a metal salt as co-catalyst. Actually, the co-catalyst plays an important role in accelerating the reaction and affecting the selectivity. Some catalysts, including cobalt salts,³ [Bu₄N]VO₃,⁴ VO(acac)₂,⁵ copper salts,⁶ iron salt,⁷ ceric ammonium nitrate,⁸ acetaldehyde,⁹ ammonium salts¹⁰ and NO₂,¹¹ have been investigated in the reaction, but the homogeneous nature of these catalytic systems leads to the difficulty of recovery of the catalyst and complexity in the process.

In the practical point of view, development of heterogeneous co-catalyst for the NHPI/O₂ system for the

selective oxidation of alcohol to carbonyl compound is still keenly desirable. To the best of our knowledge, only a few heterogeneous catalytic systems have been reported cobalt porphyrin (CoTPP) intercalated ZnAl hydrotalcite (CoTPP-Zn₂Al-LDH) is an efficient heterogeneous catalyst for the oxidation of ketone and alcohol,¹³ where excess additives were needed. In this paper, we are reporting the aerobic oxidation of alcohols by a catalytic system, consisting of NHPI and CoTPP-Zn₂Al-LDH hybrid.

2. Experimental

2.1 Materials

All reagents and solvents were of analytical grade and were obtained commercially. CoTPP-Zn₂Al-LDH was prepared according to our previous reported procedure.^{13b} Quantitative determination of the CoTPP content in the hybrid was performed by inductively coupled plasma analysis (ICP, Varian Vista-AX device). Typically, a CoTPP loading at *ca.* 0.38 mmol g⁻¹ was obtained. No impurities were found in the cyclohexanol by GC-MS (Shimadzu GCMS-2010) analysis before use.

2.2 General procedure for the aerobic oxidation of alcohols using NHPI/O₂/CoTPP-Zn₂Al-LDH system

In a typical experiment, a solution of NHPI (0.6 mmol, 20 mol%) and CoTPP-Zn₂Al-LDH (0.01 mmol of CoTPP content, 30 mg) in PhCN or CH₃CN (10 mL)

*For correspondence

was prepared in a 25 mL round-bottom flask equipped with magnetic stirrer. To this solution alcohol (3 mmol) was added and the resulting mixture was stirred at 100 or 80°C. Then dioxygen was bubbled through the solution at a rate of 20 mL min⁻¹. All the products were identified by GC-MS and quantified at different intervals during the reaction by GC-FID (Shimadzu GC-2010AF).

3. Results and Discussion

In this study, cyclohexanol was selected as the model substrate to optimize the reaction conditions. Firstly, various solvents including dichloroethane (DCE), dioxane (Diox), dimethyl formamide (DMF), acetonitrile (ACN), and cyanobenzene (PhCN), were optimized. With DMF as the solvent, much lower conversion of cyclohexanol was obtained. When dioxane was used as the solvent, the oxidation product from dioxane was observed. Other three solvents exhibited similar activities at 80°C, including low boiling solvents, ACN and DCE. We then investigated the effect of reaction temperature using PhCN as the solvent. Decreasing the temperature significantly reduced the conversion. >90% of conversion could be obtained when the temperature reached 100°C. After optimization of the amounts of NHPI and the catalyst, a high yield of 91% cyclohexanone was obtained without any other by-product. The blank reaction without catalyst showed low conversion (Table 1, entry 12), indicating that the prepared hybrid material performed as catalyst in the reaction.

It has been reported that the phthalimide N-oxyl (PINO) radical is produced from the reaction of O₂ and

NHPI in the presence of metal co-catalyst.¹² In the alcohol oxidation catalyzed by NHPI, the radical is able to abstract a hydrogen atom from the alcohol and accelerate the transformation. We suppose that in the alcohol oxidation catalyzed by NHPI and CoTPP-Zn₂Al-LDH as a co-catalyst, PINO radical would be produced in the oxidation of NHPI by O₂ and the hybrid.

Under the optimized reaction conditions, the scope of the substrates was then examined. Secondary alcohols were firstly investigated in the study. The results (Table 2, entries 2–5) clearly show that both benzylic and aliphatic alcohols can be efficiently oxidized to their corresponding ketones with excellent conversions and yields, markedly higher than the previous reported results.¹² In addition, no other by-products were observed in the oxidation of secondary alcohols, indicating the present system is an efficient method for the selective oxidation secondary alcohols. For the primary alcohols, both aldehyde and acid were observed as the products, because aldehyde was easily oxidized into the corresponding carboxylic acid with high conversion and yield.^{12c} To obtain the higher yield of the corresponding aldehyde, ACN was employed as the solvent and the reaction temperature was decreased to 80°C. In the oxidation of benzyl alcohol, moderate conversion and selectivity were obtained under the preliminary optimized conditions (Table 2, entry 6). Among the aliphatic primary alcohols and the aromatic alcohols with hetero atoms, such as 3-furanmethanol, pyridine-2-methanol and 3-thiophenemethanol, moderate yields of the corresponding aldehydes could also be obtained. It should be noted that, compared with the results without CoTPP-Zn₂Al-LDH, the conversion of the substrates increased under the catalysis with the

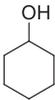
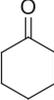
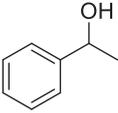
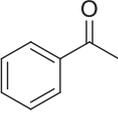
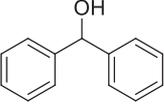
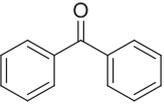
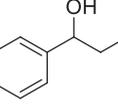
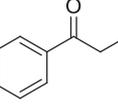
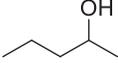
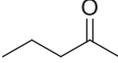
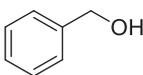
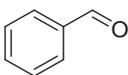
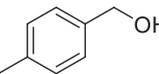
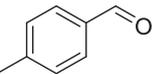
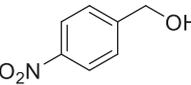
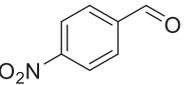
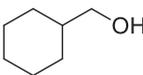
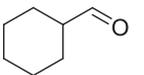
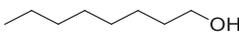
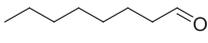
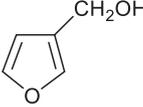
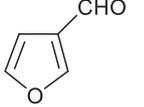
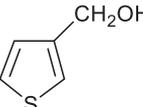
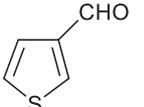
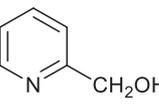
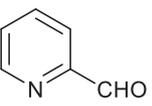
Table 1. Oxidation of cyclohexanol catalyzed by NHPI/O₂/CoTPP-Zn₂Al-LDH system.

| Entry | Solvent | T (°C) ^a | NHPI (mol%) | m (mg) ^b | C (%) ^c |
|-------|---------|---------------------|-------------|---------------------|--------------------|
| 1 | ACN | 80 | 20 | 30 | 41 |
| 2 | Diox | 80 | 20 | 30 | 81 |
| 3 | DMF | 80 | 20 | 30 | <1 |
| 4 | DCE | 80 | 20 | 30 | 66 |
| 5 | PhCN | 80 | 20 | 30 | 45 |
| 6 | PhCN | 100 | 20 | 30 | 91 |
| 7 | PhCN | 60 | 20 | 30 | 33 |
| 8 | PhCN | 100 | 20 | 15 | 78 |
| 9 | PhCN | 100 | 20 | 40 | 93 |
| 10 | PhCN | 100 | 15 | 30 | 87 |
| 11 | PhCN | 100 | 10 | 30 | 83 |
| 12 | PhCN | 100 | 20 | 0 | 68 |

Reaction conditions: cyclohexanol 3 mmol, solvent 10 mL, O₂ 20 mL/min, 24 h.

^aReaction temperature; ^bAmount of catalyst; ^cConversion of cyclohexanol; no other by-product was observed.

Table 2. Catalytic oxidation of alcohol by NHPI/O₂/CoTPP-Zn₂Al-LDH system.

| Entry | Substrate | Product | Solvent | T (°C) ^a | t (h) ^b | C (%) ^c | S (%) ^d |
|-------|---|---|---------|---------------------|--------------------|--------------------|--------------------|
| 1 |  |  | PhCN | 100 | 24 | 91(68) | >99 |
| 2 |  |  | PhCN | 100 | 28 | 93(77) | >99 |
| 3 |  |  | PhCN | 100 | 30 | 92(80) | >99 |
| 4 |  |  | PhCN | 100 | 28 | 91(78) | >99 |
| 5 |  |  | ACN | 80 | 30 | 88(75) | >99 |
| 6 |  |  | ACN | 80 | 7 | 62(40) | 77(56) |
| 7 |  |  | ACN | 80 | 16 | 82(51) | 74(46) |
| 8 |  |  | ACN | 80 | 20 | 96(78) | 92(78) |
| 9 |  |  | ACN | 80 | 10 | 75(56) | 56(44) |
| 10 |  |  | ACN | 80 | 12 | 82(69) | 36(13) |
| 11 |  |  | ACN | 80 | 44 | 72(10) | 91(81) |
| 12 |  |  | ACN | 80 | 24 | 45(10) | 95(80) |
| 13 |  |  | ACN | 80 | 44 | 79(12) | 90(82) |

Reaction conditions: alcohol 3 mmol, solvent 10 mL, O₂ 20 mL/min, NHPI 0.6 mmol, CoTPP-Zn₂Al-LDH 30 mg. All the products were identified by GC-MS. ^aReaction temperature; ^bReaction time; ^cConversion, value in parenthesis shows the result without CoTPP-Zn₂Al-LDH; ^dSelectivity, value in parenthesis shows the result without CoTPP-Zn₂Al-LDH.

hybrid, indicating the catalytic function of the material. On the other hand, the selectivity of the aldehyde increased to some extent when the primary alcohols were used as the substrates, which were obviously higher than the reported results over NHPI/O₂ systems.¹² The increase in the selectivity may be due to

the basicity of the hydrotalcites catalyst,^{13b,14} which is a representative basic material.¹⁵

Subsequently, the recyclability of the CoTPP-Zn₂Al-LDH was examined in the aerobic oxidation of cyclohexanol by NHPI. The catalyst showed no appreciable reduction of activity even after five runs

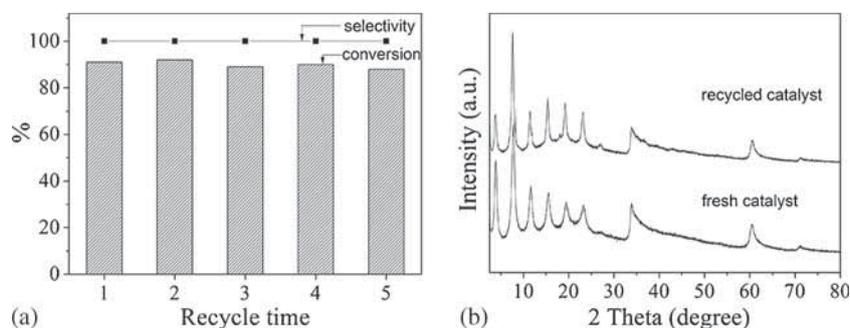


Figure 1. (A) The recyclability of the catalyst CoTPP-Zn₂Al-LDH catalyst; (B) XRD pattern of recycled and fresh catalyst. Reaction conditions: alcohol 3 mmol, solvent 10 mL, O₂ 20 mL/min, NHPI 0.6 mmol, CoTPP-Zn₂Al-LDH 30 mg.

(Figure 1A), and the selectivities were above 99%. XRD pattern for the reused catalyst suggested that the layered structure was completely preserved after several reuses (Figure 1B).

4. Conclusions

In this work, aerobic oxidation of alcohols has been investigated by NHPI combined with CoTPP-intercalated hydrotalcites. The results indicated that CoTPP-Zn₂Al-LDH is an efficient catalyst for the oxidation of alcohols to corresponding carbonyl compounds through O₂/NHPI system and tolerates a wide range of substrates. The catalyst recycling test suggested that the CoPcTs-Zn₂Al-LDH is durable and quite good under the tested reaction conditions. The work on the development of more efficient catalysts based on the hybrid and structure-activity relationship is in progress.

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