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Communications to the Editor

Oxidation of Cyclohexane to Adipic Acid Using Fe−Porphyrin as a Biomimetic Catalyst

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Abstract:

A one-pot oxidation from cyclohexane to adipic acid has been developed, catalyzed by Fe−porphyrin in the presence of molecular oxygen without any additives. When the reaction temperature is 140 °C, oxygen pressure is 2.5 MPa, concentration of catalyst is 1.33×10^{-5} mol %, and reaction time is 8 h, the yield of adipic acid reaches 21.4%. A turnover number of about 24582 is thus far the highest one among those reported for the direct oxidation from cyclohexane to adipic acid.

Introduction

Adipic acid has been found to be the most vital dicarboxylic acid industrially, widely used in the manufacture of polyamide nylon 66, urethane foams, acidulant in baking powder, plastics, and lubricant additives, as well as in the production of intermediates for pharmaceuticals, insecticides, and bactericides.[1] Most of adipic acid on the market has originated from cyclohexane,[2] which undergoes oxidation at 423−433 K and 0.9 MPa of air with a homogeneous cobalt catalyst or metaboric acid, forming the cyclohexanone and cyclohexanol intermediates (KA oils), which are subsequently oxidized into adipic acid with nitric acid as an oxidant. Succinic and glutaric acids are usually obtained as byproducts. Use of nitric acid is still preferred because it is inexpensive; however, use of a catalytic process scheme will be beneficial from the environmental standpoint. The above-mentioned two-step process poses environmental constraints, since nitric acid is a corrosive oxidizing agent (which yields NO$_x$ effluents requiring end-of-pipe treatments), and suffers from high cost, owing to a two-step operation, corrosion, stoichiometric conversion of nitric acid, and the necessity for pollution treatment.

Using green oxidants such as hydrogen peroxide or molecular oxygen is gathering increasing interest towards cyclohexane oxidation.[3,4] Hydrogen peroxide is a preferred oxidant as it only produces water as a byproduct in an environmentally friendly oxidation of cyclohexane.[5,6] Molecular oxygen is another alternative oxidant; severe reaction conditions such as high pressure and temperature are often necessary for activation of the C−H bond.[7−12] As to these processes oxidized by either hydrogen peroxide or molecular oxygen, much research has focused on the process either from cyclohexane to KA oils[7−9,13] or from KA oils to the corresponding adipic acid.[5,9,14,15] Cyclohexene as a feedstock has also been well investigated.[16] Thomas and co-workers reported a hydrogenation method to yield adipic acid from nuconic acid.[17,18] Few reports have been documented for one-pot oxidation directly from cyclohexane to adipic acid, which is a promising and economic process for producing adipic acid. Iwahama and co-workers[19] reported that a radical catalyst, i.e., *N*-hydroxyphthalimide, combined with Mn(acac)$_2$ and Co(OAc)$_2$ attained a direct conversion of cyclohexane into adipic acid in the presence of molecular oxygen. Yet, an expensive radical catalyst and two cocatalysts together with acetic acid solvent were necessary, making this process

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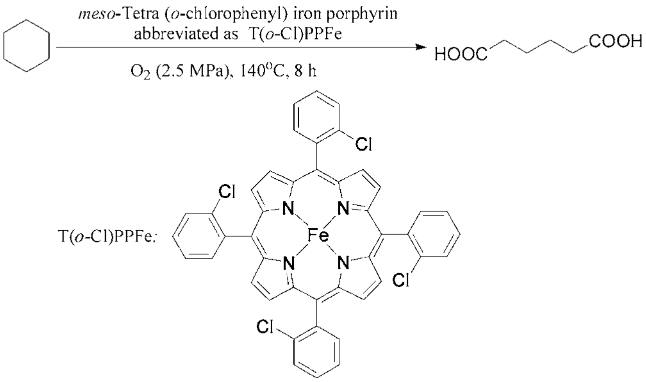
Scheme 1



less benign. Several heterogeneous catalytic systems[10−12,20] have also been explored. However, either severe reaction conditions such as temperature, pressure or acidic solvent or low activities existed in the investigated reaction systems.

In the present contribution, a novel one-pot oxidation of cyclohexane to adipic acid using molecular oxygen as an oxidant has been developed, in which metalloporphyrins proved to be effective catalysts in a solvent-free reaction system with high turnover number. In addition, this oxidation does not need any other additives including solvents. To our knowledge, there are few reports[21] using metalloporphyrins for one-pot oxidation from cyclohexane to adipic acid; the use of acetonitrile as a solvent, the low yield of adipic acid of about 7%, and the need to use more than 0.1 g of porphyrin as catalyst make the process difficult to be industrialized.

Results and Discussion

Catalytic Properties Influenced by Different Reaction Conditions. One-pot oxidation of cyclohexane to adipic acid using molecular oxygen as the only oxidant was performed as in Scheme 1.

In our endeavor for optimizing the reaction conditions for one-pot oxidation from cyclohexane to adipic acid, the existence of optimal values for investigated parameters including reaction temperature, reaction pressure, and reaction time have been discovered as shown in Table 1.

All parameters were revealed to have optimal values, and the increase or decrease of investigated parameters led to a less efficient generation of adipic acid. The optimal reaction temperature is 140 °C (entry 2). The higher temperature normally means faster oxidation but the occurrence of more side reactions, which widely exist in oxidation reactions (entries 1−3). Similar phenomena were also found while varying reaction pressure (entries 2, 5−6) and reaction time (entries 2, 7−10). The optimal values for reaction pressure and reaction time are 2.5 MPa and 8 h, respectively. These investigated rules could be attributed to the reason that further oxidation of adipic acid forms smaller oxygenates and complete oxidation forms carbon dioxide and water, widely employed in wastewater treatment.

Amount of Catalyst. It should be noted that the effect via the amount of biomimetic catalyst towards cyclohexane oxidation peaked at a concentration of 1.33×10^{-5} mol %. It is contrary to the common knowledge that more catalyst can generate more product. Under the optimal operating parameters obtained from the above, the corresponding oxidative products and TONs are shown in Figure 1.

Table 1. **One-pot oxidation of cyclohexane to adipic acid catalyzed by T(*o*-Cl)PPFe in the presence of molecular oxygen**[a]

entry	temperature (°C)	pressure (MPa)	reaction time (h)	isolated yield (%)	TON
1	130	2.5	8	0.4	689
2	140	2.5	8	14.1	24295
3	150	2.5	8	12.7	21883
4	160	2.5	8	6.2	10683
5	140	2.0	8	11.0	18953
6	140	3.0	8	11.6	19987
7	140	2.5	6	0.2	345
8	140	2.5	9	12.7	21883
9	140	2.5	10	10.0	17230
10	140	2.5	12	2.0	3446

[a] Reaction conditions: catalyst (1 mg); cyclohexane (0.14 mol); oxygen atmosphere.

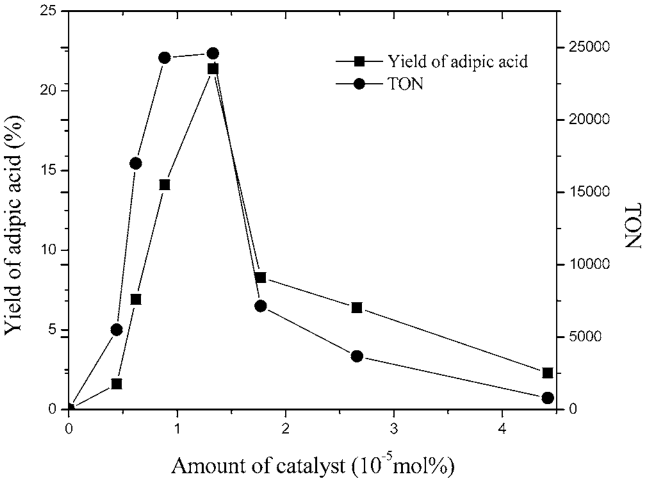


Figure 1. **Plots of yield of adipic acid and TON versus amount of catalyst. Reaction conditions: cyclohexane (0.14 mol), oxygen atmosphere (2.5 MPa), 140 °C, 8 h.**

From Figure 1, the plot of yield of adipic acid versus catalyst amount has a turning point when the concentration of catalyst is 1.33×10^{-5} mol %. As to the elucidation for this phenomenon, the reason might be the self-polymerization of T(*o*-Cl)PPFe.[22] The use of as many as 0.1 or 0.5 g of porphyrin catalyst within only 5 g of solvent in the documented patent[21] might partially explain the low activity for the above-discussed reasons.

To our best knowledge, the obtained TON (about 24582) of this present catalyst is the highest for those catalyst systems towards one-pot oxidation from cyclohexane to adipic acid. For example, TONs of about 4192, 239, and 594 could be achieved for Co/Mn cluster complex,[9] FeAlPO zeolite,[12] and *N*-hydroxyphthalimide combined with Mn(acac)$_2$ and Co(OAc)$_2$,[19] respectively.

As to the reaction mechanism, the reaction course of oxidation catalyzed by T(*o*-Cl)PPFe proceeds through a

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radical pathway; T(*o*-Cl)PPFe(IV)=O$^\bullet$ is regarded as active species. The detailed mechanism from cyclohexane to adipic acid has been further studied.

Conclusions

In conclusion, a novel, solvent-free one-pot oxidation from cyclohexane to adipic acid catalyzed by T(*o*-Cl)PPFe was successfully achieved in the presence of molecular oxygen. By far this present catalyst system, reported as a biomimetic catalyst for oxidation from cyclohexane to adipic acid, presents the highest turnover number of about 24582 in similar oxidative processes and gives an efficient alternative process for the synthesis of adipic acid.

Experimental Section

Preparation of Catalyst. *meso*-Tetra(*o*-chlorophenyl) porphyrins (hereafter abbreviated as T(*o*-Cl)PP) were synthesized according to the documented procedure.[23] Metal complexes of T(*o*-Cl)PP were synthesized using DMF as solvent, and a typical example (*meso*-tetra (*o*-chlorophenyl) iron porphyrin, abbreviated as T(*o*-Cl)PPFe) is as follows: A three-neck round-bottomed flask equipped with a thermometer, reflux condenser, and magnetic force stirrer were charged with 20 mL of DMF, 0.27 mmol T(*o*-Cl)PP and 0.30 mmol $FeCl_2$. The mixture was stirred under reflux for 2 h at 165 °C. TLC presented the complete disappearance of the starting material. Into the obtained cooled mixture, 20 mL of deionized water and 30 mL of 10% HCl were added, and a crystalline product formed. After overnight deposition, followed by filtration and dryness in a vacuum, 180 mg of crude product was obtained. Then, the crude product was dissolved in CH_2Cl_2 and purified by column chromatography (neutral Al_2O_3, CH_2Cl_2 as eluant), and T(*o*-Cl)PPFe was obtained as a green powder (160 mg). Analysis data are as follows: UV−vis(CH_2Cl_2): λ_{max}: 416.2 nm (Soret band), 545.8 nm (Q-band); IR: 2925 cm^{-1} (ν_{C-H}), 1630 cm^{-1} (ν_{C-C} benzene), 1312 cm^{-1} (ν_{C-N} pyrrole), 1008 cm^{-1} (ν_{Fe-N}), 751 cm^{-1} (δ_{C-H} benzene); the above results show that the synthetic complex was metalloporphyrin as expected.

Cyclohexane Oxidation. A typical oxidation for cyclohexane is as follows: Into a 200-mL autoclave with magnetic stirrer and temperature-controlling device were placed 15 mL of cyclohexane (0.14 mol) and 1 mg of T(*o*-Cl)PPFe (8.84×10^{-6} mol %) catalyst. After flushing several times with O_2, 2.5 MPa of O_2 was charged. The reaction was performed at 140 °C for 8 h. The oxidation products were a mixture of solids and liquids. The solid products were separated from the resulting mixtures by vacuum distillation, followed by recrystallization. The obtained product gave 2.503 g of pure adipic acid (21.4%). Identifications of the different products were carried out with melting-point testing device and IR and HPLC analysis. TON is defined as the ratio of moles of product (adipic acid) to moles of central metal (iron).

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