Clean synthesis of adipic acid

by direct oxidation of cyclohexene with H_2O_2 over peroxytungstate–organic complex catalysts

Youquan Deng,* Zufu Ma, Kun Wang and Jing Chen

Laboratory of Environmental and Applied Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P.R. China. E-mail: ydeng@ns.lzb.ac.cn

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Summary

Direct catalytic oxidation of cyclohexene to adipic acid with hydrogen peroxide over environmentally benign peroxytungstate–organic complex catalysts is performed with excellent yields and selectivities, without any organic solvent and harmful phase-transer catalyst.

Introduction

Environmental legislation and increasing public awareness of environmental issues are providing an ever-increasing need for the introduction of clean syntheses to replace traditional chemical manufacturing. An effort to cleanly synthesise adipic acid, which has been manufactured using nitric acid oxidation of cyclohexanol or cyclohexanone in most current industrial processes, has been made recently.[1–4] Research on the clean synthesis of adipic acid has also been reported recently,[5] in which cyclohexene could be efficiently oxidized to adipic acid with aqueous 30% H_2O_2 in the presence of small amounts of Na_2WO_2 and $[CH_3(n\text{-}C_8H_{17})_3HSO_4$ as a phase-transfer catalyst. The $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ as a phase-transfer catalyst is, however, relatively expensive if it is used in industry for adipic acid production, and quaternary ammoniums are generally not environmentally benign. Here we report a cheaper and environmentally benign peroxytungstate–organic complex which could be used as a highly efficient catalyst for the direct catalytic oxidation of cyclohexenes to adipic acid with hydrogen peroxide without any phase-transfer catalyst.

Results and discussion

The experimental results indicated that the organic acids as ligands have strong impact on the catalytic oxidation (Table 1). The cyclohexene conversion and the selectivity for adipic acid was 97.3 and 38.9% respectively if the peroxytungstate was only present in the reaction media. However, the selectivity for adipic acid could be greatly enhanced when both peroxytungstate and organic acids were present in the reaction media. The best catalytic performance could be achieved when oxalic acid was used as ligand, *i.e.* in addition to complete conversion of cyclohexene, 96.6% selectivity for adipic acid was obtained. The main byproducts were cyclohexanediol and pentanedioic acid. In comparing the relationship between the complex catalyst performance and the acidities and molecular structures of the organic acids as ligands listed in Table 1, it can be seen that: (1) The stronger the acidity of the organic acid, the higher yield and selectivity for apidic acid could be obtained. Since an acidic environment is essential for an oxidation reaction involving H_2O_2 as oxidant,[6] and the acidity in this reaction media was derived from the organic acids, the acidity of the reaction media would directly depend upon the acidity of the organic acids. (2) The catalytic activities of the peroxytungstate–organic complexes with a monochelate ring were higher than that with double or multiple chelate rings. For example, the acidity of tartaric acid is stronger than that of succinic acid, 1, 5-pentanedioic acid and salicylic acid, the catalytic activity, however, was relatively lower. This is probably due to the formation of multiple chelate rings between peroxytungstate and tartaric acid, which would reduce the number of peroxy species bonded to tungsten. (3) The yields and selectivities of peroxytungstate complexed with pentanedioic acid or 8-hydroxyquinoline were respectively higher than that with succinic and nicotinic acids, although the acidities of pentanedioic acid and succinic acid, or 8-hydroxyquinoline and nicotinic acid are quite similar. These may be related to the different oleophilic properties of these organic acids. Since the peroxytungstate was only water-soluble but immiscible with cyclohexane, it must penetrate from the aqueous H_2O_2 phase into the 'oil phase' before initiating oxidation of cyclohexene. When the peroxytungstate was complexed with the organic acids, the resultant catalyst system not only possessed the capability of carrying active oxygen species but also became oleophilic, and the more oleophilic a peroxytungstate–organic complex (*i.e.* more $–CH_2–$ units in the structure), the better catalyst performance is.

The pioneering works by Ishii *et al.*[7] indicated that the oxidation virtually did not occur with H_2WO_4 in water. This is probably because the cyclohexene is immiscible with water and the H_2WO_4 is only water-soluble. When the peroxytungstate was complexed with the organic acids, the resultant catalyst system not only possessed the capability of carrying active oxygen species but also became oleophilic, therefore, a very good catalyst system for the oxidation of cyclohexene could be formed.

Since the best yield and selectivity could be achieved with the peroxytungstate–oxalic acid catalyst system, the effect of the amount of catalyst on the formation of adipic acid was further investigated. The experimental results showed that the oxidation

Green Context

Millions of tonnes of adipic acid are produced each year for the manufacture of nylon-6. The conventional method for the production of adipic acid involves oxidation of cyclohexane to cyclohexanol (a step which shows poor selectivity), followed by nitric acid oxidation. This report describes a clean and direct catalytic method for the conversion of cyclohexene to adipic acid.

Stewart J. Tavener, University of York

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Table 1 Influence of organic acids as ligands on the catalyst performance in cyclohexene oxidation[a]

Ligand	Products (wt%)[b]						
						Others	
Oxalic acid	—	1.2	—	—	—	1.6	96.6
Succinic acid	—	0.2	—	—	4.2	1.5	94.0
Pentanedioic acid	—	0.2	0.1	—	3.6	1.0	95.1
Salicylic acid	—	4.7	0.7	—	—	4.5	90.1
Nicotinic acid	—	4.6	2.9	0.5	—	2.2	89.8
8-Hydroxyquinoline	—	5.8	0.8	0.5	—	2.2	90.7
Tartaric acid	—	1.7	1.1	—	—	16.6	80.6
—	2.7	39.8	—	—	—	18.6	38.9

[a] *Reaction conditions*: catalyst 1.0 mol% (relative to 0.3 mol cyclohexene), 30% H_2O_2 (134 ml), refluxed and stirred for 24 h.
[b] Other by-products were valeric acid, cyclopentanone and cyclohexanone.

Table 2 Influence of the amount of peroxytungstate–oxalic acid complex catalyst on the catalystic performance in cyclohexene oxidation[a]

Amount of catalyst (mol%)	Reaction time/h	Products (wt%)				
					Others	
0.5	24	6.6	0.5	3.5	3.5	86.0
1.0	24	1.2	—	—	1.6	96.6
1.5	8	2.3	0.3	3.4	1.9	93.5
2.0	8	0.9	—	3.7	1.1	94.2
2.5	8	0.6	0.1	1.9	1.6	95.8

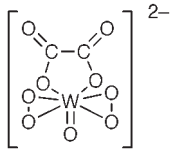
[a] Reaction conditions same as in Table 1.

reaction has to be conducted for 24 hours in order to achieve complete cyclohexene conversion and more than 90% of adipic acid selectivity when the amount of the catalyst charged was <1.5% mol (relative to the amount of cyclohexene), Table 2. However, 93.5% yield or selectivity for adipic acid could be achieved when the amount of the catalyst was increased to ⩾1.5% (mol). It is worth mentioning that such yield and selectivity was the same as that obtained from the Na_2WO_2 and $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ catalyst system reported recently by Sato *et al.*[5] This means that the expensive $[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$ PTC could be replaced by a much cheaper and simpler organic acid, *e.g.* oxalic acid, without any loss of yield and selectivity for adipic acid production, and moreover, the catalyst system itself is more environmentally friendly.

We are currently investigating the possibility of recovery and reusing the catalyst, and using oxygen or air to replace some of the H_2O_2.

Experimental

The peroxytungstate–organic complex was prepared *in situ* by adding $Na_2WO_4{\cdot}2H_2O$ (2.74 g, 7.5 mmol) and organic acids (7.5 mmol equiv.) and aqueous 30% H_2O_2 (134 ml, 1.32 mmol) into a 250 ml round-bottomed flask equipped with a mechanical stirrer, a flux condenser and a thermometer. The mixture was stirred at room temperature for *ca.* 15 min and the resultant solution changed from light yellow to orange, indicating the formation of a peroxytungstate–organic acid complex, *i.e.* $[W(O)(O_2)_2L_{(2)}]^{2-}$ ($L_{(2)}$ is an organic acid with double or multi functional groups), **1**. Cyclohexene (24.9 g, 0.3 mmol, H_2O_2: cyclohexene = 4.4:1) was added into the above solution. The mixture was initially heated at 72 °C for 3–4 h



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and then at 94 °C for 4–20 h with stirring at *ca.* 1000 rpm. The reaction was then stopped and the resultant aqueous mixture was cooled at 0 °C overnight. A white crystalline solid, apidic acid, separated out and was filtered off and after washing and drying had purity ⩾99% (GC analysis) and mp 151–152 °C. Some extra apidic acid product could be obtained if the remainder mother liquor was further evaporated. The best total yield of apidic acid was 93–95%.

After each reaction, the resulting aqueous mixture containing reactant and products was directly analyzed with HP6890/5973 GC-MS with crosslinked 5% PH ME Siloxane column, 30 m × 0.25 mm × 0.25 μm.

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