

Oxidation of Cyclohexanone and Cyclohexanol to Adipic Acid Using Hydrogen Peroxide and Supercritical Carbon Dioxide

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Abstract Supercritical carbon dioxide and hydrogen peroxide was used in the oxidation for exploring a clean and efficient process to produce adipic acid. Supercritical carbon dioxide would be both a solvent and reactant in combination with aqueous hydrogen peroxide, which made the oxidation be possible through the formation of peroxycarbonic acid as the intermediate oxidizer. The effects of temperature and reactant were also studied in this thesis.

INTRODUCTION

Adipic acid is a valuable raw material used in the production of nylon-6,6, fibers, plasticizers, and food additives[1]. Nowadays, most adipic acid is manufactured by the oxidation using HNO_3 . In the first stage, cyclohexane is oxidized with oxygen to KA oil (a mixture of cyclohexanol and cyclohexanone). In the second stage, this mixture is further oxidized to adipic acid by 40–60% HNO_3 in the presence of copper and vanadium catalysts. However, during the second stage, significant amounts of environmentally harmful NO_x effluents (NO , NO_2 , and N_2O) are produced. Therefore, an alternative non- HNO_3 route to adipic acid using cleaner oxidants is highly desirable [2].

Hydrogen peroxide is a cheap and readily available oxidant for this purpose, with the innocuous decomposition byproducts of water and oxygen. Nevertheless, the oxidation reaction will not happen without activation of hydrogen peroxide. Nowadays, converting hydrogen peroxide to a more reactive peroxy acid or adding metal catalysts are the major methods to enhance the activity of hydrogen peroxide. However, there are serious disadvantage in these processes.

Metal catalysts, composed primarily of transition metals including V, Mo, Mn, Re, and Ru, have been used in conjunction with hydrogen peroxide to form epoxides [3]. Small amounts of the catalysts could provide good selectivity and yield. However, the problems about the stability, separation and recycling of the catalyst bring additional processing challenges and expenses.

Another mean of activating hydrogen peroxide is to generate peroxy acids, which are more reactive than hydrogen peroxide. Peroxy acids can be synthesized through the acid-catalyzed reaction of a carboxylic acid with hydrogen peroxide [4]. After the oxidations, the peroxy acids will be regenerated to the carboxylic acid. These carboxylic acids must then be recovered for reuse or disposal. These processes are very complex and a large amount of industrial aqueous waste will be produced. Additionally, the potential for explosions makes

the use of traditional peroxy acids be undesirable.

It is well known that carboxylic acid reacts with hydrogen peroxide to form peroxy acids. By analogy, the reaction of supercritical CO₂ (scCO₂) with hydrogen peroxide should generate peroxycarbonic acid, which is also much more activity than hydrogen peroxide [5]. In this work, scCO₂ and hydrogen peroxide was used in the oxidation for exploring a clean and efficient process. Using scCO₂ as the reaction medium is also based on unique properties of supercritical fluids and its subsequent advantages of being nonpoisonous and nonflammable, which is beneficial to developing a inherently clean and safe oxidation process.

MATERIALS AND METHODS

Materials.

All chemicals were commercially obtained and used without further purification. They include cyclohexanone (>99%), cyclohexanol(>99%), adipic acid(>99%), H₂O₂ (30w%), CO₂(>99%).

Methods.

The cyclohexanone/cyclohexanol and hydrogen peroxide solution were added into the reactor before the reactor was sealed. CO₂ was pumped in to the reactor, and pressurized the reactor. After heated up to the required temperature, the reactor was pressurized to the desired pressure by introducing more CO₂. After the desired time under stirring, the heater was turned off. The reactor was cooled and decompressed. Then the reaction mixture was removed from the reactor.

Some crystal was precipitated after the reaction mixture had been cooled at 5 °C for 12 hours. Then the solid was filtrated and washed with cool water. The IR spectra of the product sample was measured and compared with the standard adipic acid sample, they were nearly the same. The yield of this reaction could be calculated after measuring the weight of crystals.

RESULTS

1. The effect of scCO₂

To testify the catalysis of supercritical CO₂ for the oxidation with H₂O₂, the control experiments were performed with cyclohexanone in atmospheric air and high pressure N₂. The results (Table 1) shew that, under analogous conditions, the yield of adipic acid in supercritical CO₂ environment were nearly 4 times as many as the yield in atmospheric air or a N₂ environment..

Table 1 : Control experiments for testifying the catalysis role of scCO₂
Reaction for 5h at 92.5°C and with.1:4.5 vol/vol of cyclohexanone to H₂O₂ solution

Run no.	Condition	Yield %
1	atmospheric air	3.75
2	N ₂ , 15MPa	4.10
3	CO ₂ ,15MPa	15.70

2. The effect of temperature

In order to study the effect of temperature on the oxidation, the experiments were

performed at the same condition except temperature. The experimental results (Table 2) show that, almost no adipic acid was formed at temperatures less than 88 °C, and the yield was increased with reaction temperature higher than 88 °C.

Table 2 : Effect of reaction temperature on the oxidation
Reaction was conducted for 5h at 15MPa. The volume ratio of reactant to H₂O₂ solution was 1:4.5;

T/°C	Reactant	
	Yield%	
88.0	0	0
90.3	7.25	4.89
92.5	15.70	7.12

3. The effect of reactant

In order to study the effect of reactant on the oxidation, the experiments were performed at the same condition, and the reactants were cyclohexanone, cyclohexanol and their mixture respectively. The experimental results (Table 3) show that, when the reactant was cyclohexanone, the yield were much more higher than others.

Table 3 : Effect of reactant on the oxidation
Reaction was conducted for 5h at 15MPa at 92.5°C.
The volume ratio of reactant to H₂O₂ solution was 1:4.5;

Run no.	Reactant	Yield %
1	Cyclohexanone	15.70
2	Cyclohexanol	7.12
3	Mixture(volume ratio of cyclohexanone to cyclohexanol: 1:1)	7.92
4	Mixture(volume ratio of cyclohexanone to cyclohexanol: 2:1)	8.66

CONCLUSION

With scCO₂ as the catalyst, H₂O₂ can react with cyclohexanone/cyclohexanol to form adipic acid, and the yield in supercritical CO₂ environment were much more than ones in atmospheric air or a N₂ environment..

The yield of oxidation is increased as the reaction temperature increasing. The oxidation is also influenced by reactant. Among cyclohexanone, cyclohexanol and their mixture, cyclohexanone is the most active reactant to produce adipic acid.

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