Original Article

Catalytic synthesis of cyclohexanone oxime as a raw material of nylon 6

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ABSTRACT

Nylon 6 or polycaprolactam is one of the most widely used polymers, obtained from the polymerization of caprolactam monomer resulting from the innovation of cyclohexanone oxime. Cyclohexanone oxime is obtained from the reaction of hydroxylamine and cyclohexanone oxime. This reaction depends on the parameters such as temperature, amount of raw materials, catalyst, and reaction time, which affect the reaction yield. The reaction of ammonia and cyclohexane in the presence of an aluminum silicate catalyst was used. After the progress of the reaction, we added an oxidizing agent, such as hydrogen peroxide, to the reaction medium to oxidize the ammonia present in the reaction medium and to advance the reaction of cyclohexanone towards the progress of the oxime formation reaction. The present study aims to investigate the factors affecting the catalytic production of cyclohexanone oxime to increase its production yield. Also, it investigates this reaction using different catalysts, including aluminum silicate and titanium oxide catalysts under different reaction conditions to produce cyclohexanone oxime. The obtained results showed the cyclohexanone oxime production with a yield of 90.54% in the conditions of 0.294 mol of ammonia, 0.176 mol of hydrogen peroxide, 0.178 mol of cyclohexanone, at a temperature of 72 to 75 °C and 1% catalyst. Also, the aluminum silicate catalyst showed the best yield in cyclohexanone oxime production.

Keywords: Aluminum silicate catalyst, Titanium oxide catalyst, Cyclohexane, Cyclohexanone oxime

Introduction

Cyclohexanone oxime is an organic compound containing oxime groups. It is a white crystalline solid with a molecular weight of 113.16 g/mol and a melting point of 90 °C. Oxime is a compound that has the functional group OH-N=C. It is one of the most important derivatives used to identify aldehydes and ketones. It is obtained from the reaction of hydroxylamine hydrochloride with aldehydes and ketones. All ketones, especially cyclic and liquid ketones, are quickly converted to oxime. Compounds containing oxime have medical applications such as antidotes for nerve agents. Cyclohexanone is mostly used in various industries. It is primarily used for the synthesis of caprolactam, used in the polymerization of polycaprolactam (nylon 6), fiber, and plastic. Oximes are one of the most important functional groups in organic chemistry. They act especially as protecting groups of carbonyl compounds and as intermediates in Beckman innovation [1-2]. The reaction of cyclohexanone with hydroxylamine is a well-known method for producing cyclohexanone oxime. Hydroxylamine is generally used as an unstable and intermediate liquid to produce cyclohexanone oxime.

Liquid hydroxylamine is converted to cyclohexanone oxime in the presence of cyclohexanone at 70-75 °C within 4 hours [3]. Cyclohexanone oxime can be obtained by several methods. It can be obtained using liquid hydroxylamine in the presence of cyclohexane at a temperature of 70-75 °C within several hours. Cyclohexane oxime is converted into cyclohexane oxime by using hydroxylamine sulfate or hydroxylamine chloride in the presence of cyclohexane. The industrial production method involves the reaction of cyclohexane with nitrosyl chloride, which is a free radical reaction leading to the production of cyclohexane oxime. Nylon 6 or polycaprolactam is a semi-crystalline polyamide. Unlike other nylons, it is a compression polymer, distinguishing it from other nylons. Nylon 6 is prepared by heating caprolactam to about 250°C and 5-10% water. The carbonyl oxygen binds to the water molecule. The carbonyl oxygen donates a pair of electrons to the hydrogen atom of water and separates the hydrogen atom from it. At this stage, a carbonyl gives us a proton and a free hydroxyl group. Adding water to caprolactam opens the monomer ring and converts it into amino Ɛ-caproic acid. Nylon 6 fibers are very strong and have high tensile strength. Nylon 6 fiber has high elasticity and is shiny. Nylon 6,6 is obtained from the condensation of adipic acid and hexamethylenediamine in the presence of heat and the removal of a water molecule.

Richard Edward developed a new method for the production of hydroxylamine in 1950. In this method, it is possible to increase the amount of hydroxylamine production by using a nitric oxide catalyst with hydrogen at a moderate amount of acid under low pressure. Although the required raw materials are cheap, they did not show a successful commercial synthesis due to the low conversion percentage and yield [4]. Kurt and Karl used the method of reducing nitric oxide by hydrogen in the presence of a catalyst and in an acidic environment to produce hydroxylamine. This method has a low yield. They found that using an organic compound with polar molecules that includes at least four carbon atoms can increase the yield of hydroxylamine in this method [5].

Hisama examined the oxime direct production using the reaction of a ketone or aldehyde with nitrogen monoxide and hydrogen in the presence of a platinum catalyst. He found that the catalyst amount may vary from 0.001 to 20 mmol, and the best result was obtained at 0.05 to 2 mmol [6]. Mantegazza *et al*. examined a direct catalytic process for the production of hydroxylamine using ammonia oxidation with hydrogen peroxide in the presence of a titanium silicon catalyst. It was finally revealed that increasing the titanium silicate catalyst in the reaction decreases the production yield of hydroxylamine [7]. Dal Pozzo *et al*. (2001) converted cyclohexanone to oxime using ammonia and hydrogen peroxide in the presence of a TS-1 catalyst. Decomposing hydroxylamine decreases the yield of oxime production and it results in forming an intermediate and preventing the formation of oxime [8]. Yang *et al*. (2006) produced hydroxylamine from the reaction in an aqueous medium containing acidic buffer and nitrate ion in the presence of a limited amount of pure metals such as iron. The results of comparing the samples revealed that the low amount of metal impurity in the aqueous reaction medium for the hydroxylamine synthesis reaction can significantly improve the selection rate of hydroxylamine production. The impurity of iron metal should be below 100 ppm. The catalytic activity first increases and then decreases as the level of iron decreases [6].

Song *et al*. (2006) used a titanium silicate catalyst to produce hydroxylamine. The results revealed that the catalyst behavior in this system is affected by the way of adding hydrogen peroxide. To achieve a high conversion percentage, hydrogen peroxide should be added drop by drop and gradually. The optimal temperature of this process is 75 °C. The yield decreases at higher temperatures due to the evaporation and decomposition of ammonia and hydrogen peroxide [9]. Sirijaraensre and Limtrakul examined the catalytic performance of titanium species in zeolite TS-1 for forming hydroxylamine using density functional theory with the ONIOM design. The results show that H2O2 decomposition is kinetically and thermodynamically more favorable on imperfect Ti species than on suitable species [10]. The most important application of cyclohexanone oxime is related to using its derivatives in the production of caprolactam (about 70%) as a raw material for the production of nylon 6. The remaining 30% of cyclohexanone oxime is used in the dyes, pesticides, solvents, and softeners industries. Generally, it is used as an intermediate in the production of nylon 6 and Nylon 6,6. Given what was stated above, the catalytic synthesis of cyclohexanone oxime is the raw material of nylon 6.

Materials and Methods

1-Preparation of cyclohexanone oxime

Several states have been examined in cyclohexanone oxime synthesis. In the first case, ammonia, cyclohexanone, catalyst, and hydrogen peroxide were entered into the system. In the second state, ammonia, hydrogen peroxide, and catalyst were first added to the system and finally to cyclohexanone. In the third state, all materials including ammonia, hydrogen peroxide, aluminum silicate catalyst, and cyclohexanone were entered into the system simultaneously. In the method of adding cyclohexane, aluminum silicate catalyst, ammonia, and cyclohexane were added to the flask at the beginning of the synthesis and it was stirred for 1.5 to 2 hours at 75°C using a magnet. Then, hydrogen peroxide was added drop by drop to the solution inside the flask through the dropping funnel for 1.5 hours. Then, the hydrogen peroxide solution inside the flask was mixed again for half an hour. During this time, the evaporated ammonia was returned to the flask by the condenser. Then, the heater was turned off and the solution was poured into the falcon tube and the organic and aqueous substances were separated. Then, we gave the obtained solution retention time to form the oxime.

In the method of adding cyclohexane, at the end of the synthesis, aluminum silicate catalyst, ammonia, and hydrogen peroxide were added to the flask and stirred for 1.5 to 2 hours at 75°C with a magnet. Then, the cyclohexane was added drop by drop to the solution inside the flask through a dropping funnel for 1.5 hours. Then, the hydrogen peroxide solution inside the flask was mixed again for half an hour. Then, the heater was turned off and the solution was poured into the falcon tube and the organic and aqueous substances were separated. Then, we gave the obtained solution retention time to form the oxime. In the cyclohexanone oxime synthesis method, ammonia, hydrogen peroxide, and aluminum silicate catalyst were first added to the flask at two stages for 2-2.5 hours at a temperature of 75 °C and mixed with a magnet. After the reaction, the catalyst was separated from the solution by a centrifuge. Then, the cyclohexane was poured into the flask alone and the obtained solution was gradually added to the cyclohexanone inside the flask for one hour by a dropping funnel.

In the cyclohexanone oxime synthesis method, aluminum silicate catalyst, ammonia, and cyclohexane were first added to the flask using aluminum silicate catalyst and stirred with a magnet for 2 hours at 70-75 °C. Then, hydrogen peroxide was added drop by drop and was added to the solution inside the flask by the dropping funnel for 90 minutes. Then, the hydrogen peroxide solution inside the flask was mixed again for 30 minutes. Then, the heater was turned off and the solution was poured into the falcon tube and the organic and aqueous substances were separated. Then, we gave the obtained solution retention time to form the oxime

2- Determining the optimum conditions for the cyclohexanone oxime synthesis

After performing the tests and analyzing their results, the optimal conditions in terms of the amount of hydrogen peroxide, ammonia, cyclohexane, temperature, and the amount of catalyst were determined. Then, the synthesis was performed under optimal conditions using titanium oxide and aluminum silicate 3A and 5A catalysts to determine the best catalyst type to produce cyclohexanone oxime [11].

3- Hydroxylamine sulfate

In this method, aluminum silicate catalyst, ammonia, and hydrogen peroxide were added to the flask drop by drop for 1.5 to 2 hours at a temperature of 70 to 80 °C with a magnet. Then, the sulfuric acid was added to the hydroxylamine outside the flask. Then, we added the reacted mixture of hydroxylamine and sulfuric acid to the flask in the presence of the catalyst for 30 to 45 minutes in the flask until the reaction is complete. Then, we removed the substance from the flask environment and placed it at room temperature for 24 hours to precipitate the hydroxylamine sulfate. The precipitated hydroxylamine sulfate was separated from its solution using filter paper [12].

Results and Discussion

Figure 1 presents the result of FTIR analysis of cyclohexanone oxime by adding cyclohexanone at the beginning of the synthesis without using water solvent, where peaks 2843 to 2977 are related to the C-H bond, 3187 are related to O-H bond, 1620 to 1690 are related to C=N bond, and 700 to 1260 are related to C-C bond.

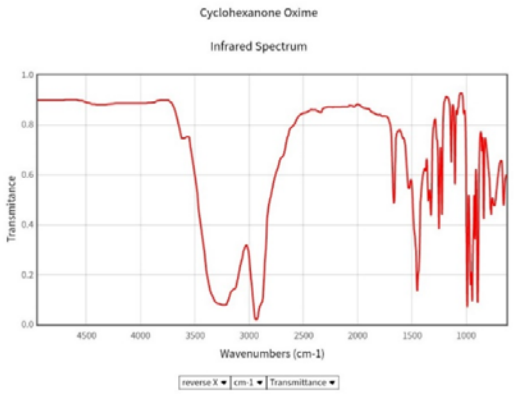
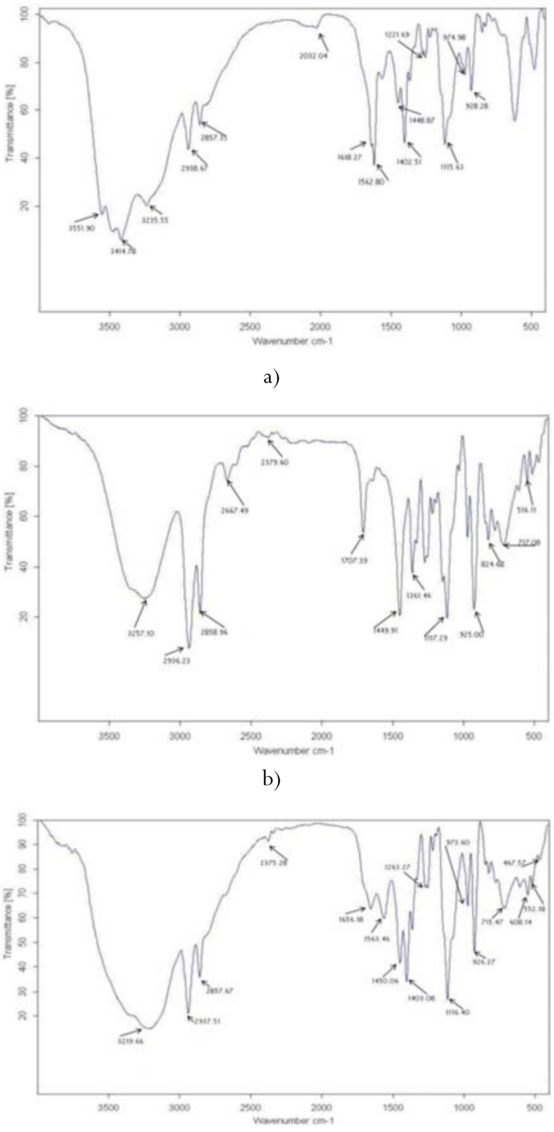


Figure 1. Sample FTIR test using the cyclohexanone standard, following international standards.



a)

b)

c)

Figyre 2. a) FTIR analysis of cyclohexane oxime No. 1 (low temperature), b) FTIR analysis of cyclohexane oxime No. 2 (ambient temperature), and c) FTIR analysis of cyclohexane oxime

The obtained results show that adding cyclohexanone at the beginning of the reaction with ammonia has the highest yield in oxime production given the catalyst type.

Table 1. The results of cyclohexanone oxime yield by adding cyclohexane at the beginning of the synthesis

Row	Aluminum silicate catalyst (%)	Ammonia (g/mole)	Hydrogen peroxide (g/mol)	Cyclohexane (g/mol)	Temperature (°C)	Time (hours)	Yield (%)
1	1	5	6	5.10	75	5	45
2	1	5	6	9.11	75	5	50
3	1	5	6	6.12	75	5	55
4	1	5	6	14	75	5	62
5	1	5	6	4.15	75	5	2.83
6	1	5	6	5.17	75	5	56.90

The analyses indicate that if ammonia and hydrogen peroxide is to form hydroxylamine at the beginning of the reaction, this reaction should take place in the presence of a suitable catalyst. However, due to the lack of a suitable catalyst, the general reaction does not take place, resulting in the formation of oxime at the end of the reaction.

Table 2. The results of adding cyclohexane yield at the end of the synthesis

Row	Aluminum silicate catalyst (%)	Ammonia (g)	hydrogen peroxide (g)	Cyclohexane (g)	Temperature (°C)	Time (hours)	Yield (%)
1	1	5	6	14	75	5	8.20
2	1	5	6	4.15	75	5	9.20
3	1	5	6	5.17	75	5	30

At the end of the reaction, if we add cyclohexanone, oxime formation does not take place due to the non-formation of stable hydroxylamine at the beginning of the reaction and the unsuitable catalyst.

Table 3. The results of cyclohexanone oxime synthesis yield during two stages

Row	Aluminum silicate catalyst (%)	Ammonia (g/mole)	Hydrogen peroxide (g/mol)	Cyclohexane (g/mol)	Temperature (°C)	Time (hours)	Yield (%)
1	1	5	6	14	75	5	0
2	1	5	6	4.15	75	5	0
3	1	5	6	5.17	75	5	0

In the oxime production reaction, adding hydrogen peroxide to the reaction medium, which includes ammonia and cyclohexanone, causes the ammonia to oxide. Adding hydrogen peroxide to the reaction medium will not affect the reaction.

Table 4. Effect of hydrogen peroxide amount on cyclohexanone oxime yield

Row	Aluminum silicate catalyst (%)	Ammonia (g/mole)	Hydrogen peroxide (g/mol)	Cyclohexane (g/mol)	Temperature (°C)	Time (hours)	Yield (%)
1	1	375.1	5.1	85.3	75	5	65
2	1	375.1	65.1	85.3	75	5	67
3	1	375.1	8.1	85.3	75	5	68
4	1	375.1	95.1	85.3	75	5	70
5	1	375.1	1.2	85.3	75	5	75

There is a direct association between ammonia and cyclohexane in the reaction. Therefore, based on the obtained data, the more ammonia is added to the medium, the oxime production yield decreases. It is due to reason that an excessive amount of ammonia does not react completely with cyclohexane and ammonia remains unreacted in the product and contaminates the medium, resulting in a reduction or no formation of oxime at the end of the reaction.

Table 5. Effect of ammonia amount on cyclohexanone oxime yield

Row	Aluminum silicate catalyst (%)	Ammonia (g/mole)	Hydrogen peroxide (g/mol)	Cyclohexane (g/mol)	Temperature (°C)	Time (hours)	Yield (%)
1	1	25.1	56.1	85.3	75	5	5.70
2	1	375.1	56.1	85.3	75	5	9.67
3	1	5.1	56.1	85.3	75	5	8.65
4	1	87.1	56.1	85.3	75	5	6.63
5	1	2	56.1	85.3	75	5	5.62

The temperature was changed between 65 and 85 °C in the synthesis to examine the effect of temperature on the production yield of cyclohexanone oxime. The results revealed that increasing temperature between 65 and 75 °C increases the formation of oxime and yield. Due to the greater condensation of ammonia and the cyclohexane structure destruction at a temperature of 80 to 85 °C, the reaction does not proceed in the right direction. It causes the complete formation of oxime and reduced yield.

Table 6. The temperature effect on the cyclohexanone oxime yield

Row	Aluminum silicate catalyst (%)	Ammonia (g/mole)	Hydrogen peroxide (g/mol)	Cyclohexane (g/mol)	Temperature (°C)	Time (hours)	Yield (%)
1	1	375.1	56.1	85.3	65	5	9.67
2	1	375.1	56.1	85.3	70	5	8.68
3	1	375.1	56.1	85.3	75	5	5.70
4	1	375.1	56.1	85.3	80	5	4.69
5	1	375.1	56.1	85.3	85	5	67

To examine the cyclohexane effect on the production yield of cyclohexanone oxime, this material was used at 4.2 to 5.6 g/mol. Based on the obtained results, the yield of the reaction and oxime formation is increasing with increasing cyclohexane. It is due to the industrial nature of cyclohexane and the presence of impurities. The purity ratio is lower than the ideal value calculated for the reaction. Therefore, by increasing the amount of cyclohexane given its purity, the lack of complete oxime formation is compensated.

Table 7. The effect of cyclohexane amount on the cyclohexanone oxime yield

Row	Aluminum silicate catalyst (%)	Ammonia (g/mole)	Hydrogen peroxide (g/mol)	Cyclohexane (g/mol)	Temperature (°C)	Time (hours)	Yield (%)
1	1	375.1	56.1	2.4	75	5	5.63
2	1	375.1	56.1	55.4	75	5	8.65
3	1	375.1	56.1	9.4	75	5	3.67
4	1	375.1	56.1	25.5	75	5	8.69
5	1	375.1	56.1	6.5	75	5	7.70

Based on the results of cyclohexane oxime formation with an aluminum silicate catalyst, a yield of about 70% was obtained. This yield was due to increasing the amount of catalyst due to catalyst and synthesis type since the catalyst becomes inactive according to time and temperature. Hence, by increasing the amount of catalyst up to one gram, this problem was solved in the synthesis.

Table 8. Effect of catalyst on cyclohexanone oxime yield

Row	Aluminum silicate catalyst (%)	Ammonia (g/mole)	Hydrogen peroxide (g/mol)	Cyclohexane (g/mol)	Temperature (°C)	Time (hours)	Yield (%)
1	2.0	375.1	56.1	85.3	75	5	9.49
2	4.0	375.1	56.1	85.3	75	5	8.54
3	6.0	375.1	56.1	85.3	75	5	3.61
4	8.0	375.1	56.1	85.3	75	5	8.65
5	1	375.1	56.1	85.3	75	5	5.69

Examining the results determined the optimal conditions for the production of cyclohexanone oxime in terms of yield. These conditions are presented in **Table 9**.

Table 9. Optimum conditions for cyclohexanone oxime production

Substance	Amount (g/mol)
Hydrogen peroxide	6
Ammonia	5
Cyclohexanone	17.5
temperature	75

Conclusion

Nylon 6 is one of the most widely used polymer materials obtained from caprolactam monomer. Cyclohexanone oxime is needed for producing caprolactam. It is obtained from the reaction of hydroxylamine and cyclohexanone. In the present study, the catalytic synthesis and factors affecting its yield, including temperature, time, amount of reactants, and the catalyst type were examined. Investigating various methods of cyclohexanone oxime production revealed that adding cyclohexanone at the beginning of the reaction shows a better performance compared to other methods and leads to cyclohexanone oxime production. However, other methods lead to small amounts of formation or no formation of the oxime. Since the cyclohexanone substance used in this study is industrial and industrial substances have a lower purity than the laboratory samples, and according to the test performed, the purity percentage of cyclohexanone is predicted to be about 70%. Based on the obtained results, it can be estimated that if cyclohexanone is purer according to the molecular mass, the amount of cyclohexane in this reaction will be almost half of ammonia, and we have a more optimal production economically.

Increasing the temperature on the production yield of cyclohexanone oxime is effective up to a specified temperature range, but it has no effect after that temperature. For this reaction, increasing the temperature up to 75 °C increases the reaction yield, but it has no effect from 75 to 85 °C. Also, the ammonia effect on the reaction yield is such that if the amount of ammonia is more than the specified value, the complete reaction will not take place and it will remain at the end of the reaction and prevent the formation of the true oxime. Also, the hydrogen peroxide effect on the reaction yield was investigated. As long as ammonia is present in the medium, increasing its amount increases the cyclohexane oxime yield, and its excess amount has no effect on the reaction and causes waste of raw materials since hydrogen peroxide enters the medium for oxidation with ammonia, which later reacts with cyclohexanone in the form of hydroxylamine. Also, increasing cyclohexanone in the oxime formation reaction will increase the product yield given the purity and molecular mass, if it is added to the reaction. Otherwise, we will have additional cyclohexanone in the reaction medium, which prevents oxime formation. Additionally, the effect of different catalysts on the cyclohexanone oxime production yield was examined. The catalysts were slightly ground to make the contact surface of the catalyst with the materials faster during the reaction.

The use of catalysts for greater yield was also examined and the results showed that as long as the amount of catalyst is not reduced (the catalyst is still in the reaction medium), it will not affect the reaction yield negatively. The use of aluminum silicate catalysts 3A and 5A provides the highest yield in oxime production up to 91%. Based on the results of using an aluminum silicate catalyst and examining its effect on cyclohexanone oxime production yield, it is recommended to recycle the catalyst and use it to produce cyclohexanone oxime and to investigate the effect of raw material concentration on cyclohexanone oxime production reaction yield.

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