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Silica Gel Supported Trifluoromethanesulfonic Acid Catalyzed Beckmann Rearrangement of Cyclohexanone Oxime in Liquid Phase

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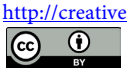

Abstract

The liquid phase Beckmann rearrangement of cyclohexanone oxime (CHO) using fuming sulfuric acid as a catalyst is a traditional method for preparing ε-caprolactam (CPL). This process has drawbacks, such as environmental pollution, corrosion of equipment, and low added value of by-product ammonium sulfate. This article designed and prepared a green silica gel-supported trifluoromethanesulfonic acid catalyst for the liquid-phase Beckmann rearrangement of CHO to prepare (CPL). The influencing factors of catalyst preparation and the optimal reaction conditions for Beckmann rearrangement were investigated. It was found that the optimal conditions for catalyst preparation were as follows: raw material silica gel:trifluoromethanesulfonic acid = 1:0.2 (mass ratio), room temperature, stirring time of 2.5 hours, and solvent of acetonitrile, silica gel mesh size is 100 - 200. The optimal reaction conditions for Beckmann rearrangement are CHO: catalyst = 1:2 (mass ratio), temperature of 130˚C, solvent of benzonitrile, volume of 30 mL/g CHO, and reaction time of 4 hours. Under the above conditions, the conversion of CHO is 90%, and the selectivity of CPL is 90%.

Keywords

Beckmann Rearrangement, Silica Gel, Trifluoromethanesulfonic Acid, Cyclohexanone Oxime

1. Introduction

Amide is an organic compound in which the hydroxyl group in a carboxylic acid is replaced by an amino or amino group. This type of substance has a wide range

of applications in the industrial field, including pharmaceuticals and pesticides. Usually, one of the methods for synthesizing amides is by reacting carboxylic acid derivatives with amines, or by reacting carboxylic acids with amines in the presence of condensation agents. Although these synthesis methods are very effective, they require the use of toxic raw materials, produce a large number of by-products, have low atomic utilization rates, cause serious environmental pollution, and do not comply with the principles of green chemistry. Therefore, using more environmentally friendly methods to synthesize amides has become one of the development directions of modern chemical synthesis, such as Beckmann rearrangement reaction. The Beckmann rearrangement reaction is known for its simple operation, high selectivity, and atomic economy, which can easily prepare various structures of primary and secondary amides. A typical application in industry is the preparation of CPL through the Beckmann rearrangement reaction of CHO. CPL is almost always used to synthesize nylon 6 fibers [1], and nylon 6 fibers are commonly used to produce civilian silk, carpets, and industrial silk, which are widely used in transportation, computers, consumer goods, etc. [2] [3]. In addition, CPL is used as a pharmaceutical raw material to synthesize pentenetetrazole, methylheptazidinol, and lauroyl urea to produce antiplatelet drugs 6-aminohexanoic acid [4], azithromycin [5], antimalarial drugs, and laurylazone. It can also be converted into essential amino acids such as L-lysine for nutrition and biology [6], with a wide range of uses. There are two processes for the rearrangement of CHO to prepare CPL. One is the gas-solid phase process, but due to the high reaction temperature, the stability of the catalyst in this process still needs to be improved. Another popular process for producing CPL is the liquid-phase Beckmann rearrangement method, which has many advantages, such as simple process, mild reaction conditions, high reactant conversion and high selectivity. However, the use of strong acids in this process results in equipment being prone to corrosion, requiring the treatment of residual acids and producing a large amount of low value-added ammonium sulfate. These issues need to be addressed. Therefore, it is urgent to develop an advanced solid acid catalyst material to replace liquid-fuming sulfuric acid, and related research has attracted widespread attention from scholars at home and abroad.

Katada *et al*. [7] loaded monolayer SiO_2 onto three types of oxides, Al_2O_3, ZrO_2, and TiO_2, respectively, as catalysts for Beckmann rearrangement studies. Jain's research group [8] developed Fe_2O_3@SiO_2 as a catalyst, directly converting aldehydes or ketones into amides in one pot. Khayyat *et al*. [9] developed TS-1 molecular sieve as catalyst for Beckmann rearrangement experiment. The experimental results show that it has excellent catalytic performance, the conversion of CHO is 94%, and the maximum selectivity of CPL is 100%. Ren *et al*. [10] developed the Beckmann rearrangement experiment using Bronsted acidic ionic liquid as catalyst. The experimental results showed that when the molar ratio of CHO to catalyst was 1:3 and the reaction time was 2 hours at 90˚C, the conversion of CHO was 100% and the selectivity of CPL was 95%. After several reactions, the yield of

CPL remained at a high level. The advantages of this method are environmental protection, high efficiency, low cost and recyclability. Guo *et al*. [11] developed Beckmann rearrangement experiment using 3-methyl-1-(propyl-4-sulfonyl) imidazolium methanesulfonate as catalyst. The results showed that when the optimal molar ratio of $ZnCl_2$ to [$PhSO_3$mim] [MSA] was 0.02, the selectivity of CPL was 94% at 90˚C for 1 hour, and the yield of CPL remained at a high level after 10 reactions. Zhang's research group [12] developed Beckmann rearrangement experiment using trifluoroacetic acid as catalyst. Experiments show that the conversion of this method is 100%, the yield is almost 100%, and there is no by-product. Kalkhambkar's research group [13] developed Cu/SBA-15 as a solid acid catalyst for Beckmann rearrangement research. Gao's research group [14] developed a new method for Beckmann rearrangement of ketoxime catalyzed by carbon tetrabromide/triphenylphosphine. This method does not need to add acids or metals, and has good tolerance of functional groups and high yield. Allam's research group [15] developed a new method to directly synthesize primary amides from aldehydes catalyzed by scandium trifluoromethane sulfonate under microwave conditions. This method has fast reaction rate, mild reaction conditions and high yield.

In response to the problems caused by previous catalysts, this article attempts to use silica gel loaded trifluoromethanesulfonic acid as a catalyst to improve catalytic performance and further explores the optimal catalyst preparation and Beckmann rearrangement reaction process conditions.

2. Experimental Materials and Methods

2.1. Materials

Nitrogen was purchased from Zhejiang Minxing Gas Co., Ltd., and trifluoromethanesulfonic acid (≥99%) was purchased from Hefei Bomei Biotechnology Co., Ltd.; Cyclohexanone oxime (≥97%), acetonitrile (≥99%), 1,2-dichloroethane (≥99%), 1,4-dioxane (≥99.5%), dimethyl sulfoxide (≥99%), and benzonitrile (≥99%) were purchased from China National Pharmaceutical Group Chemical Reagent Co., Ltd.; Cyclohexanone (≥99.5%) and n-heptane (≥98%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.; Acetonitrile (≥99%) and caprolactam (≥99%) were purchased from Shanghai McLean Biochemical Technology Co., Ltd.

2.2. Methods

Catalyst preparation: In a muffle furnace, a certain quantity of silica gel underwent calcination at 400˚C for 24 hours. A three-necked flask was charged with 2 g of silica gel and 60 mL of dichloromethane [15]. Subsequently, under nitrogen gas protection, 0.4 g of chlorosulfonic acid was titrated at room temperature by rapidly stirring for 2.5 hours. The solvent was then evaporated using a rotary evaporator. The resulting powder was subjected to calcination in a tube furnace (under nitrogen) at 150˚C for 24 hours. The reaction principle is shown in **Figure 1**.

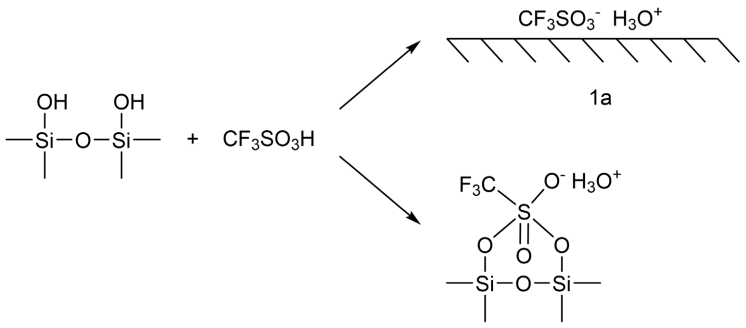

Figure 1. Principle of silica gel loaded trifluoromethanesulfonic acid.

Beckman rearrangement: Under nitrogen protection at 130˚C, 2 g of catalyst, 1 g of CHO, and 30 mL of benzonitrile were combined in a three-necked flask equipped with a thermowell and condensation reflux device. The mixture was stirred for 4 hours. After completion of the reaction, the sample was extracted from the centrifuge, and 0.1 g of the internal standard n-heptane was introduced to the sample. Analysis was carried out using a GC-9600A gas chromatograph. The reaction principle is shown in Figure 2.

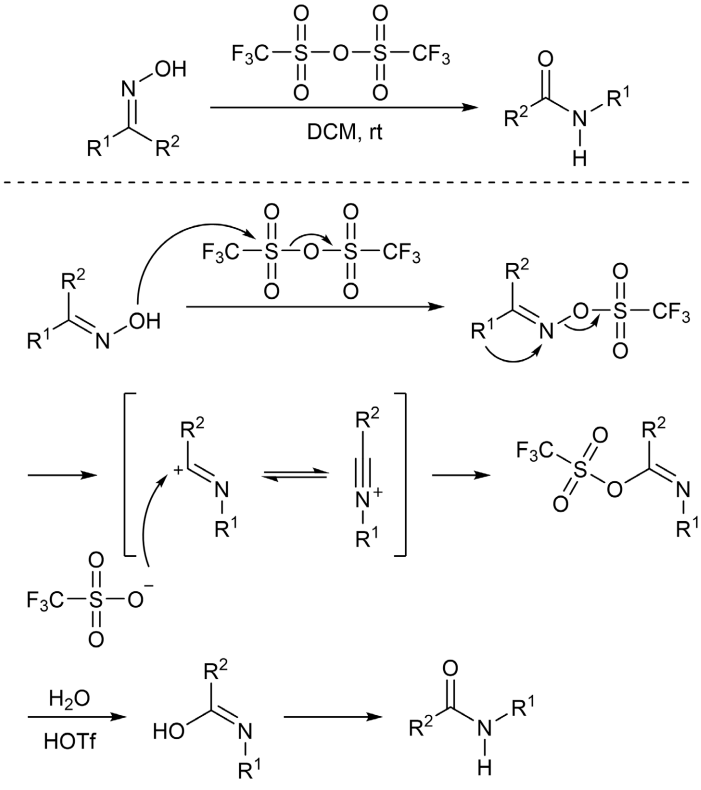

Figure 2. Principle of Beckmann rearrangement under the action of trifluoromethylsulfonic anhydride.

2.3. Measurement of Catalyst Acidity

The catalyst used in the test is the one with the best catalytic effect, namely the

highest conversion of CHO and selectivity of CPL. The preparation conditions are as follows: silica gel is roasted at 400˚C for 24 hours, 2 g of silica gel and 0.4 g of trifluoromethanesulfonic acid are taken, solvent is 30 mL of acetonitrile, stirred under nitrogen protection at room temperature for 2.5 hours, and then placed in a tube furnace for 150˚C nitrogen protection roasting for 24 hours.

Table 1. Catalyst acid value results

	Dropwise dosage of NaOH solution (mL)
1	3.04
2	3.02
3	2.94
Average value	3.01
Acid value	1.5 (mmolH^+/g)

Based on the results in Table 1, it can be concluded that the measured acidity value is slightly lower than the theoretical acidity value for all loads. This may be due to the release of a portion of free trifluoromethanesulfonic acid during storage, resulting in a decrease in acidity value.

3. Catalyst Characterization

3.1. Infrared Analysis

The instrument used in this article is the Thermo Scientific Nicolet iS20 Fourier infrared spectrometer produced by the model company. The test parameters are as follows: the resolution is set to 4 cm^{-1}, 32 scans were conducted, and the test wavenumber range is limited to 400/600 - 4000 cm^{-1}.

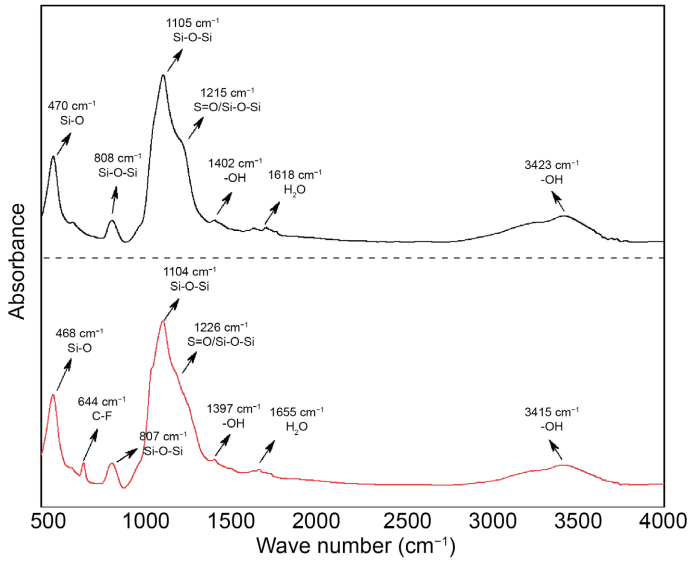

Figure 3. Infrared spectrum of silica gel loaded trifluoromethanesulfonic acid.

The infrared spectrum of the silica gel loaded trifluoromethanesulfonic acid sample is shown in **Figure 3**, which has similar characteristics to the silica gel loaded chlorosulfonic acid. The absorption peaks at 1104 cm^{-1}, 807 cm^{-1}, and 468 cm^{-1} originate from various vibration forms of Si-O [16]. The absorption peaks at 3415 cm^{-1}, 1655 cm^{-1}, and 1397 cm^{-1} are related to the vibration of hydroxyl groups in silica gel and bound water [17]. The absorption peak at 1226 cm^{-1} shows a certain fluctuation, which is a mixed absorption peak of Si-O and S=O stretching vibration [16] [17]. It is worth noting that the silica gel loaded trifluoromethanesulfonic acid sample exhibits a significant absorption peak at 644 cm^{-1}, which originates from the C-F stretching vibration in the trifluoromethanesulfonic acid structure [18]. Trifluoromethanesulfonic acid was successfully crosslinked with silica gel.

3.2. Thermogravimetric Analysis of Catalysts

According to the blue curve and peak position in **Figure 4**, it can be seen that there is not much change in catalyst quality before around 260˚C. By around 340˚C, the quality significantly decreases, possibly due to the decomposition of trifluoromethanesulfonic acid loaded on silica gel at around 340˚C, resulting in a sharp decrease in catalyst quality.

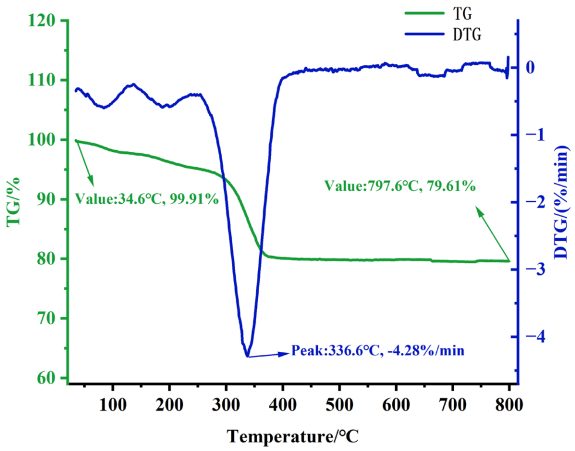

Figure 4. Thermogravimetric analysis of silica gel loaded trifluoromethanesulfonic acid.

3.3. BET

The BET test of the catalyst prepared in this article was carried out using the American company model Micromerities Tristar. Testing process: In a nitrogen atmosphere, the sample in the sample preparation tube is desorbed, followed by physical adsorption testing. The equilibrium interval is 10 seconds, and automatic degassing occurs during testing.

The nitrogen adsorption and desorption curve of the sample shows a clear III-type adsorption isotherm and has a significant H_3-type hysteresis loop structure, indicating that the sample is a mesoporous material and does not contain a microporous structure. Other relevant information is shown in **Figure 5** and **Table 2**.

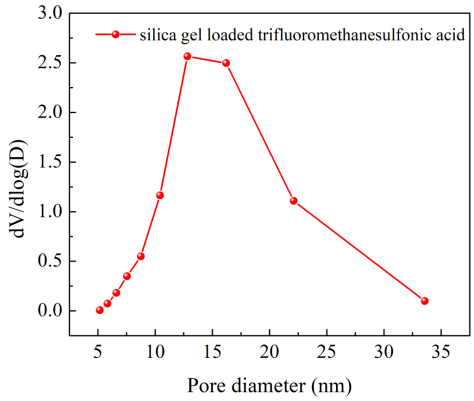

Figure 5. Pore size distribution of silica gel loaded trifluoromethanesulfonic acid.

Table 2. Comprehensive information table of samples.

Sample	Specific surface area (m^2/g)	Pore volume (mL/g)	Average pore diameter (nm)
Silica gel loaded trifluoromethanesulfonic acid	174	0.93	14.1

3.4. NH_3-TPD

The NH_3-TPD curve of trifluoromethanesulfonic acid loaded silica gel is shown in **Figure 6**, with a programmed maximum temperature of 600˚C. Compared to the NH_3-TPD curve of the carrier silica gel shown in **Figure 7**, the catalyst loaded with trifluoromethanesulfonic acid showed an additional ammonia desorption peak in the high-temperature range (300˚C - 450˚C), and the peak area significantly increased in the low-temperature range (50˚C - 200˚C), indicating a significant increase in total acid content. Compared to the desorption peak in the low-temperature range, the desorption peak area of ammonia in the high-temperature range is larger, indicating that the loading of trifluoromethanesulfonic acid provides more strong acid sites.

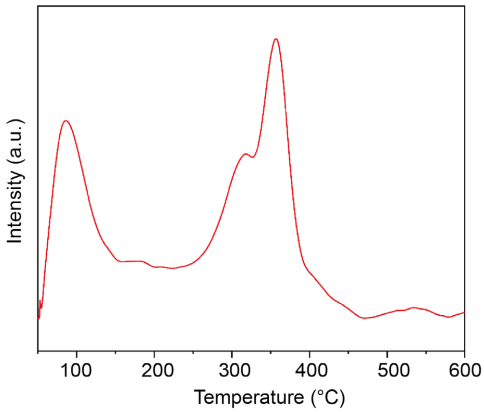

Figure 6. Silica gel loaded trifluoromethanesulfonic acid NH_3-TPD diagram.

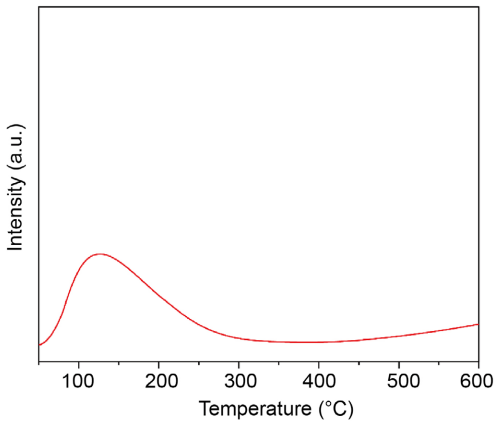

Figure 7. NH_3-TPD curve of carrier silica gel.

4. Results and Discussion

4.1. Effect of Solvent Dehydration on Experiments

One of the key factors affecting the formation of side reactions in the reaction system is whether the solvent contains water. Firstly, the solvent used in the catalyst preparation process, such as acetonitrile and the solvent used in the Beckmann rearrangement reaction, such as benzonitrile, is dehydrated. Then, experiments are conducted, and the measured results are shown in **Table 3**.

Table 3. Effect of dehydration on the reaction.

Whether to remove water	Conversion (%)	Selectivity (%)	
	CHO	CPL	CH
Underwatered	90	80	10
Dewatering	90	90	5

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, acetonitrile 25 mL, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, benzonitrile 30 mL, nitrogen protection.

CHO is prone to hydrolysis reactions in the presence of water. When conducting experiments, there is a competitive relationship between rearrangement reaction and hydrolysis reaction, so inhibiting the side reaction hydrolysis reaction becomes the key to improving the experimental effect. This experiment compared the effects of solvent dehydration and non-dehydration on the experimental results. From the results in **Table 3**, it can be seen that solvent dehydration has a significant effect on improving the conversion of CHO and the selectivity of CPL. Afterwards, the reaction solvent was treated by dehydration.

4.2. Effect of Silica Gel Mesh Number on Rearrangement Reaction during Catalyst Preparation Process

The effect of silica gel mesh size on the experiment was studied while keeping other

quantities unchanged, as shown in Figure 8.

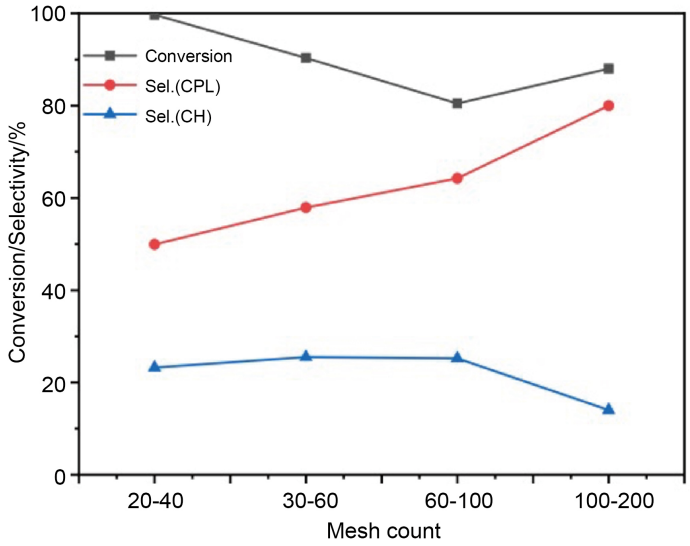

Figure 8. Effect of silica gel mesh on rearrangement reaction.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, acetonitrile 25 mL, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, benzonitrile 30 mL, nitrogen protection.

From Figure 8, it can be seen that increasing the amount of silica gel results in an initial increase in the conversion of CHO, then reaching the highest point at 60 - 100 mesh, and then beginning to decrease. The selectivity of CPL has been consistently increasing, reaching its maximum at 100 - 200 mesh. This may be because as the mesh size increases, the silica gel particles become smaller and the adsorption effect changes, making it easier to load trifluoromethanesulfonic acid, resulting in a consistently higher selectivity for CPL. Therefore, considering 100 to 200 mesh sizes comprehensively, it is the optimal mesh size for silica gel loaded trifluoromethanesulfonic acid for Beckmann rearrangement.

4.3. Effect of Solvent Types on Rearrangement Reaction during Catalyst Preparation Process

Keeping other amounts unchanged, the effect of solvent types on the experiment during catalyst preparation was studied, as shown in Figure 9.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, solvent 25 mL, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, benzonitrile 30 mL, nitrogen protection.

From Figure 9, it can be seen that when acetonitrile is used as the solvent, the conversion of CHO is the highest and the selectivity of CPL is also the highest. This may be due to the presence of CN groups in the acetonitrile solvent, which

has a catalytic effect on trifluoromethanesulfonic acid loaded on silica gel. In addition, acetonitrile has a lower boiling point, lower polarity, and lower water content in these solvents, resulting in less hydrolysis and loss of trifluoromethanesulfonic acid, which can be more loaded on silica gel, ultimately leading to optimal catalytic performance.

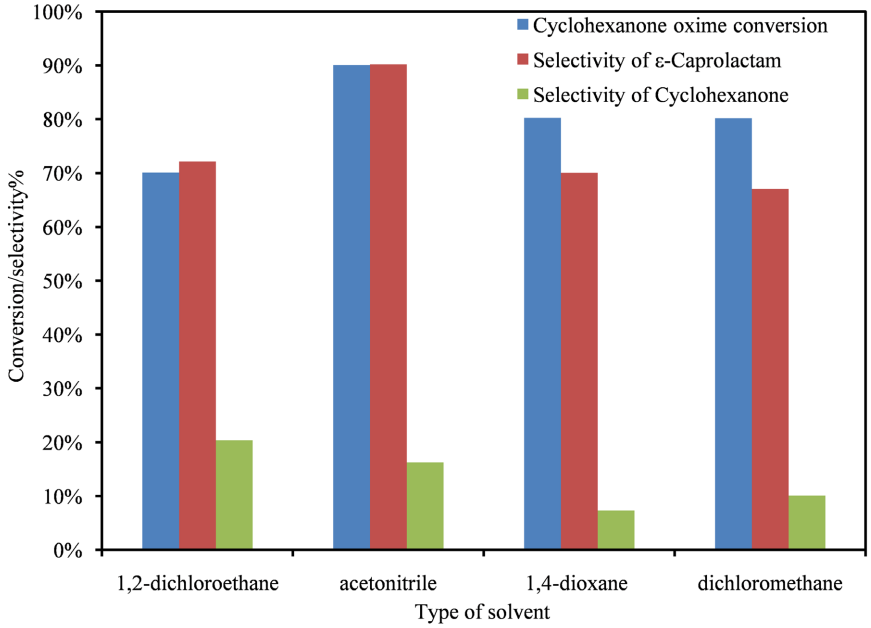

Figure 9. Effect of solvent types on rearrangement reaction.

4.4. Effect of Stirring Time on Rearrangement Reaction during Catalyst Preparation Process

The effect of stirring time on the experiment was studied while keeping other quantities unchanged, as shown in Figure 10.

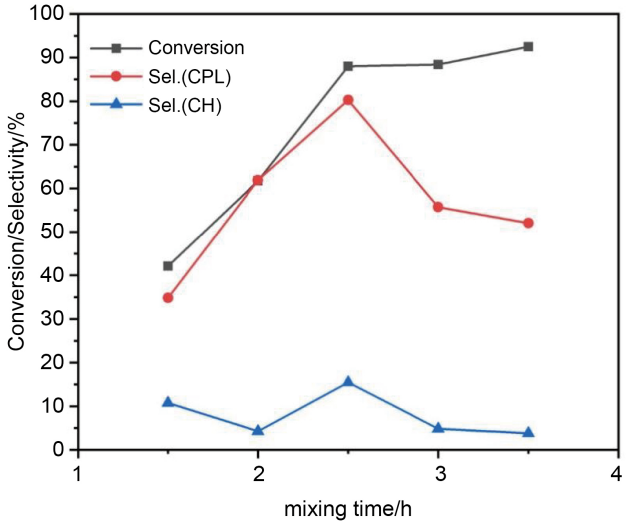

Figure 10. Effect of mixing time on rearrangement reaction.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, acetonitrile 25 mL, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, benzonitrile 30 mL, nitrogen protection.

From Figure 10, it can be seen that as the stirring time increases, the conversion of CHO first increases and then remains basically unchanged. When it reaches 3 hours, it reaches its maximum, while the selectivity of caprolactam first increases and then decreases. When it reaches 2.5 hours, it reaches its maximum. This may be because at 2.5 hours, trifluoromethanesulfonic acid was fully loaded on the silica gel. As the stirring time increased, the acid loaded on the silica gel fell off and the catalyst structure was destroyed, leading to a gradual decrease in the conversion of CHO and the selectivity of CPL. Due to the small difference in CHO conversion between 3 and 2.5 hours, but the significant difference in CPL selectivity, a stirring time of 2.5 hours is considered the optimal stirring time for silica gel loaded trifluoromethanesulfonic acid for Beckmann rearrangement.

4.5. Effect of Solvent Volume on Rearrangement Reaction during Catalyst Preparation Process

The effect of solvent volume on the experiment during the catalyst preparation process was studied, while keeping other amounts unchanged. The results are shown in Figure 11.

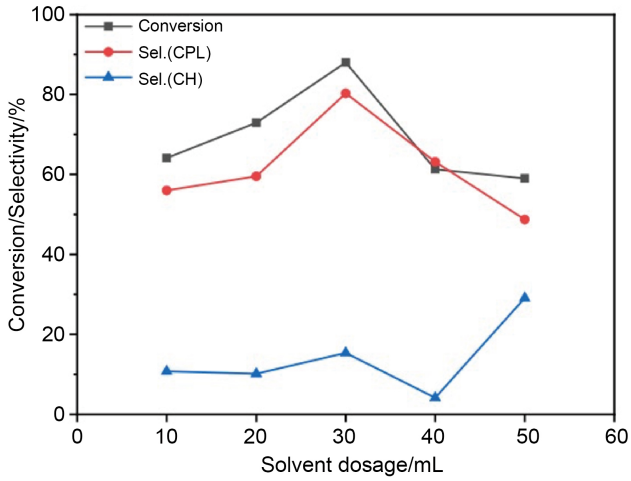

Figure 11. Effect of solvent volume during catalyst preparation process.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, acetonitrile, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, benzonitrile 30 mL, nitrogen protection.

From Figure 11, it can be seen that as the solvent volume increases, the conversion of CHO increases, and the selectivity of CPL also increases. When the solvent volume increases to 25 mL, the conversion of CHO and the selectivity of CPL

reach their maximum values. However, as the volume further increases, the conversion of CHO and the selectivity of CPL gradually decrease. This may be because the larger volume leads to a decrease in the concentration of trifluoromethanesulfonic acid, making it difficult to fully load with silica gel. In addition, the use of more solvents also increases costs. Therefore, considering all factors, 25 mL is the optimal stirring volume for silica gel loaded trifluoromethanesulfonic acid in Beckmann rearrangement.

4.6. Effect of Solvent Types on Rearrangement Reactions

The effect of catalyst dosage on the experiment in Beckmann rearrangement was studied, keeping other amounts unchanged. The results are shown in Figure 12.

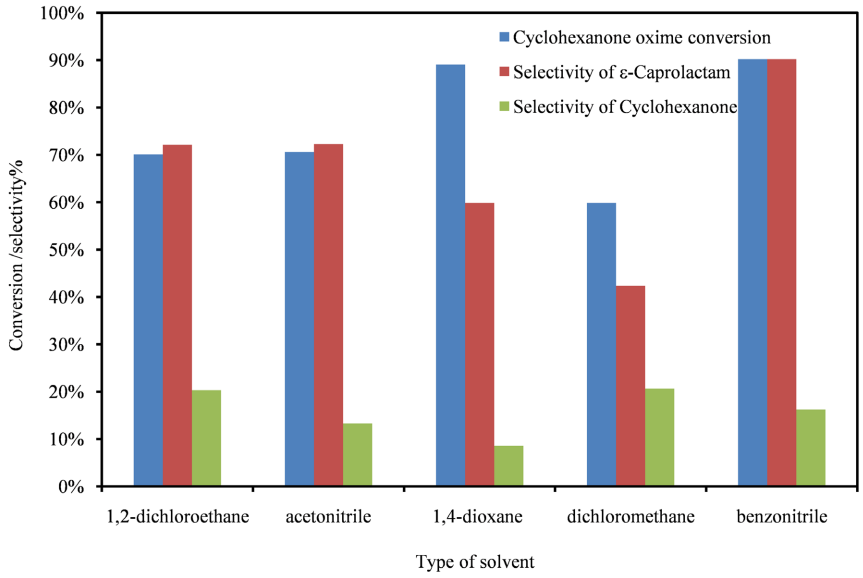

Figure 12. Effect of solvent types on experiments.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, acetonitrile 25 mL, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, solvent 30 mL, nitrogen protection.

From Figure 12, it can be seen that the conversion of CHO and the selectivity of CPL for dichloromethane, acetonitrile, and 1,4-dioxane are not high. This may be due to the lower boiling points of dichloromethane, acetonitrile, and 1,4-dioxane, with heating temperatures of 30˚C, 60˚C, and 90˚C respectively, resulting in a slow reaction rate and a low conversion of CHO due to the low heating temperature. At the same time, too low a temperature results in the inability to achieve optimal catalyst activity, resulting in lower selectivity of CPL. The boiling point of benzonitrile is relatively high, and the experimental temperature can be carried out at a higher temperature of 130˚C, resulting in a faster reaction rate. At the same time, the higher temperature leads to the optimal catalyst activity, which in turn leads to higher selectivity of CPL. Therefore, considering comprehensively

that benzonitrile is the optimal solvent for silica gel loaded trifluoromethanesulfonic acid for Beckmann rearrangement.

4.7. Effect of Reaction Temperature on Rearrangement Reactions

The effect of reaction temperature on the experiment in Beckmann rearrangement was studied, keeping other quantities unchanged. The results are shown in Figure 13.

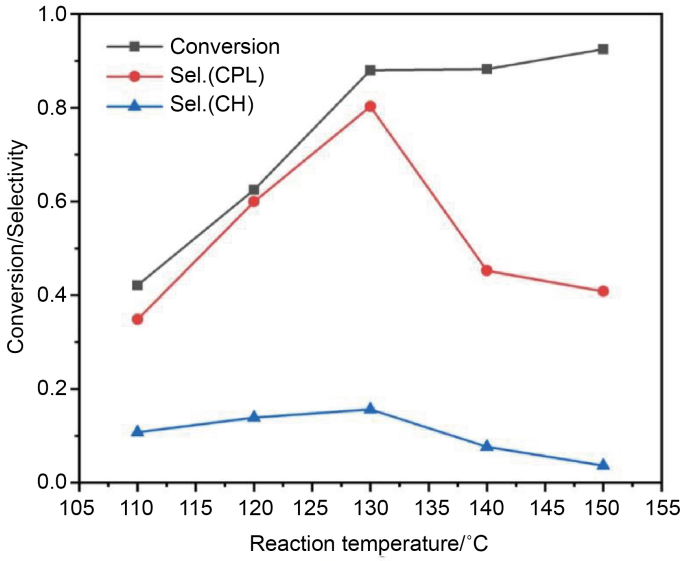

Figure 13. Effect of temperature on experiments.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, acetonitrile 25 mL, nitrogen protection.

Reaction conditions: CHO 1 g, catalyst 2 g, benzonitrile 30 mL, nitrogen protection.

From Figure 13, it can be seen that temperature has a significant impact on the Beckmann rearrangement of CHO. As the temperature increases, the conversion of CHO increases, and the selectivity of CPL also increases. At 130˚C, the conversion of CHO and the selectivity of CPL reached their peak. As the temperature continues to rise, the conversion of CHO and the selectivity of CPL decrease instead. This may be due to the condensation reaction between CPL and CH at too high a temperature. It may also be due to the reduced activity of the catalyst, even causing partial decomposition, resulting in a gradual decrease in the selectivity of CPL. Therefore, 130˚C is the optimal temperature for silica gel loaded trifluoromethanesulfonic acid for Beckmann rearrangement.

4.8. Effect of Catalyst Amount on Rearrangement Reaction

The effect of catalyst dosage on the experiment in Beckmann rearrangement was studied, keeping other amounts unchanged. The results are shown in Figure 14.

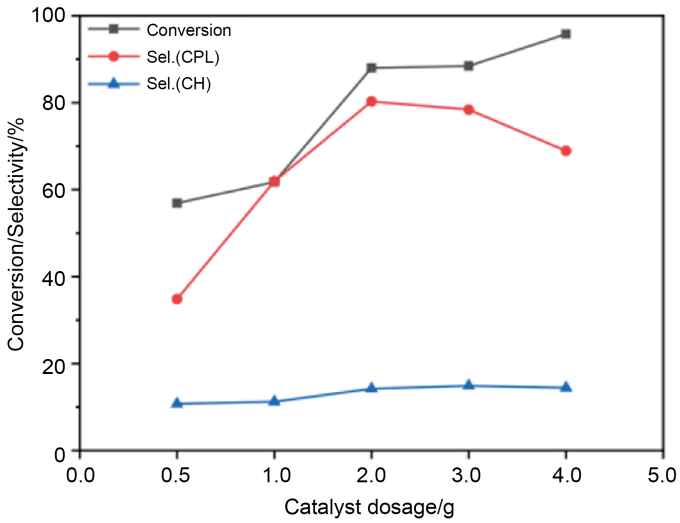

Figure 14. Effect of catalyst amount on rearrangement reaction.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, acetonitrile 25 mL, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, benzonitrile 30 mL, nitrogen protection.

From **Figure 14**, it can be seen that as the amount of catalyst used increases, the conversion of CHO increases, and the selectivity of CPL also increases. When the amount of catalyst is 2 g, the selectivity of CPL reaches its maximum. Continuing to increase the amount of catalyst, the selectivity of caprolactam gradually decreases. When the amount of catalyst reaches the maximum conversion of CHO 1 g, increasing the amount of catalyst gradually reduces the conversion of CHO. This may be due to the reduction of reaction space due to the excessive amount of catalyst, resulting in insufficient reaction. It may also be due to the catalyst adsorbing too many products and reactants, making it difficult for CHO to react and CPL to be detected. Due to the fact that the conversion of CHO remains relatively unchanged with the amount of 2 g catalyst compared to the amount of 1 g catalyst, the selectivity of CPL is significantly improved. Therefore, considering the amount of catalyst, 2 g is the optimal amount of catalyst for silica gel supported trifluoromethanesulfonic acid for Beckmann rearrangement.

4.9. Effect of Solvent Volume on Rearrangement Reaction

The effect of solvent volume on the experiment in Beckmann rearrangement was studied, keeping other quantities unchanged. The results are shown in **Figure 15**.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, nitrogen protection

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, benzonitrile, nitrogen protection.

From **Figure 15**, it can be seen that as the solvent volume increases, the conversion of CHO increases, and the selectivity of CPL also increases. At 30 mL, the conversion of CHO and the selectivity of CPL reach their maximum. Continuing

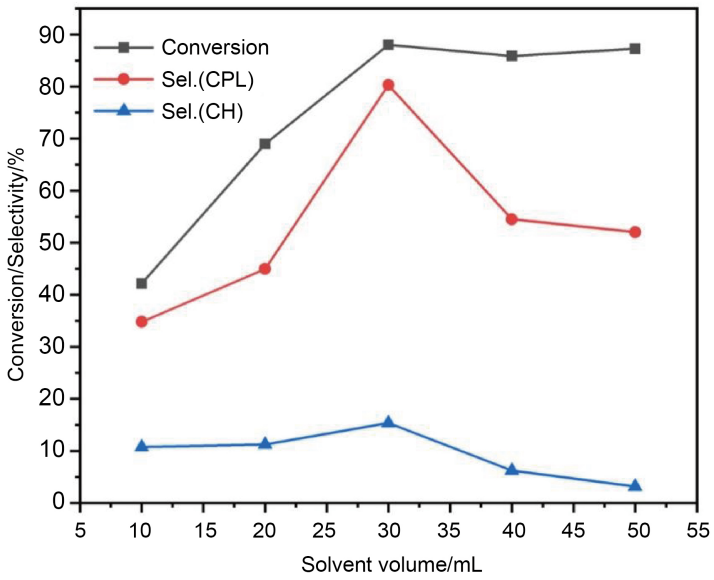

Figure 15. Effect of solvent volume on rearrangement reaction.

to increase the volume, the conversion of CHO and the selectivity of CPL gradually decrease. This may be because the volume is too large, which leads to a lower concentration of CHO and makes the reaction difficult. Additionally, the increase in solvent size increases costs. Therefore, a solvent volume of 30 mL is considered the optimal volume for Beckmann rearrangement.

4.10. Effect of Catalyst Reuse Times

The number of times a catalyst can be reused while maintaining a certain level of activity and selectivity is an important indicator of its performance. In this chapter's experiment, the catalyst with the best catalytic effect, namely the one with the highest CHO conversion and CPL selectivity, was selected for the experiment. Then, it was washed with acetone three times and finally dried at 80˚C. Repeat the Beckmann rearrangement experiment using the dried catalyst, and the results are shown in **Table 4**.

Table 4. Effect of catalyst reuse times.

Reuse Times	Conversion (%)	Selectivity (%)	
	CHO	CPL	CH
1	90	90	5
2	83	86	9
3	80	80	15
4	65	75	16
5	50	70	20

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1

g, trifluoromethanesulfonic acid 0.2 g, acetonitrile 25 mL, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, benzonitrile 30 mL, nitrogen protection.

According to the data in Table 4, after 3 repetitions of the catalyst, the selectivity of CPL remained relatively stable, but the conversion of CHO significantly decreased. This may be due to several reasons: firstly, with the repeated use of the catalyst, the quality of the catalyst gradually decreases, resulting in a decrease in the number of sulfonic groups on top; secondly, during the reaction process, the interaction between magnetic particles may cause partial damage to certain catalysts; finally, the accumulation of raw materials and products may clog the pores of the catalyst, thereby affecting its catalytic performance. However, it is important to repeat experimental data indicating that the selectivity of the catalyst for CPL has not changed much, so the catalyst can still be reliably reused.

4.11. Effect of Reaction Time on Rearrangement Reactions

The effect of reaction time on the experiment in Beckmann rearrangement was studied, keeping other quantities unchanged. The results are shown in Figure 16.

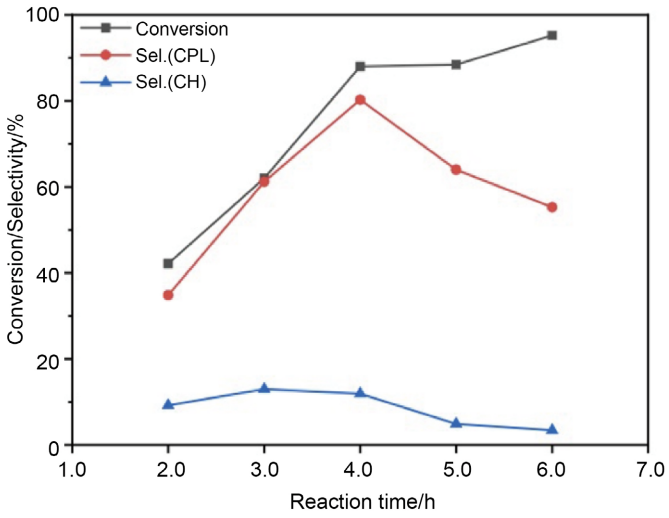

Figure 16. Effect of reaction time on rearrangement reaction.

Catalyst preparation conditions: Normal atmospheric temperature, silica gel 1 g, trifluoromethanesulfonic acid 0.2 g, acetonitrile 25 mL, nitrogen protection.

Reaction conditions: 130˚C, CHO 1 g, catalyst 2 g, benzonitrile 30 mL, nitrogen protection.

From Figure 16, it can be seen that as the reaction time increases, the conversion of CHO first increases and then remains basically unchanged. When it reaches 4 hours, it reaches its maximum, while the CPL selectivity first increases and then decreases. When it reaches 4 hours, it reaches its maximum. This may be because as the reaction time increases, on the one hand, the generated CPL is prone to polymerization, leading to a gradual decrease in the selectivity of caprolactam. On

the other hand, the catalyst adsorbs more products and reactants, making it difficult for CHO to react or CPL to be detected, resulting in a gradual decrease in the conversion of CHO and the selectivity of CPL.

5. Conclusion

This article studies the loading of trifluoromethanesulfonic acid over silica gel as a solid acid catalyst to evaluate its catalytic performance for Beckmann rearrangement reactions, and improves the catalytic process to find the optimal operating conditions. It was found that the optimal conditions for catalyst preparation were as follows: raw material silica gel:trifluoromethanesulfonic acid = 1:0.2 (mass ratio), room temperature, stirring time of 2.5 hours, and solvent of acetonitrile, silica gel mesh size is 100 - 200. The optimal reaction conditions for Beckmann rearrangement are CHO:catalyst = 1:2 (mass ratio), temperature of 130˚C, solvent of benzonitrile, volume of 30 mL/g CHO, and reaction time of 4 hours. Under the above conditions, the conversion of CHO is 90%, and the selectivity of CPL is 90%. The catalyst can be recycled and easily recovered with good repeatability, and the process is simple, green, and environmentally friendly. It has good industrial application prospects.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Wu, Y., Inoue, M., Sakakura, S. and Hyodo, K. (2024) *γ*-Lactam Synthesis from Cyclobutanone *via* Transoximation and the Beckmann Rearrangement. *Organic & Biomolecular Chemistry*, **22**, 4364-4368. https://doi.org/10.1039/d4ob00566j

[2] Yang, J., He, W., Zhang, M., Hou, J., Wu, S. and Wang, X. (2024) Solubility Behavior and Thermodynamic Properties of Caprolactam in Four Pure Solvents and Two Cosolvent Mixtures. *Fluid Phase Equilibria*, **582**, Article ID: 114101. https://doi.org/10.1016/j.fluid.2024.114101

[3] Cazzador, G., Manzato, L., Ronchin, L., Sadraoui, C., Vavasori, A. and Zanella, M. (2022) A New Sustainable Multistep Catalytic Process from Benzene to Caprolactam: Amination, Hydroximation and Beckmann Rearrangement Promoted and Catalyzed by Trifluoroacetic Acid. *Catalysis Letters*, **153**, 2763-2774. https://doi.org/10.1007/s10562-022-04207-9

[4] Yang, W., Jung, S., Lee, J., Lee, S.W., Kim, Y.T. and Kwon, E.E. (2023) Selective Recovery

of Caprolactam from the Thermo-Catalytic Conversion of Textile Waste over γ-Al_2O_3 Supported Metal Catalysts. *Environmental Pollution*, **329**, Article ID: 121684. https://doi.org/10.1016/j.envpol.2023.121684

[5] Minor, A., Goldhahn, R., Rihko-Struckmann, L. and Sundmacher, K. (2023) Chemical Recycling Processes of Nylon 6 to Caprolactam: Review and Techno-Economic Assessment. *Chemical Engineering Journal*, **474**, Article ID: 145333. https://doi.org/10.1016/j.cej.2023.145333

[6] Ling, W., Zhou, Y., Zhao, J. and Yao, G. (2022) Study on Enhanced Nitrogen Removal of Caprolactam Production Wastewater. *IOP Conference Series*: *Earth and Environmental Science*, **1035**, Article ID: 012010. https://doi.org/10.1088/1755-1315/1035/1/012010

[7] Katada, N., Tsubouchi, T., Niwa, M. and Murakami, Y. (1995) Vapor-Phase Beckmann Rearrangement over Silica Monolayers Prepared by Chemical Vapor Deposition. *Applied Catalysis A: General*, **124**, 1-7. https://doi.org/10.1016/0926-860x(94)00257-6

[8] Jain, P.U. and Samant, S.D. (2018) A Facile One-pot Transformation of Aromatic Aldehydes/ketones to Amides: Fe_2O_3@SiO_2 as an Environmentally Benign Core-Shell Catalyst. *ChemistrySelect*, **3**, 1967-1975. https://doi.org/10.1002/slct.201703155

[9] Khayyat, S.A., Selvin, R. and Umar, A. (2017) Beckmann Rearrangement of Cyclohexanone Oxime Using Nanocrystalline Titanium Silicalite-1 (TS-1). *Journal of Nanoscience and Nanotechnology*, **17**, 2170-2176. https://doi.org/10.1166/jnn.2017.12724

[10] Ren, C., Wang, Z., Gao, Q., Li, J., Jiang, S., Huang, Q., *et al.* (2023) Novel Brønsted Acidic Ionic Liquids as High Efficiency Catalysts for Liquid-Phase Beckmann Rearrangement. *Catalysts*, **13**, Article 978. https://doi.org/10.3390/catal13060978

[11] Guo, X., Wang, Z., Yang, Y., Zhang, J., Liu, Y., Mu, Z., *et al.* (2024) Highly Efficient Catalyzed by Imidazolium-Based Dual-Sulfonic Acid Functionalized Ionic Liquids for Liquid Phase Beckmann Rearrangement: Experiments and COSMO-RS Calculations. *Green Chemical Engineering*, **5**, 108-118. https://doi.org/10.1016/j.gce.2023.01.002

[12] Zhang, J.S., Riaud, A., Wang, K., Lu, Y.C. and Luo, G.S. (2013) Beckmann Rearrangement of Cyclohexanone Oxime to ε-Caprolactam in a Modified Catalytic System of Trifluoroacetic Acid. *Catalysis Letters*, **144**, 151-157. https://doi.org/10.1007/s10562-013-1114-3

[13] Kalkhambkar, R.G. and Savanur, H.M. (2015) Highly Efficient Synthesis of Amides from Ketoximes Using Trifluoromethanesulphonic Anhydride. *RSC Advances*, **5**, 60106-60113. https://doi.org/10.1039/c5ra07789c

[14] Gao, P. and Bai, Z. (2017) Carbon Tetrabromide/Triphenylphosphine-Activated Beckmann Rearrangement of Ketoximes for Synthesis of Amides. *Chinese Journal of Chemistry*, **35**, 1673-1677. https://doi.org/10.1002/cjoc.201700191

[15] Allam, B.K. and Singh, K.N. (2011) Highly Efficient One-Pot Synthesis of Primary Amides Catalyzed by Scandium(III) Triflate under Controlled MW. *Tetrahedron Letters*, **52**, 5851-5854. https://doi.org/10.1016/j.tetlet.2011.08.150

[16] Ma, Y., Wang, J., Wang, L. and Yu, Y. (2020) Structure and Thermal Stability of Column Chromatography Silica Gel. *Coal and Chemical Industry*, **43**, 154-157. (In Chinese)

[17] Sun, Y., Deng, X., Xu, Z., Bian, D. and Zhou, X. (2007) Sulphuration and Characterization of PE Non-Woven Film by Chlorosulfonic Acid. *Journal of Functional Polymers*, No. 3, 272-276. (In Chinese)

[18] Hu, J., Yan, H., Hu, H. and Fang, Z. (2018) Effect of Trifluoromethanesulfonic Acid Metal Salts on the Curing of Benzoxazine and Thermo Stability of Its Cured Product. *Thermosetting Resin*, **33**, 12-20. (In Chinese)