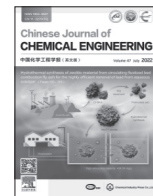




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Full Length Article

Preparation of aldoxime through direct ammoximation using titanium silicalite-1 catalyst



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ABSTRACT

The liquid phase direct ammoximation of 5-isooctyl salicylaldehyde with ammonia and hydrogen peroxide was studied using titanium silicalite-1 (TS-1) catalyst. The effect of reaction parameters on the yield of the product was studied, which include reaction temperature, reaction time, molar ratio of ammonia to aldehyde as well as hydrogen peroxide to aldehyde. The influence of the amount of catalyst on the reaction results was also investigated. The maximum 5-isooctyl salicylaldoxime yield of 98.76% was achieved under the following optimal reaction conditions: the molar ratio of 5-isooctylaldehyde to hydrogen peroxide and ammonia of 1:1.4:1.6, the reaction temperature of 70 °C, the amount of TS-1 of 17.5 g·mol⁻¹ (5-isooctyl salicylaldehyde), and the feeding time of 2 h. This method has the mild reaction conditions and avoids the shortcomings of traditional methods. Moreover, useless inorganic salts by-products are avoided, and there is no environmental pollution.

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1. Introduction

Solvent extraction is widely used in hydrometallurgy field due to its good selectivity and high metal recovery [1]. In recent years, with the rapid development of solvent extraction technologies and the increasing demand for exploiting low-grade ores, as well as the environmental protection, solvent extraction (SX) technology will play more important role in the metallurgical industry. Since 1960s, the hydrometallurgical technologies have been more and more practically applied, especially in non-ferrous metals solvent extraction plants. For a long time, people used smelting method to produce various metals, but the process requires high grade of ores. Moreover, the smelting process is complicated, and has serious air pollution and large waste of resources. With the discovery of new reagents for metals recovery in the mid-1960s, the metals such as copper produced by hydrometallurgical technologies increased rapidly. Nowadays the reagents used in metals recovery mainly include oximes, β -diketones, ternary amines and complex compounds [2]. Among them, hydroxyoximes are the most attrac-

tive, especially aromatic oximes, which promoted a rapid development of hydrometallurgy in mine chemistry and have been widely used in metals recovery.

5-isooctyl salicylaldoxime (ISAO) has excellent affinity with various metals, as a consequence, which can be used as the key component of many commercial extractants. The traditional preparation method of ISAO is via the oximation reaction of 5-isooctyl salicylaldehyde (ISA) using hydroxylamine salts in the presence of solvent such as toluene. However, this method has many drawbacks, such as low atomic utilization rate, long and complex production process, and high operation cost. Especially, during the production process, a large number of by-products, such as ammonium sulfate or ammonium chloride solution, will be generated, and is absolutely forbidden to discharge directly and have to be treated via evaporation under higher temperature, indicating that higher cost would be paid to treat these useless salt solutions. As a result, finding a new way to avoid the by-products of useless inorganic salts attracted much interesting in recent years. As is known, direct ammoximation is a suitable choice to solve this issue, while it should find an excellent catalyst to achieve direct ammoximation because the catalyst has significant effects on the yield and purity of the products.

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With the development of titanium silicalite molecular sieve, the excellent selective catalytic function of TS-1 was favored [3]. Together with H_2O_2 , titanium silicalite molecular sieve has been widely used in the catalytic oxidation of various organic compounds, especially in the ammoximation of organic compounds. As a green catalyst, TS-1 has been widely used in various catalytic oxidation reactions with H_2O_2 [4–6].

The reported studies focused on reaction mechanism [7–13], functional theory and kinetics [14–16], optimization of reaction parameters [6,17], preparation and post-treatment of titanium silicate [18–21], deactivation and regeneration of catalysts [22–24]. Moreover, the application of microreaction system in ammoximation attracted many interests [25].

Chu *et al.* [26] used density functional theory to study the mechanism of ammoximation of cyclohexanone over TS-1 catalyst. The non-catalytic oxidation of cyclohexanone with hydroxylamine in water showed that water not only contributed to proton transfer, but also stabilized the proton transfer process by hydrogen bonding. As far as the ammoximation of ketones or aldehydes on titanium silicate is concerned, it is generally believed that the typical side reaction is deep oxidation [5]. In the performance of catalysts, hydrophilicity/hydrophobicity, porosity and the properties of Ti active sites are considered to affect the selectivity of products [27,28].

Nowadays there are two kinds of understanding about ammoximation reaction mechanism. One is imine mechanism, which considered that cyclohexylamine intermediate was firstly generated by non-catalytic reaction of cyclohexanone and ammonia, and then oxidized by H_2O_2 on Ti active center in zeolite channel [3]. This mechanism involves the imine intermediate of cyclohexanone and ammonia. The other is hydroxylamine mechanism, which included hydroxylamine intermediate formed by oxidation of ammonia on Ti site by H_2O_2 , and subsequent non catalytic ammoximation of ketone and hydroxylamine [29]. The key step of this mechanism was the formation of hydroxylamine. However, the formation of imine species, which was unstable, often decomposes back to a ketone. Therefore, it is believed that this mechanism plays a secondary role in the ammoximation of cyclohexanone over TS-1 catalyst. The most commonly accepted mechanism is that hydroxylamine was formed *via* catalytic oxidation of ammonia by hydrogen peroxide on Ti active site and then non catalytic oxidation of ketone and hydroxylamine in homogeneous phase to form oxime.

Recent years, more and more attention has been paid to the environment. As one of the main directions of chemical progress in the new century, green chemistry is widely advocated. Each atom in the raw materials involved in the reaction is required to enter the product without producing any other by-products. There is “zero discharge” of waste, and the raw materials, catalysts and solvents are all non-toxic and harmless. There is no environmental pollution during the production process, and environmentally friendly products are produced. The ammoximation process has the characteristics of mild conditions, high reaction conversion rate and selectivity, simple process, and environmental friendliness. The outcomes contain only target products and water, which makes up for various shortcomings of the traditional process and meets the requirements of green chemical industry.

Up to now, the synthesis of ISAO from ISA catalyzed by TS-1 has not been studied in detail. The traditional process of oximation *via* hydroxylamine salts has the disadvantages of complicated synthesis steps, producing plenty of ammonium salts, high production cost, serious pollution, and difficult post-treatment. As is described, direct ammoximation has the advantages of high conversion rate, excellent selectivity, and simple production process. Especially, the useless inorganic salts can be avoided, indicating environmental friendliness and low operation costs. Therefore,

the green synthesis (direct ammoximation) of ISAO with hydrogen peroxide as an oxidant and TS-1 as a catalyst was studied. The effect of reaction parameters on the yield of ISAO was investigated, including reaction temperature and time, molar ratio of ammonia to aldehyde as well as hydrogen peroxide to aldehyde.

2. Materials and Methods

2.1. Reagents and materials

TS-1 molecular sieve powder was provided by Shanghai Gechi Chemical Co., Ltd (Shanghai, China). Hydrogen peroxide (H_2O_2 , 30 % (mass)), ammonia (NH_3 , 25 % (mass)) and *tert*-Butyl alcohol (*t*-BuOH) were purchased from Chongqing Chuandong Chemical (Group) Co., Ltd (Chongqing, China). Sulfuric acid (H_2SO_4), and toluene (C_7H_8) were obtained from Xilong Scientific Co., Ltd (Shantou, China). All reagents are analytical grade and used as received without further purification. And distilled water (DI water) was used throughout the whole experimental investigation.

2.2. Characterization of materials

Fourier transform infrared spectroscopy (FTIR) was utilized for structural analysis between 500 cm^{-1} and 4000 cm^{-1} with FT-IR Spectrometer (Nicolet6700, Thermo Fisher Scientific Company, American). Gas chromatograph-mass spectrometry (GCMS-QP2010, Shimadzu Co., Japan) was used for qualitative and quantitative of organic substances. The gas chromatography (GC) analysis was performed with a Varian 3800 gas chromatograph, equipped with a flame ionization detector (FID). The chromatograph was fitted with a DB-5MS fused silica capillary column ($30\text{ m} \times 0.25\text{ mm}$ i.d., $0.25\text{ }\mu\text{m}$ film thickness). Helium ($1.0\text{ mL}\cdot\text{min}^{-1}$) was used as the carrier gas. The injection and detector ports were retained at $230\text{ }^\circ\text{C}$ and $280\text{ }^\circ\text{C}$, respectively. After the sample injection at $60\text{ }^\circ\text{C}$, the oven temperature increased to $280\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. High Performance Liquid Chromatography (1260 Infinity II, Agilent Technologies Inc., American) analyses was performed with an instrument equipped a 250 mm Sapphire-C18 reverse-phase column (film thickness of $5\text{ }\mu\text{m}$, internal diameter of 4.6 mm).

2.3. Ammoximation reaction

The reaction was carried out in a 250 mL four-neck round bottom flask equipped with a thermometer and a mechanical stirrer. TS-1 (1.2 g), ISA (80 mmol), *tert*-Butyl alcohol (22 g) and water (18 g) were added to the reactor. When the temperature of the reaction reached $65\text{ }^\circ\text{C}$, ammonia (160 mmol) and hydrogen peroxide (104 mmol) were added dropwise to feed, and the reaction was continued for 0.5 h after the addition was completed.

The aqueous layer was extracted with toluene (25 g) when the mixture was cooled. The loaded organic layers were combined and washed firstly with 5% sulfuric acid (mass). After finished acid washing, the organic phase obtained was washed with water for three times. A viscous light yellow liquid oxime was obtained *via* distillation under reduced pressure. The intermediates and final products were analyzed by thin layer chromatography (TLC) to monitor the reaction process. Finally, the samples were analyzed by high performance liquid chromatography and infrared spectroscopy, which confirmed the synthesis of ISAO.

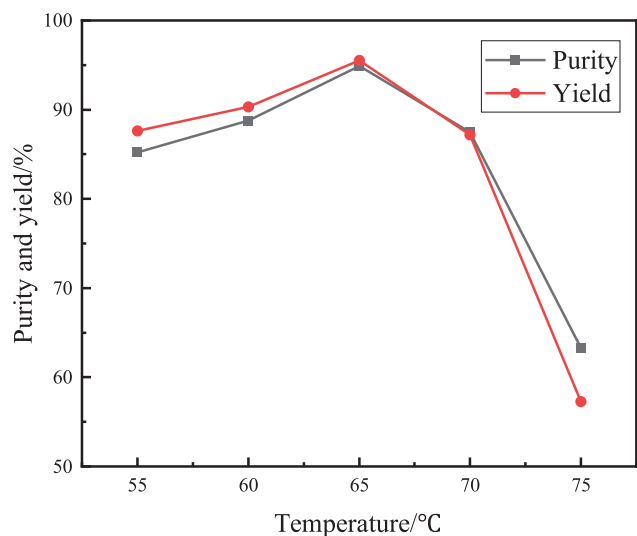


Fig. 1. The effects of temperature on ISAO formation. Reaction conditions: 80 mmol of ISA, 160 mmol of NH_3 aqueous solution, 104 mmol of H_2O_2 , 1.2 g of TS-1, and the feeding time of 1 h.

3. Results and Discussion

3.1. Effect of temperature on the ammonia oxidation reaction of ISA

It can be seen from Fig. 1, the purity and yield of ISAO increased with increasing temperature. However, when the temperature exceeded 65 °C, the purity and yield of the oxime decreased. The TS-1 showed a good catalytic activity within a certain range, and the reaction dominated by ammoxidation still showed excellent reaction efficiency. The higher temperature has advantages of improving the catalytic activity of the catalyst, but which has drawbacks of accelerating the side reactions such as the oxidation of ISA and aldol condensation.

By-products can deepen the color of the products (liquid), changing from light amber to deep red or even brown. From the results, when the reaction temperature was 65 °C, the ammoxidation reaction was the main reaction, and the side reaction was less important.

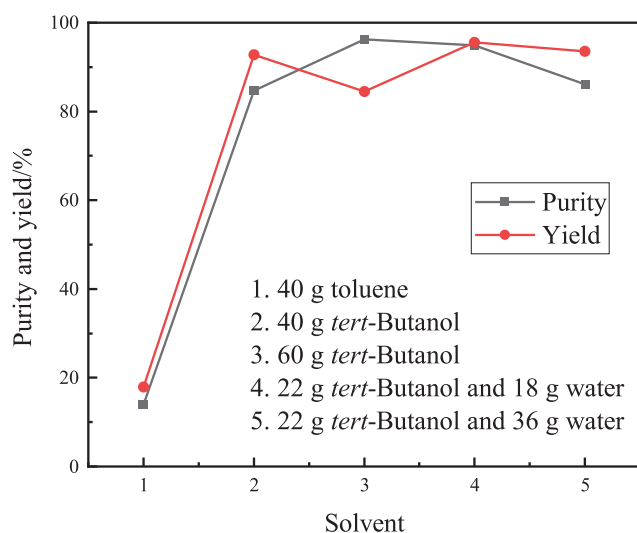


Fig. 2. Effect of solvents on ISAO formation. Reaction conditions: 80 mmol of ISA, 160 mmol of NH_3 aqueous solution, 104 mmol of H_2O_2 , 1.2 g of TS-1, temperature 65 °C, and the feeding time of 1 h.

3.2. Effect of solvents on the ammoxidation of ISA

The effect of solvents on the ammoxidation of ISA is presented in Fig. 2. It can be seen from Fig. 2 that when only 40 g of toluene was added as solvent, the reaction results were not good, and the reactants were not fully dispersed in the system. When only 40 g of *tert*-Butyl alcohol was added as solvent, the reaction results were better and the reactants were evenly dispersed. However, when 60 g of *tert*-Butyl alcohol was added, the yield was lower. When 22 g of *tert*-Butyl alcohol and 18 g of water were added as mixed solvent, the yield was the best. When 22 g of *tert*-Butyl alcohol and 36 g of water were added, the reactants were diluted and the reaction efficiency decreased. Therefore, 22 g of *tert*-Butyl alcohol and 18 g of water is the most suitable.

3.3. Effect of ratio of H_2O_2 /ISA on the ammoxidation of ISA

The effect of H_2O_2 /ISA ratio on the ammoxidation of ISA was investigated (See Fig. 3). As is shown in Fig. 3, when the mole ratio of H_2O_2 /ISA was 1.0, the utilization efficiency of hydrogen peroxide was low and the yield of ISAO was not high. With increasing the ratio of H_2O_2 /ISA, the yield of the products increased. The results showed that the decomposition rate of H_2O_2 was higher than the theoretical value, and the loss of H_2O_2 was caused by ineffective decomposition and ineffective oxidation. When the molar ratio of H_2O_2 /ISA increased to 1.4, the yield of ISAO decreased significantly, and excessive H_2O_2 began to oxidize the intermediate hydroxylamine and the reactant ISA, resulting in poor selectivity. Therefore, the optimum mole ratio of H_2O_2 /ISA was 1.3.

3.4. Effect of ratio of NH_3 /ISA on the ammoxidation of ISA

As is shown in Fig. 4, the purity and yield of ISAO were significantly improved within a certain range with increasing the ratio of ammonia to aldehyde. Theoretically, the molar ratio of ammonia to ISA is 1, and no excessive ammonia can provide a stable alkaline environment for ammonia oxidation. But hydroxylamine was easy to decompose, resulting in a low conversion and poor selectivity. With the increase of ammonia, part of ammonia provided an alkaline environment, hydroxylamine tended to be stable, and the purity and yield of ISAO began to increase. When the molar ratio

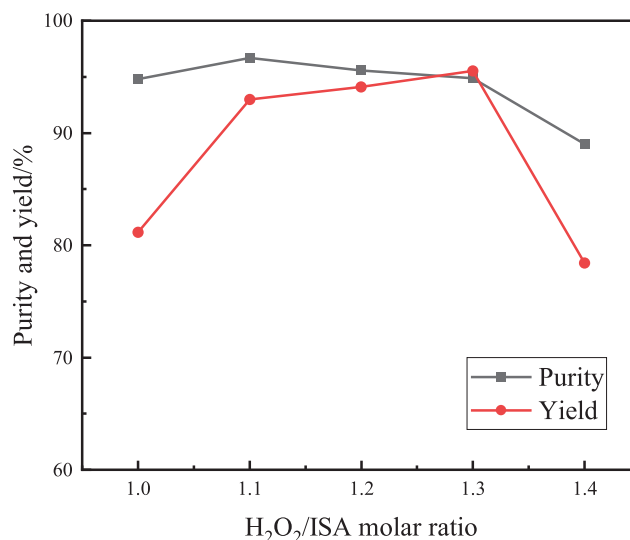


Fig. 3. Effect of H_2O_2 /ISA molar ratio on ISAO formation. Reaction conditions: 80 mmol of ISA, 160 mmol of NH_3 aqueous solution, 1.2 g of TS-1, temperature 65 °C, and the feeding time of 1 h.

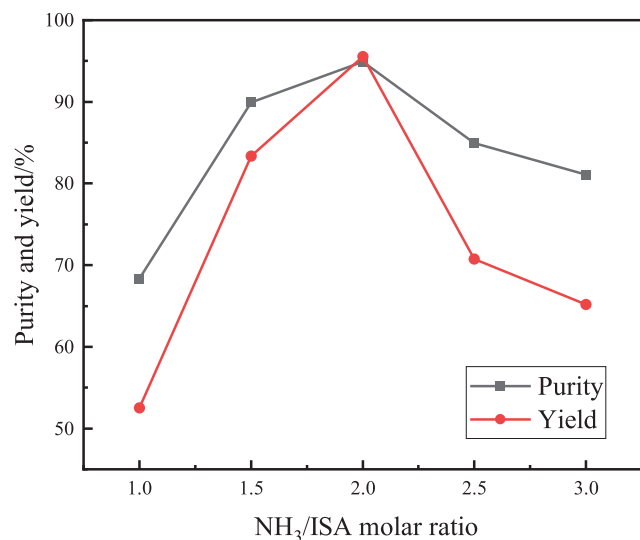


Fig. 4. Effect of NH_3/ISA molar ratio on ISAO formation. Reaction conditions: 80 mmol of ISA, 104 mmol of H_2O_2 , 1.2 g of TS-1, temperature 65°C , and the feeding time of 1 h.

reached up to 2.0, the reaction effect was the best. When the amount of ammonia continues to increase, the alkali concentration of the system was too high, which accelerated the decomposition of H_2O_2 . According to the reaction mechanism [30], when the amount of hydroxylamine added in the reaction process was decreased, the second step of ISAO reaction was also decreased, and the side reaction of ISA increased. The conversion of ISA and the selectivity of ISAO decreased significantly.

3.5. Effect of the amount of catalyst on the ammoxidation of ISA

The effect of catalyst concentration on the ammoxidation of ISA is shown in Fig. 5. The purity and yield of ISAO increased with increasing the catalyst amount in the range of 0.8–1.2 g (ISA dosage was 80 mmol). The active sites of the catalyst are too little to catalyze enough hydroxylamine, resulting in the accumulation of acetaldehyde in the system and low conversion and selectivity.

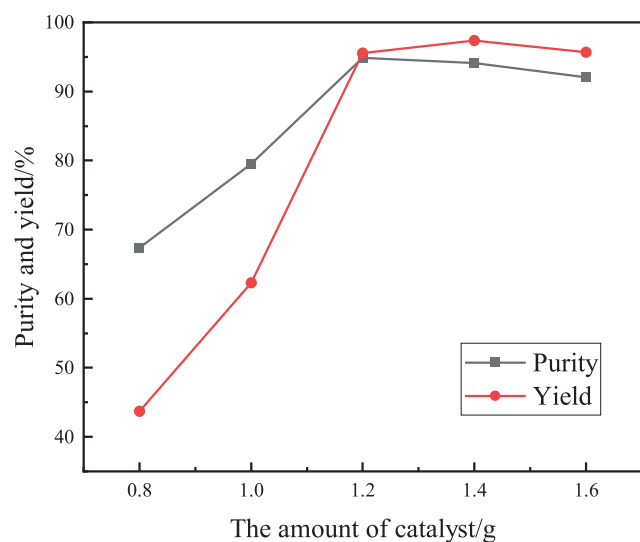


Fig. 5. Effect of the amount of catalyst on ISAO formation. Reaction conditions: 80 mmol of ISA, 160 mmol of NH_3 aqueous solution, 104 mmol of H_2O_2 , temperature 65°C , and the feeding time of 1 h.

The active sites increased with increasing the TS-1 amount. The ammoxidation reaction increased and the side effects were inhibited, so the conversion and selectivity increased rapidly.

Even if the amount of catalyst increases to 1.6 g or above, the reaction results remain unchanged. In order to obtain enough active centers and catalytic intermediates, the optimal amount of catalyst should be 1.4 g, which can obtain better aldehyde conversion and oxime selectivity.

3.6. Effect of the feeding time on the ammoxidation of ISA

The purity and yield of oxime are the lowest when the hydrogen peroxide feeding time is 0 h (Fig. 6). At this time, a large amount of hydrogen peroxide in the system can directly oxidize the aldehyde and lead to the deep oxidation of ISA. According to the hydroxylamine mechanism, with the ineffective consumption of hydrogen peroxide, the amount of direct catalytic reaction with NH_3 was reduced, and sufficient hydroxylamine intermediates cannot be produced, resulting in low conversion.

The effective utilization rate of H_2O_2 increased and the content of free H_2O_2 decreased with increasing the feeding time. When it was 1 h, the concentration of hydrogen peroxide in the system was the optimal to produce hydroxylamine. With the extension of the feeding time, the effective utilization rate of H_2O_2 increased and the content of free H_2O_2 decreased. As a result, the probability of side reactions was low, and therefore, the conversion rate of ISA was increased. The experimental results showed that the appropriate feeding time was 2 h.

3.7. Optimization of reaction parameters by orthogonal experiment

In order to investigate the effects of reaction temperature, amount of catalyst, reaction time, molar ratio of ammonia to ISA and molar ratio of hydrogen peroxide to ISA on the yield of ISAO, the yield of ISAO at four levels was investigated, and the experiments were designed as $L_{16}(4^5)$ with five factors and four levels. The influencing factors and level parameters are shown in Table 1 and the orthogonal test results are shown in Table 2.

The main effect diagram of influencing factors on average yield is shown in Fig. 7. As is shown in Fig. 7, the order of influence degree of five factors on ISAO yield was as follows:

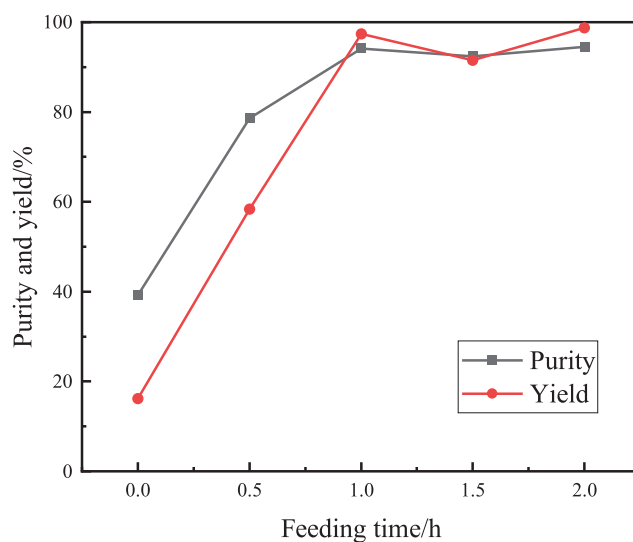


Fig. 6. Effect of feeding time of H_2O_2 on ISAO. Reaction conditions: 80 mmol of ISA, 160 mmol of NH_3 aqueous solution, 104 mmol of H_2O_2 , 1.2 g of TS-1, temperature 65°C .

$A > E > D > C > B$, that is, temperature $>$ H_2O_2/ISA molar ratio $>$ NH_3/ISA molar ratio $>$ feeding time $>$ amount of catalyst. As a result, the optimum conditions of the orthogonal test were $A_4B_3C_4D_2E_2$ (the reaction temperature of 70 °C, the amount of catalyst of 1.4 g, the feeding time of 2 h, the NH_3/ISA molar ratio of 1.6, and the H_2O_2/ISA molar ratio of 1.2).

Table 1
Influencing factors and level factors

Factors	Level			
	1	2	3	4
A: Temperature/°C	55	60	65	70
B: Amount of catalyst/g	1.0	1.2	1.4	1.6
C: Feeding time/h	0.5	1.0	1.5	2.0
D: NH_3/ISA molar ratio	1.4	1.6	1.8	2.0
E: H_2O_2/ISA molar ratio	1.1	1.2	1.3	1.4

Table 2
Orthogonal experiment and results

Test serial number	A	B	C	D	E	Purity/%	Yield/%
1	55	1.0	0.5	1.4	1.1	76.06	48.10
2	55	1.2	1.0	1.6	1.2	77.97	51.12
3	55	1.4	1.5	1.8	1.3	42.80	14.57
4	55	1.6	2.0	2.0	1.4	69.96	45.25
5	60	1.0	1.0	1.8	1.4	64.11	37.31
6	60	1.2	0.5	2.0	1.3	54.62	27.85
7	60	1.4	2.0	1.4	1.2	91.33	82.77
8	60	1.6	1.5	1.6	1.1	82.18	69.87
9	65	1.0	1.5	2.0	1.2	90.16	81.31
10	65	1.2	2.0	1.8	1.1	81.77	73.61
11	65	1.4	0.5	1.6	1.4	95.06	98.68
12	65	1.6	1.0	1.4	1.3	78.44	56.74
13	70	1.0	2.0	1.6	1.3	85.27	80.31
14	70	1.2	1.5	1.4	1.4	92.50	88.91
15	70	1.4	1.0	2.0	1.1	87.98	85.65
16	70	1.6	0.5	1.8	1.2	93.58	92.88

Because the total degree of freedom of the orthogonal table must be greater than the sum of the experimental factors and the interaction degrees of freedom, the column (Amount of catalyst) with smaller mean square deviation was regarded as the “error column” for variance analysis. That is, the interaction was not considered. The range analysis results are shown in Table 3.

In statistics, the P-value is an index to measure the difference between the control group and the experimental group. The P value indicates the degree of non-rejection of the null hypothesis. When the P value is less than 0.05, it indicates that there is a significant difference between the two groups. According to Table 3, the test results showed that temperature (A) and oxime ratio (E) have a significant effect on the material dropping time (C) and oxime ratio (D), and a greater impact on the yield of orthogonal test.

The results in Table 4 showed that among the 4 levels in group A, level 2 and level 3 were divided into two groups, and the difference between the means sharing one letter was not statistically significant. And level 1 and level 4 did not share a letter, indicating that the difference between level 1 and level 4 was significant, and the expected yield was the largest, so the optimal reaction temperature was level 4.

It can be seen from Table 5 that among the 4 levels of group E, the difference between level 1 and level 4 was significant, and the expected yield was the largest, so the optimal H_2O_2/ISA molar ratio was level 4. The other two factors can be directly based on the factor level in the range analysis and the yield was worth the optimal level of $B_3C_4D_2$. Therefore, the optimal reaction parameter (obtain

Table 3
Analysis of variance significance test

Source	DF	Adj SS	Adj MS	F-Value	P-Value
A	3	5550.4	1850.1	22.28	0.015
C	3	352.8	117.61	1.42	0.391
D	3	998.9	332.96	4.01	0.142
E	3	2297.6	765.85	9.22	0.050
Error	3	249.1	83.04		
Total	15	9448.8			

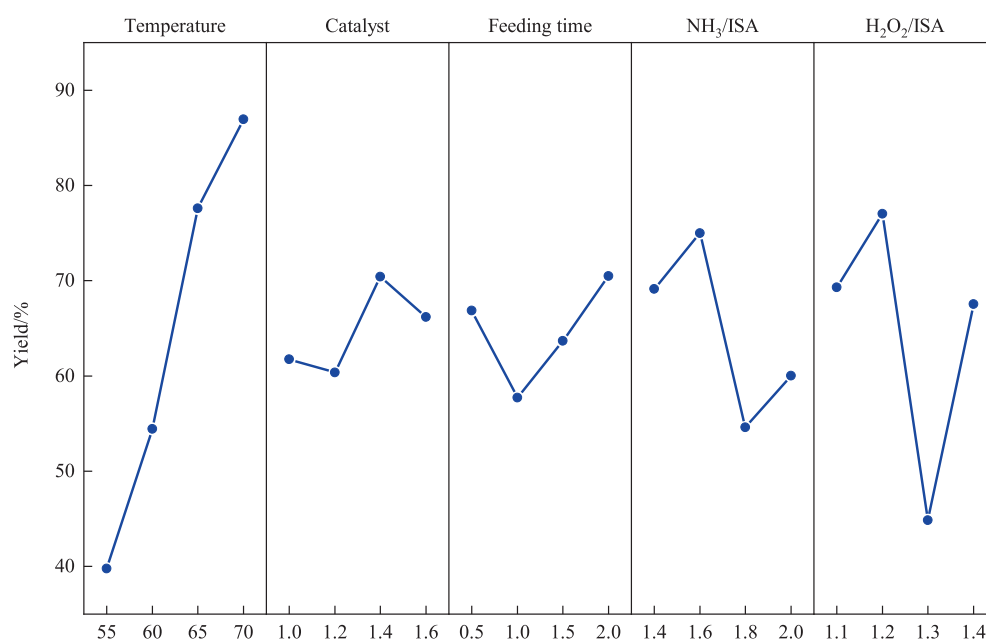


Fig. 7. Main effects plot for means.

Table 4

Tukey pairwise comparisons: response = Yield, Term = A

A	N	Mean	Grouping		
4	4	86.9375	A		
3	4	77.5850	A	B	
2	4	54.4500		B	C
1	4	39.7600			C

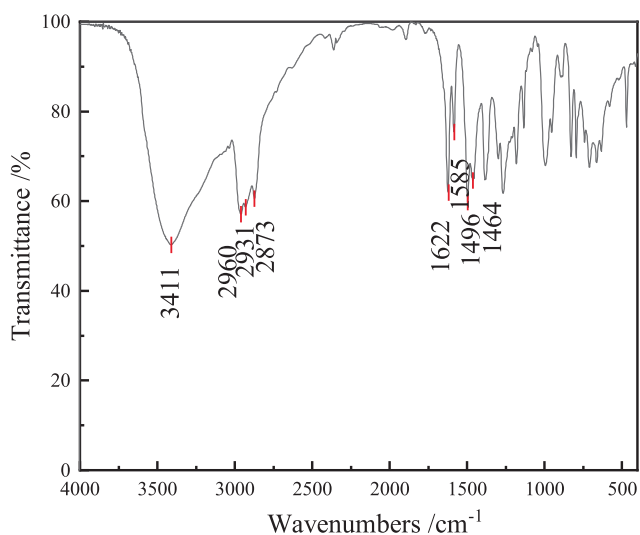
Note: N means the level number of each factor.

Table 5

Tukey pairwise comparisons: response = Yield, Term = E

E	N	Mean	Grouping		
4	4	77.0200	A		
3	4	69.3075	A	B	
2	4	67.5375	A	B	
1	4	44.8675		B	

Note: N means the level number of each factor.

**Fig. 8.** FT-IR spectra of ISAO.

the highest yield) was $A_4B_3C_4D_2E_4$ (the reaction temperature of 70 °C, the amount of catalyst of 1.4 g, the feeding time of 2 h, the NH_3 /ISA molar ratio of 1.6, and the H_2O_2 /ISA molar ratio of 1.4).

Based on the results of the orthogonal experiment, the best condition is $A_4B_3C_4D_2E_2$. Through the analysis of variance, the param-

eters with a significant impact on the results and the differences under the same factor level are compared, indicating that the best condition is $A_4B_3C_4D_2E_4$. Therefore, the experiments were performed under these two sets of parameters ($A_4B_3C_4D_2E_2$ and $A_4B_3C_4D_2E_4$), and the yields of the two were 96.54% and 98.76%, respectively. It is determined that $A_4B_3C_4D_2E_4$ (the reaction temperature of 70 °C, the amount of catalyst of 1.4 g, the feeding time of 2 h, the NH_3 /ISA molar ratio of 1.6, and the H_2O_2 /ISA molar ratio of 1.4) is the final reaction condition.

The experiment was repeated three times under the optimal reaction conditions, and the yields obtained were 97.86%, 98.35% and 98.76%, respectively, indicating that the actual application can be achieved under these conditions. And the TS-1 catalyst was recycled 5 times under this condition, and the yield can still reach more than 90%.

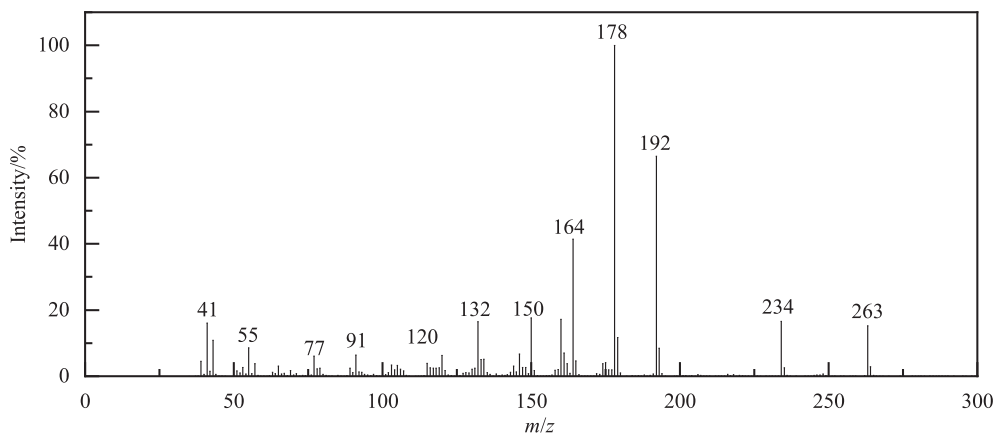
3.8. Structural characterization of the product

The products prepared under the optimal reaction conditions previously optimized were characterized by Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of the samples (Fig. 8) show a wide peak at 3411 cm^{-1} , which is designated as the O—H bond of phenolic and oxime hydroxyl, and a sharp peak at 1622 cm^{-1} is potentially attributed to C=N bond in the C=NOH group [31]. Several peaks at 2960 cm^{-1} , 2931 cm^{-1} , 2873 cm^{-1} , which can be attributed to aromatic and alkyl C—H bond stretching. The C=C double bond of aromatic ring appears at 1585 cm^{-1} , 1496 cm^{-1} and 1464 cm^{-1} . These results confirmed the identity of ISAO.

In order to further confirm that the substance as-obtained is the target product of ISAO intestine, GCMS was further used for identification and analysis. The mass spectrogram is shown in Fig. 9. It can be seen from Fig. 9 that the pair m/z : 263(M^+), 234, 192, 178, 164, 150, 132, 120, 91, 77, 55, 41 is consistent with the characteristics of the target product, 5-isooctyl salicylaldehyde [32]. Therefore, combining infrared spectroscopy and mass spectrometry analysis, it can be determined that the substances as-obtained are target products.

4. Conclusions

In this study, the TS-1 catalyst ammoxidation method was used to synthesize 5-isooctyl salicylaldehyde. The orthogonal experiments were designed to optimize the reaction conditions, and the optimized synthesis conditions were obtained: The dosage of ISA is 80 mmol, the reaction temperature of 70 °C, the amount of TS-1 is 1.4 g, the feeding time of 2 h, and the NH_3 /ISA molar ratio

**Fig. 9.** Mass spectrum structure of ISAO.

of 1.6, and the H_2O_2 /ISA molar ratio of 1.4, and the mass ratio of solvent (*tert*-Butyl alcohol to water) of 22:18. The results revealed that the yield of ISAO was as high as 98.76%. The reaction temperature and the amount of hydrogen peroxide have significant effects on the yield of ISAO. The green hydrometallurgical extraction has mild reaction conditions, avoiding the production of useless inorganic salt by-products, and no environmental pollution.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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