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Preparation of 2,6-Naphthalic Acid by Liquid Phase Oxidation of 2,6-Diisopropyl Naphthalene

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An orthogonal experiment was carried out and the effects of bromine, metal ions additives and organic nitrogen compounds on the yield of 2,6-naphthalic acid were discussed. The results shown that influence order for the yield of 2,6-naphthalic acid in the orthogonal experiment were: reaction temperature > feed flux > catalyst dosage > Co/Mn. High temperature could cause the cleavage of naphthalene ring and low temperature could not give rise to the full oxidation of intermediate products, then the suitable temperature could be 473 K. It is good for producing 2,6-naphthalic acid to decrease the feed flux and increase the catalyst dosage. However, there was no significant influence of Co/Mn for the yield of 2,6-naphthalic acid.

Key Words: Oxidation, 2,6-Naphthalic acid, 2,6-Diisopropyl naphthalene.

INTRODUCTION

2,6-Naphthalic acid (2,6-NDCA) and its derivates are important monomers for producing various kinds of polyester and polyurethane materials as well as liquid crystal compounds[1]. The major preparation methods included Henkel method, isomerization method, carboxy group transfer reaction, 2,6-dimethylnaphthalene oxidation, 2,6-diisopropyl naphthalene oxidation and other methods[2-4]. The raw materials for 2,6-diisopropyl naphthalene oxidation are easy to obtain and the separation was relatively simple and the route for this synthetic technology was the most economical. Thus this method has become one of the hotspots for the investigations on the preparation of 2,6-naphthalic acid[5-7].

The purpose of the present study was to producing 2,6-naphthalic acid by liquid phase oxidation of 2,6-diisopropyl naphthalene. The effects of incipient concentration, catalyst concentration, ratio between cobalt and manganese, reaction temperature, different bromides, metallic compound additives and nitrogenous compound additives on 2,6-diisopropyl naphthalene oxidation were examined. Finally the relatively appropriate reaction conditions were screened out for the reference for industrial design and implement process.

EXPERIMENTAL

The experiment was carried out in different batches, firstly the reaction materials, solvents, catalysts were prepared into a solution of 300 mL in proper proportions. The solution was added into the reactor, the air in the reactor was exhausted by introducing nitrogen gas after tight sealing. Pressurization was then carried out with nitrogen gas to a final pressure at *ca.* 1 MPa, the inlet valve and the outlet valve were shut off, the power supply was switched on for heating, subsequently the valve for cooling water in the end gas condensation tube at the same time and the stirring was started. Nitrogen gas was continuously introduced during the process for increasing temperature in order to guarantee the synchronized increase in pressure and temperature. After the temperature and the pressure increased to the preset values, the heating power was adjusted in order to maintain the temperature in the reactor constant and the stirring speed was adjusted to 900-950 rpm. Finally the nitrogen gas was switched to the air and the reaction was triggered.

Analytical method: The sampling was carried out for every a short period during the reaction and the ingredients in the sample were determined by using a HP6890-MS5973 gas chromatograph-mass spectrometer and quantitative analysis was carried out by using a Shimadzu GC-9A gas chromatograph. The chromatographic column was a SE-54 capillary column and the detector was a hydrogen flame ion detector (FID).

RESULTS AND DISCUSSION

Orthogonal experiment and the results: The factors of experimental tests to be used in the orthogonal design included reaction temperature, ratio between cobalt and manganese, 2,6-diisopropyl naphthalene feeding rate and molar ratio between the catalyst and the raw materials and the parameters for examination were the yield of the product 2,6-naphthalic acid and the yield of the side product trimellitic acid. The levels and factors of orthogonal design was shown in Table-1, the experimental conditions and the results were shown in Table-2.

TABLE-1
UTILIZATION OF DIPN OXIDATION NDCA UTILIZATION FACTOR LEVELS ORTHOGONAL DESIGN TO WATCH

Item		Factor			
		T(K)	Co + Mn/ 2,6-DIPN	Co/Mn	Quantity of flow (mL/min)
Factor	1	443	3:1	1:1	5
	2	423	1.5:1	3:1	2
	3	473	0.5:1	1:3	10

2,6-DIPN = 2,6-diisopropyl naphthalene

According to the experimental results in Table-2, we can obtain the results as follows: 2,6-naphthalic acid was a target product and its yield should be as high as possible, while trimellitic acid was a major side product and it stood for the probability for oxidative cleavage during 2,6-diisopropyl naphthalene oxidation, which may seriously affect the yield of the target product, thus its yield should be as low as possible. It can be found from the results in Table-2 that among the four factors for examination, the effects on the yield of the target product 2,6-naphthalic acid were successively: reaction temperature > feeding rate > catalyst concentration > ratio between cobalt and manganese, while the effects on the yield of trimellitic acid were successively: reaction temperature > catalyst concentration > feeding rate > ratio between cobalt and manganese; the optimal reaction conditions within the examined range were as followed: the temperature was 170 ºC, the catalyst concentration [Co + Mn]: diisopropyl naphthalene (molar ratio) = 3:1, [Co]: [Mn] = 1:3, the feeding rate was 5 mL/min. Verification experiments were carried out at the optimal conditions, the yield of 2,6-naphthalic acid was 74.9 % and the yield of trimellitic acid was 14.1 %, which was higher than that at the conditions in the orthogonal experiment.

Effects of the promoter on the oxidation of 2,6-diisopropyl naphthalene: Bromine is a kind of renewable source for chain-initiating radicals as a kind of promoter and it can significantly promote the oxidation reaction. The present study examined the effects of different bromides on the liquid phase catalytic oxidation of 2,6-diisopropyl naphthalene and related experimental conditions and the results were shown in Table-3. Other experimental conditions were as followed: the pressure P = 2 MPa, T = 170 ºC, acetic acid = 1000 mL, 2,6-diisopropyl naphthalene = 10 g.

It can be found from Table-3 that the yields of 2,6-naphthalic acid from 2,6-diisopropyl naphthalene oxidation did not differ significantly when potassium bromide and tetrabromoethane were used as the additives, but they were significantly higher than the yields when hydrogen bromide was used as the additive and the amount of trimellitic acid by disrupting naphthalene ring also decreased when tetrabromoethane was used as the catalytic additive, but the mechanism for the promoter bromine on the disruption of naphthalene ring is still unclear, further investigations are still required.

TABLE-2
UTILIZATION OF DIPN OXIDATION NDCA ORTHOGONAL DESIGN TABLE UTILIZATION

No	Experiment condition				Experimental results	
	T (K)	Co+Mn/2, 6-DIPN	Co/Mn	Feeding flow rate (mL/min)	2,6-NDCA yield (%)	TMA yield (%)
1	443	3:1	1:3	2	72.8	13.5
2	423	3:1	1:1	5	48.8	7.40
3	473	3:1	3:1	10	47.9	27.4
4	443	1.5:1	3:1	5	70.2	17.4
5	423	1.5:1	1:3	10	32.1	13.8
6	473	1.5:1	1:1	2	48.9	27.7
7	443	0.5:1	1:1	10	42.1	20.7
8	423	0.5:1	3:1	2	33.7	15.0
9	473	0.5:1	1:3	5	48.7	28.9
K_{1N}	1.851	1.695	1.536	1.677	–	–
K_{1T}	0.5168	0.4836	0.5590	0.5376	–	–
K_{2N}	1.145	1.512	1.398	1.554	–	–
K_{2T}	0.3628	0.5894	0.5983	0.5622	–	–
K_{3N}	1.455	1.245	1.518	1.221	–	–
K_{3T}	0.8402	0.6468	0.5625	0.6200	–	–
R_N	0.706	0.450	0.138	0.456	–	–
R_T	0.4774	0.1632	0.0393	0.0824	–	–

Remarks: in this table, K_{1N}, K_{2N}, K_{3N}, R_N were the sums and the ranges for the experimental results with the yield of 2,6-NDCA as the examination parameters, while K_{1T}, K_{2T}, K_{3T}, R_T were the sums and the ranges for the experimental results with the yield of trimellitic acid as the examination parameters; higher R value indicated that the effects of this factor on the experiment were much significant.

TABLE-3
DIFFERENT DIPN OXIDATION OF UTILIZATION ROHS THE INFLUENCE

Bromide	Co + Mn/2,6-DIPN (mol/mol)	Co/Mn/Br	Feeding flow rate × 10^3/(mol/min)	Yield (%)	
				2,6-NDCA	Trimellitic acid
Potassium bromide	3	1:3:1	0.472	66.2	16.5
Tetrabromo ethane	3	1:3:1	0.472	68.0	11.8
Hydrogen bromide	3	1:3:1	0.472	60.3	13.2

Effects of metals on the oxidation of 2,6-diisopropyl naphthalene: The effects of metal ion additives in the manganese-cobalt catalytic system were significant and they can accelerate the main reaction. Therefore, the present study carried out investigations on the effects of different metal ions on the oxidation of 2,6-diisopropyl naphthalene, related experimental results and the results were listed in Table-4 (other experimental conditions were as followed: the pressure P = 2 MPa, T = 443 K, acetic acid = 1000 mL, 2,6-diisopropyl naphthalene = 10 g).

Firstly, the effects of potassium ion on the oxidation of 2,6-diisopropyl naphthalene were examined. The yield of the 2,6-naphthalic acid continuously increased with the increase in potassium ion and the effects of the increase in potassium ion on the improvement in 2,6-naphthalic acid yield was very significant when Co/Mn (molar ratio) was lower than 6, but continuous increase in potassium ion can not further increase 2,6-naphthalic acid yield when it went beyond this range. Moreover, the content of the side product trimellitic acid did not change significantly with the increase in potassium ion, indicating that the concentration of potassium ion did not affect the disruption of naphthalene ring, but it may affect the oxidation of isopropyl.

According to the data in Table-5, it was found that sodium acetate also showed the same effects and the effects of sodium acetate and potassium acetate at the same concentration on 2,6-diisopropyl naphthalene oxidation were the same, indicating that base metals had significant effects during the oxidation of 2,6-diisopropyl naphthalene.

Effects of other metal ions were also examined, magnesium acetate tetrahydrate was added in the reaction system, it was found the addition of magnesium acetate tetrahydrate decreased the probability of naphthalene ring disruption and the yield of trimellitic acid in comparison to the effects of potassium acetate at the same concentration, but it also decreased the yield of 2,6-naphthalic acid at the same time.

Small amount of rare earth metal compound cerium acetate in the reaction system, it can be found from the results in Table-4 that the yields of 2,6-naphthalic acid and trimellitic acid both showed certain increased after small amount of cerium acetate was added in the reaction system, thus it can be considered that the inclusion of cerium acetate increase 2,6-diisopropyl naphthalene in general. Previous investigations on the functions of cerium in the oxidation of aromatic hydrocarbon showed that cerium acetate had two major functions in the reaction system, one was that the rate for aromatic hydrocarbon oxidation was improved in general by the synergistic action between Co and Mn. On the other hand, it was beneficial for inhibiting the precipitation of the catalyst Mn and thus improving the water content in the reaction system. Previous studies have shown that copper also showed relative good synergistic action with cobalt and manganese.

Conclusion

The optimal conditions for oxidation were determined by examining the effects of different experimental conditions in the orthogonal test: the reaction pressure was 2 MPa, the temperature was 443 K, the catalyst concentration Co + Mn/ diisopropyl naphthalene (molar ratio) = 3:1, Co/Mn = 1:3, the feeding rate was 5 mL/min furthermore, the effects on the yield of the target product 2,6-naphthalic acid were successively: the reaction temperature > the feeding rate > the catalyst concentration > the proportion of cobalt and manganese, while the effects on the yield of trimellitic acid were successively: the reaction temperature > the catalyst concentration > the feeding rate > the proportion of cobalt and manganese.

Among the metal ion additives, base metal ions can improve the yield of 2,6-naphthalic acid and the yield of 2,6-naphthalic acid also gradually increased with the increase in potassium ion concentration, however, continuous increase in potassium ion concentration can not improve the yield of 2,6-naphthalic acid when the concentration of potassium ioin was increased to a certain level, but it can decrease the yield on the contrary, moreover, base metals had no significant effects on the disruption of naphthalene ring. The addition of magnesium ion and cerium ion can increase the yields of 2,6-naphthalic acid to some extent, but the addition of copper ion can inhibit the oxidation of 2,6-diisopropyl naphthalene.

TABLE-4
DIFFERENT METAL EFFECT ON DIPN OXIDATION

Base metal	Co+Mn/2,6-DIPN (mol/mol)	Co/Mn/Br/metal ion	Feeding flow rate × 10^3 (mol/min)	Yield (%)	
				2,6-NDCA	Trimellitic acid
Potassium acetate	3, 3	1:3:1:0, 1:3:1:1	0.472, 0.472	60.3, 66.8	13.2, 15.9
Potassium acetate	3	1:3:1:2	0.472	71.9	14.2
Potassium acetate	3	1:3:1:6	0.472	75.7	15.5
Potassium acetate	3	1:3:1:9	0.472	74.9	14.1
Sodium acetate	3	1:3:1:1	0.472	67.1	14.1
Magnesium acetate tetrahydrate	3	1:3:1:2	0.472	62.2	11.8
Cerium acetate	3	1:3:1:0.2	0.472	63.6	20.5
Cupric acetate	3	1:3:1:1	0.472	40.7	2.5

TABLE-5
NITROGEN COMPOUNDS EFFECT ON DIPN OXIDATION

Base metal	Co+Mn/2,6-DIPN (mol/mol)	Co/Mn/Br	Feeding flow rate × 10^3 (mol/min)	Yield (%)	
				2,6-NDCA	Trimellitic acid
Guanidine carbonate	3	1:3:1	0.472	49.8	7.7
Tricyanic acid	3	1:3:1	0.472	64.1	9.2
Tricyanic acid	3	1:3:1	0.472	67.0	8.4

Nitrogenous compound additives can inhibit the disruption of naphthalene ring to some extent, particularly that cyanurotriamide and tricyanic acid were very beneficial for decreasing trimellitic acid production and it did not affect the oxidation of 2,6-diisopropyl naphthalene and the subsequent transformation into 2,6-naphthalic acid. The addition of guanidine carbonate can also inhibit the disruption of naphthalene ring, but guanidine carbonate may be involved in the oxidation of isopropyl and then other intermediate products may be produced, thus the yield of 2,6-naphthalic acid was reduced, therefore, it can be considered to carry out investigations on how to improve the rate for 2,6-diisopropyl naphthalene oxidation at the same time of adding nitrogenous compounds.

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