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Preparation of Salicylic Nitrile through Direct Catalytic Dehydration of Salicylamide with Immobilized Phosphoric Acid as Catalyst

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Salicylic nitrile was prepared through direct catalytic dehydration of salicylamide under high temperature using immobilized phosphoric acid as catalyst. The catalytic performances of different catalysts were evaluated according to the analytic results of GC-MS, and the feasibility about the preparation of salicylic nitrile by direct catalytic dehydration of salicylamide was investigated according to the composition of product determinated by GC analysis (area nomalization). Experimental results indicated the comprehensive property of silica gel supported phosphoric acid was the best one among all of the catalysts utilized in this study. When the temperature of catalyst bed was 480 ± 10º and silica gel supported phosphoric acid was utilized as catalyst, the conversion ratio of salicylamide was 88.79%, the selectivity to salicylic nitrile was 97.97% and the yields of salicylic nitrile could up to 86.99%. Meanwhile, the experimental results showed the increase of temperature of catalyst bed could result in the increase of the conversation of salicylamide, but much more by-product could be formed when the temperature of catalyst bed was too high.

Keywords: Salicylamide, Salicylic nitrile, Catalytic dehydration, Immobilized phosphoric acid, Selectivity.

INTRODUCTION

The importance of salicylic nitrile as pharmaceutical and agricultural intermediates has been well established. For example, salicylic nitrile could be utilized for the synthesis of bunitrolol, one of β-recepter bolockers for the treatment of arrhythmia, angina and hypertension [1]. Salicylic nitrile could also be utilized for the preparation of azoxystrobin, one of the efficient agricultural fungicides with broad-spectrum and ability of intaking absorption [2]. Meanwhile, salicylic nitrile has obtained important application in the production of some perfumes and liquid crystal materials, *etc*. [3].

There are several methods applied for preparing salicylic nitrile, such as dehydration of salicylaldoxime in the presence of dehydrant [4-8], selective oxidation of benzonitrile [9], isomerization of 1,2-benzisoxazole [10], catalytic ammoxidation of *o*-cresol [11,12], dehydration of salicylamide in the presence of dehydrant [13-16], cyanylation of methyl salicylate [17] and hydroxylation of halogenated benzonitrile [18], *etc*. But, all of the above methods have disadvantage in some extent, for example, the dehydrants for conversing salicylaldoxime or salicylamide to salicylic nitrile usually related with toxic compounds including phosgene or *bis*(trichloromethyl)carbonate, the yields for preparing salicylic nitrile through catalytic ammoxidation of *o*-cresol is usually at a lower level, and the hydroxylation of halogenated benzonitrile needs to be carried out with harsh condition.

In order to avoid these disadvantages in present method for preparing salicylic nitrile, herein, a method for the synthesis of salicylic nitrile from salicylamide through direct catalytic dehydration with immobilized phosphoric acid as catalyst is reported.

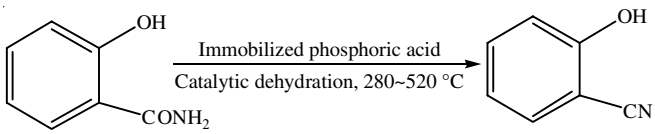
EXPERIMENTAL

All reagents were of analytical reagents and used without further purification. Salicylamide (99%, industrial product), phosphoric acid, absolute ethanol, artificial zeolite (chemically pure), silica gel (GF_{254}, TLC), aluminium oxide), molecular sieve (3Å), silicon dioxide and zirconium dioxide (CP) were procured from Sigma-Aldrich, USA.

Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets on a Nicolet Nexux 670 spectrometer. Sixteen scans at a resolution of 4 cm^{-1} were averaged over wavenumbers range of 4000~400 cm^{-1} and referenced against air. The analysis of GC-MS was carried out with gas chromatography-mass spectrometer (TRACE1310 ISQ, Thermo Fisher Scientific Co.) and analytical conditions were as follows: chromatographic column was SPV-5 type (30 m × 0.25 mm), temperature of vaporization room was 260 ºC, temperature of detector was 290 ºC, column temperature program that started from an initial temperature of 60 ºC (hold for 2 min), ramped at the rate of 10 ºC min^{-1} upto 260 ºC (hold for 15 min).

Preparation of catalyst: About 200 g of molecular sieve was added into 500 g of 30% aqueous solution of phosphoric acid with continuous stirring for 4 h at room temperature, then the mixture was settled down for 24 h before filtration. The filter residue was dried at 110 ºC for 12 h and the molecular sieve supported phosphoric acid, one of catalysts utilized for the catalytic dehydration of salicylamide in this study was obtained. The other catalysts of immobilized supported phosphoric acid could be prepared according to the above procedure.

Catalytic dehydration of salicylamide: Salicylamide (68.60 g) was added into a three-necked flask and the necks of flask were erected with thermometer, stirrer and Claisen distilling head. The Claisen distilling head was linked with fixed-bed reactor that pillowed with the immobilized supported phosphoric acid and heated with twisted electric heating wire. The fixed-bed reactor was connected with collecting bottle, which was soaked into ice brine and a vacuum device. The salicylamide was transformed into steam by heating the flask and the steam was passed through the fixed-bed reactor with the assistance of vacuum take-off. The steam of salicylamide was dehydrated at specific temperature with the catalyzing of supported phosphoric acid (**Scheme-I**).



Scheme-I: Route for preparing salicylic nitrile

RESULTS AND DISCUSSION

Main components in the typical product of dehydration: According to the experimental results completed by our team, the dehydrated product of salicylamide catalyzed by zirconium dioxide supported phosphoric acid was the most complex one among all of the products that catalyzed by immobilized supported phosphoric acid. The dehydrated product of salicylamide catalyzed by ZrO_2 supported phosphoric acid at 480 ± 10 ºC was analyzed by GC-MS (Fig. 1). Meanwhile, the MS spectra of component at different retaining time (RT) are shown in Figs. 2-7.

The ascription of MS spectra concerned with the dehydrated product of salicylamide catalyzed by ZrO_2 supported immobilized phosphoric acid is shown in Table-1.

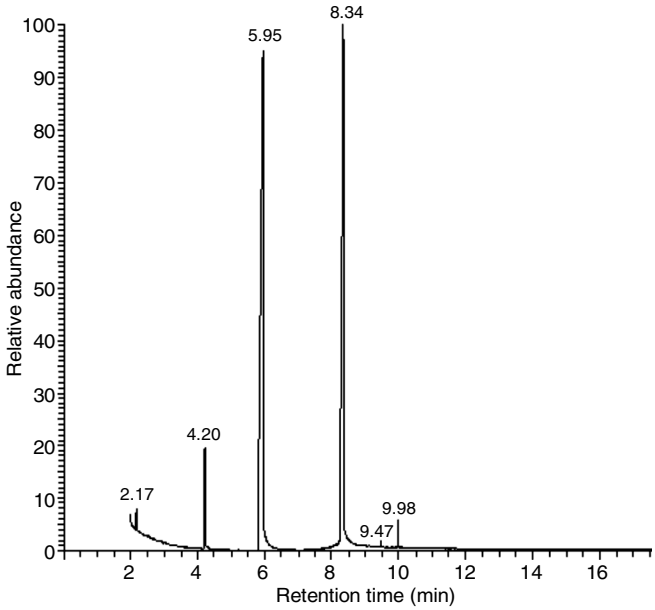


Fig. 1. GC spectrum of catalytic dehydration product of ZrO_2 supported phosphoric acid

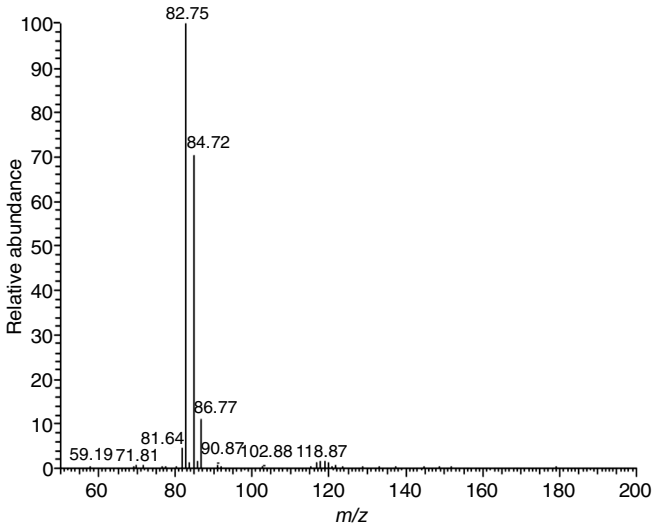


Fig. 2. MS spectrum of component at RT = 2.17 min

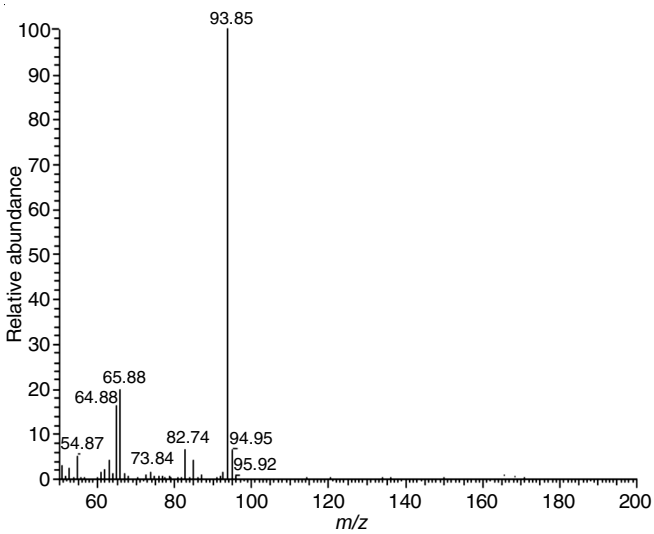


Fig. 3. MS spectrum of component at RT = 4.20 min

TABLE-1
MAIN COMPONENT OF DEHYDRATION PRODUCT CATALYZED BY ZrO_2 SUPPORTED IMMOBILIZED PHOSPHORIC ACID

RT (min)	2.17	4.20	5.95	8.34	9.47	9.98
Component	Chloroform	Phenol	Salicylic nitrile	Salicylamide	Phenyl (2-phenoxy)benzoate	Phenyl salicylate

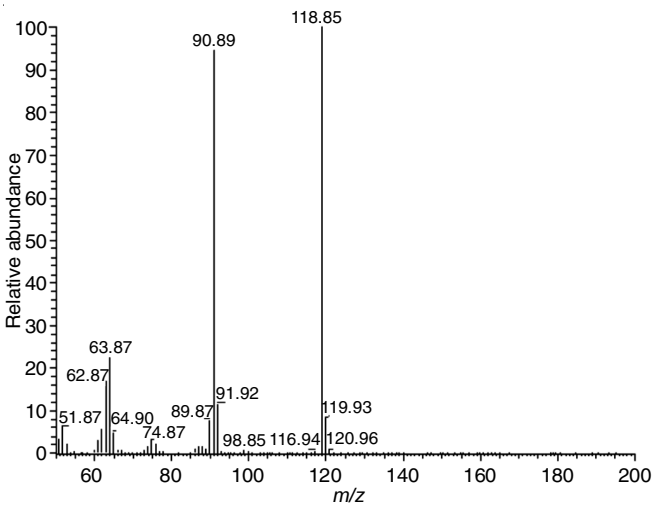


Fig. 4. MS spectrum of component at RT = 5.95 min

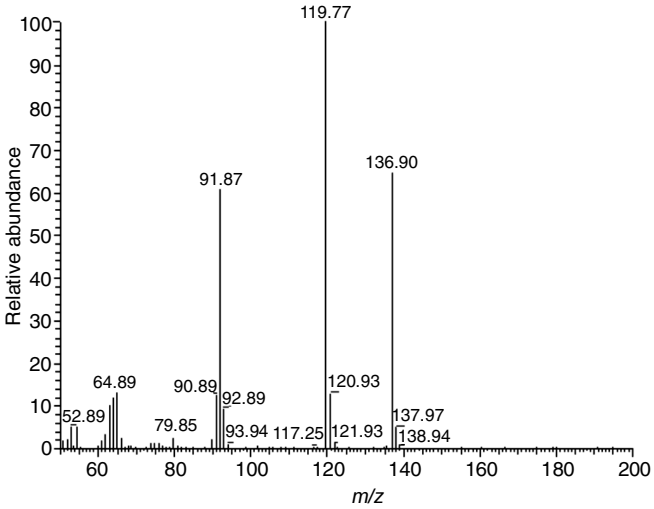


Fig. 5. MS spectrum of component at RT = 8.34 min

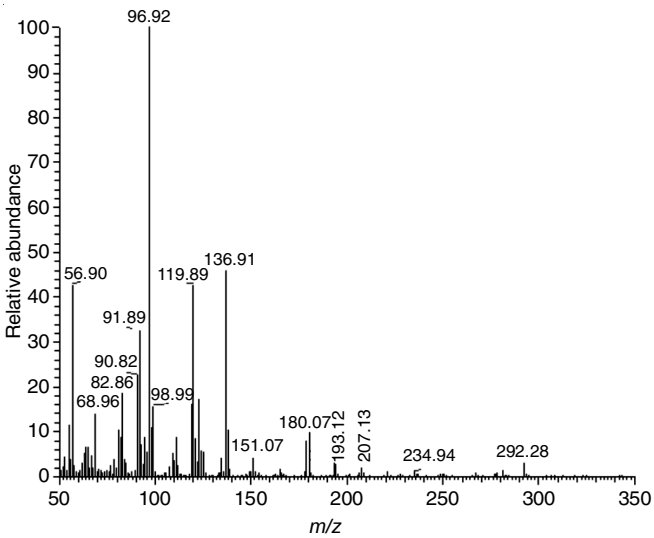


Fig. 6. MS spectrum of component at RT = 9.47 min

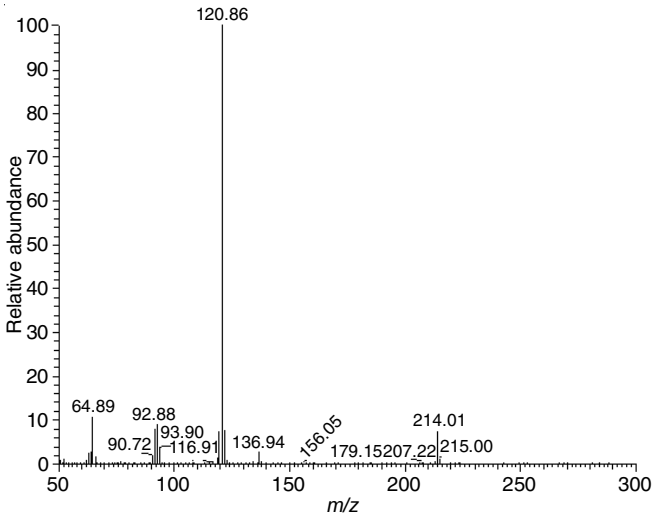


Fig. 7. MS spectrum of component at RT = 9.98 min

The component at RT = 2.17 min was ascribed to chloroform that utilized as solvent for dissolving the dehydrated product. From Table-1, it could be seen that there were phenol, phenyl(2-phenoxy)benzoate and phenyl salicylate except salicylamide and salicylic nitrile in the dehydrated product. The reasons that led to these results might concerned with the formation of by-product in the dehydrating process of salicylamide. Salicylamide could transformed into salicylic nitrile by dehydration with the catalyzation of ZrO_2 supported phosphoric acid, but a decarboxyamidation of salicylamide might arise in the same process and resulted in the formation of phenol. The phenol could react with salicylamide with the catalytic action of immobilized phosphoric acid and converted into phenyl salicylate or phenyl(2-phenoxy)benzoate.

FT-IR analysis of dehydrating product and its ascription: The FT-IR spectra of salicylamide and its dehydrated product at 480 ± 10 ºC catalyzed by ZrO_2 supported phosphoric acid are shown in Fig. 8. Compared with the FT-IR spectrum of salicylamide, it could be seen there were some absorption peaks reflected the existence of phenol, nitrile, ester and ether in the FT-IR spectrum of dehydrated product catalyzed by ZrO_2 immobilized phosphoric acid beside that reflected the existence of amide. A broad band at 2230 cm^{-1} was assigned to C≡N stretching vibration, 1690 cm^{-1} was assigned to C=O stretching vibration of ester, 1250 cm^{-1} was assigned to C-O stretching vibration of phenol and aryl ether, 3400 and 3190 cm^{-1} were assigned to O-H and N-H stretching vibration and the peak at 1630 cm^{-1} was assigned to C=O stretching vibration of amide.

Main components of dehydrating product catalyzed by different immobilized phosphoric acid and their content: The GC and HPLC method could be used for the determination of salicylamide and salicylic nitrile [19,20]. In this study, the main components in the dehydrated product obtained from different immobilized phosphoric acid at 480 ± 10 ºC was analyzed by GC-MS using the adjusted condition as reported

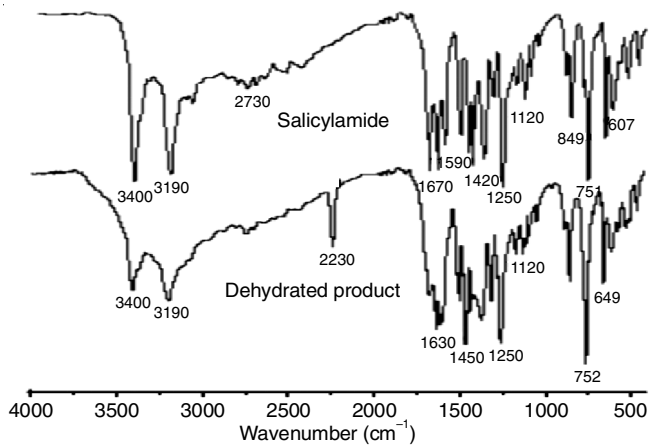


Fig. 8. FT-IR spectra of salicylamide and its catalytic dehydration product

earlier [19], and area nomalization method was used to evaluate their content in the dehydrated product. The results are listed in Table-2.

According to Table-2, a conversion ratio of salicylamide using different catalyst and the selectivity to salicylic nitrile could be obtained and the results are listed in Table-3. From Tables 2 and 3, it could be seen that there existed obvious difference concerned with the catalytic property of different immobilized phosphoric acid. The dehydrating reaction catalyzed by silica gel supported phosphoric acid could behave the best conversion ratio of salicylamide, while that catalyzed by artificial zeolite supported phosphoric acid could behave the best selectivity of salicylic nitrile among all of reactions catalyzed by different immobilized phosphoric acid. Among all of the catalysts utilized in present investigations, silica gel supported phosphoric acid was the best one that could provide optimal integrated performance. If silica gel supported phosphoric acid was utilized as the catalyst for dehydrating reaction of salicylamide at 480 ± 10 ºC, the yields of salicylic nitrile could up to 86.99%.

Influence of bed temperature on dehydrating reaction of salicylamide: In order to investigate the influence of bed temperature on the dehydrating reaction of salicylamide, silica gel supported phosphoric acid was utilized at different bed temperature, and the main components and their content in the dehydrated product were studied. The experimental results are showed in Table-4. It could be seen that an increase of bed temperature could result in the increase of the conversion ratio of salicylamide and yields of salicylic nitrile, while the content of by-product in the dehydrated product also increased with the increase of bed temperature in some content.

Conclusion

The preparation of salicylic nitrile through direct catalytic dehydration of salicylamide under high temperature with immobilized phosphoric acid as catalyst was investigated. The type of catalyst and the temperature had significant influence on the dehydrating reaction of salicylamide and the silica gel supported phosphoric acid was the best one among all of catalysts utilized in this study. When the bed temperature was 480 ± 10 ºC and silica gel supported phosphoric acid was utilized as the catalyst for the dehydration of salicylamide, the yields of salicylic nitrile could up to 86.99%.

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TABLE-2
MAIN COMPONENTS OF PRODUCT OBTAINED FROM DIFFERENT CATALYST AND THEIR CONTENT

Catalyst	Phenol (%)	Salicylic nitrile (%)	Salicylamide (%)	Phenyl (2-phenoxy)benzoate (%)	Phenyl salicylate (%)
H_3PO_4-molecular sieve	0	19.10	80.56	0.23	0.12
H_3PO_4-artificial zeolite	0	11.74	88.26	0	0
H_3PO_4-aluminium oxide	24.12	50.78	24.94	0.16	0
H_3PO_4-silica gel	0	86.99	11.21	1.56	0.24
H_3PO_4-SiO_2	1.02	33.63	65.01	0	0.34
H_3PO_4-ZrO_2	3.0	56.64	39.58	0.12	0.66

TABLE-3
CONVERSION RATIO OF SALICYLAMIDE USING DIFFERENT CATALYST AND THE SELECTIVITY TO SALICYLIC NITRILE

Catalyst	H_3PO_4-molecular sieve	H_3PO_4-artificial zeolite	H_3PO_4-aluminium oxide	H_3PO_4-silica gel	H_3PO_4-SiO_2	H_3PO_4-ZrO_2
Conversion ratio of salicylamide (%)	19.44	11.74	75.06	88.79	34.99	60.42
Selectivity to salicylic nitrile (%)	98.25	100	67.65	97.97	96.11	93.74

TABLE-4
MAIN COMPONENTS OF PRODUCT OBTAINED FROM DIFFERENT TEMPERATURE AND THEIR CONTENT

Bed temperature (°C)	280 ± 10	320 ± 10	360 ± 10	400 ± 10	440 ± 10	480 ± 10	520 ± 10
Salicylic nitrile (%)	3.27	10.16	31.90	53.11	72.16	86.99	88.13
Salicylamide (%)	96.23	89.50	67.51	45.91	26.35	11.21	7.11
Phenyl (2-phenoxy)benzoate	0	0.28	0.47	0.81	1.29	1.56	3.09
Phenyl salicylate	0	0.06	0.12	0.17	0.20	0.24	1.67

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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