The mild liquid-phase synthesis of 3-picoline from acrolein diethyl acetal and ammonia over heterogeneous catalysts

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Abstract: The liquid-phase synthesis of 3-picoline from the reaction of acrolein diethyl acetal and ammonia over ion-exchanged resins (D402 and D002) and HZSM-5 (Si/Al = 25) was carried out in a batch reactor. Various influencing parameters, including by the addition of water, ion-exchanged resins, reaction temperature and HZSM-5, were systematically investigated. The results showed that the reaction could be directly conducted, and organic acid wasn't utilized. The highest yield of 3-picoline reached up to 24% using HZSM-5 as catalyst at 110 ºC.

1. Introduction

3-picoline is an important chemical, which is widely applied for various fields such as medicines and pesticides [1-3]. Traditionally, 3-picoline is manufactured from the condensation of formaldehyde, acetaldehyde and ammonia in a fixed-bed reactor [4]. Besides the low yield of 3-picoline, it generates many 4-picoline in the final products. Due to the short internal of boiling points between 3-picoline and 4-picoline, it is extremely difficult to separate them. Acrolein/ammonia is an ideal pathway for the synthesis of 3-picoline [5]. In theory, it can achieve 100% selectivity of 3-picoline. However, the major drawback is serious polymerization from acrolein and/or its related intermediate. Our groups [3, 6] reported that this problem was absolutely solved while employing acrolein diethyl acetal as raw material. In this route, the liquid-phase reaction has many advantages, eg., low temperature, less byproducts and higher yield of 3-picoline, as compared to the gas-phase one. To the best of our knowledge, there is only one report about the liquid-phase synthesis of acrolein diethyl acetal and ammonia toward 3-picoline so far [7]. In this synthetic pathway, at least three problems are appeared, and they are as follows: (i) using a lot of organic acid like acetic acid; (ii) homogeneous catalyst; (iii) separated injection. There is no doubt that the development of a novel process is highly necessitated.

In this work, ion-exchanged resins (D402 and D002) and HZSM-5 are respectively employed for the liquid-phase synthesis of 3-picoline in a batch reactor. Some important factors are explored and a ca. 24% yield of 3-picoline is obtained.

2 Experimental

2.1 Materials
All the chemicals were commercially purchased.

2.2 Synthesis of 3-picoline
The reaction was conducted under reflux condition and atmospheric pressure. In brief, acrolein diethyl acetal, ammonium acetate, ethylene glycol monobutyl ether and/or water (mass ratio: 1/2/3/0.7) were firstly mixed in a round-bottomed flask and then they were vigorously stirred for 10 min. After, D402 or D002 or HZSM-5 (mass ratio of (acrolein diethyl acetal)/solid catalyst = 1/1) was added into the above-mentioned mixture. The reaction was conducted at a certain temperature (90 ~ 130 ºC) for 60 min. Then, the products were cooled to room temperature. Qualitative and quantitative analysis of liquid products were carried out using a Varian Saturn 2200/CP 3800 GC/MS spectrometer, equipped with a flame ionization detector (FID) and two CP-Wax 52CB fused silica capillary columns (15 m × 0.32 mm). In the qualitative analysis of liquid products, isopropyl alcohol was added and employed as an internal standard.

3 Results and discussion

3.1 Effect of adding water
Fig. 1 shows the effect of adding water on the yield of 3-picoline. One can see that the yield of 3-picoline is only ca. 1.7% at 90 ºC while the system contains no water before the reaction. The byproduct is mostly solid, arising from the polymerization of acrolein diethyl acetal and/or the intermediates containing acrolein in the presence of ammonia. After adding water, the yield of 3-picoline is increased up to ca. 5.3%. Clearly, this way can accelerate the reaction rate. Under reaction conditions, acrolein is generated from the hydrolysis of acrolein diethyl acetal and water. At the same time, ammonia is produced from he decomposition of ammonium acetate. Then, acrolein interacts with ammonia to finally generate 3-picoline. Accordingly, adding water can strengthen the hydrolysis of acrolein diethyl acetal, thereby, resulting in increasing the yield of 3-picoline. Generally, the yield of 3-picoline is extremely low, because it is absence of acid sites for catalyzing the reaction on the D402.

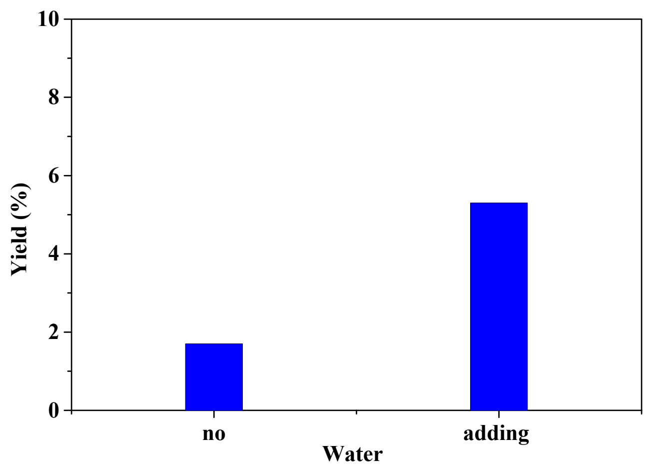

Fig. 1 Effect of the addition of water.

3.2 Effect of ion-exchanged resin
Fig. 2 shows the effect of different ion-exchanged resins on the yield of 3-picoline. It is observed that the yield of 3-picoline is ca. 13.0% using D002 resin as catalyst at 110 ºC. Obviously, D002 exhibits a stronger catalytic activity, as compared to D402. It is the most probably attributed to the higher concentration of acid sites in the former. In addition, increasing the reaction temperature, the yield of

3-picoline reaches up to 19.4% when the reaction temperature is from 110 °C to 130 °C.

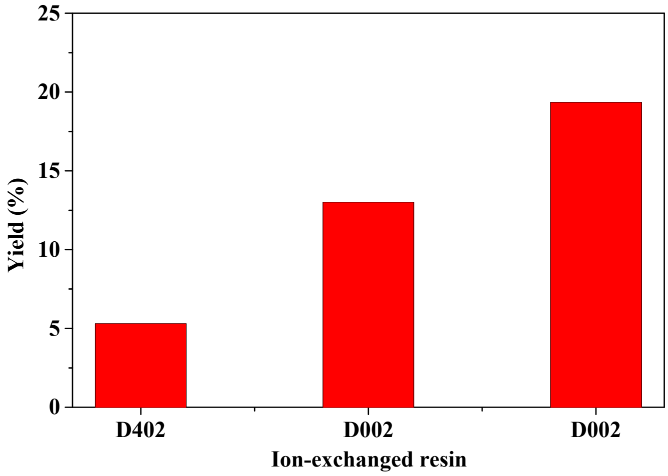

Fig. 2 Comparison with different ion-exchanged resins.

3.3 Effect of HZSM-5

Table 1 Results of 3-picoline over HZSM-5

Catalyst	Reaction conditions	Yield (%)
HZSM-5	110 °C	24.1
	130 °C	No
	Separated injection	No
	Ammonia as nitrogen source	No

Table 1 lists the effect of HZSM-5 on the yield of 3-picoline. It is found that the yield of 3-picoline is 24.1% while HZSM-5 is used as catalyst. Compared to ion-exchanged resins, HZSM-5 shows the better catalytic activity. This is due to that HZSM-5 possesses higher specific surface area and more concentrations of acid sites. Increasing the reaction temperature, the violent reaction is occurred. To improve the amount of 3-picoline, some useful ways are tried to deal with this reaction. On the one hand, two separated pipelines are injected into the reaction system. In this case, it is much difficulty to operate this reaction due to less water. On the other hand, ammonia replacing of ammonium acetate is directly used as nitrogen source. After the reaction, a lot of solid substances are generated, which is mainly attributed to the polymerization of acrolein in the existence of ammonia.

4 Conclusion

A simple heterogeneous catalytic method was proposed to prepare 3-picoline from the condensation of acrolein diethyl acetal, water and ammonia under liquid conditions. This method possesses many advantages, eg., easy to operation, no organic acid and direct mixing reaction. Kinds of factors such as types of catalysts and reaction temperature were investigated. The results showed that a ca. 24% yield of 3-picoline over HZSM-5 was obtained at 110 °C.

Acknowledgments

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