



Short communication

Preparation of pyridine and 3-picoline from acrolein and ammonia with HF/MgZSM-5 catalyst

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ABSTRACT

Pyridine and 3-picoline were prepared from acrolein and ammonia using HF/MgZSM-5 as catalyst. The HF/MgZSM-5 catalyst was produced from modification of HZSM-5 by HF and $Mg(NO_3)_2$. It was found that the micro-pore structure of the HZSM-5 carrier would be destroyed when Mg and HF were loaded. This corrosion process could be promoted by employing HF onto MgZSM-5 carrier comparing with HZSM-5 one, because of the damage of MgO to ZSM-5 stability. A micro-mesoporous HZSM-5 zeolite with fewer and weaker acid sites was prepared after HF modification. Under the optimized conditions, a total yield of 68% can be reached, with 36% being 3-picoline and 30% being pyridine.

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1. Introduction

Pyridine and 3-picoline are important intermediates in the production of pesticides, pharmaceuticals and cosmetics [1–3]. Currently, the industrial production of pyridine and 3-picoline is mainly performed through the reaction of formaldehyde, acetaldehyde and ammonia over a gaseous fluidized bed reactor. However, there are many difficulties, such as low yield of 3-picoline, high operation cost and product separation of 3-picoline [4]. An effective way of producing high yield of pyridine and 3-picoline is to condensate acrolein (AN) and ammonia. This is mainly conducted over a fluidized bed. By this method, the yield of pyridine bases can reach as high as 70%, and the yield of 3-picoline can reach 60% after the addition of acetaldehyde or propanal [5]. Although, a high selectivity to 3-picoline could be got through condensation between acrolein and ammonia. However, there are short-comings such as the short catalyst lifetime, complicated operation and high equipment cost. Experimentally, oxygen, water, ketones, aldehyde, alcohol and propylene oxide were pumped in to reduce catalyst deactivation and pipe plug for a fixed bed method [5–8]. However, it brought a series of problems, such as acrolein oxidation, product complexity and separation difficulties.

Solid acid catalysts with high surface area, such as $Al_2O_3-SiO_2$, TiO_2 and $F-M-Al_2O_3$, show good catalytic performance with a yield of

pyridine bases reaching about 70%, while that of 3-picoline is 44–57% [5,9]. Especially, the alkali-modified HZSM-5 [10–12] and HF modified Al_2O_3 [13] catalysts with particular pore structure and surface properties are effective catalysts in the synthesis of pyridine and 3-picoline from formaldehyde, acetaldehyde and ammonia. However, HZSM-5 zeolite modified by HF has never been used in the synthesis of 3-picoline.

In this paper, the pyridine and 3-picoline were prepared from acrolein and ammonia through a fixed bed reactor with a HF and $Mg(NO_3)_2$ modified HZSM-5 catalyst. Various factors for catalyst preparation and reaction conditions on the yield of pyridine and 3-picoline were investigated.

2. Experimental

2.1. Chemicals

HZSM-5 zeolites were supplied by Nankai Molecular Sieve Catalyst Plant. Acrolein, hydrofluoric acid, magnesium nitrate and ammonia were all supplied as analytical reagents.

2.2. Catalyst preparation

The MgZSM-5 catalyst were modified by impregnation of 130 gram HZSM-5 with 100 mL 0.62 M magnesium nitrate solution at a temperature 100 °C for 8 h and then activated by calcination at 700 °C for 4 h. The HF/MgZSM-5 catalyst was further modified from impregnation of the

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above MgZSM-5 catalyst with 100 mL 0.62 M NH_4HF_2 solution at the same condition above and then activation. The HF/HZSM-5 was prepared when only NH_4HF_2 solution was impregnated over HZSM-5 zeolite as the same catalyst preparation process.

The regeneration of HF/MgZSM-5 catalyst was conducted three times at 600 °C in air and steam atmospheres for 4 h, regarded as HF/MgZSM-5-reactivated-n. n is the number of regeneration time.

2.3. Characterization of catalyst

X-ray diffraction spectroscopy (XRD) was performed with a Bruker D8-Advance X-Ray diffraction spectrometer. Fourier transform infrared (FT-IR) spectroscopy was recorded on a Varian 3100 spectrometer, equipped with a DTGS detector. N_2 -physisorption was carried out on a Quantachrome Autosorb-1C/TCD Automatic Chemisorption with a TCD detector at liquid- N_2 temperature. Temperature programmed desorption of NH_3 (NH_3 -TPD) was measured by a Micromeritics AutoChemII2920 chemisorption analyzer with a TCD detector.

2.4. Products preparation

The acrolein and ammonia were firstly preheated at 250 °C before mixing with each other above the catalyst bed in the fixed bed reactor. At the same time, the preheated water vapor and nitrogen were added to reduce the deactivation of catalyst and polymerization of acrolein. The specific reaction apparatus was shown in Fig. 1.

3. Results and discussion

3.1. Catalytic activities

Table 1 shows the yield of pyridine and 3-picoline over various catalysts. No pyridine based reaction products have been collected over HZSM-5. It is probably because that the reaction products were deposited in the micropores of the HZSM-5 catalyst due to the small pore diameter and high diffusion resistance. The fast inactivation of HZSM-5 catalyst would accelerate polymerization, leading to channel blockage. We have also found that the white catalyst changed the color to black after reaction. The yields of pyridine bases using HF/HZSM-5 and HF/MgZSM-5 as catalysts are obviously higher than that using MgZSM-5 and HZSM-5 as catalysts. It shows the fact that HF offers a great help in yield for both HF/HZSM-5 and HF/MgZSM-5 catalysts.

The yield of pyridine and that of 3-picoline are similar, which indicates their similar synthesis mechanism. However, the selectivity of 3-picoline is higher than that of pyridine when the catalyst shows a good selectivity to total pyridine bases. The low selectivity to 3-

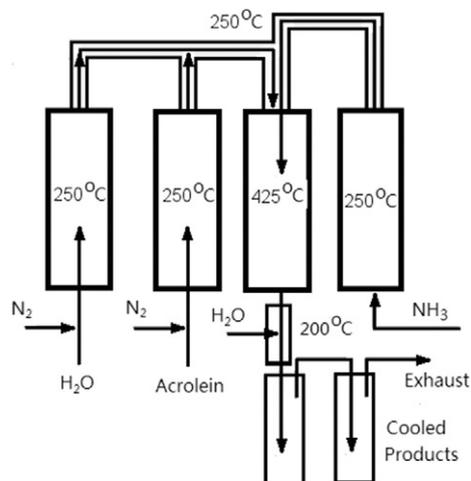


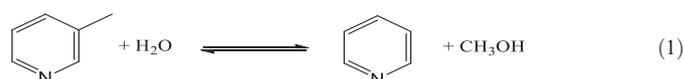
Fig. 1. Fixed-bed reactive apparatus for condensation of acrolein and ammonia.

Table 1
Yield of pyridine and 3-picoline over various catalysts.

Catalysts	Pyridine/%	3-Picoline/%	Others/%	Pyridines/%
HZSM-5	–	–	–	–
MgZSM-5	4.55	4.26	0	8.81
HF/HZSM-5	25.82	25.91	1	52.73
HF/MgZSM-5	26.59	30.38	1.9	58.86
HF/MgZSM-5-reactivated-1	28.3	32.1	1.68	62.07
HF/MgZSM-5-reactivated-2	17.24	18.15	0.53	35.92
HF/MgZSM-5-reactivated-3	11.02	11.88	0.41	23.31

Conditions: $\rho_{\text{AN}} : \rho_{\text{H}_2\text{O}} : \rho_{\text{NH}_3} = 1 : 2 : 2$, 500 h^{-1} , 4 h, 425 °C.

picoline is probably due to demethylation reaction of 3-picoline to pyridine [14] as shown in Eq. (1).



The HF/MgZSM-5-reactivated-1 catalyst shows a little higher yield than the yield before the regeneration, but it is deactivated quickly. This might be due to the loss of F on the catalyst surface as shown in Eq. (2).



It is apparent that the regeneration of the catalyst should be improved. Comparing the catalytic results of HF/MgZSM-5-reactivated-1, HF/MgZSM-5-reactivated-2 and HF/MgZSM-5-reactivated-3, the catalyst surface properties could not be restored completely after the regeneration. The decrease of V_{total} , S_{total} , S_{mic} , S_{mic} and V_{mic} shown in Table 2 shows the carbon deposition on reaction pores. The diameter of micropores only decreased from 6.54 to 6.40 Å. Because pyridine bases are mainly produced on weak Lewis acid sites (*w*-LAS) and hydroxyl groups of ZMS-5 catalyst, the HF/MgZSM-5-reactivated-1 catalyst can keep high catalytic activity even through carbon deposition occurs on the strong Lewis acid sites (*s*-LAS) [15]. With the continuous carbon deposition on HF/MgZSM-5-reactivated-2 and HF/MgZSM-5-reactivated-3, large part of pores and acid surface are covered, which leads to decrease of pyridine bases production.

Fig. 2 shows the yields of pyridine and 3-picoline versus reaction time. It is observed that the yields of pyridine, 3-picoline and other pyridine bases during every two hours increase firstly and decrease dramatically after the 6 h. The highest 62% yield of pyridine bases (about 32% of 3-picoline, 28% of pyridine and 2% other pyridine bases) is obtained between 2 to 4 h, with a sharp decrease for the 3-picoline production after 4 h. The yield of 3-picoline is higher than that of pyridine because the catalyst has higher activity during the first 4 h. It is consistent with the results of various catalysts as shown in Table 1.

Acrolein or propylene imine intermediate may favor cycloaddition and Diels-Alder reaction to produce pyridine and 3-picoline products

Table 2
The textural properties of different catalysts.

Catalysts	V_{total} cm^3/g	S_{total} m^2/g	V_{mic} cm^3/g	S_{mic} m^2/g	S_{ext} m^2/g	D_{mic} Å	D_{mes} Å
HZSM-5	0.240	389	0.132	316	73.4	6.20	24.6
MgZSM-5	0.226	308	0.103	256	52.4	4.58	29.3
HF/HZSM-5	0.251	356	0.140	304	52.1	6.26	28.1
HF/MgZSM-5	0.219	330	0.107	249	80.7	6.54	26.6
HF/MgZSM-5-deactivated	0.068	61.5	0.017	35.4	26.1	6.60	
HF/MgZSM-5-reactivated	0.152	233	0.072	184	49.5	6.40	

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