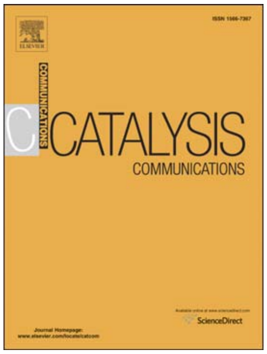

Preparation of pyridine and 3-picoline from acrolein and ammonia with HF/MgZSM-5 catalyst

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PII: S1566-7367(16)30058-9
DOI: doi: 10.1016/j.catcom.2016.02.011
Reference: CATCOM 4592

To appear in: *Catalysis Communications*

Received date: 3 July 2015
Revised date: 4 February 2016
Accepted date: 9 February 2016

Please cite this article as: Xian Zhang, Zhen Wu, Wei Liu, Zi-sheng Chao, Preparation of pyridine and 3-picoline from acrolein and ammonia with HF/MgZSM-5 catalyst, *Catalysis Communications* (2016), doi: 10.1016/j.catcom.2016.02.011

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 micropore 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.

Keywords：acrolein；pyridine；3-picoline；ZSM-5；mesoporous

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-commings 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 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]. Espacially, 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-pocline.

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 grams HZSM-5 with 100 mL 0.62 M magnesium nitrate solution at a temperature 100 ^oC for 8 h and then activated by calcination at 700 ^oC for 4 h. The HF/MgZSM-5 catalyst was further modified from impregnation of the 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 for three times at 600 ^{o}C in air and steam atmosphere for 4 hours, 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

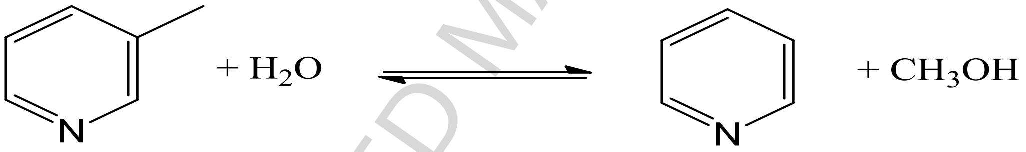
The acrolein and ammonia were firstly preheated at 250 ^{o}C before mixing with each other above the catalyst bed in the fixed bed reactor. At the same time, the preheated water vapor and nitrogen were added to reduce the deactivation of catalyst and polymerization of acrolein. The specific reaction 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-picoline is probably due to demethylation reaction of 3-picoline to pyridine [14] as shown in *Eqn. 1*.



(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 *Eqn. 2*.

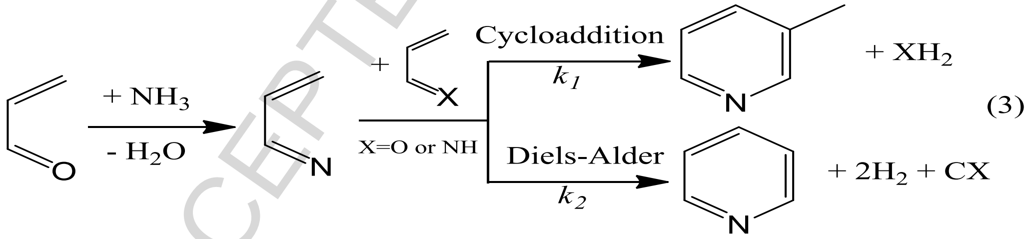
$$\text{M-F} + H_2O \longrightarrow \text{M-OH} + HF \qquad (2)$$

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.

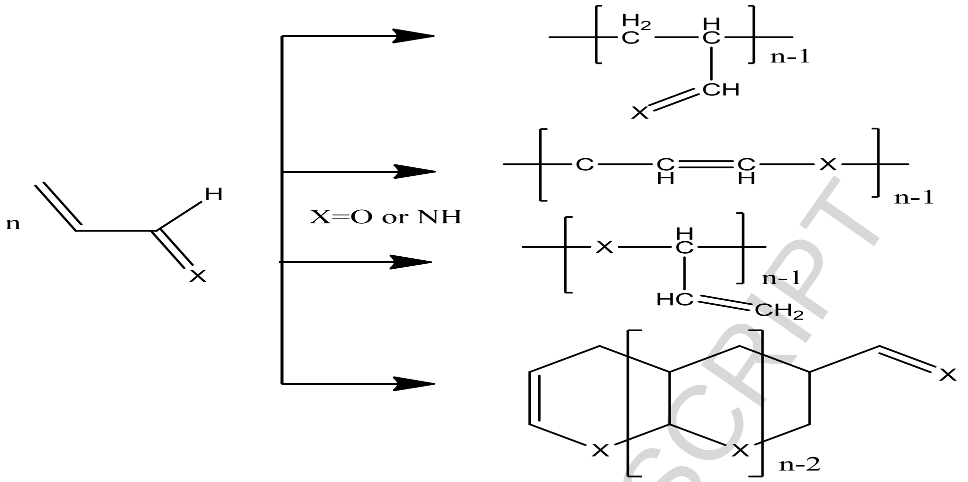
Fig.2 shows the yields of pyridine and 3-picoline versus reaction time. It is observed that the yields of pyridine, 3-picoline and other pyridine bases during every two hours increase firstly and decrease dramatically after the 6 hours. The highest 62% yield of pyridine bases (about 32% of 3-picoline, 28% of pyridine and 2% other pyridine bases) is obtained between 2 to 4 hours, with a sharp decrease for the 3-picoline production after 4 hours. The yield of 3-picoline is higher than that of pyridine because the catalyst has higher activity during the first four hours. 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 [15-17] as shown in *Eqn.3*.



(3)

The total yield of pyridine bases has dropped to about 5% between 10 to 12 hours because the acrolein or propylene imine intermediate are so active that the polymer byproducts are produced, which leads to catalyst coking. At the same time, the total yield of pyridine bases decreases sharp at the 6th time. Some polymerizations of acrolein and/or propylene imine were shown in *Eqn.4*.



(4)

A white plastic polymer could be seen after the tars solid byproducts were washed by method. It is possibly caused by *s*-LAS and often leads to channel blockage. Other unsaturated intermediate might also take part in the above four polymerizations [17]. However, the main polymerization byproduct is not clear.

3.2 Catalytic properties

The XRD patterns of various catalysts are shown in Fig. S1, it shows similar ZSM-5 framework with lower peak intensity after HF modification [18, 19]. The hydroxyl stretching region (A) and ZSM-5 framework (B) for the HZSM-5, MgZSM-5, HF/HZSM-5 and HF/MgZSM-5 are depicted in Fig. 8. The band of $SiOH(SiO)_3$ at 1749 cm^{-1} is weak and there are the strong bands at 1674-1648 cm^{-1}, which are attributed to Si(OH)Al [18]. The broad bands at 3450-3200 cm^{-1} are attributed to Si(OH)Al associated with hydrogen bond [20]. The bands at 3419 and 3250 cm^{-1} over MgZSM-5 are attributed to the Mg(OH) and Si(OH)Mg. The intensity of hydroxyl stretching bands decrease after HF etched over the zeolite surface because the OH^- group is partly occupied by F^- ion, which leads to BAS converting to LAS [18]. Nevertheless, F^- ion could also occupy O^{2-} atom in the Al-O framework to from $Al(OH)_xF_y$ ($x + y < 3$) and make the hydroxyl group bands (3419 and 3648 cm^{-1}) shift to higher wavenumbers (3448 and 3674 cm^{-1}) [13, 18].

The band at 1399 cm^{-1} in Fig. 3B is attributed to Al-H group since Al species are extracted from the framework by HF [21]. While the band of 1627 cm^{-1} is attributed to the water in framework. All of the ZSM-5 framework bands at 1229, 1113, 794, 625, 584, 553 and 455 cm^{-1} could be seen in the spectra of the four catalysts [22]. However, the new bands at 1160 and 1076 cm^{-1} shifted from 1113 cm^{-1} are attributed to the external asymmetric stretching vibrations. The related peak intensities decrease because of zeolite framework containing Mg or F. At the same time, Mg not only stays on the zeolite surface, but also enters into pores as the bands (625, 553, 584 and 455 cm^{-1}) intensities decrease. The new bands at 728 and 686 cm^{-1} of HF/HZSM-5 and HF/MgZSM-5 catalysts are attributed to the symmetric stretching vibration assigned to zeolite framework containing F. The weaker interaction of HF with ZSM-5 in HF/MgZSM-5 than HF/HZSM-5 suggests that the reaction of MgO with HF, which leads to the formation of MgF_2. This would depress the damage to ZSM-5 framework. The band at 924 cm^{-1} is attributed to extra atoms for the HF/MgZSM-5 and HZSM-5 catalysts, which have the similar framework IR spectra.

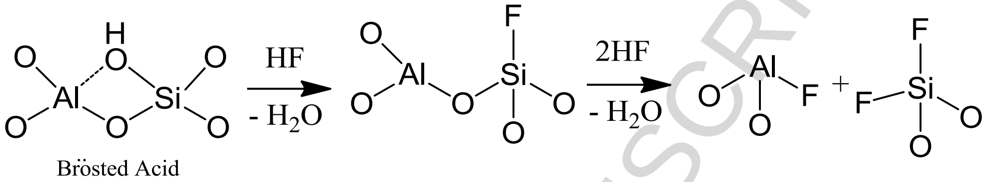
The N_2 adsorption desorption isotherms (A) and SF pore diameter distribution (B) of different catalyst samples are depicted in Fig. 4. The all isotherms exhibit a type Ⅳ curve due to the micro-mesoporous structure. The curves of SF pore diameter distribution show that there are two kinds of micropores, one of which is smaller and the other is bigger than that of HZSM-5. It approved the formation of MgO in a micropore leading to the micropore expansion and the neighboring one shrinkage. The mesopores, caused by HF modification in HF/MgZSM-5 and HF/HZSM-5, are of 27.2 and 29.2 Å respectively. These mesopores come from collapse of neighboring micropores and may be helpful for their high catalytic activities. Fewer mesopores could be seen in the HF/MgZSM-5 than the HF/HZSM-5 as the neutralization of MgO with HF.

Table 2 shows the textural properties of different catalysts. The decrease of D_{mic}, V_{mic} and S_{mic} for MgZSM-5 catalyst suggests the blockage of micropores because of the formation of MgO in micropores. And also, the V_{total} and S_{total}

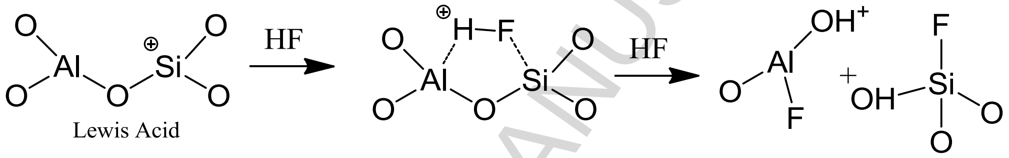
decrease. The decrease of S_{ext} and increase of D_{mes} indicates the aggregation of HZSM-5 grains. The increase of D_{mic}, D_{meso}, V_{mic} and V_{total} and decrease of S_{total}, S_{mic} and S_{ext} for HF/HZSM-5 show that HF dissolve amorphous species deposited in the micropores and some micropore walls to make mesopores. The fresh mesopore diameters are four times than that of micropore ones [21]. The S_{ext} and S_{total} of HF/MgZSM-5 increase more obviously than that of MgZSM-5. It shows that catalyst grains become smaller for HF/HZSM-5 than for MgZSM-5 and 5. The deactivated HF/MgZSM-5 catalyst has fewer pores than the fresh one is due to the deposited carbon. After it was regenerated, same deposited carbon was burned, but not all. The regeneration method has a great effect for the catalyst activation.

The catalyst acidities of various catalysts are summarized at Table 3 from the NH_3-TPD curves shown in Fig. 5. One can see that there are only three NH_3 desorption temperature (T_1, T_2 and T_3) for all catalysts. The peaks of T_1=130-250 °C, T_2=190-350 °C and T_3=450-550 °C can be assigned to the terminal silanol groups, the Brönsted acid sites (BAS) and proton acid sites, the strong BAS from internal pore and LAS, respectively [23, 24]. The NH_3 desorption temperatures of HZSM-5 and MgZSM-5 catalysts at three kinds acid sites shift to lower temperatures, such as T_1 from 150-159 °C to 134-146 °C, T_2 from 345-347°C to 192-250 °C and T_3 from 490-541 °C to 460-462°C. It is said that the strong BAS and LAS are changed to weak ones. At the same time, the HZSM-5 and MgZSM-5 catalysts contains a large quantity of acid sites (1099.6 and 2037.4 μmol/g) and have low yields of pyridine bases (0 and 8.81%), while the HF/HZSM-5 and HF/MgZSM-5 catalysts contains a small quantity of acid sites (56.6 and 245.5 μmol/g) and high yields of pyridine bases (52.73 and 58.86%). It can be concluded that the yield of pyridine bases is determined by both concentration and strength of acid sites. The samples modified by HF containing weaker and fewer acid sites show good catalytic activities. However, a certain amount of BAS and *w*-LAS are highly helpful for the acrolein activation and pyridine bases formation because of the higher selectivity for HF/MgZSM-5 than HF/HZSM-5 catalyst [13, 15].

From the above analysis, we conclude that the reactions between HF and HZSM-5 zeolite shown in *Eqn. 5* and *Eqn. 6*. Amounts of BAS and LAS have decreased and weakened by HF modification.

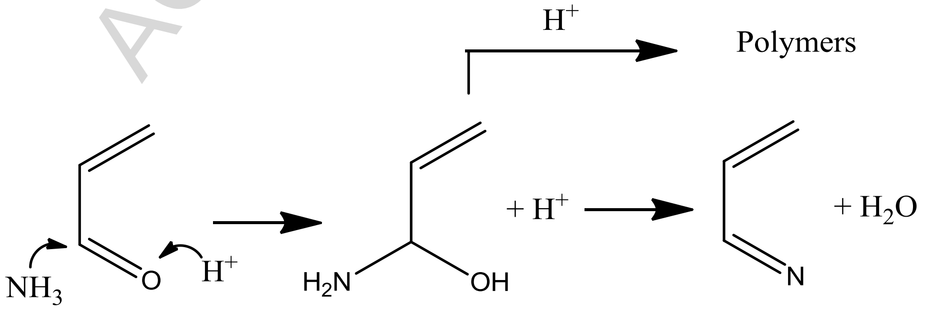


(5)



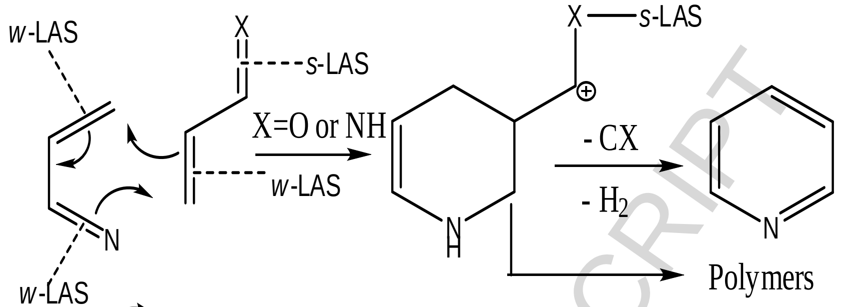
(6)

It was reported that the production of pyridine bases involves both hydroxyl groups and LAS. However, *s*-LAS might favor the polymerization products, which included coke precursors [15]. It is argued that the presence of two types of LAS exhibit high activity and selectivity in the 3-picoline synthesis by condensation of acrolein with ammonia [9]. And also, desorption of NH_3 from strong acid sites is difficult and leads to decrease of propylene imine formation. The proton sites and hydroxyl groups could catalyze the formation of propylene imine from acrolein as shown in *Eqn. 7*.



(7)

A certain concentration of BAS and *w*-LAS might be favorable to flat-adsorption of propylene imine and synthesis of 3-picoline. On the contrary, a high concentration of strong acid sites might be favorable to point-adsorption of propylene imine and synthesis of pyridine and polymers. The synthesis reactions of pyridine and 3-picoline are shown in *Eqn*. 8 and *Eqn*. 9. The good diffusion of products in big micropores could decrease coking and increase catalyst lifetime.



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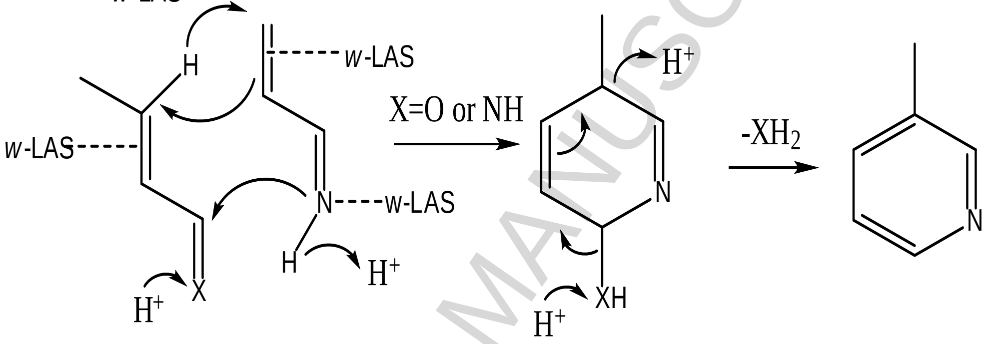

(9)

4 Conclusion

A 68 % yield of pyridine and 3-picoline from the condensation of acrolein and ammonia was observed by using HF/MgZSM-5 as catalyst. The improved catalytic activity is seen with MgZSM-5 modified by HF. It is because that the fresh acid sites for HF/MgZSM-5 are less and weaker than that before modification. In addition, it is concluded that the formed bigger micropores and mesopores can prolong catalyst lifetime and reduce diffusion resistance.

Acknowledgments

We are grateful to the financial supports from the Project #21376068 for National Natural Science Foundation (NSFC), the Colleges and Universities' Scientific Research Project of Inner Mongolia Autonomous Region (NJZZ13017) and the Innovation training program of Inner Mongolia University.

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Figures:

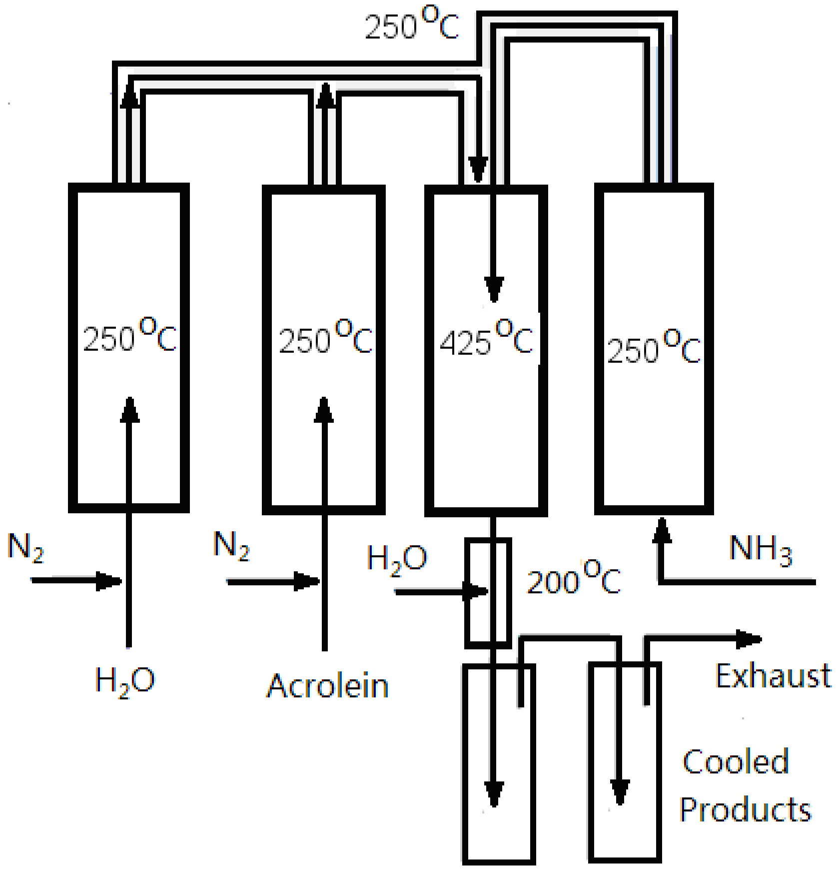
Fig.1 Fixed-bed reactive apparatus for condensation of acrolein and ammonia.

Fig.2 Yield of pyridine and 3-picoline versus reaction time.

Fig.3 FT-IR spectra (A) 4000～2500 cm^{-1} and (B) 1800～400 cm^{-1} of (a) HZSM-5, (b) MgZSM-5, (c) HF/HZSM-5 and (d) HF/MgZSM-5.

Fig.4 The N_2-adsorption and desorption isotherms (A) and pore diameter distribution (B) of (a) HZSM-5, (b) MgZSM-5, (c) HF/HZSM-5 and (d) HF/MgZSM-5.

Fig.5 NH_3-TPD curves of (a) HZSM-5, (b) MgZSM-5, (c) HF/HZSM-5 and (d) HF/MgZSM-5



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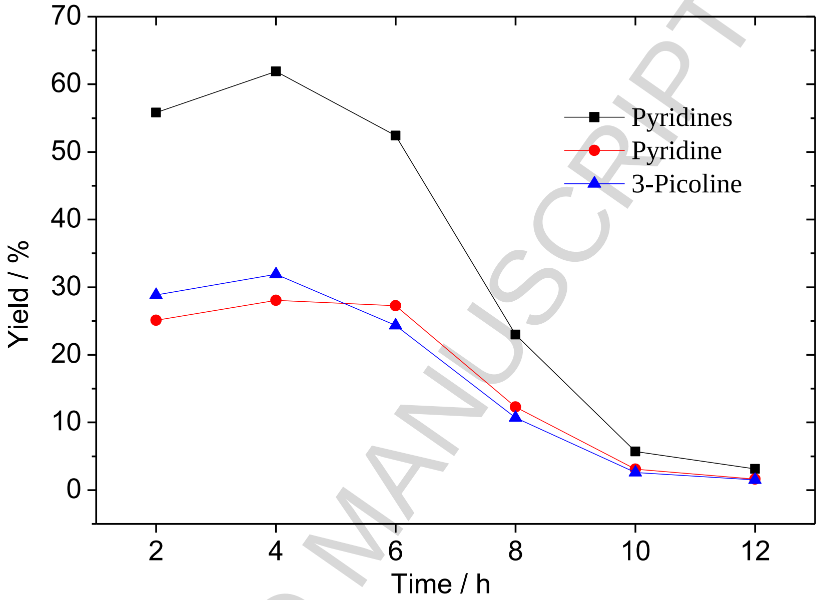
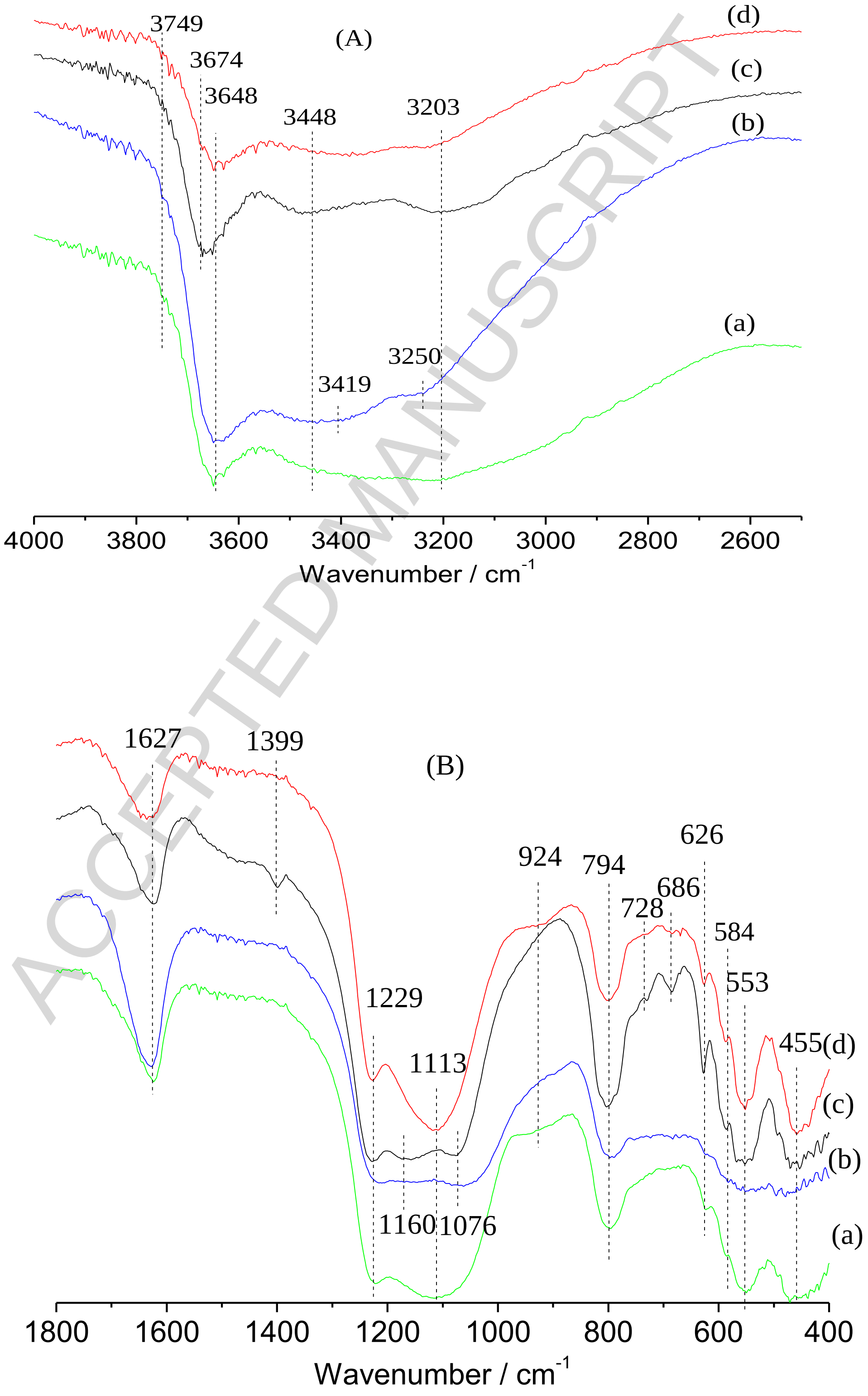


Fig.2 Yield of pyridine and 3-picoline versus reaction time.

Conditions: HF/MgZSM-5 Catalyst, n_{AN} / n_{H2O} / n_{NH3}=1 / 2 / 2, 500 h^{-1}, 425 ^{o}C.



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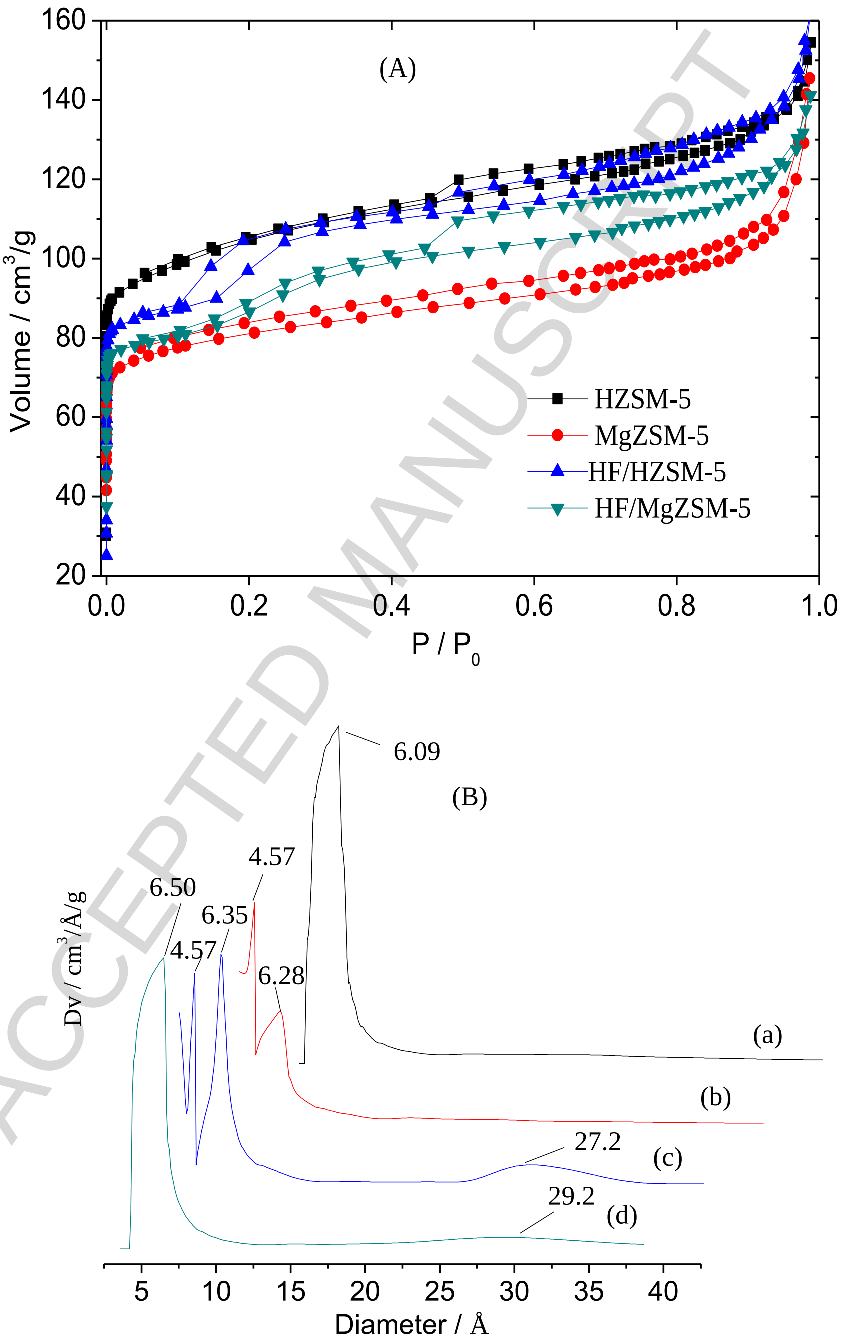

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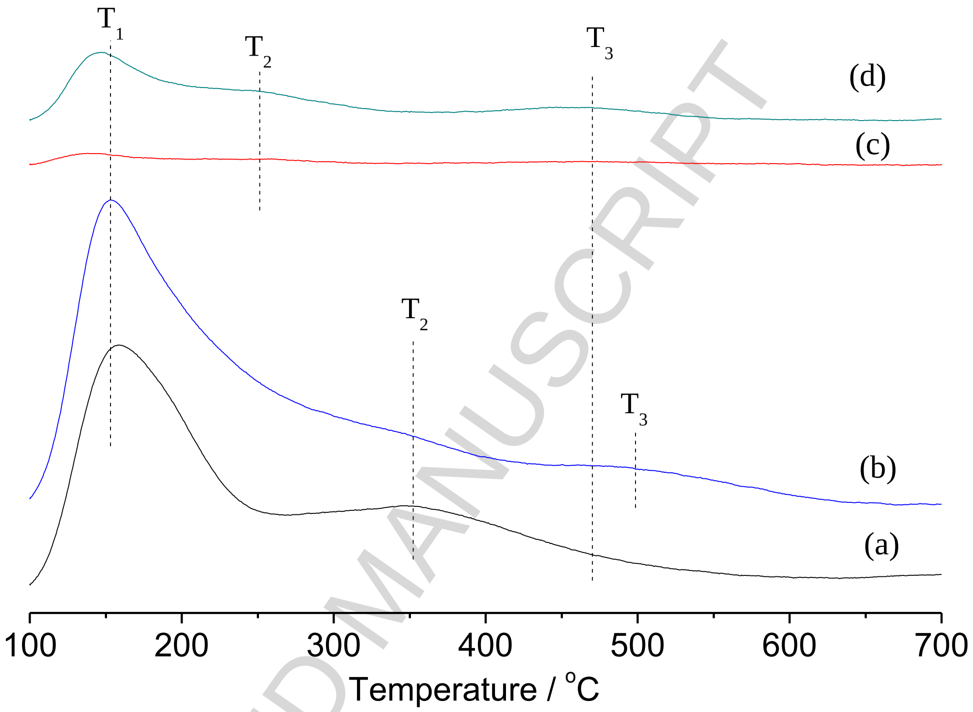


Fig.5 NH_3-TPD curves of (a) HZSM-5, (b) MgZSM-5, (c) HF/HZSM-5 and (d) HF/MgZSM-5.

Tables:

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

Table 2 The textural properties of different catalysts

Table 3 Acidity of different catalysts from the NH_3-TPD data

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

Conditions: n_{AN}: n_{H2O}: n_{NH3} =1: 2: 2, 500 h^{-1}, 4 h, 425 ^oC.

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

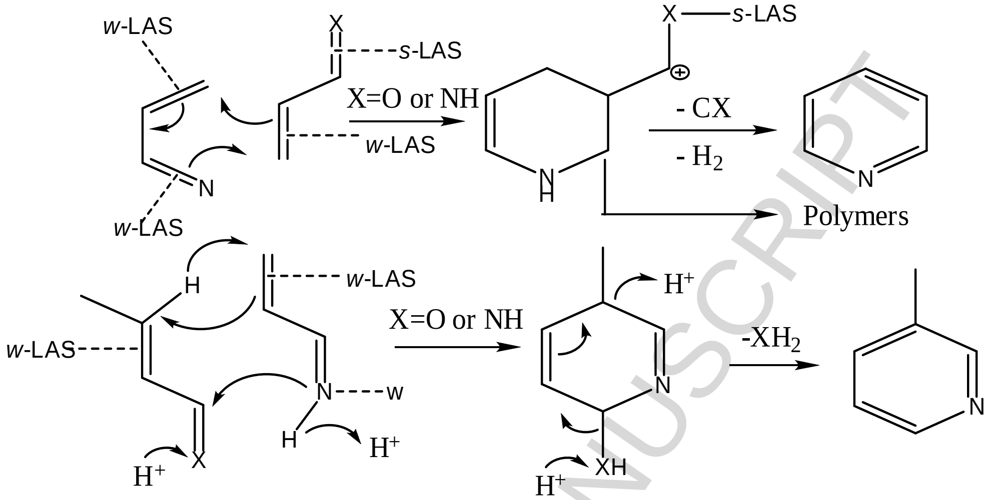
Table 2 The textural properties of different catalysts

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	

Table 3 Acidity of different catalysts from the NH_3-TPD data

Catalysts	Desorption temperature（T_m, °C）and acid sites（A_{Tm}, μmol/g）						
	A_T	T_1	A_{T1}	T_2	A_{T2}	T_3	A_{T3}
HZSM-5	1099.6	159	667.1	345	288.3	492	144.2
MgZSM-5	2037.4	150	1008.7	347	207.1	541	822.6
HF/HZSM-5	56.6	138	17.7	192	17.4	462	21.5
HF/MgZSM-5	245.5	146	111.6	250	78.3	460	45.6

Graphical abstract：



The HF/HZSM-5 and HF/MgZSM-5 catalysts, containing weaker and fewer Brösted and Lewis acid sites than HZSM-5 and MgZSM-5, have great help for the synthesis of pyridine and 3-picoline. The flat-adsorption of propylene imine on weak Lewis acid sites favors the production of 3-picoline. A strong adsorption leads to pyridine or polymer products. The bigger micropores and mesopores formed under further corrosion of HF solution have prolonged the catalyst lifetime.

Highlights

- As high as 68% yield of pyridine and 3-picoline was achieved from concentration of acrolein and ammonia.
- A HF/MgZSM-5 catalyst containing certain weaker and fewer acid sites after HF modification.
- The catalytic active centers might be fresh weak Lewis acid sites.
- The bigger micropores and mesopores formed by HF modification prolonged catalyst lifetime.