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Synthesis of Pyridine Bases over Ion-exchanged Pentasil Zeolite

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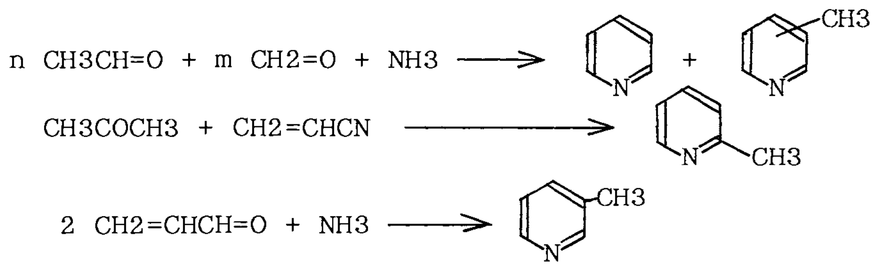
The catalytic activity of pentasil zeolite for the synthesis of pyridine bases from aldehydes and ammonia was found to depend upon the Si/Al ratio and the metal cation. The best choices are 30 to 120 of Si/Al ratios and metal cations such as Tl(I), Pb(II), Co(II) and Zn(II).

Pyridine bases are key intermediates for pharmaceuticals and agricultural chemicals.[1)] The industrial vapor phase pyridine bases is classified into the following three routes; 1) condensation of aldehydes and ammonia to form pyridine bases (Eq. 1),[2)] 2) condensation of acrylonitrile and acetone to form α-picoline (Eq. 2)[3)] and 3) condensation of acrolein and ammonia to form β-picoline (Eq. 3).[4)] These reactions include condensation, cyclization and dehydrogenation.



(1)
(2)
(3)

Among them, the route (1) is the most versatile one, because, by changing the combination of substrates, pyridine and/or picolines can be synthesized at some controlled ratios. First of all, we examined various solid acid catalysts on this reaction (Table 1). Both the total yield of pyridine bases and the ratio of pyridine (the most versatile one) among pyridine bases are the highest with pentasil type zeolites such as H-ZSM-5 and Silicalite. Other type zeolites, such as H-A, H-X, H-Y and H-M, and typical solid acids, such as SiO_2-Al_2O_3, gave a little poor results. These results mean that, for the vapor phase synthesis of pyridine bases, both the medium acidity and the pentasil structure are preferable.

Taking H-ZSM-5 as the best zeolite catalyst, the influences of the Si/Al atomic ratio were examined (Fig. 1). A mild increase in total yield was observed with the increase of the Si/Al ratio till 80 to 120. But over these ratios, the total yield decreased with the increase of the Si/Al ratio. These results indicate that, in the higher acidity region, too much acidity retards the catalytic activity because of coke formation (rapid decay of the activity). Whereas in the lower acidity region, the catalytic activity is proportional to the acid amount.

Table 1. Catalytic activities of various solid acids in the vapor phase synthesis of pyridine bases

Catalyst	Yield/% based on aldehydes				
	pyridine	α-picoline	γ-picoline	β-picoline	Total
SiO_2-Al_2O_3	33	4	4	11	52
H-A	25	1	4	6	36
H-X	20	6	6	9	41
H-Y	27	5	8	14	54
H-M	17	2	4	8	31
H-ZSM-5	42	3	5	11	61
Silicalite	41	3	5	12	61

Reaction conditions; Flow type reactor with fixed catalyst bed, SV=1000 h^{-1} T=450 ℃, $CH_3CH=O/CH_2=O/NH_3=2/1/4$ (molar ratios). H-ZSM-5(Si/Al=88) was synthesized following the literature,[5] and was identified by XRD. Silicalite: UCC's S-115.

The great increase in the yield of pyridine bases was observed by ion-exchange of the pentasil zeolite with metal cations, such as Tl(I), Pb(II), Co(II) and Zn(II) (Table 2). Other cations, such as Ag(I), Cu(II), Ni(II) and Cd(III), did not show any effect on the catalytic activity. To investigate the effect of the ion-exchage, the acidity was measured by the GC-pulse adsorption of pyridine. A mild decrease in the acidity was observed, but no clear difference was observed for each ion-exchanged zeolite. Therefore, other properties of metal cation itself, such as dehydrogenation activity, which is necessary for the synthesis of pyridine bases, might have to be taken into consideration.

The influences of the Si/Al ratio in Pb-ZSM-5 on the yield of pyridine bases are shown together with the results for H-ZSM-5 (Fig. 1). The similar changes are observed for both zeolites, as has been discussed above.

To estimate the reaction pathway for piridine bases, the influences of the molar ratio of aldehydes were examined over Pb-ZSM-5 catalyst (Fig. 2). With the increase of formaldehyde/acetaldehyde molar ratio, the yields of α - and γ -picolines decreased almost linearly with the increase of pyridine yield. Both α - and γ -picolines were not synthesized when the $CH_2=O/CH_3CH=O$ molar ratio exceeded 0.8. β -Picoline began to be formed when the $CH_2=O/CH_3CH=O$ molar ratio exceeded 0.5, then gradually increased.

Table 2. Influences of ion-exchange in ZSM zeolites over the synthesis of pyridine bases

Catalyst	Yield/% based on aldehydes				
	pyridine	α -picoline	γ -picoline	β -picoline	Total
H-ZSM-5	42	3	5	11	61
Tl-ZSM-5	63	6	3	9	81
Pb-ZSM-5	60	7	4	8	79
Co-ZSM-5	57	6	8	7	78
Zn-ZSM-5	58	6	6	9	79
Tl-ZSM-11	60	5	5	8	78
Pb-ZSM-11	57	5	5	9	76
Ag-ZSM-5	42	3	6	11	62
Cu-ZSM-5	42	3	5	10	60
Ni-ZSM-5	42	3	4	11	60

ZSM-11 was synthesized following the patent literature.[6)]

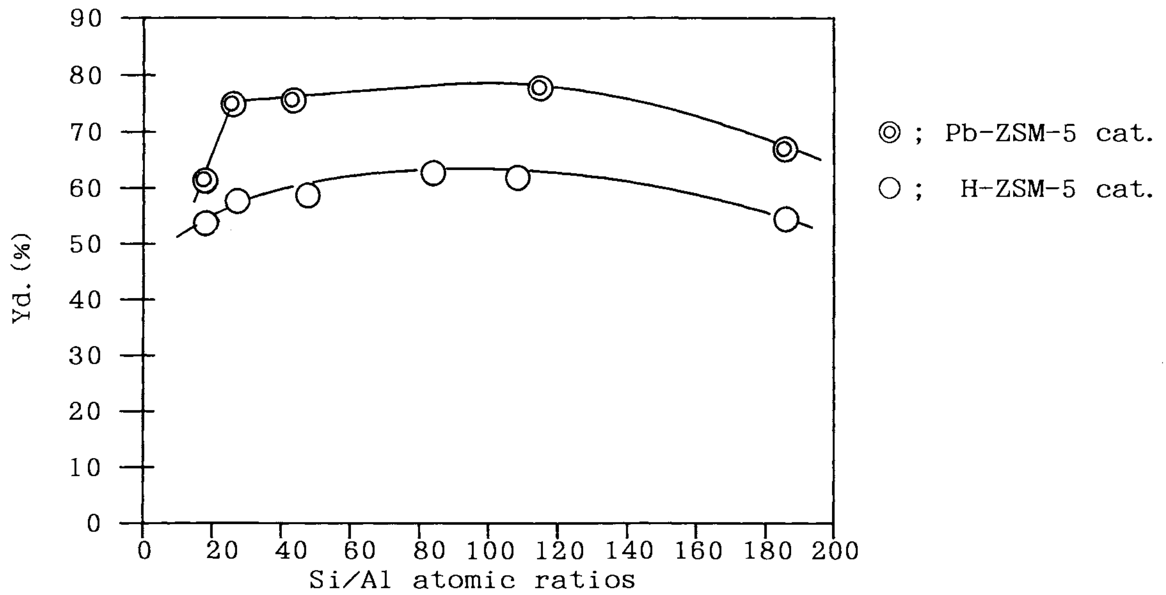


Fig. 1. Influences of Si/Al atomic ratios on the yield of pyridine bases.

These data coincide with the reaction system proposed by A. E. Tschitschibabin, as shown schematically below.

1) formaldehyde/acetaldehyde=0

3 CH3CH=O + NH3 ⟶ α - & γ -picolines + H2 + 3 H2O (4)

2) formaldehyde/acetaldehyde=0.5

2 CH3CH=O + CH2=O + NH3 ⟶ pyridine + H2 + 3 H2O (5)

3) formaldehyde/acetaldehyde=1.0

2 CH3CH=O + 2 CH2=O + NH3 ⟶ β -picoline + H2 + 3 H2O (6)

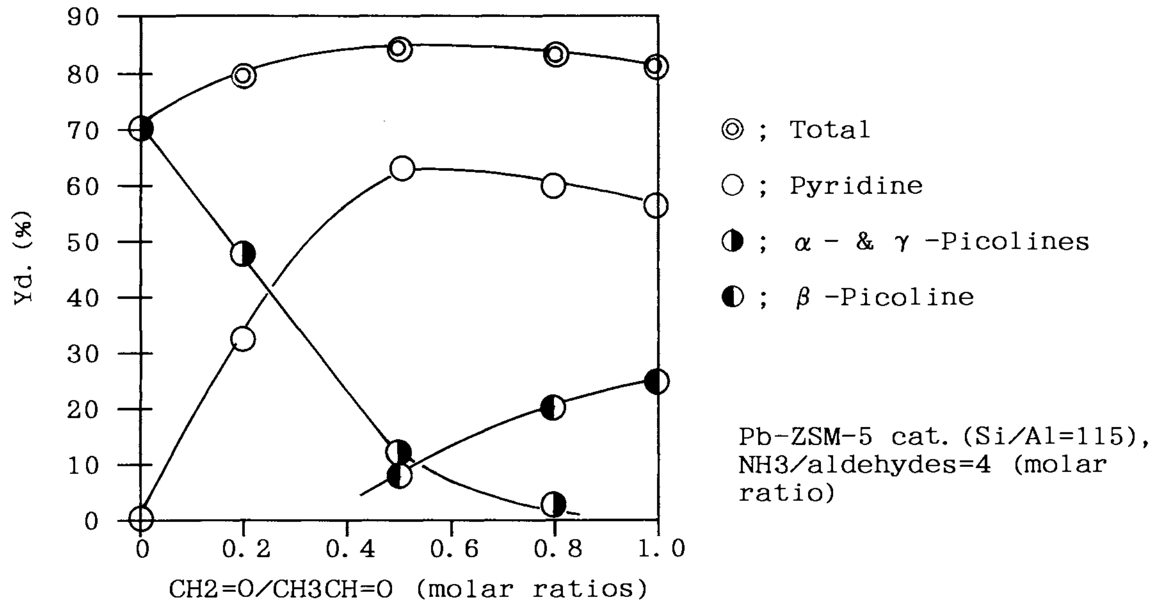


Fig. 2. Influences of formaldehyde/acetaldehyde moloar ratios on the yield of pyridine bases.

The results in Fig. 2 exhibit the preference of pyridine formation (Eq. 5) to picolines fromation (Eqs. 4 and 6).

In conclusion, the pentasil zeolite with medium Si/Al ratios (30 to 120), which was ion-exchanged with a metal cation such as Pb(II), Tl(I), Zn(II) or Co(II), exhibited a high catalytic performance for the synthesis of pyridine bases from aldehydes and ammonia.

References

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4) Japanese Patent (unexamined) 52-31075 (1977).
5) T. Yashima, Syokubai, 23, 232 (1982).
6) U. S. Patent 3709979 (1873).

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