SYNTHESIS OF PYRIDINES OVER ZEOLITES IN GAS PHASE

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday for his achievements in organometallic chemistry and catalysis and for his long-term friendship.

Pyridine and its methyl derivatives were synthesized in vapor phase from ethanol, formaldehyde and ammonia over zeolites H-ZSM-5, Beta, mordenite and over SiO_2. Both the Si/Al molar ratio and modification of zeolite with zinc strongly influenced the selectivity in pyridine and alkylpyridines formation. The highest yield of pyridine was obtained over ZSM-5 modified with zinc and the highest pyridine-to-alkylpyridines ratio was achieved over H-ZSM-5 with high Si content (Si/Al ratio 140). The conversion of ethanol and the selectivity in pyridine formation were correlated with the acidity of used catalyst.

Keywords: Pyridine; Pyridine bases; ZSM-5; Ethanol; Gas-phase reactions; Heterogeneous catalysis; Zeolites; Acidity.

Pyridine bases are key intermediates for the synthesis of various pharmaceuticals, agricultural chemicals, surface agents, disinfectants and other fine chemicals, such as vitamin B, nicotinamide and nicotinic acid, which play an important role in metabolism. Pyridine itself is also used as a solvent for extraction and some special applications[1]. The pharmaceutical industry needs pyridine bases of high purity, which cannot be obtained from coal tars. Most pyridine bases have been mass-produced by the Chichibabin condensation, which involves gas-phase reactions of acetaldehyde, formaldehyde and ammonia on an amorphous silica–alumina catalyst. However, the selectivity for pyridine is rather low owing to many byproducts and the process is accompanied by heavy coking of the catalyst[2].

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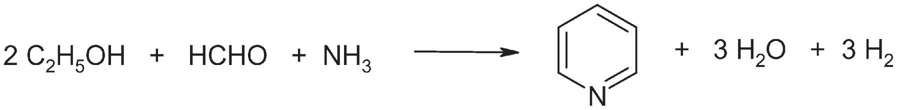
The reaction of aldehydes or ketones with ammonia over pentasil zeolite catalysts is the most general synthetic method for the manufacture of pyridine bases. The first examples of catalytic application of zeolites in production of pyridine and picolines date back to the early eighties[3]. These reactions include condensation, cyclization and dehydrogenation. Both the total yield of pyridine bases and the ratio of pyridine to pyridine derivatives are the highest with pentasil zeolites, such as H-ZSM-5 due to their unique channel structure. It is expected that the zeolite shape-selectivity plays a decisive role in condensation reactions, leading to pyridine, pyrrole and furan derivatives, limiting the formation of bulkier reaction intermediates or even reaction products[4]. Other types of zeolites, such as A, H–X and H–Y and typical solid acids, such as SiO_2–Al_2O_3, provided poor results especially with regard to the selectivity[5]. Alcohols (except for methanol) can substitute expensive and very reactive carbonyl compounds in this process. Suitable catalysts for the preparation of pyridine from ethanol, formaldehyde and ammonia are usually mixed metal oxide catalysts (e.g. Zn/Al/Si, Cd/Al/Si), zeolites (e.g. H-ZSM-5) and zeolites modified with metal cations such as Zn, Pb, W, Cd or Co [6–8]. The activity and the lifetime of H-ZSM-5 catalysts are influenced not only by modification with metals but also by temperature and conditions of catalyst calcination[6].

The objective of this contribution is to report the synthesis of pyridine bases in a gas-phase reaction using ethanol, formaldehyde and ammonia as reactants over zeolites differing in channel structure and architecture, and concentration of acid sites, namely zeolites Beta, mordenite and ZSM-5, unmodified and treated with zinc. In addition, pure SiO_2 was used for comparison.



EXPERIMENTAL

Catalysts

ZSM-5 zeolites (Si/Al 14.1 and 21.8) were supplied by VURUP, Slovakia, ZSM-5 zeolite (Si/Al 75) by Conteka, Switzerland and ZSM-5 zeolites (Si/Al 40 and 140) by Zeolyst, U.S.A. Zeolite Beta (Si/Al 13, 75 and 150) and mordenite (Si/Al 10) were synthesized in the J. Heyrovský Institute of Physical Chemistry, Prague, Czech Republic. Protonized forms of these zeolites were prepared by four-fold ion-exchange with 0.5 M ammonium nitrate solution. Silica (specific surface area 194 m^2/g) was supplied by Merck.

The catalysts were modified by impregnation of 10 g of zeolite with 1.5 M aqueous solutions of zinc nitrate at room temperature for 1 h, then the water was evaporated and the catalysts were activated by calcination at 600 °C for 20 h.

Catalytic Tests

The reaction mixture of ethanol, aqueous solution of formaldehyde and ammonia in the molar ratio 1:0.21:1.24 was fed with nitrogen into a stainless steel fixed bed reactor at 400 °C and a space velocity of 0.5 h^{-1}. The reaction was carried out in an excess of ethanol, because formaldehyde is very reactive and the formed paraformaldehyde causes plugging of the tubes of the reactor. Prior to the reaction the catalysts were activated by calcination at 600 °C for 20 h. The reactor (i.d. 8 mm) was packed with 1 g of a catalyst (particle size 0.3–0.6 mm). The stream of reaction products was cooled to about 5 °C and collected in a flask. Unreacted ethanol was analyzed by gas chromatography at 190 °C and pyridine and alkylpyridines at 250 °C using Chrompack CP 9001 equipped with FID and a Porapack QS packed column. The reactions were repeated twice and the experimental error was less than 5%.

The total acidity of the catalysts was measured by temperature programmed desorption of ammonia (NH_3–TPD). The NH_3–TPD spectra were measured using a gas flow reactor connected to a thermal conductivity detector (TCD). 100 mg of a catalyst were dried in a stream of N_2 at 600 °C for 30 min, then cooled to 200 °C and saturated with ammonia during 1 h. The catalyst was kept at 200 °C for 3 h to remove physisorbed ammonia. Desorption was then programmed from 200 °C at the beginning up to the desired 600 °C. The temperature was increased at a rate of 10 °C/min.

FTIR spectra of the zeolites were recorded at room temperature using self-supported zeolite wafers of a thickness of 10–14 mg/cm^2 and the spectra were normalized to a sample thickness of 10 mg/cm^2. An FTIR spectrometer Nicolet Magna-550 with an MCT low-temperature detector was used. Prior to adsorption and measurement of spectra, the zeolites were activated in vacuum at an increasing temperature of 5 °C/min up to 450 °C and kept at this temperature overnight. Adsorption of deuterated acetonitrile on activated zeolites was carried out at room temperature at pressure 950 Pa with subsequent evacuation. Positions and relative intensities of the bands were evaluated by a Fourier self-deconvolution procedure of the spectra.

RESULTS AND DISCUSSION

The catalytic activity of various zeolite catalysts was tested in the condensation of ethanol, formaldehyde and ammonia leading to pyridine and its derivatives. In the reaction using zeolites Beta and ZSM-5 as catalysts, total conversion of formaldehyde was achieved. Conversion of ethanol over H-ZSM-5 catalyst (Si/Al ratio 140) decreased from 64 to 45%, while the selectivity to pyridine changed from 21 to 28% during 28 h of time-on-stream (Table I). In addition to pyridine, picolines (methylpyridines) and lutidines (dimethylpiridines) were formed as the main byproducts. Formaldehyde and ethanol were the key reactants; therefore the yield of pyridine was based on ethanol and also on formaldehyde. Since the conversion of formaldehyde was always total the selectivities are based on ethanol. In parallel with decreasing conversion of ethanol, a decrease in the concentration of picolines and lutidines was observed while the concentration of the primary product, pyridine, steadily increased.

The influence of the zeolite structure on the yield of pyridine was studied using protonized forms of the zeolites mordenite, Beta and ZSM-5 and, for comparison, also with amorphous silica (Fig. 1). Before the reaction all cata-

TABLE I
Conversion of ethanol and selectivity for pyridine, picolines and lutidines over unmodified zeolite H-ZSM-5 (Si/Al ratio 140; Conteka), calcined at 600 °C for 20 h

Time-on-stream h	Conversion of ethanol %	Selectivity, %			Pyridine/ alkylpyridines molar ratio
		pyridine	picolines	lutidines	
1	64.2	20.9	3.7	11.2	1.4
3	53.6	24.9	3.8	12.4	1.5
7	56.3	24.7	3.3	11.3	1.7
14	49.0	27.6	2.9	10.9	2.0
28	45.6	27.9	2.5	10.4	2.1

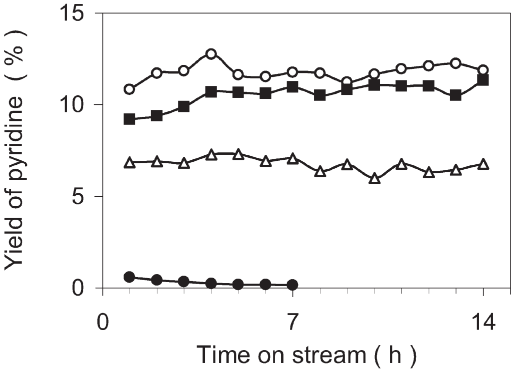


FIG. 1
Influence of catalyst on the yield of pyridine: Beta zeolite (○), H-ZSM-5 (■), mordenite (△), silica (●)

lysts were activated at 600 °C for 20 h. The yield of pyridine over amorphous silica was less than 0.6% at the beginning of the kinetic run and decreased further during the time-on-stream (TOS). Amorphous silica was practically inactive after 7 h of TOS. The reaction carried out over mordenite afforded yields of pyridine between 6.0–7.3% and the formation of pyridine was stable during 14 h of TOS. The highest yield of pyridine (between 10.8 and 12.7%) was achieved over zeolite Beta with the Si/Al ratio equal to 75, which was the superior catalyst among all the investigated zeolites. The yield of pyridine achieved over the ZSM-5 catalyst was about 3% lower than over zeolite Beta. In a similar way to zeolite Beta, also over ZSM-5 the yield of pyridine was constant for at least 14 h of TOS.

In the pyridine synthesis from ethanol, formaldehyde and ammonia, almost all formaldehyde is usually consumed during the reaction. Figure 2 depicts the influence of the Si/Al ratio of the zeolite Beta on the conversion of ethanol and the yield of pyridine based on formaldehyde after 14 h of TOS. An average conversion of ethanol over zeolite Beta possessing the highest concentration of aluminium was 84.8% during this time span and the obtained yield of pyridine was 30.9%. The conversion of ethanol only slightly decreased (81%) with an increase in the Si/Al ratio to 75 while the yield of pyridine remained practically constant (32.2%). However, a substantial decrease in the concentration of acid sites in zeolite Beta with the Si/Al ratio 150 caused a decrease in both the ethanol conversion (60.6%) and the yield of pyridine (26.7%). These results strongly indicate that the concentration of acid sites (probably also their density) is important for

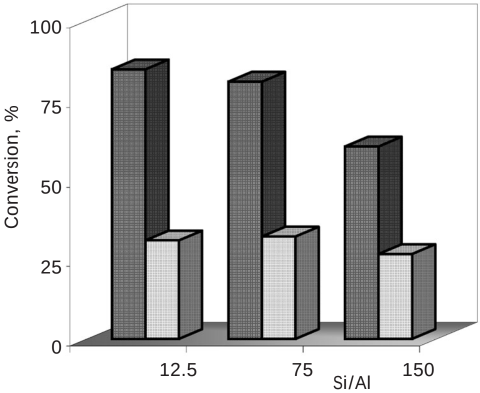


FIG. 2
Effect of Si/Al ratio in Beta zeolite: conversion of ethanol (■), pyridine (□) based on formaldehyde during 14 h of TOS

subsequent reactions. It can be inferred that in order to increase the concentration of reactant molecules in zeolite channels, on increase in the concentration of acid sites is necessary. All the tested catalysts exhibited stable conversion during 14 h of TOS.

The FTIR spectrum of the parent H-ZSM-5 zeolite activated at 450 °C overnight (Fig. 3) displays two bands in the OH region, between 3800 and 3500 cm^{-1}. Typical bands characteristic of bridging OH groups of zeolites were found for H-ZSM-5 at 3612 cm^{-1}. Adsorption of acetonitrile-d_3 on H-ZSM-5 resulted in complete disappearance of this absorption band while the band of silanol (Si–OH) OH groups was not significantly affected. The interaction of acetonitrile-d_3 with acid sites of the ZSM-5 zeolite resulted in

TABLE II
Concentration of Brönsted and Lewis acid sites in the H-ZSM-5 structure determined by FT-IR spectrometry using acetonitrile-d_3

Si/Al ratio	Brönsted sites, mmol/g	Lewis sites, mmol/g
14.1	0.46	0.30
21.8	0.30	0.24
40	0.24	0.08
75	0.10	0.02
140	0.05	0.02

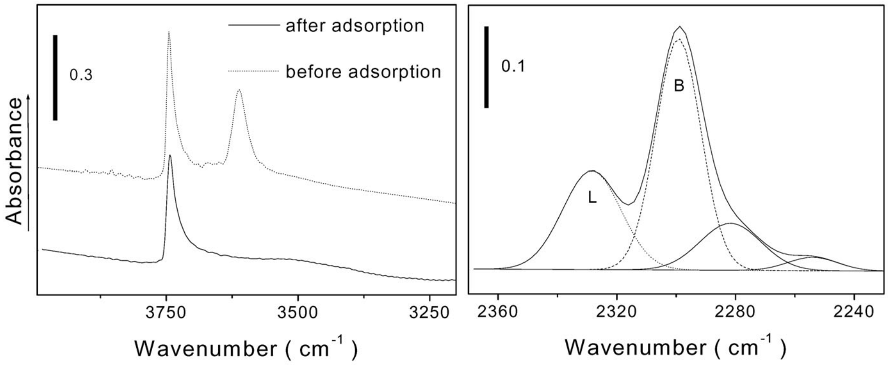


FIG. 3
Infrared spectra of H-ZSM-5 (Si/Al 80) calcined at 600 °C for 20 h

the appearance of two new absorption bands in the IR spectrum due to its interaction with both Brönsted (B) and Lewis (L) acid sites[9]. Quantitative evaluation of the concentration of Brönsted and Lewis acid sites for ZSM-5 zeolites with different Si/Al ratios is shown in Table II.

The concentration of acid sites of H-ZSM-5 decreased with increasing Si/Al ratio from 1.1 (Si/Al 14.1) to 0.06 (Si/Al 140) and no particular preference to decreasing the concentration of Brönsted or Lewis acid sites was observed.

Despite this sharp decrease in the total concetration of acid sites (Fig. 4), the average conversion of ethanol in 14 h of TOS drops only slightly, e.g. from 80.4 to 70.3% over ZSM-5 zeolites with the Si/Al ratios 14.1 and 75, respectively. A further increase in the Si/Al ratio up to 140 led to a substantial decrease in the conversion of ethanol amounting only to 47.5%. As regards role of concentration of acid sites on the resulting ethanol conversion, the behavior of ZSM-5 zeolites was the same as of zeolite Beta. This confirms the critical role of the concentration of acid sites as achieving a reasonable activity in this condensation reaction. The decrease in the conversion of ethanol was accompanied by an increase in pyridine selectivity from 13.8 to 25.1%.

The concentration of acid sites in ZSM-5 zeolite, expressed as the Si/Al ratio, influenced also the selectivity for individual condensation products,

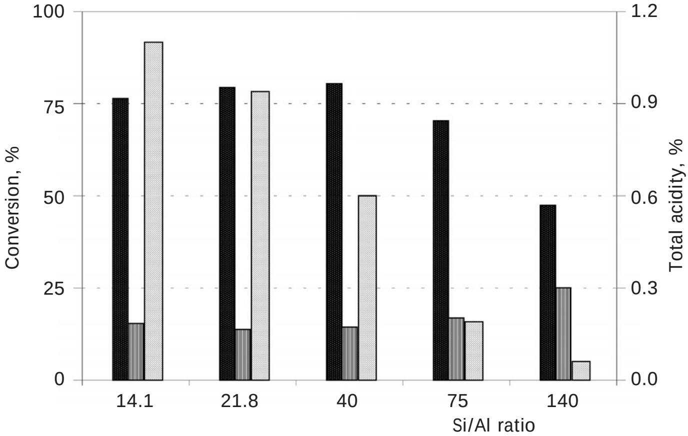


FIG. 4

Influence of the Si/Al ratio on conversion, selectivity and total acidity of the H-YSM-5 catalyst: average ethanol conversion during 14 h of TOS (black), average selectivity for pyridine during 14 h of TOS (dark grey), total acidity (light grey) presented here as the molar ratio of pyridine to other pyridine bases (picolines and lutidines; Fig. 5).

The highest ratio of pyridine/pyridine bases was obtained over H-ZSM-5 (140) zeolite. The ratio increased with time-on-stream and after 14 h reached 2.03. It can be inferred that alkyl derivatives of pyridine are preferably produced on the external surface of the ZSM-5 zeolite due to the restricted shape selectivity of the transition state[10]. Deactivation of the zeolite surface by coke formation, which proceeds in the course of the reaction, reduced the rate of the formation of alkylpyridine derivatives. Over more acid H-ZSM-5 zeolites with a high content of Al, alkylpyridines were preferred products (the ratio is below 1.0), which is associated with a higher overall activity of the ZSM-5 zeolites.

To improve the yield of pyridine, the H-ZSM-5 zeolites were impregnated with zinc nitrate. Figure 6 depicts the influence of zinc loading on the average selectivity of pyridine formation during 14 h of TOS. Modification of ZSM-5 zeolite (Si/Al 75) with 0.5 wt.% of zinc loading increased the selectivity of pyridine from 15 to 29%. In the case of Zn-ZSM-5 loaded with 1 wt.% of Zn, the increase in the selectivity was even higher (from 15 to 38% over Zn-ZSM-5, although the conversion of ethanol decreased from 71 to 63%). The catalytic test carried out with ZSM-5 zeolite modified with 3 wt.% of Zn showed, that during the first hour of time-on-stream the selec-

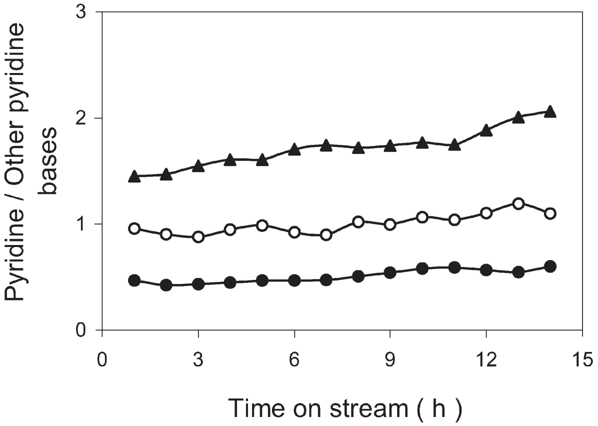


FIG. 5
Influence of the Si/Al ratio in the zeolite framework on the ratio of pyridine to other pyridine bases: 21.8 (●), 75 (○), 140 (▲)

tivity for pyridine was more than 40%; however, the zeolite catalyst deactivated very rapidly. Thus, the average selectivity decreased to 21% during 14 h of TOS. On the other hand, it should be stressed that the selectivity for pyridine over Zn-ZSM-5 was still higher than over the unmodified zeolite.

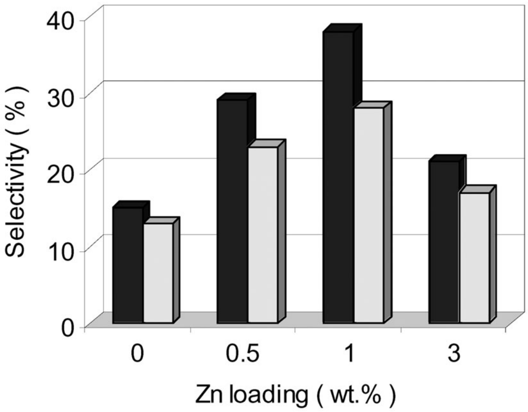


FIG. 6
Influence of Zn loading on the selectivity of catalysts: Si/Al 75 (■), 21.8 (□)

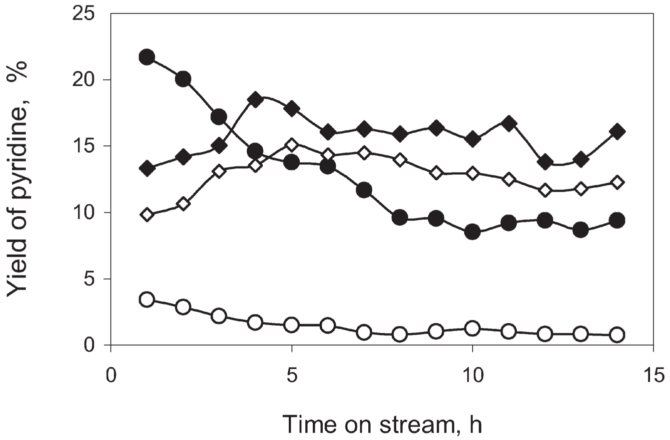


FIG. 7
Influence of impregnation on the yield of pyridine: 1.5 wt.% Zn-H form (◆), 1.5 wt.% Zn-NH_4 form (◇), 5 wt.% Zn-H form (●), 5 wt.% Zn-NH_4 form (○)

The same dependence on the Zn loading was observed also over ZSM-5 catalysts with the Si/Al ratio equal to 28.1. However, the selectivity for pyridine was always lower than the selectivity achieved over higher-silica ZSM-5. But also the effect of non-steady-state performance of the catalyst on the changes of selectivity at short TOS cannot be excluded.

The zeolite catalysts discussed above were prepared by impregnation of the H form of zeolite ZSM-5 with zinc nitrate. We have also tested the Zn-ZSM-5 catalyst (Si/Al 140) prepared by direct modification with zinc nitrate of the ammonium form of ZSM-5. A comparison of the pyridine yields (based on ethanol) over Zn-ZSM-5 catalysts prepared in different ways is shown in Fig. 7. As it is seen from this figure, H-ZSM-5 catalysts modified with zinc provided higher yields of pyridine than the catalysts prepared from the NH_4 form of the same zeolite. In particular, very high differences in the yields were observed between catalysts modified with 5 wt.% of zinc. As was mentioned above, zeolite catalysts with higher loadings of zinc were more selective in the first hour of TOS. Unfortunately, with increasing time-on-stream they were quickly deactivated. This is documented also by the results with the catalyst Zn-ZSM-5 containing 5% of Zn, which deactivated during the first 7–8 h.

The study of the condensation reaction of ethanol, formaldehyde and ammonia to pyridine has shown that unmodified H-ZSM-5 and Beta zeolite catalysts possess a similar activity, in contrast to the low activity of mordenite. Conversion of ethanol decreases with increasing Si/Al ratio; however, zeolites with lower silica contents are more selective. Their activity remains practically stable during 14 h of TOS. Modification of the ZSM-5 catalyst with zinc increases the activity and selectivity of the reaction. The highest selectivity of pyridine formation was achieved over catalysts with the Si/Al ratio from 75 to 280 and a Zn loading of about 1 wt.%. At higher zinc loadings, the selectivity of pyridine formation decreases.

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