



Synthesis of Picolines Over Metal Modified HZSM-5 Catalyst

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A series of metal (*i.e.* Pb, Cd, Zn, Co, Cr) modified H-ZSM-5 catalysts were prepared by an ion-exchange method and were characterized by XRD, FT-IR, NH₃-TPD and N₂ adsorption techniques. Their catalytic activity was evaluated in the Chichibabin condensation of acetaldehyde and ammonia giving 2-picoline, 4-picoline and a small amount of pyridine as the product. The catalyst coking behaviour was also characterized by TG measurement. The characterization results showed that the crystal structure of H-ZSM-5 was well reserved and the active metal ions were evenly spread in the ZSM-5 framework. The surface acidity was enhanced a lot after the metal modification. Catalytic results showed that metal incorporated catalysts greatly increased the total yield of pyridine bases, especially which of 2-picoline and 4-picoline, meanwhile the ratio of 2-picoline/4-picoline was also enhanced.

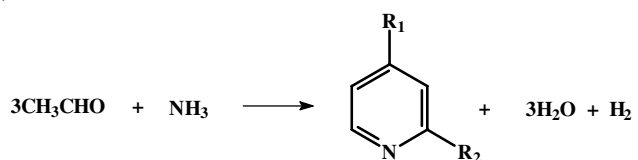
Keywords: ZSM-5, Ion-exchange, 2-Picoline, 4-Picoline.

INTRODUCTION

Pyridine and picolines are useful intermediates in the synthesis of herbicides, pharmaceuticals, surface-active agents, disinfectants and other fine chemicals, such as vitamin B, nicotinamide and nicotinic acid. Most picolines have been mass-produced by the Chichibabin condensation, which involves gas-phase reactions of acetaldehyde, formaldehyde and ammonia¹⁻⁵. Usually 2-picoline and 4-picoline are formed as the by products in this reaction. However, with the development of economy, the demand of 2-picoline and 4-picoline is increasing. 2-picoline is mainly used in the synthesis of fertilizer synergist, rubber additives, dyes intermediates, photosensitive film material, *etc.* 4-Picoline is used for the synthesis of isoniazid, phosphate-solubilizing antidote in medicine industry and also used in the field of the pesticide, dye, rubber additives, synthetic resin, especially for the synthesis of 4-vinyl pyridine. Chichibabin condensation of ammonia and acetaldehyde is a method to synthesis of 2-picoline and 4-picoline.

ZSM-5 zeolite has intrinsic acidity, capability to incorporate trivalent cations other than Al in framework and three-dimensional porosity and therefore, has been explored extensively as a catalyst for the aldehyde-ammonia condensation reaction in recent years⁴⁻⁹. It is expected that the zeolite shape-selectivity plays an important role in condensation reactions, leading to pyridine, 2-picoline and 4-picoline and limiting the formation of bulkier reaction intermediates. The reactions include condensation, cyclization and dehydrogenation.

Balanced equation for key products of the CH₃CHO and NH₃ reaction is as follows.



2-Picoline: R₁ = H, R₂ = CH₃

4-Picoline: R₁ = CH₃, R₂ = H

The activity of the catalyst is in connection with its acidity which is an important property that governs the yield and selectivity^{5,10}. In order to adjust the surface acidity of the catalyst, several methods have been used to modify H-ZSM-5, such as impregnation^{5,6,11}, ion-exchange⁵, chemical vapor deposition (CVD)^{12,13}, atom-planting method^{14,15} and sublimation treatment¹⁶. To our best of knowledge, study of the influence of incorporated metal on the catalytic performance in the condensation of acetaldehyde and ammonia are limited. Therefore, in the present work, ion-exchange technique was employed to prepare a series of metal incorporated H-ZSM-5 catalysts. The investigated metals include Pb, Cd, Zn, Co and Cr. The catalytic performance of these catalysts for the condensation of acetaldehyde and ammonia was evaluated and the coking performance was also investigated.

EXPERIMENTAL

Catalyst preparation: The original HZSM-5 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 120$ mol/mol) was supplied by Nanjing Refinery, which was calcined at 823 K for 5 h before using.

The metal was incorporated respectively by an ion-exchange technique with water as the solvent. The metal precursors used to prepare the catalysts were: $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In a typical experiment, 3 g HZSM-5 was added into 75 mL nitrate salt aqueous solution with a concentration of 0.125 mol/L. After stirring at 363 K for 24 h, the slurry was filtrated and washed with distilled water. Finally, the samples were dried at 373 K for 6 h and then calcined at 823 K for 4 h. These samples were denoted as Pb-ZSM-5, Cd-ZSM-5, Cr-ZSM-5, Zn-ZSM-5 and Co-ZSM-5, respectively.

Activity measurements: The vapor phase condensation of ammonia and acetaldehyde was carried out in a fixed bed reactor ($\phi 20 \times 6$) at 673 K and atmospheric pressure. The catalyst bed temperature was measured with a thermocouple placed at the center of reactor cross-section. The 20 wt. % acetaldehyde aqueous solution was fed from the top of the reactor using a chromatographic pump (USA). Ammonia was fed from a pressurized cylinder and adjusted by mass flow controllers. Prior to this, 1 g of the catalyst diluted with 1.5 g quartz sand was loaded into the reactor. A 1: 7 molar ratio of aldehyde/ammonia was introduced into the reactor at GHSV of 1000 h^{-1} . The product was cooled and condensed using ice-cold water and collected per hour at the bottom. A sufficient number of ice-cooled traps were used to collect all lower boilings. The products were finally analyzed by GC 9160 equipped with FID using a capillary column of FFAP. Yield of pyridine bases (2-picoline, 4-picoline and pyridine) were calculated on the basis of carbon balance with calibration. As a result of the polymerization of acetaldehyde, the content of acetaldehyde consumed can't be calculated. The selectivity was calculated based on the content of carbon in the acetaldehyde reacted is the same with the content of carbon in pyridine, 2-picoline and 4-picoline. The yield ratio of 2-picoline/4-picoline was also calculated and discussed.

Catalyst characterization: The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX 2000 instrument with $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. Thermal analysis was carried out using a simultaneous DSC-TGA instrument (SDT Q600, TA, USA) and performed at a uniform heating rate of 20 K min^{-1} under air atmosphere. The surface area and pore characteristics of the samples were measured by means of a Beishide 3H-2000 instrument. Before the adsorption of N_2 at 77 K, the samples were degassed at 673 K for 3 h. Total specific surface areas (S_{BET}) of the samples were determined by applying the BET (Brunauer-Emmett-Teller) model to nitrogen adsorption data obtained in the relative pressure range from 0.01 to 0.12. Total pore volumes were estimated from the amount of nitrogen absorbed at a relative pressure of 0.99. The t -plot method was employed to evaluate the volume of micropore (V_{microp}). The average pore diameter (D_p) was obtained from the BET data. NH_3 -TPD was carried out with a quartz reactor, a TCD detector and 100 mg sample at atmospheric pressure. The system was quenched at 823 K for 1 h in a He

flow of 30 mL min^{-1} . After cooling to 373 K, NH_3 was introduced by a pulsed injection with the He flow until saturation. The sample was quenched again at the temperature for 1 h to remove the excess NH_3 . Desorption was then performed under the same He flow with a ramp of 10 K min^{-1} to 973 K.

RESULTS AND DISCUSSION

XRD patterns of all the samples show the characteristic MFI diffraction peaks and similar peak positions in Fig. 1, which indicates that the ZSM-5 crystal structure is not destroyed during the ion-exchange treatment⁵. Moreover, no metal containing phases are detected suggesting a highly dispersed metal species on the zeolite.

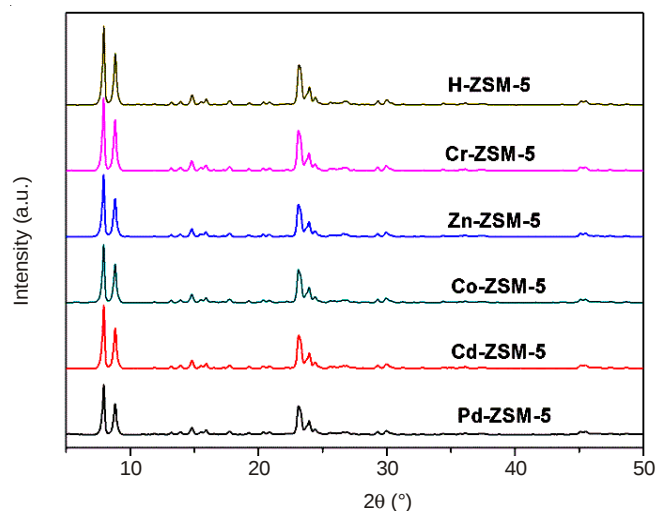


Fig. 1. XRD patterns of metal modified and original samples

Fig. 2 shows the IR spectra of the samples. The absorption bands at 1220, 1100, 800 and 455 cm^{-1} are typical of siliceous materials. These absorption bands are the external asymmetric stretching, internal asymmetric stretching, external symmetric stretching and the bending vibration peak of the T-O (Si or Al), respectively¹⁶. As a result of the asymmetric stretching mode in double-ring blocks, a characteristic band at 551 cm^{-1}

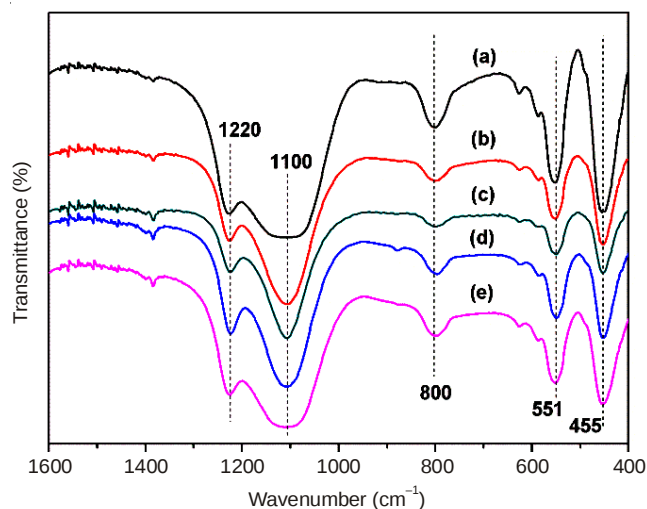


Fig. 2. IR spectra of (a) H-ZSM-5, (b) Pb-ZSM-5, (c) Co-ZSM-5, (d) Cd-ZSM-5 and (e) Zn-ZSM-5 samples

is observed in each of the catalysts, which suggests that all the catalysts have the MFI structure. As reported, the optical density ratio of the 550 and 450 cm^{-1} is about 0.72 for the pure MFI sample¹⁷. The intensity ratios of the 550 and 450 cm^{-1} for (a) HZSM-5, (b) Pb-ZSM-5, (c) Co-ZSM-5, (d) Cd-ZSM-5 and (e) Zn-ZSM-5 are 0.47, 0.77, 0.86, 0.75 and 0.66, respectively. It is concluded that metal incorporated has a certain influence on the crystallinity of HZSM-5 and the MFI structure of these catalysts is well reserved. These results are in accordance with the XRD results.

Table-1 summarizes the BET surface area, pore volume and average pore size of the samples. It can be seen that the specific surface area decreases slightly after the modification. The modification of Cd, Zn, Co and Cr make the pore volume and pore size slightly increase, while that of Pb behaviour the opposite way. The expanding pore volume and pore size may be due to the destruction of zeolite framework in the ion-exchange process, for these aqueous solutions of metal nitrates have weak acidity which can lead to the dealumination of the framework and result in the meso- or macro-pores in the zeolite^{18,19}. The declining pore volume and pore size may be ascribed to the much bigger Pb atom replacing the original small H atom during the ion-exchange process. Consequently, the decrease of XRD peak intensity in Fig. 1 can be explained as the framework of zeolite was partly destroyed, or the incorporated metal covered the zeolite structure. On the whole, the surface area and pore characteristics do not change too much during the ion-exchange process.

The NH_3 -TPD curves of the samples are depicted in Fig. 3. The curves have two peaks corresponding to two kinds of acid sites, *i.e.* the weak sites associated with the TPD peak at around 480-650 K and the strong sites related to the peak at around 700-850 K. After the metal modification, the peak area of the weak acid sites increases largely, while that of the strong acid sites decreases. The top temperature of the weak peak also slightly shifts to higher position when the curve of metal modified sample is presented. The change of Pb-ZSM-5 is the biggest, of which the top temperature shifts to 570 K with that of the original sample 550 K. Since the ion-exchange process is the exchange of H^+ in the ZSM-5 framework to metal ions, it is deduced that the declining strong acid sites are mainly Brønsted acid sites and the increasing weak acid sites are mainly Lewis acid sites. The metal incorporation greatly increases the total amount of acid sites, especially that of the weak acid sites. The ratio of the acid amount of HZSM-5/Co-ZSM-5/Zn-ZSM-5/Cd-ZSM-5/Cr-ZSM-5/Pb-ZSM-5 is about 1: 1.36: 1.35: 1.29: 1.15: 1.68. The influence of Pb metal on the catalyst surface acidity is the most significant.

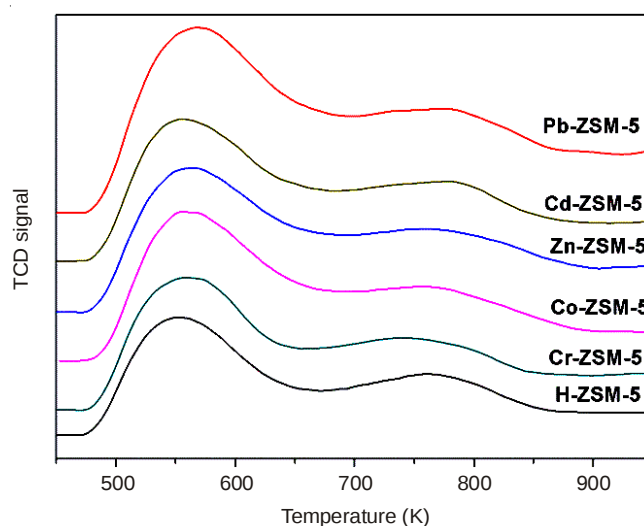


Fig. 3. NH_3 -TPD curves of the original and metal modified ZSM-5 samples

Result of thermal analysis of the samples used after 8 h is presented in Fig. 4. The slightly declining of TG curve before 473 K is ascribed to desorption physically adsorbed water, for water is one of the products in this reaction. The one occurred from 573 to 1073 K is undoubtedly due to the burning of coke formed during the reaction of acetaldehyde and ammonia. The content of coke is equal to the losing weight of catalysts. We can see that the carbon deposition of modified catalysts is higher than that of the parent HZSM-5, which is probably ascribed to the covered surface pores and the destruction of ZSM-5 framework which would restrict the diffusion of the products²¹. However, that of Pb-ZSM-5 is the lowest among the modified samples.

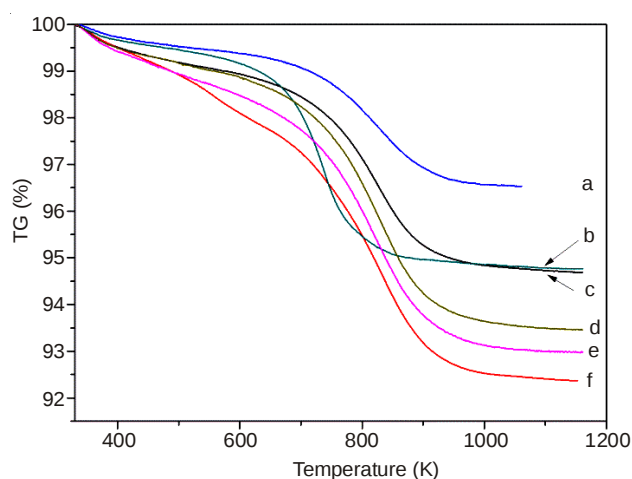


Fig. 4. TG curves of used samples: (a) H-ZSM-5, (b) Cr-ZSM-5, (c) Pb-ZSM-5, (d) Zn-ZSM-5, (e) Cd-ZSM-5 and (f) Co-ZSM-5

TABLE-1
TEXTURAL PROPERTIES OF DIFFERENT CATALYSTS

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{microp} (cm^3/g)	V_{mesop} (cm^3/g) ^a	Dp (nm)
H-ZSM-5	357	0.297	0.075	0.222	3.33
Pb-ZSM-5	356	0.290	0.089	0.201	3.26
Cd-ZSM-5	352	0.303	0.069	0.234	3.44
Zn-ZSM-5	340	0.328	0.072	0.256	3.85
Cr-ZSM-5	342	0.390	0.104	0.286	4.56
Co-ZSM-5	346	0.298	0.078	0.217	3.42

^a $V_{\text{mesop}} = V_{\text{total}} - V_{\text{microp}}$

Figs. 5-7 depicts the yield of 2-picoline, 4-picoline, total pyridine bases and selectivity of 2-picoline and 4-picoline as a function of time on stream (TOS), respectively. Although the influence of time on stream is small, the following trends are observed. The total yield of pyridine bases increases to a maximum value with an initial increase in time on stream prior to declining with further increase in time on stream and it seems to be steady after reaction for 2 or 3 h for most samples except Pb-ZSM-5, the time of which is 5 h. The highest yields of pyridine bases over these catalysts are also obtained when the reaction proceeds for 2 or 3 h, which are 50.3 % (Co-ZSM-5), 84.1 % (Pb-ZSM-5), 61.1 % (Zn-ZSM-5), 56.2 % (Cr-ZSM-5), 73.2 % (Cd-ZSM-5) and 42.5 % (HZSM-5), respectively. The yields of metal modified catalysts are superior to that of HZSM-5. The HZSM-5 catalyst used in the synthesis of 2-picoline and 4-picoline was less reported. From the reported literatures^{5,14,16}, we can see that the yield of pyridine and 3-picoline is about 55-70 %, which is lower than that of Pb-ZSM-5 catalyst in the present work. Sile *et al.*²⁰ reported that the yields of 2-picoline and 4-picoline catalyzed by the $\text{Al}_2\text{O}_3\text{-CrCl}_3$ catalyst were 27 and 11 %, respectively. Rao *et al.*⁶ reported that the total yield of 2-picoline and 4-picoline catalyzed by the Pb-Cr- $\text{Al}_2\text{O}_3\text{-SiO}_2$ catalyst was 80.6 %. These yields of 2-picoline and 4-picoline are also lower than that of our work.

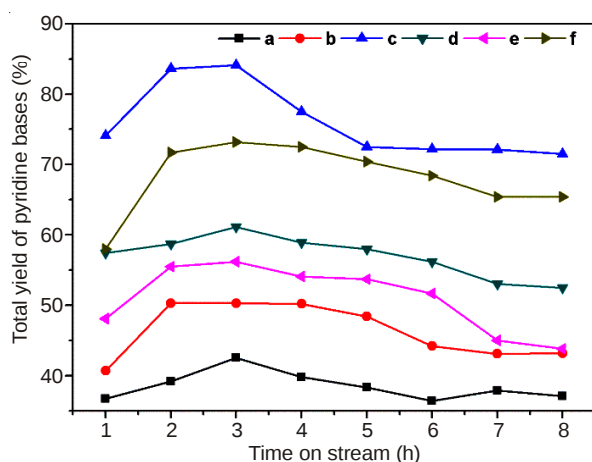


Fig. 5. Total yield of pyridine bases *versus* time on stream. (a) H-ZSM-5, (b) Co-ZSM-5, (c) Pb-ZSM-5, (d) Zn-ZSM-5, (e) Cr-ZSM-5, (f) Cd-ZSM-5

Fig. 6 depicts the yield and selectivity of 2-picoline over varied samples. Fig. 6 showed that the influence of TOS on selectivity is negligible for all the samples. Samples of Cd-ZSM-5 and Pb-ZSM-5 occupy the highest place in the selectivity plot, of which the selectivity is about 58 and 56 %, respectively. The following line belongs to Zn-ZSM-5 with a value of about 52 %. Selectivities of the other catalysts are below 50 %, about 45 % (Co-ZSM-5, Cr-ZSM-5) and 41 % (HZSM-5). In general, the selectivity of metal incorporated catalysts is higher than the original HZSM-5, which indicates that the introduction of metal species could change the product distribution and make it prone for 2-picoline production. As a result of the behaviour of total pyridine bases yield and 2-picoline selectivity, the trends of 2-picoline yield are similar to that of yield of pyridine bases: the highest yields of 2-picoline are obtained at reaction for 2 or 3 h, which are 47.1 % (Pb-

ZSM-5), 42.4 % (Cd-ZSM-5), 31.8 % (Zn-ZSM-5), 25.4 % (Cr-ZSM-5), 22.5 % (Co-ZSM-5) and 15.7 % (Mg-ZSM-5), respectively. The highest one (47.1 %) is almost three times as that of the initial H-ZSM-5 catalyst (17.5 %). Such increase in 2-picoline yield is not only due to the increase of pyridine bases yield from 42.5 to 84.1 %, but also due to the increase of 2-picoline selectivity from 41 to 56 %.

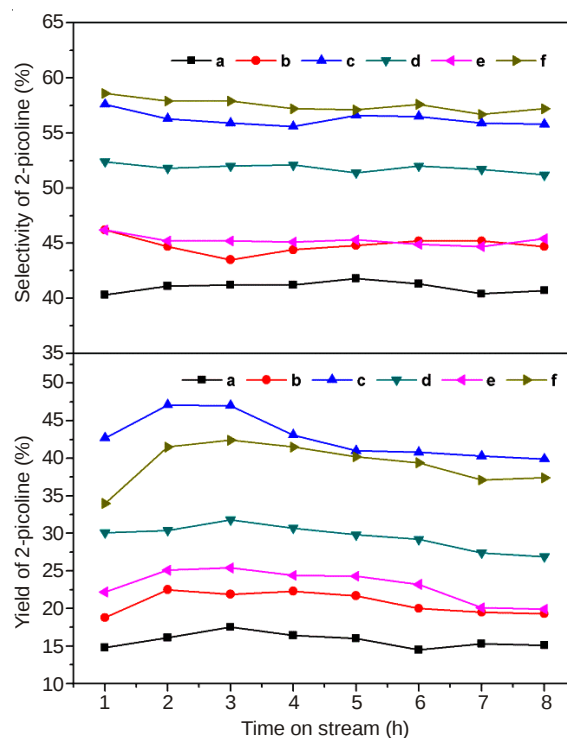


Fig. 6. Yield and selectivity of 2-picoline *versus* time on stream. (a) H-ZSM-5, (b) Co-ZSM-5, (c) Pb-ZSM-5, (d) Zn-ZSM-5, (e) Cr-ZSM-5, (f) Cd-ZSM-5

Fig. 7 shows the influences of TOS on the yield and selectivity of 4-picoline. As is shown in this figure, sample of H-ZSM-5 occupies the highest place in the selectivity plot, of which the selectivity is about 53.8 %. The following line belongs to Co-ZSM-5 with a value of about 50.7 %. The selectivity of the other catalysts is below 50 %, about 40 % (Cd-ZSM-5, Pb-ZSM-5) and 44 % (Zn-ZSM-5, Cr-ZSM-5). In general, the selectivity of metal incorporated catalysts is lower than the original H-ZSM-5. The highest yields of 4-picoline are also obtained at reaction for 2 or 3 h, which are 34.1 % (Pb-ZSM-5), 27.7 % (Cd-ZSM-5), 25.8 % (Zn-ZSM-5), 26.0 % (Cr-ZSM-5) and 25.5 % (Co-ZSM-5), respectively. Comparing with the initial HZSM-5 catalyst (21.4 %), the highest one (34.1 %) increases by 12.7 %. Such increase in 4-picoline yield is mainly due to the promotion of pyridine bases.

Fig. 8 depicts the change of 2-picoline to 4-picoline ratios as a function of TOS. These catalysts had a high initial 2-picoline to 4-picoline ratio, varied from 0.7 to 1.6 and no specific trend was observed with the increase of TOS. As can be seen that the ratio of Cd-ZSM-5, Pb-ZSM-5 and Zn-ZSM-5 samples are bigger than 1, which are varied from 1.44 to 1.60, 1.36 to 1.49, and 1.17 to 1.28, respectively. That of the other two samples are below 1, which are in the range of 0.94-1.07 (Cr-ZSM-5), and 0.86-1.01 (Co-ZSM-5), respectively.

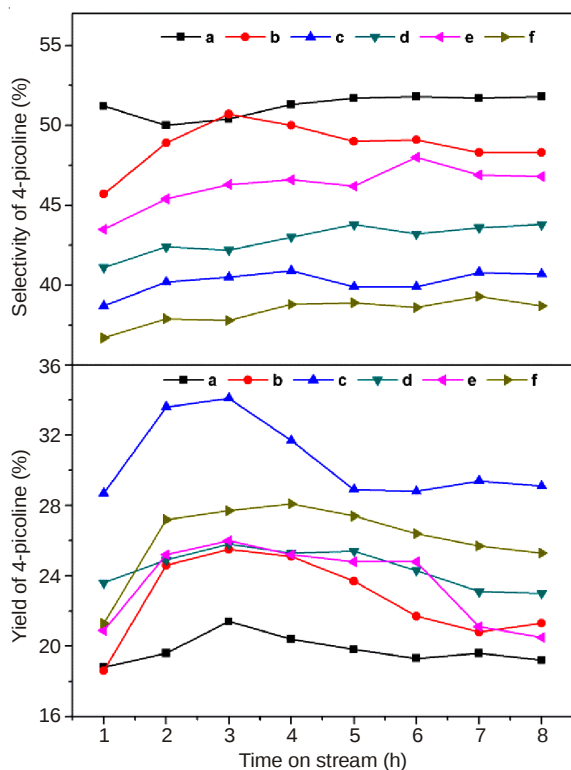


Fig. 7. Yield and selectivity of 4-picoline versus time on stream. (a) H-ZSM-5, (b) Co-ZSM-5, (c) Pb-ZSM-5, (d) Zn-ZSM-5, (e) Cr-ZSM-5, (f) Cd-ZSM-5

The ratios of all the metal incorporated catalyst are higher than that of H-ZSM-5 (0.75-0.82) in addition to that of Mg-ZSM-5 catalyst at the reaction carrying on 2 and 5 h. Ion-exchange treatment increases the selectivity of 2-picoline but decreases that of 4-picoline.

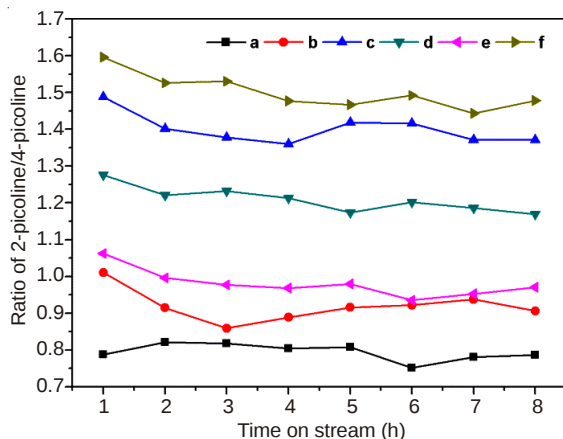


Fig. 8. 2-Picoline/4-picoline ratio versus time on stream. (a) H-ZSM-5, (b) Co-ZSM-5, (c) Pb-ZSM-5, (d) Zn-ZSM-5, (e) Cr-ZSM-5, (f) Cd-ZSM-5

All these results discussed above show that the yield of pyridine bases can be greatly enhanced by the introduction metal ion into the ZSM-5 zeolite. These metal modified samples, especially Pb-ZSM-5 and Cd-ZSM-5 sample, not only enhances the yield of picolines, but also has a unique selectivity to 2-picoline. This may be due to the change of distribution of surface acidity, which is a very important factor influencing the catalytic activity and selectivity in Chichibabin

reaction^{21,22}. The increasing amount of surface acidity may be the reason for the high picoline yield, while the increasing amount of weak acid sites are account for the unique selectivity of 2-picoline.

Conclusion

Highly dispersed and MFI structure well reserved Pb, Cd, Zn, Co, Cr modified ZSM-5 catalysts were obtained by the ion-exchange method. The surface area and pore properties were also showed small change after the modification. However, the amount of surface acidity, especially the weak acidity, increased a great deal of the modified samples. Catalytic experiments revealed that the metal incorporated catalysts gave higher yields of pyridine bases than the original HZSM-5. Among them, performance of Pb-ZSM-5 and Cd-ZSM-5 was better than that of the rest catalysts in terms of yields of total pyridine bases and selectivity of 2-picoline. The yields of pyridine bases for Pb-ZSM-5 and Cd-ZSM-5 were 84.1 % and 73.2 %, respectively and the selectivity of 2-picoline were 56.3 and 58.6 %, respectively. However, the coking of the metal incorporated catalysts was worse than the initial zeolite, which may be due to the restriction of diffusion of the products after modification. Moreover, the coking of Pb-ZSM-5 was the least among the modified samples which also gave the highest yield of pyridine bases.

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