Study on catalyst for pyridine synthesis

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Abstract: The synthesis of pyridine from aldehydes and ammonia was performed over ZSM-5 catalyst. The catalytic activity in reaction was correlated with the acidity of the zeolite catalysts. In this study a few of ZSM-5 ($m(SiO_2)/m(Al_2O_3) = 120$) were prepared and modified with Co^{2+}, Fe^{3+}. The surface acidity was determined by Py-IR technique. It was found that CoZSM-5 and FeZSM-5 have fewer Lewis acid sites than HZSM-5. The decrease of Lewis acid sites leads to decreasing the ability of NH_3 adsorption, this phenomenon insures that there are adequate acid sites discovering and reacting with aldehydes. It is advantageous to the reaction. By using a CoZSM-5 catalyst, the yields of pyridine base can reach 78%. The study provides a theoretical base for preparing high activity and high selective catalyst for pyridine synthesis.

Key words: pyridine; catalyst; ZSM-5

Pyridine is an important chemical intermediate in the manufacture of agricultural chemicals and various pharmaceuticals. It is also useful as a solvent in the polymer and textile industries. Pyridine is obtained either as a by-product of the coal tar industry or by chemical synthesis through a catalytic reaction between ammonia and a carbonyl compound. The synthesis of pyridine from aldehydes and ammonia was performed over an amorphous aluminosilicate catalyst. This catalyst provides a reasonable yield of pyridine at the beginning of the reaction. However, after repeated operation cycles some drawbacks appeared which made these catalysts unacceptable from a commercial point of view. Specifically, ① Large amounts of carbonaceous deposition reduced the catalytic activity; ② The selectivity of the reaction for pyridine and alkylpyridine became very poor; ③ The catalysts showed poor thermal stability; ④ The activity of the used catalyst was difficult to regenerate completely. Recently, crystalline aluminosilicate (especially ZSM-5) catalyst began to replace amorphous aluminosilicates. ZSM-5 is an important industrial solid acid catalyst, playing a key role in the fields of fuel processing and synthesis of fine chemicals owing to its shape-selective properties. ZSM-5 also exhibits good properties in condensation reaction from aldehydes and ammonia. The yields of pyridine and 3-methlypyridine can increase 30% over modified ZSM-5 catalysts[1-5]. In this study a few zeolites ($m(SiO_2)/m(Al_2O_3) = 120$) were prepared and modified with Co^{2+}, Fe^{3+}. The surface acidity was determined by Py-IR technique. Their catalytic activities in condensation reaction of aldehydes and ammonia were correlated to provide a theoretical base for preparing high activity and high selective catalyst.

Received 2003-06-09.

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1 Experiment

Water glass, distilled water, $Al_2(SO_4)_3$, $NH_2CH_2(CH_2)_4CH_2NH_2$, NaOH at desired procedures, the NaZSM-5 zeolite was prepared through hydrothermal synthesis by mixing. After washing and filtration until pH of the filtrate was 8 to 9, it was then dried at 110 ℃ for 12 h and finally calcined in air at 540 ℃ for 4 h, the ZSM-5 framefork was confirmed by XRD measurement. The NaZSM-5 was further ion exchanged with 0.5 mol/L NH_4NO_3 at 90 ℃, followed by washing and filtration until the concentration of Cl^- ion in the filtrate became 10^{-6} or blow. NH_4ZSM-5 was dried, calcined and HZSM-5 was obtained. HZSM-5 zeolite was modified with various cations like Co^{2+}, Fe^{3+} by the impregnation with 0.1 mol/L $Co(NO_3)_2$ or $FeCl_3$ at 100 ℃ during 24 h. After repetition of washing and filtration until the concentration of NO_3^{-1} or Cl^- ion in the filtrate became 10^{-6} or blow, MeZSM-5 were dried at 110 ℃ for 12 h, calcined at 540 ℃ for 4 h.

The condensation reactions were carried out using a glass tube reactor with 12.6 mm internal diameter. The reaction was carried out at 450 ℃ with 1 000 h^{-1} weight hourly space velocity. The reaction products were analyzed by gas chromatography.

X-ray powder diffraction spectra were recorded with Cu Kα radiation using a model D/max-RB powder diffractometer.

Py-IR spectra were recorded using a model Bruker FT-IR. Temperature of adsorption is 200 ℃

and pressure of equation is 0.01 Pa.

2 Results and Discussions

The reaction of formaldehyde, aldehyde with ammonia was carried out over various ZSM-5 catalysts. The results are summarized in Tab.1. It can be seen that CoZSM-5 exhibited the highest activity and selectivity.

Tab.1 Effect of modification on the catalytic activity

Catalyst	Yield of pyridine w/%	Yield of pyridine base w/%
HZSM-5	42	60
CoZSM-5	55.6	78
FeZSM-5	50	68

Fig. 1 shows the XRD spectra of HZSM-5, CoZSM-5 and FeZSM-5 samples. It can be concluded that the structure of MZSM-5 was not destroyed by impregnation and calcination.

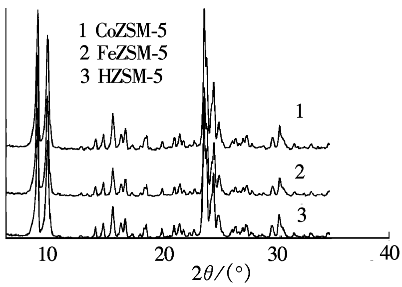


Fig.1 XRD spectra of HZSM-5, CoZSM-5, and FeZSM-5 samples

Fig.2 shows the Py-IR spectra of HZSM-5, CoZSM-5 and FeZSM-5 samples. We can find that there are strong peaks (1 450 cm^{-1}, 1 540 cm^{-1}) responding to Bronsted acid and Lewis acid on HZSM-5 sample. It further indicates that there is much Bronsted acid and Lewis acid on surface of HZSM-5. When modified with Co^{2+} and Fe^{3+}, CoZSM-5 and FeZSM-5 have fewer Lewis acid sites than that of HZSM-5, while the Bronsted acid changes a little.

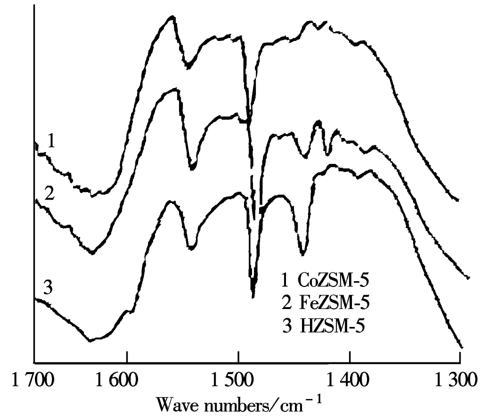
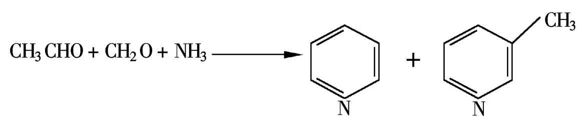
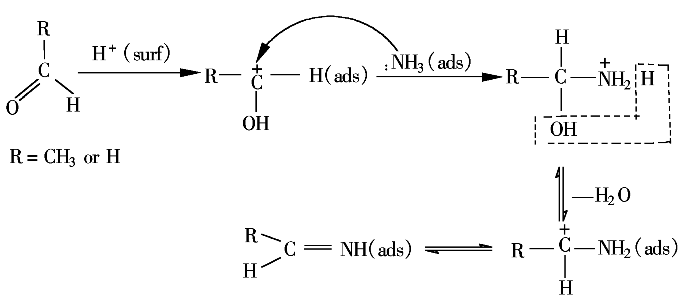


Fig.2 Py-IR spectra of HZSM-5, CoZSM-5, and FeZSM-5 samples

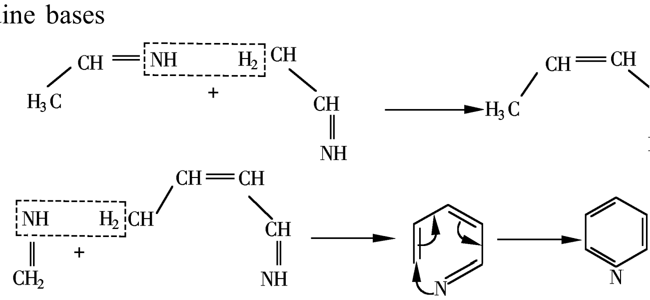
The yield of pyridine is 60% with HZSM-5 as catalysts. While the yield of pyridine increases rapidly CoZSM-5 and FeZSM-5 are employed. The relationship between the surface acidity of ZSM-5 zeolite and the catalytic activity in condensation reaction will be discussed below.



1) Formation of imines[6]



2) Formation of pyridine bases



The reactants are adsorbed near or at acidic sites, forming adsorbed ammonia and carbonium ions. Nucleophilic addition occurs at the surface of the catalyst followed by the loss of water to form imines. The adsorbed imines further react to generate pyridine.

Aluminosilicates can readily adsorb ammonia and are known to promote the formation of stable surface carbocations. Bronsted acid of HZSM-5 can react with adsorbed aldehyde to form carbocations and Lewis acid can receive solo electric of ammonia. Therefore the catalyst activity is closely related to the surface acidity of the catalyst. When HZSM-5 is modified with Co^{2+}, Fe^{3+}, fewer Lewis acid sites than that of HZSM-5 are presented. There are more Lewis acid sites on the HZSM-5 surface and thus a high temperature is required to promote ammonia disorption and to expose the acid sites for forming carbonium ions. The decrease of Lewis acid reduced the ability of adsorption for ammonia, which favored the condensation reaction

3 Conclusion

HZSM-5 zeolite was modified with Co^{2+}, Fe^{3+} cations by the impregnation method. CoZSM-5 and FeZSM-5 had fewer Lewis acid sites than that of HZSM-5, which decreased the ability of NH_3 adsorption; this effect gave rise to adequate exposed acid sites to interact with aldehydes, improving the formation of desired products. Using a CoZSM-5 catalyst, the yields of pyridine base can reach 78%.

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合成吡啶催化剂的研究

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摘要: 醛(酮)氨法合成吡啶可用 ZSM-5 作催化剂, 本文研究了 ZSM-5 催化剂的表面酸性与催化合成吡啶活性之间的关系.合成了硅铝质量比为 120 的 ZSM-5, 并用钴、铁对其进行改性, 用吡啶红外光谱技术测定了 ZSM-5 的表面酸性.研究表明用 Co^{2+},Fe^{3+} 离子对 HZSM-5 进行改性, Lewis 酸中心明显减少, 对氨的吸附能力下降, 这种现象保证了足够多的酸中心暴露和醛反应, 有利于吡啶碱的形成, 吡啶碱产率可达 78%.该研究为制备高活性、高选择性的合成吡啶催化剂提供了理论依据.

关键词: 吡啶; 催化剂; ZSM-5

中图分类号: TQ253.2