Mechanism of pyridine bases prepared from acrolein and ammonia by in situ infrared spectroscopy

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ABSTRACT

The in situ infrared spectroscopy of acrolein and ammonia over HF/MgZSM-5 was investigated to check the adsorption reaction of acrolein and ammonia. It was proved that propylene imine intermediate came up during the condensation process of adsorbed acrolein with ammonia. The strong adsorption of C=O helps the formation of propylene imine. The reaction order and active energy were calculated according to the intensity of acrolein infrared spectroscopy. The synthesis of 3-picoline is likely to go through a flat adsorption of propylene imine and a deamination of amino dihydropyridine.

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1. Introduction

3-Picoline is an important chemical intermediate in the synthesis of pharmaceuticals, agriculture and fine chemicals [1,2]. Pyridine and 3-picoline was prepared from acrolein and ammonia because of a higher yield with no 4-picoline [3], comparing to that from formaldehyde, acetaldehyde and ammonia [4]. The Chichibabin mechanism [5,6] shows that the production of pyridines from saturated aldehyde and ammonia involves imine intermediate. Although, there is still no detailed mechanism for the condensation of acrolein and ammonia to 3-picoline, so that the fact that no 3-picoline could be produced between acetaldehyde and ammonia reaction, where the products are 2-picoline and 4-picoline [7], is paid little attention to and admitted in some literatures [8,9].

Acrolein was considered to be the reaction intermediate in the condensation of formaldehyde, acetaldehyde and ammonia, as pyridine and 3-picoline were the common pyridine products comparing to that of acrolein and ammonia [4]. And also, it was reported that the production of 3-picoline undergoes a process of propylene imine formation [10], which was confirmed but never investigated until now. Literatures [8,10–12] reported that the formation of 3-picoline from acrolein or propylene imine underwent a hydrogenation and dehydrogenation process, which is inconsistent with the result of 3-picoline prepared from acrolein and ammonium acetate in acetic acid solution with a liquid-phase reactor [13].

Caibin Wang and Li [14] concluded that the catalyst reactive sites in favor of 3-picoline product were Brönsted acid sites over HF-Al$_2$O$_3$ catalyst, however, Ivanova et al. [15] insisted on the interaction of weak Lewis acid sites and Brönsted acid sites of Al$_2$O$_3$–SiO$_2$ catalyst. On the other hand, a strong Lewis acid site favored decomposition to pyridine product and polymerization to tars products, while, the Brönsted acid sites were less important than the Lewis ones. Ivanova et al. [16] preferred to the presence of two types of Lewis acid sites exhibiting high activity and selectivity to 3-picoline over SO$_4{}^{2-}$/TiO$_2$ catalyst. It is necessary to analyze and study further the catalysis of acid sites for abrogating theses arguments. And also, it is not clear that the adsorption of acrolein and formation of pyridine, involving to the decomposition reaction occurring before or after the 3-picoline formation.
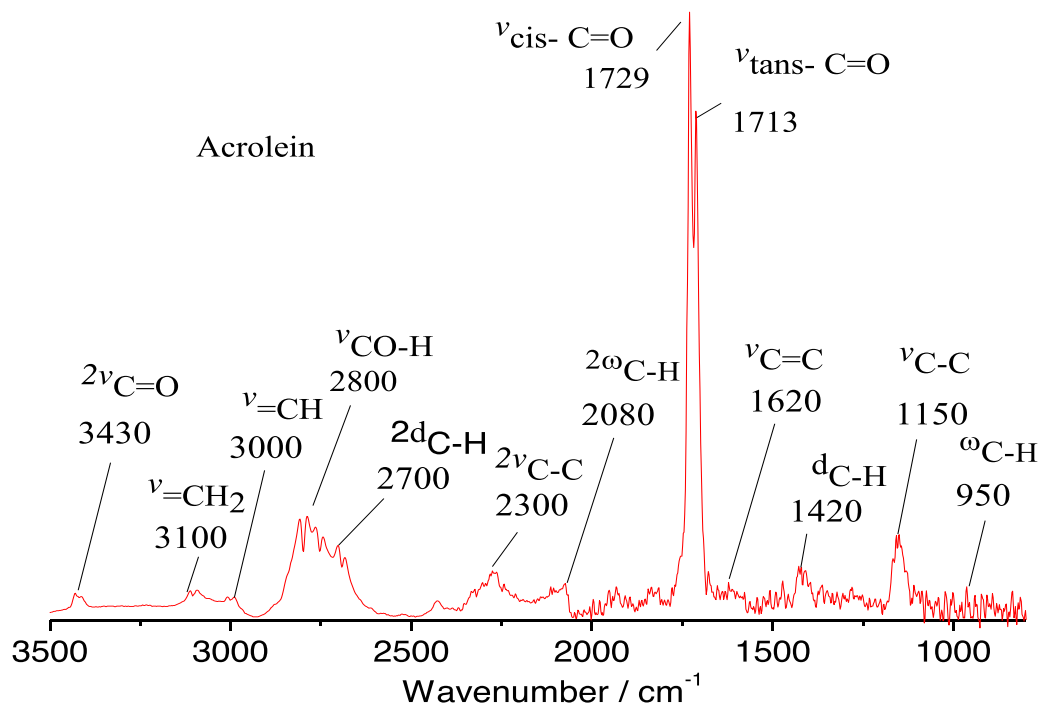
Fig. 1. FT-IR spectrum of acrolein at room temperature.

The present study describes the adsorption and reaction of acrolein and ammonia over HF/MgZSM-5 catalyst by in-situ infrared spectroscopy in order to understand the mechanism of pyridine and 3-picoline formation.

2. Experimental

2.1. Catalyst preparation

The catalyst were modified by impregnation of 130 g of HZSM-5(Si/Al = 25, Nankai University Catalyst Factory) with 100 mL 0.62 M $Mg(NO_3)_2$ solution at a temperature 90 °C for 8 h and then dried. After that, 100 mL 0.62 M NH_4HF_2 solution followed to impregnate the prepared solid with the same condition and then calcinated at 700 °C for 4 h to get a HF/MgZSM-5 catalyst.

2.2. Characterization and methods

A varian 3100 FT-IR spectroscopy with a MCT detector and a quartz in-situ IR transmission cell-reactor with a CaF_2 window (Dalian Institute of Chemical Physics, Chinese Academy of Sciences) and a oil diffusion pump vacuum system are used to record the IR spectrums of acrolein and its reaction products. The IR detecting condition was followed as: speed = 40 KHz, filter = 5 Hz, resolution = 2 cm^{-1}, under sampling ratio = 2, sensitivity = 1, Co-add = 32, wavenumber = 4000–400 cm^{-1}.

2.3. Experimental procedure

Acrolein with 95% (in mass), supplied by HuBei Xinjing new material limited company, was firstly purified through distillation before used. Ammonia was supplied by heating commercial ammonium acetate (AR). Potassium bromide was appropriative for IR spectroscopy and supplied by Germany Meck Company.

The procedure was conducted as following: (1) The HF/MgZSM-5 catalyst and KBr were firstly mixed and milled with a mass ration of 1:99 at a total weight of 175 mg, and then pressed into a self-supported 13 mm transparent wafer. The wafer was mounted

Table 1
Wavenumber and assignments of IR spectra of acrolein.

Wavenumber	Assignments		
cm^{-1}	Bond	Vibration	Intensity
3468–3395	C=O	2υ	Weak
3200–3050	=CH$_2$	υ	Weak
3050–2950	=CH—	υ	Weak
2950–2750	CO—H	υ	Strong
2750–2600	C—H	2δ	Medium
2380–2200	C—C	2υ	Medium
2200–2040	C—H	$2g$	Medium
1750–1660	HC=O	υ	Strong
1630–1550	C=C	υ	Weak
1438–1250	C—H	δ	Medium
1180–1109	C—C	d	Medium
1000–800	C—H	g	Weak

Note: υ, δ and g denote stretching, bending and deformation; 2 denotes the double frequency.

into the sample holder of the IR cell-reactor and then removed the impurities at 350 °C for 2 h under vacuum condition. After the temperature was cooled down, the background spectrum was collected. (2) Then, acrolein was inhaled and adsorbed on the catalyst wafer, at the same time, the adsorption and desorption IR spectrum of acrolein were recorded at various temperature and vacuity. (3) The in situ IR spectrums of adsorbed acrolein were recorded after fresh acrolein and ammonia was inhaled respectively. (4) After ammonia and acrolein was inhaled orderly, the in situ IR spectrums of ammonia condensation with acrolein were recorded at various temperature and time.

3. Results and discussion

3.1. IR spectrum of acrolein

On the basis of the vibrational spectroscopic study of acrolein as reported [17], we made tentative assignments to IR bands in Fig. 1,