

Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Towards the sustainable production of pyridines *via* thermo-catalytic conversion of glycerol with ammonia over zeolite catalysts

Lujiang Xu, Zheng Han, Qian Yao, Jin Deng, Ying Zhang*, Yao Fu* and Qingxiang Guo

Received (in XXX, XXX) XthXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

DOI: 10.1039/b000000x

In this study, the renewable pyridines can be directly produced from glycerol and ammonia via thermo-catalytic conversion process with zeolites. The major factors, including catalyst, temperature, weight hourly space velocity of glycerol to catalyst (WHSV), the molar ratio of ammonia to glycerol, which may affect the pyridines production, were investigated systematically. The optimal conditions for producing pyridines from glycerol was achieved with HZSM-5 (Si/Al=25) at 550 °C with the WHSV of glycerol to catalyst at 1 h⁻¹ and the ammonia to glycerol molar ratio at 12:1. The carbon yield of pyridines was up to 35.6%. The addition of water to the feed decreased the pyridines yield, because water competed with glycerol on the acid sites of the catalyst and therefore impacted the acidity of the catalyst. After five reaction/regeneration cycles, a slightly deactivation of the catalyst was observed. The catalysts were investigated by N₂ adsorption/desorption, XRD, XRF and NH₃-TPD and the results indicated that the deactivation could be due to the structure change and the acid site loss of the catalyst. The reaction pathway from glycerol to pyridines was studied and the main pathway should be that glycerol was initially dehydrated to form acrolein and some by-products such as acetaldehyde, acetol, acetone, *etc.*, and then acrolein, the mixture of acrolein and acetaldehyde, or other by-products reacted with ammonia to form imines and finally pyridines.

Introduction

The pyridine substructure is one of the most prevalent heterocycles found in natural products, pharmaceuticals, and functional materials.^{1,2} Pyridines (pyridine, 2-methylpyridine, 3-methylpyridine and 4-methylpyridine) are widely used as building blocks for the synthesis of agrochemicals and pharmaceuticals due to their high chemical activity and biological activity. They have also been used as solvent as well as catalysts in the chemical industry.^{3,4} Traditionally, pyridines were produced from coal tar as a by-product of the coal gasification. Pyridines produced by this method couldn't meet the increasing demand of market, which resulted in the development of alternative synthetic methods of pyridines from acyclic molecules (carbonyls, dicarbonyls, dicyano alkanes, alkenes, and alkynes) over zeolites (HZSM-5, HY and H-β).⁵⁻⁹ Formaldehyde, acetaldehyde and acrolein are used to produce pyridines industrially. However, these feedstocks are non-renewable fossil based materials. In industry, formaldehyde is produced by the catalytic oxidation of methanol.¹⁰ Acetaldehyde is mainly produced by the oxidation of ethylene via the Wacker process.¹¹ Acrolein is prepared by oxidation of propene.¹² The chemical properties of these aldehydes are unstable and prone to aggregation. Furthermore, formaldehyde and acrolein are highly toxic and carcinogenic.^{13,14} Therefore, it would be highly desirable to find a renewable and environment friendly feedstock to produce pyridines in large scale.

Glycerol, as a co-product in the production of biodiesel by

transesterification of vegetable oils or animal fats, is a potentially desired candidate. About 1kg of crude glycerol is generated for every 9 kg of biodiesel produced.¹⁵ Recently, glycerol has a remarkable production increase because of the demand and the production boosts of biodiesel. The anticipated production of glycerol will be 1.54 million tonnes in 2015.^{16,17} However, because the market demand for glycerol is far less than its production, the market price of glycerol has decreased rapidly from around 1200 USD/ton in 2000 to 400 USD/ton in 2010.¹⁸ Such an inexpensive feed makes the development of processes for the conversion of glycerol into other value-added chemicals.

Compared with the aldehydes which are used to produce pyridines, glycerol is renewable, nontoxic and chemically stable. Therefore, utilizing glycerol for pyridines production could have a tremendous technical impact. More than sixty years ago, Cullinane et al. mentioned the formation of pyridine and derivatives by reacting ammonia, urea or ammonia salts with glycerol for about 10 hours, but the selectivity and yield of pyridine were too low to be applied in industry.¹⁹ Acrolein is an important intermediate in the production of pyridines from formaldehyde and acetaldehyde. Many literatures reported that acrolein could be produced from glycerol via catalytic gas phase dehydration process.^{16, 20-29} The recent development of glycerol to acrolein over different acid catalysts, such as zeolites, metal oxides, heteropolyacids (HPAs) supported on metal oxides, and the effects of catalyst pore structure and acid properties on the dehydration of glycerol have been reviewed and well documented.^{16,20,21} Dubois et al. synthesized pyridines by a two-step method that included: 1) glycerol dehydration to acrolein,

acrolein enrichment and separation, and 2) reaction of the acrolein from the preceding step with the additional acetaldehyde to form pyridines.³⁰ Gullu et al. synthesized pyridines from glycerol and inorganic ammonium salts via micro-assisted pyrolysis.³¹

In this study, zeolite catalysts were employed to convert glycerol into pyridines in one step via the thermo-catalytic conversion process. Ammonia served as both carrier gas and reactant. Different catalysts, MCM-41, β -zeolite, ZSM-5 (Si/Al=50) and HZSM-5 with different Si/Al ratios (Si/Al=25, 50, 80) were screened. The major factors, including catalyst, reaction temperature, WHSV of glycerol to catalyst, the molar ratio of ammonia to glycerol and water content in the feeding solution were investigated systematically. The stability of the catalyst was tested by five reaction/regeneration cycles. The catalyst of each cycle was characterized by N_2 adsorption/desorption, X-Ray Diffraction (XRD), X-ray Fluorescence (XRF), and temperature programmed desorption of ammonia (NH_3 -TPD) analyses. The reaction pathway was also investigated.

Experimental Section

Materials

Ethanol (≥ 99.5 , AR), glycerol (≥ 99.5 , AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Pyridine (≥ 99.5 , AR), 2-methylpyridine (≥ 99.5 , AR), 3-methylpyridine (≥ 99.5 , AR), and bi-cyclohexane (≥ 99.5 , AR) were purchased from Aladin Chemical Reagent Co. Ltd. All these chemicals were used as received. NH_3 (≥ 99.995 , AR), N_2 (99.999%), Ar (99.999%), He (99.999%) and standard gas were purchased from Nanjing Special Gases Factory.

Catalysts and characterizations

MCM-41, β -zeolite, ZSM-5 (Si/Al=50) and HZSM-5 with different Si/Al ratios (Si/Al=25, 50, 80) were purchased from the Catalyst Plant of Nankai University. The typical properties of these catalysts are shown in Table 1. The particle size of the catalysts was about 40 meshes.

The XRD patterns were analyzed by a RigakuD/MAX-2500 diffractometer in a 2θ range of $5-80^\circ$ (with a 2θ step of 0.02°) using Cu K α radiation ($k = 1.5406 \text{ \AA}$). The N_2 adsorption / desorption isotherms of the catalysts were measured at -196°C using the COULTER SA 3100 analyzer. The surface area of the catalyst was calculated by the Brunauer–Emmett–Teller (BET) method. The Si/Al ratio of zeolites was measured by XRF (Shimadzu Corporation, Japan). The data was analyzed using the semi-quantitative program UniQuant.

For the NH_3 -TPD tests, about 200 mg of sample were put in a reactor and pre-treated, in situ, for 1 h at 500°C in a flow of argon. After cooling to 90°C , ammonia adsorption was performed by feeding pulses of reactant grade ammonia ($>99.995\%$) to the reactor using a flow of dry argon ($>99\%$) of 60 ml/min. After the catalyst surface became saturated the sample was kept at 90°C for 2 h to remove the ammonia. Ammonia was thermally desorbed by rising the temperature with a linear heating rate of approximately $8^\circ\text{C}/\text{min}$ from 90°C to 700°C . The amount of desorbed NH_3 was measured by a gas chromatograph (GC-SP6890, Shandong Lu-nan Ruihong Chemical Instrument Co., Ltd., Tengzhou China) with a thermal conductivity detector

(TCD).

Apparatus for thermo-catalytic conversion of glycerol over zeolites to pyridines

As shown in Figure S1, a bench-top continuous flow reactor consisting of a quartz tube reactor heated by a furnace and a condensation tube bathed in liquid nitrogen was used for these experiments. The catalyst bed supported by quartz wool was built up in the heating zone of the reactor. The liquid feed was fed into the reactor with a peristaltic pump under a certain flow rate and purged with ammonia. Volatile products were trapped in the condensation tube cooled with liquid N_2 .

Product Analysis

The liquid produced were analyzed by GC-MS (Thermo Trace GC Ultra with an ISQ i mass spectrometer) equipped with a TR-35MS capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ mm}$). Split injection was performed at a split ratio of 50 using helium (99.999%) as carrier gas. The GC heating ramp was: 1) hold at 40°C for 3 min, 2) heat to 180°C at $5^\circ\text{C}/\text{min}$, 3) heat to 280°C at $10^\circ\text{C}/\text{min}$, and 4) hold at 280°C for 5 min.

The total amount of liquid products was determined by the weight difference of the condensation tube before and after the experiment. The coke at the end of the run was measured after the reaction by weighing the catalyst. The carbon yield of coke was further determined by elemental analysis.

The glycerol and major liquid products were quantified by gas chromatography (GC 1690, Kexiao, China) employing a $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ fused-silica capillary column (HP-Innowax, Agilent). The liquid sample was mixed with bi-cyclohexane as the internal standard and diluted by ethanol. The GC operating conditions were as follows: carrier gas: nitrogen; injection port: 250°C in a split mode; detector (FID): 250°C ; heating ramp: heating up from 40°C to 250°C at a rate of $10^\circ\text{C}/\text{min}$, and holding at a final temperature for 5.0 min.

The gas products were analyzed by collecting the gas in gas bags. The gas bags were weighed before and after reaction and their contents were analyzed using gas chromatography (GC-SP6890, Shandong Lu-nan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China) with two detectors, a TCD for analysis of H_2 , CO, CH_4 , and CO_2 separated on TDX-01 column, and a FID (flame ionization detector) for gas hydrocarbons separated on Porapak Q column. The moles of gas products were determined by the normalization method with standard gas.

The conversion of glycerol, the yield of coke, gases, pyridines and aromatics, and the selectivity of pyridines and gases were calculated from Equation 1 to 7.

$$1. \text{ Glycerol Conversion (\%)} = \frac{\text{Moles of glycerol reacted}}{\text{Moles of glycerol fed}} \times 100\%$$

$$2. \text{ Coke yield (C \%)} = \frac{\text{Moles of carbon in solid residue}}{\text{Moles of carbon in glycerol fed}} \times 100\%$$

$$3. \text{ Gases yield (C \%)} = \frac{\text{Carbon moles in gases}}{\text{Moles of carbon in glycerol fed}} \times 100\%$$

$$4. \text{ Pyridines yield (C \%)} = \frac{\text{Moles of carbon in Pyridines}}{\text{Moles of carbon in glycerol fed}} \times 100\%$$

$$5. \text{ Aromatics yield (C \%)} = \frac{\text{Moles of carbon in aromatics}}{\text{Moles of carbon in glycerol fed}} \times 100\%$$

$$6. \text{ Pyridine selectivity (\%)} = \frac{\text{Moles of carbon in specific pyridine}}{\text{Total moles of carbon in all pyridines}} \times 100\%$$

$$7. \text{ Gas selectivity (\%)} = \frac{\text{Moles of carbon in specific gas}}{\text{Total moles of carbon in gases identified}} \times 100\%$$

Results and Discussion

Catalyst property effect on glycerol conversion with ammonia

The appropriate catalyst was essential to selectively obtain target products in the thermo-catalytic conversion process. Six catalysts with different properties were tested in this study. The typical properties of these catalysts are shown in Table 1. Table 2 summarizes the detailed results of thermo-catalytic conversion of glycerol over different zeolites at 500 °C. It can be seen that the

Table 1. Typical property of the catalysts

Catalyst	BET Surface area (m ² /g)	Pore diameter (nm)	Si/Al	Total acid (μmolg ⁻¹)
β-Zeolite	640	0.7	50	683.3
MCM-41	1000	3.8	50	260.0
ZSM-5	420	0.5	50	255.5
HZSM-5-1	350	0.5	50	293.6
HZSM-5-2	370	0.5	25	580.6
HZSM-5-3	375	0.5	80	92.4

products from thermo-catalytic conversion of glycerol were coke, gases, pyridines and a little aromatics. The detected gases were CO, CH₄, C₂H₄ and C₃H₆. Trace amount of CO₂ was also produced during this process, because when the gases passed through the Ca(OH)₂ solution, very small amount of white precipitant could be observed. However, CO₂ was difficult to be detected by GC due to its reaction with ammonia to form ammonium carbonate. Since the amount of CO₂ was small and it was hard to give accurate data, we didn't report it in Table 2.

As shown in Table 2, when there was no catalyst, the conversion of glycerol was only 5.6%. Gases and coke were the major products, and only trace amount of pyridines (below 1 % carbon yield) were detected in the liquids. Then, three kinds of catalysts, β-zeolite, MCM-41 and ZSM-5 with different acid content and pore structure were screened firstly. When these zeolites were introduced, glycerol was almost completely

Table 2. Thermo-catalytic conversion of glycerol with ammonia over various catalysts.

Entry	1	2	3	4	5	6	7
Catalyst	Blank	β-Zeolite	MCM-41	ZSM-5	HZSM-5-1	HZSM-5-2	HZSM-5-3
Si/Al	-	50	50	50	50	25	80
Glycerol conversion (%) a	5.6	92.6	100	100	100	100	100
Overall carbon Selectivity (C %)							
Coke	20.7	30.1	19.4	13.7	13.0	13.2	14.5
Gases	41.8	47.3	54.3	53.6	52.7	47.5	50.9
Pyridines	-	15.3	9.7	19.2	22.8	26.0	20.9
Aromatics	-	0.5	0.3	0.4	0.6	0.9	0.4
Pyridines selectivity (%)							
Pyridine	-	63.8	66.4	71.1	69.3	67.3	72.3
2-methylpyridine	-	10.5	11.0	11.1	12.1	10.0	8.8
3-methylpyridine	-	24.1	21.5	16.8	17.9	21.4	16.1
4-methylpyridine	-	1.6	1.1	2.0	1.7	1.3	2.8
Other alky pyridines	-	<1	<1	<1	<1	<1	<1
Gases selectivity (%)							
CO	85.1	71.2	69.9	70.1	78.8	80.3	76.4
CH ₄	5.9	5.8	8.6	5.9	6.4	5.3	7.2
C ₂ H ₄	3.5	13.0	15.3	15.5	12.3	11.9	14.0
C ₃ H ₆	1.5	9.0	6.2	8.5	2.5	2.5	2.4

Reaction conditions: reaction temperature, 500 °C; HZSM-5, Si/Al=25, 1g; WHSV, 1hr⁻¹; NH₃ to glycerol molar rate, 8:1; glycerol content, 100%. a. Mole conversion: mol%; b. Carbon yield: carbon mol%.

converted and the conversion of glycerol increased to nearly 100%. Compared with β -zeolite and MCM-41, more pyridines were produced by using ZSM-5, and the carbon yield reached about 20%. The kinetic diameter of pyridines was about 0.585 nm, which was similar to the pore diameter of ZSM-5.^{5,32} ZSM-5 is consisted of two perpendicularly intersecting channels. The larger one has a near circular pore structure with dimensions of $0.54 \times 0.56 \text{ nm}^2$, and the smaller channels have a geometry of $0.51 \times 0.54 \text{ nm}^2$. The intersection of these channels which contains the proposed active site is approximately a 0.9 nm cavity.³³ More coke and less pyridines were produced by using β -zeolite. Although β -zeolite has intersecting channels similar to ZSM-5, this zeolite is a mixture of three polymorphs which is different from ZSM-5.³⁴ Furthermore, as shown in the Table 1, the total acid content of β -zeolite was up to $683.3 \mu\text{mol g}^{-1}$, which was much more than ZSM-5. Thus, more coke was produced in the thermo-catalytic conversion of glycerol over β -zeolite process. Compared with ZSM-5, more gases and coke, and less pyridines were produced by using MCM-41. The acid content of MCM-41 was similar to ZSM-5. The difference of the product distribution may be caused by the different structure between ZSM-5 and MCM-41. MCM-41 possesses hexagonally packed arrays of channels with pore diameter around 3.8 nm, which has no shape selectivity to pyridines.^{35,36}

Usually, acid is an important factor to influence the product distribution. Converting ZSM-5 to HZSM-5 can introduce acid to the catalyst but keep its pore structure, therefore, HZSM-5/1 with same Si/Al ratio (50) as ZSM-5 was selected to investigate the acid effect. Compared the results in Table 2, entries 4 and 5, the introduction of acid slightly changed the coke and gases production. However, it increased the pyridines yield from 19.2% to 22.8%. Since the alumina contents of the zeolite determine the acid site densities of the catalyst which may influence the product distribution, two other HZSM-5 samples with silica to alumina ratios 25 and 80 were also tested in this study. The total acid contents of these catalysts determined by NH_3 -TPD are shown in Table 1, and the detailed information can be seen in supplementary information (Figure S2). The acid density decreased with the Si/Al ratio increase. As shown in Table 2, entries 5-7, with the Si/Al ratio increased from 25 to 80, the yield of pyridines decreased, and the HZSM-5-2 (Si/Al=25) which possessed the highest acid concentration resulted in the highest pyridines yield among all the catalysts, and the yield of pyridines reached about 26%. Therefore HZSM-5 (Si/Al=25) was selected as the optimal catalyst in the following study.

The effect of temperature on the pyridines production from glycerol

The temperature effect on the glycerol conversion with ammonia was investigated in the temperature range of 300 to 600 °C. As shown in Fig. 1a, the yield of coke decreased and the yield of gases increased with temperature increasing. The conversion of glycerol increased from 68.2 % to 100 % from 300 to 450 °C, and the pyridines yield also increased from 3.2 % to 23.3 %. The highest yield of pyridines (32.1 %) was obtained at about 550 °C. If the temperature increased to 600 °C, the yield of pyridines decreased to 8.1 %. Meanwhile, the yield of aromatics increased from 2.2 to 15.9 %. It indicated that temperature at around 550 °C is in favor of pyridines production.

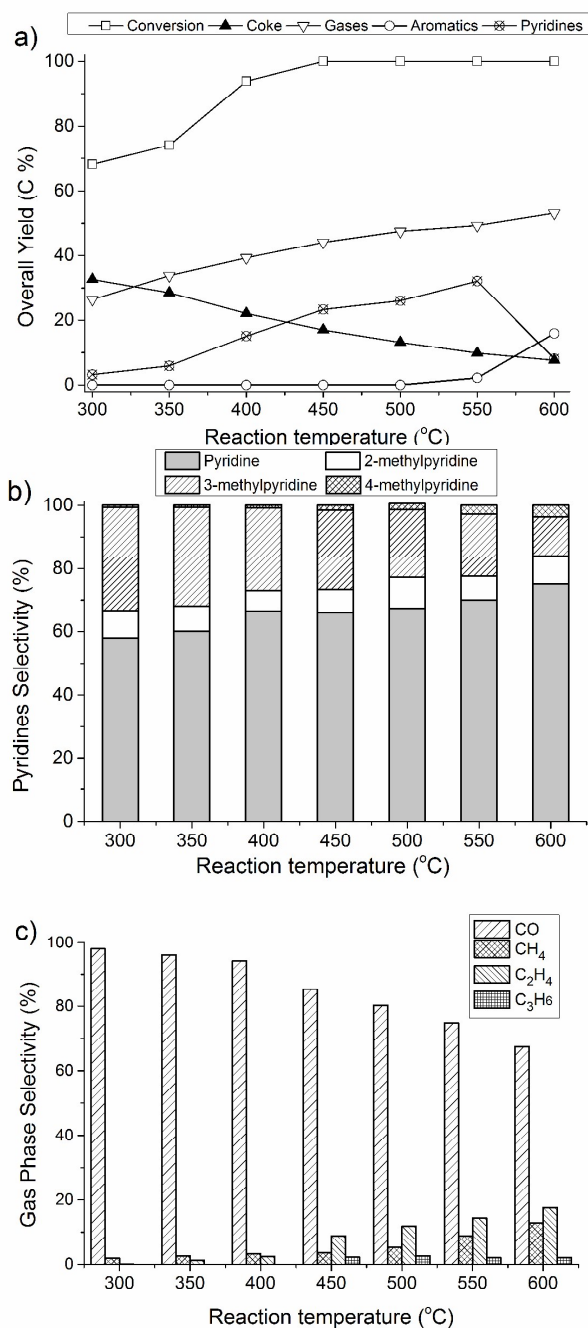


Fig. 1 The effect of reaction temperature on the overall yield (a), pyridines selectivity (b), the gas selectivity (c) obtained via thermo-catalytic conversion of glycerol. (Reaction conditions: catalyst, HZSM-5, Si/Al=25; catalyst usage, 1g; glycerol feed rate, 1 ml/h; NH_3 flow rate, 40 ml/min, glycerol content, 100%)

Fig. 1b shows the effect of reaction temperature on the pyridines selectivity. Pyridine and 3-methylpyridine are the major products. Meanwhile, small amount of 2-methylpyridine and trace amount of 4-methylpyridine were also produced. With temperature increasing from 300 to 600 °C, the pyridine selectivity increased from 58 % to 75.1 and the 4-methylpyridine selectivity increased from 0.6% to 3.7%. The 3-methylpyridine selectivity decreased from 32.7 % to 12.2 %. The selectivity of 2-methylpyridine showed no regularity in entire temperature range.

The pyridines distribution change could be explained by previous findings. Pyridine is most likely formed from the reaction of acrolein and acetaldehyde with ammonia, 3-methylpyridine is the major product from the reaction of acrolein with ammonia, 2-methylpyridine is mainly from the reaction of acrolein and acetone with ammonia and 4-methylpyridine was from the reaction of acetaldehyde with ammonia.⁶ With temperature increasing, the cracking reaction of glycerol became severe, and more acetaldehyde as the by-product would be produced in the glycerol dehydration process, while there is nearly no change on the acetone production.²² As a result of above reasons, as temperature increased, the selectivity of pyridine and 4-methylpyridine increased but 3-methylpyridine decreased significantly.

Fig. 1c shows the effect of temperature on the gas product distribution. The main products detected in the gas phase were CO and some olefins. The CO selectivity decreased but CH₄ and C₂H₄ selectivity increased with temperature. No C₃H₆ was detected when the reaction temperature was lower than 450 °C. At higher temperature, the selectivity of C₃H₆ was constant at 3 %. At a lower temperature, side reactions in this process were not notable and the product distribution of gases was simple; while, at a higher temperature, the side reactions such as cracking, decarbonylation, oligomerization, become more significant. Thus the selectivity of olefins and hydrocarbons increased with the temperature increasing.

The effect of WHSV of glycerol to catalyst on the pyridines production

The WHSV was defined as the ratio of the mass flow rate of glycerol to the mass of catalyst used for reaction. During the experiments, the mass flow rate of glycerol was ranged from 0.5-2 g/h while the mass of catalyst was kept constant at 1 g. Fig. 2 shows the glycerol conversion, the overall yield of coke, gases, pyridines, aromatics and the selectivity of pyridines as a function of the WHSV. When the WHSV was less than 1 h⁻¹, the conversion of glycerol was 100%, and then with the WHSV increased from 1 to 2 h⁻¹, the conversion of glycerol decreased from 100% to 73.8%. With the WHSV increasing, the carbon yield of coke, gases and aromatics decreased from 10.7% to 7.6%, 52.9% to 40.6%, and 3.7% to 1.4%, respectively. While the pyridines yield firstly increased from 27.8% to 35.6% as the WHSV increased from 0.5 to 1 h⁻¹, and then decreased gradually to 23.7% as the WHSV further increased to 2 h⁻¹. A lower WHSV would result in overreaction of the glycerol over the catalyst which caused the yield of pyridines decrease and the yield of gases and coke increase. A higher WHSV would lead to the incomplete reaction of glycerol over catalyst and the conversion of glycerol decreased. As shown in Fig. 2b, as the WHSV increased from 0.5 to 2 h⁻¹, the distributions of pyridines had almost no change. The main products of pyridines were pyridine and 3-methylpyridine, and their selectivity was kept at about 70% and 20%, respectively. Meanwhile, the selectivity of by-products 2-methylpyridine and 4-methylpyridine was also kept at about 8% and 3%, respectively. Thus, the optimal WHSV of glycerol to catalyst for producing pyridines was about 1 h⁻¹, and the yield of pyridines was about 35.6 %.

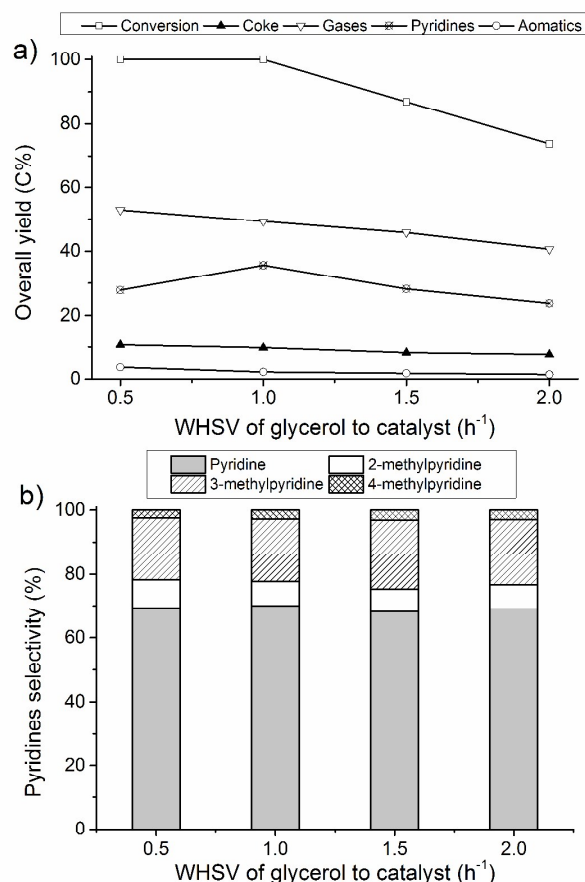


Fig. 2 The effect of WHSV of glycerol to catalyst on the pyridines distribution, (a) overall yield; (b) pyridines selectivity. (Reaction conditions: 550 °C; HZSM-5, Si/Al=25, 1g; NH₃ to glycerol molar ratio, 12:1; glycerol content, 100%.)

The effect of ammonia to glycerol molar ratio on the pyridines production

The effect of ammonia to glycerol molar ratio on glycerol thermo-catalytic conversion to pyridines was investigated by fixing the WHSV of glycerol to catalyst at 1 h⁻¹ and the mass of catalyst at 1g, while changing the flow rate of ammonia. The molar ratio of ammonia to glycerol was in the range from 4:1 to 20:1. In this study, the ammonia served not only as the reagent but also as the carrier gas. Different ammonia to glycerol molar ratio would result in different reaction time of glycerol and the pyrolytic vapor in the system. As shown in Fig. 3a, with the molar ratio of ammonia to glycerol rising from 4:1 to 20:1, the conversion of glycerol kept at 100%, and the total carbon yield of the detected products was above 90%. The coke yield decreased from 14.1% to 8.8%, while the gas yield increased from 45.2% to 55.9%. The carbon yield of aromatics was very low and kept at about 2%. During this process, a higher ammonia to glycerol ratio, that is a higher ammonia flow rate, could cause the reaction time of feedstock stream over catalyst decreased, which could cause the reaction from glycerol to pyridines insufficient. In contrast, a lower ammonia flow rate, which could cause the reaction time of feedstock stream over catalyst increased, and led to the further reaction of pyridines. When the molar ratio of ammonia to

glycerol was at 12:1, the yield of pyridines reached 35.6%. Fig. 3b shows that the major product distribution in pyridines didn't change significantly, and the main products were still pyridine and 3-methylpyridine. The selectivity of pyridine, 2-methylpyridine, 3-methylpyridine and 4-methylpyridine were about 70 %, 8 %, 20 % and 2%, respectively.

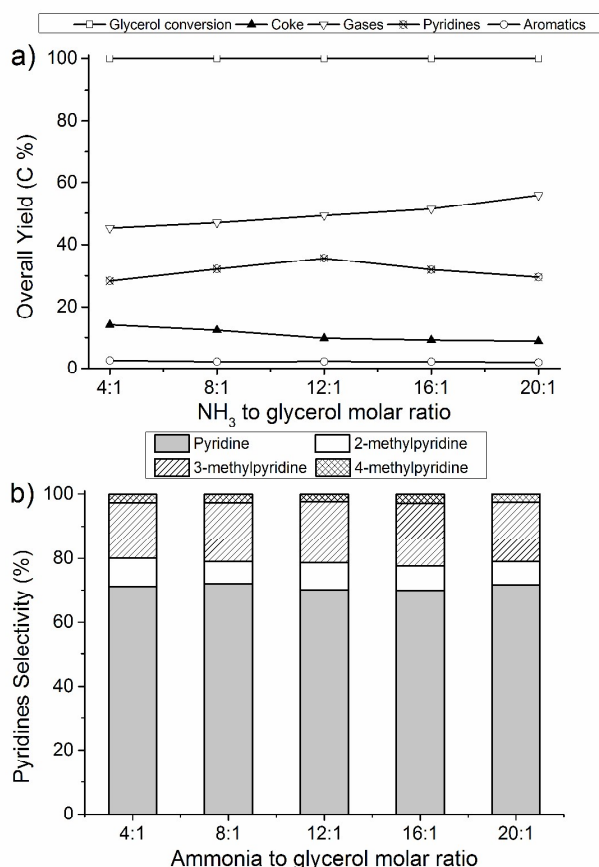


Fig. 3 The product distribution and the pyridines selectivity obtained from thermo-catalytic conversion of glycerol with different ammonia to glycerol molar ratio, (a) overall yield; (b) pyridines selectivity. (Reaction conditions: 550 °C; HZSM-5, Si/Al=25, 1g; WHSV, 1; glycerol content, 100%)

The effect of water content of glycerol-water solution on the pyridines production

Crude glycerol obtained from biodiesel production usually contains a lot of water, which can influence the product distribution and the acrolein yield in the glycerol gas phase dehydration process.²³ In this study, glycerol gas phase dehydration is an essential process which may influence the yield and selectivity of pyridines. The experiments of thermo-catalytic conversion of glycerol / water solution with different water content were carried out. Table 3 shows the effect of the water content in the solution on the pyridines production. The pyridines yield decreased from 35.6 to 28.5 % with the water content in the feed increased from 0 to 80%. Meanwhile, the selectivity of pyridine increased from 70.7 to 78.2 %. There was a slight decrease of the selectivity to 2-methylpyridine and 3-methylpyridine with increasing water content. Based on Table 2, the acidity of catalyst is an important factor for producing

Table 3. The effect of water content in the glycerol-water solution on the yield and selectivity on the pyridines production.

Entry	1	2	3	4	5
Water content (wt %)	0	20	40	60	80
Overall carbon yield (C %)					
Coke	9.8	9.3	8.5	7.3	6.4
Gases	49.3	49.3	51.6	52.7	56.8
Pyridines	35.6	34.5	34.7	29.9	28.5
Aromatics	2.2	2.2	2.4	2.5	2.6
Pyridines selectivity (%)					
Pyridine	70.7	70.2	71.0	75.5	78.2
2-methylpyridine	8.6	8.1	7.9	5.8	3.5
3-methylpyridine	17.8	18.7	18.2	16.2	16.1
4-methylpyridine	2.9	3.0	2.9	2.5	2.2
Other alkylpyridines	<1	<1	<1	<1	<1

Reaction conditions: reaction temperature, 550 °C; catalyst, HZSM-5, Si/Al=25; catalyst usage, 1g; NH₃ flow rate, 60 ml/min, glycerol content, 100%. a. Carbon yield: carbon mol%.

pyridines in the thermo-catalytic conversion of glycerol with ammonia process. Because water competes with glycerol on the acid sites of the catalyst²³ and therefore impacts the acidity of the catalyst, it is intelligible that the pyridines yield decreases with increasing the water content. Furthermore, it was found that the selectivity of acrolein and acetaldehyde increased and the selectivity of acetone decreased with increasing water content.^{22,23} As mentioned previously, pyridine is mainly formed by acrolein and acetaldehyde, and 2-methylpyridine is mainly formed by acrolein and acetone.^{3,4} Thus, the selectivity of pyridine increased and the selectivity of 2-methylpyridine decreased with increasing the water content.

Catalyst stability study

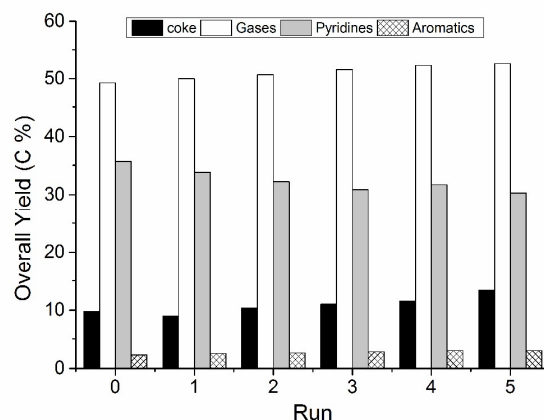
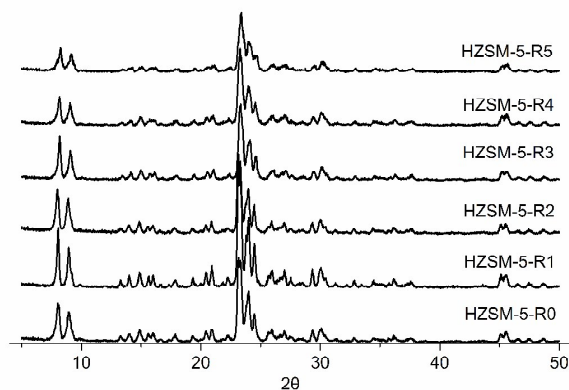


Fig. 4 The recycle of catalyst recycle. (Reaction conditions: reaction temperature, 550 °C; HZSM-5, Si/Al=25, 1g; the WHSV, 1; the NH₃ to glycerol molar ratio, 12:1; each run was 1h; glycerol content, 100%)

Table 4. Typical property of the catalysts before and after each recycles

Catalyst	BET Surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Si/Al ^a	Total acid (μmolg ⁻¹) ^b
HZSM-5-R0	370	0.200	25.0	580.6
HZSM-5-R1	331.9	0.198	26.3	442.1
HZSM-5-R2	312.7	0.176	26.3	363.5
HZSM-5-R3	304.4	0.172	26.4	318.2
HZSM-5-R4	295.4	0.167	26.7	254.6
HZSM-5-R5	288.0	0.165	27.1	206.2

a. The Si/Al: the ratio of silicon to aluminum in the zeolites; b. The detailed NH₃-TPD of the recycled catalysts was shown in the supplementary information (Figure S3).

**Fig. 5** The X-Ray diffraction patterns of the recycled catalysts.

To study the stability of the catalyst during the thermo-catalytic conversion of glycerol with ammonia, five reaction/regeneration cycles of catalyst were conducted. For each cycle, the reaction was performed with a WHSV of 1 h⁻¹ at 550 °C for 1h. After the reaction, the spent catalyst was regenerated in an air stream at 600 °C for 3 hours to remove the coke. As shown in Fig. 4, after used for 5 times, the yield of pyridines decreased from 35.6% to 30.3%, while the yields of gases and coke increased from 49.3% to 52.6% and 9.8% to 13.0%, respectively. The yield of aromatics didn't change a lot and kept at around 2.5%. Based on these results the catalyst slightly deactivated in this glycerol conversion process.

In order to understand the reason for the gradual decrease of activity of the catalyst, some characterizations were conducted, including N₂ adsorption/desorption, XRD, XRF and NH₃-TPD. Based on the N₂ adsorption/desorption results shown in Table 4, the surface area and pore volume of catalyst exhibited a decrease from 370 m²g⁻¹ and 0.200 cm³g⁻¹ (fresh catalyst) to 288 m²g⁻¹ and 0.165 cm³g⁻¹ (after five times reaction/regeneration cycles), respectively. This indicated that the pore structure of catalyst were somehow collapsed or blocked. To investigate the structure changes of catalyst before and after regeneration, XRD was also conducted. As shown in Fig. 5, the crystal structure of HZSM-5 changed slightly after regeneration. A decrease in the intensity of

the peak at ~8° (2θ) indicated a decrease of crystallinity of HZSM-5.^{23,37,38} The XRD patterns also showed a decrease in intensity for the peak at ~24° (2θ), which indicated that aluminum was somehow removed from the framework.³⁹ To estimate the loss of aluminum, the Si/Al ratio of HZSM-5 was studied by XRF. The Si/Al ratio increased from 25.0 to 27.1 after regeneration, indicating that less than 8 mol% of aluminum was lost after 5-times regeneration. The acid sites of HZSM-5 are important for its activity. The NH₃-TPD was used to measure the total acid of HZSM-5 after each reaction/regeneration cycle. As shown in Table 4, the total acid sites of HZSM-5 decreased from 580.6 to 206.2 μmol·g⁻¹. The great change should be related to the ammonia atmosphere. Based on the above study, the reason for the gradual deactivation of the catalyst was the structure change and the acid site loss. Better catalysts should be developed in the future study.

The reaction pathway of glycerol to pyridines

To further study the pathway from glycerol to pyridines, a series of experiments, such as catalytic dehydration of glycerol under N₂ atmosphere, thermo-catalytic conversion of different oxygenated chemicals which could be formed in the glycerol catalytic dehydration process, were carried out in this study. The detailed product distribution of glycerol catalytic dehydration was shown in the supplementary information (Table S1). It can be seen that the main feedstocks for pyridines production such as acrolein, acetol, acetaldehyde and acetone could be produced in the glycerol dehydration process. They were employed as the feedstocks for producing pyridines via thermo-catalytic conversion process. The detailed product distribution is shown in Table 5. When acrolein and the mixture of acrolein and acetaldehyde were feedstocks, the product distribution and pyridines selectivity were similar to that of glycerol. Acetaldehyde mainly produced 2-methylpyridine and 4-methylpyridine, while acetol or acetone, mainly produced 2,4,6-trimethylpyridine. When the feedstocks were the mixture of acrolein and acetol or acrolein and acetone, the main product in the pyridines was 2-methylpyridine.

Based on all above investigation, the reaction pathways for the production of pyridines by thermo-catalytic conversion glycerol with ammonia is proposed and summarized in Fig. 6. Glycerol initially underwent a dehydration process to form acrolein. At the same time, the glycerol also underwent a cracking process to form some other oxygenated chemicals as the by-products, including acetaldehyde, acetol, acetone, etc. Then, these oxygenated chemicals reacted with the ammonia to form imine compounds, which were the intermediates in the pyridines production process.^{4,9,31} Finally, the imine compounds could be further converted to pyridines via the catalytic condensation reaction. According to the product distribution of thermo-catalytic conversion of glycerol and different oxygenated compounds for producing pyridines in the Table 5, the reaction of acrolein to pyridines and the mixture of acrolein and acetaldehyde to pyridines were the main reactions during this process. Meanwhile, certain amount of coke, CO_x, hydrocarbons and H₂O were also formed as the side products during the whole process via the decarbonylation, cracking and oligomerization reactions.

Table 5. Summary of thermo-catalytic conversion of different oxygenated compounds with ammonia for the mechanism study ^a.

	Entry 1	Entry 2	Entry 3	Entry 4	Entry 5	Entry 6	Entry 7	Entry 8
Feedstocks	Glycerol	Acrolein	Acetaldehyde	Acetol	Acetone	Acrolein + Acetaldehyde	Acrolein + Acetol	Acrolein + Acetone
Molar ratio	-	-	-	-	-	1:1	1:1	1:1
Overall carbon yield (C %)								
Coke	13.2	15.6	10.4	13.2	12.8	13.5	14.4	13.9
Gases	47.5	47.6	50.1	50.4	51.3	49.7	48.8	49.3
Pyridines	26.0	33.7	35.9	27.6	29.4	35.0	30.5	31.6
Aromatics	0.9	2.4	2.5	2.8	2.4	2.5	2.1	2.2
Pyridines selectivity (%)								
Pyridine	67.3	61.2	7.6	18.8	3.0	74.3	25.0	14.9
2-methylpyridine	10.0	5.6	65.3	21.1	5.8	4.2	48.3	60.9
3-methylpyridine	21.4	33.2	1.4	<1	18.9	15.1	13.8	18.2
4-methylpyridine	1.3	<1	25.7	9.7	<1	6.4	5.6	<1
Other alkylpyridines ^b	<1	<1	<1	50.4	72.3	<1	7.3	6.0

a. All the conversion of the feedstocks in this study was 100%, all the reaction temperature was at 500°C; b: Other alkylpyridines: 2,5-dimethylpyridines, 2,6-dimethylpyridines, 2,4,6-trimethylpyridine *etc.*;

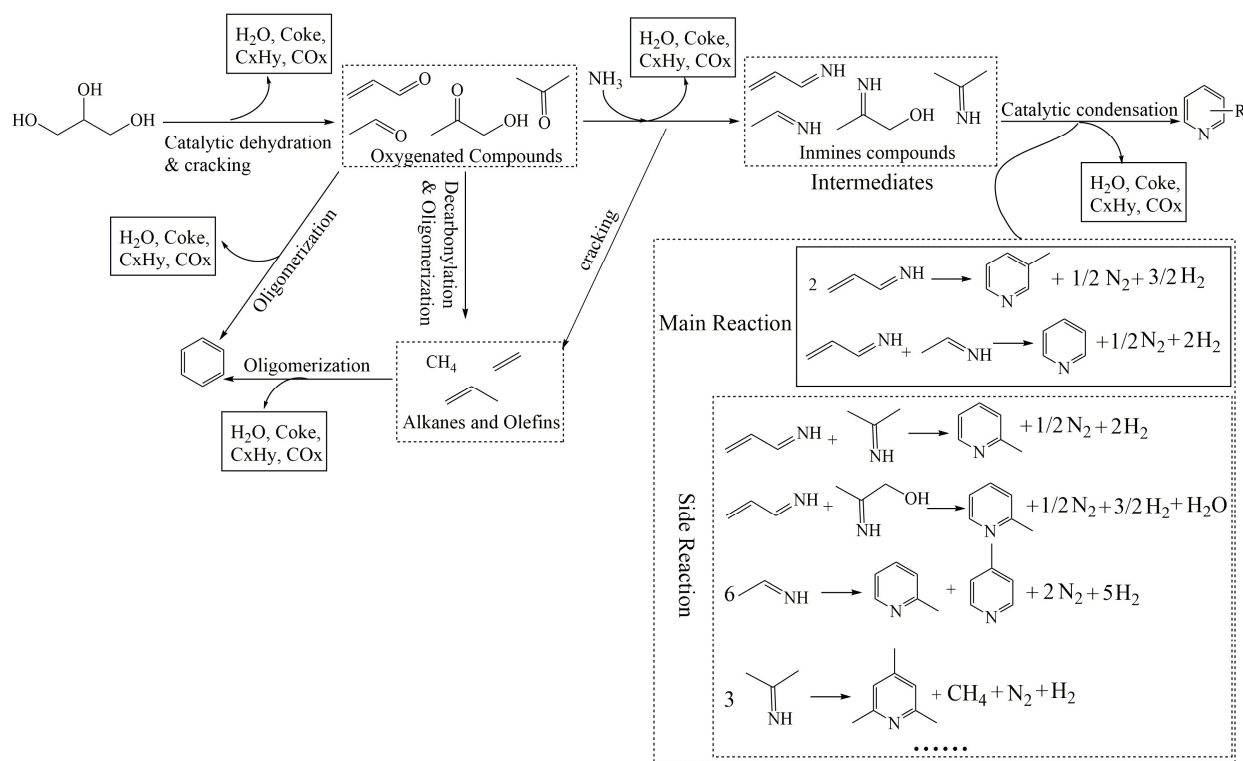


Fig. 6 The proposed reaction pathway from glycerol to pyridines.

Conclusions

This study demonstrates that pyridines can be synthesized directly from renewable glycerol in the fixed bed reactor over zeolites under ammonia atmosphere via thermo-catalytic conversion process. In this process, ammonia served not only as the carrier gas, but also as the reactive nitrogen source. Among

10 different catalysts, HZSM-5 with Si/Al ratio as 25 showed best reactivity for pyridines production due to the desired pore structure and acidity. Temperature displayed significant effect on the product distribution. The maximum yield of pyridines was obtained at 550 °C. The 15 WHSV of glycerol to catalyst investigation indicated that a lower WHSV could cause the overreaction of glycerol,

while a higher WHSV would cause the insufficient glycerol conversion to pyridines. The desired WHSV was about 1h^{-1} . Because ammonia served as both reactant and carrier gas, to supply sufficient reactant and keep desired reaction time, appropriate ammonia to pyridines molar ratio was important on glycerol conversion to pyridines. The addition of water to the feed decreased the pyridines yield, because water competed with glycerol on the acid sites of the catalyst and therefore impacted the acidity of the catalyst. Under the optimal conditions, the highest carbon yield of pyridines was 35.6%. After five reaction/regeneration cycles, a slightly irreversible deactivation of the catalyst was observed, which could be due to the structure change and the acid site loss of the catalyst. The reaction pathway from glycerol to pyridines was that glycerol was initially dehydrated to form acrolein and some by-products such as acetaldehyde, acetol, acetone, etc., and then acrolein, the mixture of acrolein and acetaldehyde, or other by-products reacted with ammonia to form imines and finally pyridines.

Acknowledgments

The authors sincerely thank Professor George W. Huber (University of Wisconsin - Madison) for giving valuable suggestions on the experiments and article writing of this work. The authors are also grateful to the National Basic Research Program of China (2013CB228103), NSFC (21325208, 21172209, 21402181), the Program for Changjiang Scholars and Innovative Research Team in University of the Ministry of Education of China and the Fundamental Research Funds for the Central Universities (wk 2060190040) for the financial support.

Notes and references

- 30 Collaborative Innovation Center of Chemistry for Energy Materials, Anhui Province Key Laboratory of Biomass Clean Energy, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, China. Fax: (+86) 551-6360-6689 E-mail: zhzhying@ustc.edu.cn (Ying Zhang); fuyao@ustc.edu.cn (Yao Fu).
- 35 † Electronic Supplementary Information (ESI) available: [The scheme of the fixed bed reactor for glycerol conversion; NH_3 -TPD spectra of the catalysts; The liquid product distribution of glycerol dehydration over zeolites with nitrogen.]. See DOI: 10.1039/b000000x/
- ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

References

- G. D. Henry, *Tetrahedron*, 2004, **60**, 6043-6061.
- M. Movassaghi, M. D. Hill, and O. K. Ahmad, *J. Am. Chem. Soc.*, 2007, **129**, 10096-10097.
- K. S. K. Reddy, I. Sreedhar, K. V. Raghavan, *Appl. Catal.-A: Gen.*, 2008, **339**, 15-20.
- K. S. K. Reddy, C. Srinivasakannan, K. V. Raghavan, *Catal. Surveys from Asia*, 2012, **16**, 28-35.
- S. Shimizu, N. Abe, A. Iguchi, M. Dohba, H. Sato, K. I. Hirose, *Micropor. Mesopor. Mater.*, 1998, **21**, 447-451.
- S. Shimizu, N. Abe, A. Iguchi, H. Sato, *Catal. Surv. Asia*, 1998, **2**, 71-76.
- J. R. Calvin, R. D. Davis, C. H. McAteer, *Appl. Catal.-A: Gen.*, 2005, **285**, 1-23.
- F. Jin, F., G. Y. Wu, Y. D. Li, *Chem. Eng. Technol.*, 2011, **34**, 1660-1666.
- Y. Higashio, T. Shoji, *Appl. Catal.-A: Gen.*, 2004, **260**, 251-259.
- D. E. Webster and I. M. Rouse, US 4208353 A, 1977.

- G. A. Renberg, US 3291839 A, 1962.
- D. Arntz, A. Fischer, M. Höpp, S. Jacobi, J. Sauer, T. Ohara, T. Sato, N. Shimizu, and H. Schwind, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, 2012.
- I. Broder, P. Corey, P. Brasher, M. Lipa, P. Cole, *Environ. Health Perspect.*, 1991, **95**, 101-104.
- Z. Feng, W. Hu, Y. Hu, M. Tang, *Proc. National Acad. Sci.*, 2006, **103**, 15404-15409.
- Y. G. Zheng, X. L. Chen, and Y. C. Shen, *Chem. Rev.*, 2008, **108**, 5253-5277.
- B. Katryniok, S. Paul, F. Dumeignil, *ACS Catal.*, 2013, **3**, 1819-1834.
- L. Z. Tao, B. Yan, Y. Liang, and B. Q. Xu, *Green Chem.*, 2013, **15**, 696-705.
- Y. Nakagawa and K. Tomishige, *Catal. Sci. Technol.*, 2011, **1**, 179-190.
- N. M. Cullinane, S. J. Chard and R. Meatyrd, *J. Chem. Soc. Chem. Ind.*, 1948, **67**, 142-143.
- L. Z. Tao, S. H. Chai, Y. Zuo, W. T. Zheng, Y. Liang, B. Q. Xu, *Catal. Today*, 2010, **158**, 310-316.
- Y. Choi, H. Park, Y. Yun, J. Yi, *ChemSusChem*, 2014, DOI: 10.1002/cssc.201402925.
- A. Corma, G. W. Huber, L. Sauvinaud, and P. O'Connor, *J. Catal.*, 2008, **257**, 163-171.
- Y. T. Kim, K. D. Jung, E. D. Park, *Micropor. Mesopor. Mater.*, 2010, **131**, 28-36.
- S.H. Chai, H. P. Wang, Y. Liang, B. Q. Xu, *Green Chem.*, 2008, **10**, 1087-1093.
- B. Katryniok, S. Paul, V. Belliere-Baca, P. Rey, F. Dumeignil, *Green Chem.*, 2010, **12**, 2079-2098.
- D. Cespi, F. Passarini, G. Mastragostino, I. Vassura, S. Larocca, A. Iaconi, A. Chiericato, J.-L. Dubois, F. Cavani, *Green Chem.*, 2014, DOI: 10.1039/c4gc01497a.
- C. H. Zhou, J. N. Beltrami, Y.X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2007, **37**, 527-549.
- X. Li, C. Zhang, C. Qin, C. Chen and J. Shao, CN 101070276, 2007.
- C. J. Zhou, C. J. Huang, W. G. Zhang, H. S.Zhai, H. L. Wu, Z. S. Chao, *Stud. Surf. Sci. Catal.*, 2007, **165**, 527-530.
- J. L. Dubois, J. F. Devaux, US 20120283446 A1, 2012.
- Bayramoglu, D., G. Gurel, et al., *Turk. J. Chem.*, 2014, **38**, 661-670.
- B. Singh, S. K. Roy, K. P. Sharma, T. K. Goswami, *J. Chem. Technol. Biotechnol.*, 1998, **71**, 246-252.
- T. R. Carlson, G. A. Tompsett, W. C. Conner, and G. W. Huber, *Top. Catal.*, 2009, **52**, 241-252.
- Q. H. Xia, S. C. Shen, J. Song, *J. Catal.*, 2003, **219**, 74-84.
- C. T., Kresge, M. E. Leonowicz, W. J. Roth, *Nature*, 1992, **359**, 710-712.
- M. H. Lim, C. F. Blanford, A. Stein, *J. Am. Chem. Soc.*, 1997, **119**, 4090-4091.
- T. R. Carlson; Y. T. Cheng, J. Jae and G. W. Huber, *Energy Environ. Sci.*, 2011, **4**, 145-161.
- C. H. Ding, X. S. Wang, X. W. Guo and S. G. Zhang, *Catal. Commun.*, 2008, **9**, 487.
- S. J. Wang, G. W. Guo, L. Q. Zhao and R. H. Wang, *Chin. J. Catal.*, 1992, **13**, 38.

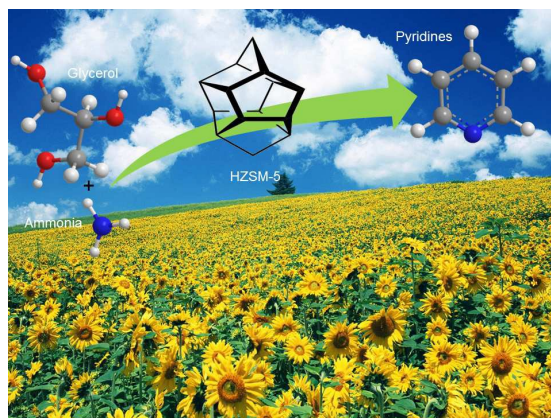
40

Graphic abstract

Towards the sustainable production of pyridines via thermo-catalytic conversion of glycerol with ammonia over zeolite catalysts

Lujiang Xu, Zheng Han, Qian Yao, Jin Deng, Ying Zhang*, Yao Fu* and Qingxiang Guo

Collaborative Innovation Center of Chemistry for Energy Materials, Anhui Province Key Laboratory of Biomass Clean Energy, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, China.



Thermo-catalytic conversion of renewable glycerol with ammonia over HZSM-5 for producing pyridines with high yield and high selectivity.