



Enhancement of indoles production and catalyst stability in thermo-catalytic conversion and ammonization of furfural with NH₃ and N₂ environments



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ARTICLE INFO

Article history:

Received 15 June 2016

Received in revised form 20 July 2016

Accepted 5 August 2016

Available online 6 August 2016

Keywords:

Diluted ammonia

Thermo-catalytic conversion

Ammonization

Furans

Indole

Catalyst stability

ABSTRACT

Thermo-catalytic conversion and ammonization (TCC-A) is a novel and promising thermochemical conversion process for the direct production of N-heterocycles under NH₃ atmosphere, which is similar to the pyrolysis technology through introducing exogenous nitrogen. Since NH₃ served as the carrier gas and reactant, it played an important part in the process. The introduction of N₂ into NH₃ significantly enhanced the indoles production and catalyst stability in the TCC-A process of bio-derived furans. Under the optimized TCC-A conditions of furfural, NH₃ being diluted by 25% N₂ at 600 °C with WHSV as 1.5 h⁻¹ and gas flow rate at 40 ml/min, the carbon yields of N-containing chemicals and indoles reached 46.51% and 33.04%, respectively, which increased by 90.54% and 203.96% compared with those in pure NH₃. Using furan derivatives as the feedstock, diluted NH₃ also showed positive effect on the production of N-containing chemicals. Functional groups in the furan derivatives strongly affect the product distribution. It was found that the increase of indoles production from furfural was because the generation of 2-furonitrile via the side reaction pathway to form coke was inhibited by the dilution of NH₃. The catalysts were tested via five reaction/regeneration cycles in pure and diluted NH₃ atmosphere and characterized by N₂ adsorption/desorption, XRD, XRF, NH₃-TPD analyses and SEM. Compared in pure NH₃, the catalysts in N₂ diluted NH₃ was more stable, which could be due to the lower degree of dealumination, structure damage, and acid site loss.

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1. Introduction

Lignocellulosic biomass is an important alternative source of carbon that can be used for producing renewable fuels and commodity chemicals [1–4]. The development of energy-efficient processes for biomass conversion is a top priority to face the petroleum shortage and associated environmental issues worldwide [5,6]. Thermo-catalytic conversion and ammonization (TCC-A) is a novel and promising thermochemical conversion for the direct production of N-heterocycles through introducing exogenous NH₃, which is similar to the pyrolysis technology in NH₃ atmosphere [7]. With this method, N-heterocycles including pyrroles, pyridines and indoles can form directly from various lignocellulosic biomass and bio-derived molecules [8–13]. HZSM-5 zeolite was reported to be the best in achieving high conversions

from biomass into N-containing chemicals during TCC-A process, mainly due to its unique structure and acid sites [14,15]. Previously, it has been reported that biomass first thermally decomposes (or pyrolyze) and undergoes rearrangement reactions to form furanic species and other light oxygenated chemicals (glycolaldehyde, hydroxyacetone and aldehydes, etc.) during TCC-A process, which are the intermediates of N-heterocycles. These intermediates are further converted into N-containing chemicals through the acid-catalyzed reactions [7]. The conversion of bio-derived furans over HZSM-5 has been employed as the model reaction for TCC-A of the real biomass in an attempt to elucidate the reaction chemistry. Xu et al. obtained 32% carbon yield of indoles from furan in a lab-scale bench-top continuous flow reactor [8]. However, furan cannot be easily produced in a large quantity from abundant lignocellulosic biomass [16–19]. Furan is industrially produced through either the gas-phase or liquid-phase decarbonylation of bio-derived furfural over supported Pd catalyst [20–22]. Furfural has recently been emphasized as one of the top value-added chemicals derived from biomass, being identified as one of the most promising chemicals

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produced in the lignocellulosic biorefineries [23–26]. Furfural is produced from renewable agricultural sources such as food crop residues and wood wastes [27,28]. The largest producing country of furfural is China (~70% total production capacity) [29]. More than 80 chemicals have been derived directly or indirectly from furfural according to the literature [30], such as furfuryl alcohol, other 5-membered oxygencontaining heterocycles (furan, methylfuran, furfurylamine, furoic acid) and so on [24]. The maximal carbon yield (20.79%) of indoles was achieved via TCC-A of furfural by using HZSM-5 catalyst at 650 °C in our previous study [12]. However, there were still some shortcomings of the bio-derived furans process, especially for furfural, such as low indoles yield, coking, and low catalyst stability.

Previous studies of TCC-A process focused on selecting TCC-A reactor apparatus, optimizing reaction conditions and screening feedstocks with pure NH₃ gas flow [7–12]. The price of pure NH₃ gas is kind of expensive [31]. We found that the introduction of N₂ into NH₃ remarkable increased N-containing chemicals yield and indoles selectivity for TCC-A of furfural. Diluting NH₃ with cheap and inert N₂ will make the TCC-A process more economical. Meanwhile, the carrier gas circulation could also help to reduce the operating cost and realize large-scale industrialization [32,33]. However, besides the non-consumed NH₃, other gas products were produced during the reaction, which made NH₃ diluted. Therefore, it is necessary to investigate the effect of the diluted NH₃ as the carrier gas on the TCC-A process.

In this study, N₂ was mixed with pure NH₃ to get the diluted NH₃ carrier gas and tested for TCC-A of furfural to indoles over HZSM-5. The optimal temperature, diluted NH₃ concentration, weight hourly space velocity (WHSV), residence time and diluted NH₃ flow rate on the production of indoles from furfural were studied systematically. Moreover, different furan derivatives including, furfuryl alcohol (FA), 5-methyl furfural (5-MF) and 5-hydroxymethylfurfural (HMF) on TCC-A process in different atmosphere was also investigated. The effect of N₂ diluted NH₃ on TCC-A pathway of furfural over HZSM-5 was discussed. The effect of diluted NH₃ on the reusability of HZSM-5 was also tested. The catalysts and the ones undergoing five reaction/regeneration cycles in different atmosphere were characterized by N₂ adsorption/desorption, X-ray diffraction (XRD), X-ray fluorescence (XRF), temperature programmed desorption of ammonia (NH₃-TPD) analyses and scanning electron microscope (SEM).

2. Experimental section

2.1. Materials

Furfural (AR), furan (AR), FA (AR), 5-MF (AR), anhydrous ethanol (AR), benzene (AR), toluene (AR), xylene (AR), pyridine (AR), 2-methylpyridine (AR), 3-methylpyridine (AR) and 4-methylpyridine (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Bicyclohexyl (AR), pyrrole (AR), aniline (AR), indole (AR), 2-methylindole (AR), 3-methylindole (AR), 4-methylindole (AR), and 2, 4-dimethylindole (AR) were purchased from Aladin Chemical Reagent Co. Ltd. HMF (AR) was provided by Hefei Leaf Biotech Co. Ltd. NH₃ (≥99.995%), N₂ (99.999%), Ar (99.999%) and standard gases were purchased from Nanjing Special Gases Factory. All chemicals were used without further purification.

A commercial HZSM-5 catalyst from Catalyst Plant of Nankai University (Si/Al = 25) was used in these experiments. The catalyst was calcined at 550 °C (5 °C min⁻¹) for 3 h in a muffle furnace before being pelletized and sieved to 20–40 mesh size.

2.2. Experimental unit and procedure

A lab-scale bench-top continuous flow reactor (Fig. S1) was used for the TCC-A experiments. The quartz tube reactor heated by a furnace with temperature control instrument and a condensation tube bathed in liquid N₂. For TCC-A experiments, the feedstock was directly fed into the reactor by an automatic sampler at a certain speed and purged with different proportions of NH₃ and N₂ at room temperature. Quartz wool was used to support the catalyst particles and prevent solids from exiting the catalyst bed. The products formed in the catalyst bed were swept directly to condenser tube. The condensable liquid product was collected in the condenser tube bathed in liquid N₂. The non-condensable gas product was collected using a gasbag. After the TCC-A experiment, the spent catalyst was regenerated in an air stream (100 ml/min) at 550 °C for 3 h to remove the coke.

2.3. Product analysis and data processing

The liquid product was analyzed by gas chromatography (GC1690, Kexiao, China) with an HP-INNOWAX column (30 m × 0.250 mm × 0.25 μm) and GC-MS (Thermo Trace GC Ultra with a Polaris Q ion trap mass spectrometer) with a TR-35MS capillary column (30 m × 0.25 mm × 25 μm).

Gases were identified by injecting known gases and quantified by injecting known gas mixture volumes via gas chromatograph (GC-SP6890, Shandong Lu-nan Ruihong Chemical Instrument Co., Ltd., Tengzhou, China) using a thermal conductivity detector (TCD) for analysis of H₂, CO, CH₄, and CO₂ separated on TDX-01 column, and a flame ionization detector (FID) for gas hydrocarbons separated on Porapak Q column.

WHSV was calculated by dividing the feedstock mass flow rate by the mass of catalyst present inside the reactor as shown in Formula (1). Yield was calculated based on the amount of carbon present in the product species divided by the amount of carbon present in the feed stocks as shown in Formula (2)–(5). Selectivity was calculated based on the amount of carbon present in all product species of that type in Formula (6).

$$\text{WHSV} = \frac{\text{Mass flow rate of feedstock}}{\text{Mass usage of catalyst in the catalyst bed}} \quad (1)$$

$$\text{Coke yield (C mol\%)} = \frac{\text{Moles of carbon in solid residue}}{\text{Moles of carbon in feedstocks}} \times 100\% \quad (2)$$

$$\text{Gases yield (C mol\%)} = \frac{\text{Moles of carbon in gases}}{\text{Moles of carbon in feedstocks}} \times 100\% \quad (3)$$

$$\begin{aligned} \text{N-containing chemicals yield (C mol\%)} \\ = \frac{\text{Moles of carbon in N-containing chemicals}}{\text{Moles of carbon in feedstocks}} \times 100\% \end{aligned} \quad (4)$$

$$\text{Aromatics yield (C mol\%)} = \frac{\text{Moles of carbon in aromatics}}{\text{Moles of carbon in feedstocks}} \times 100\% \quad (5)$$

$$\begin{aligned} \text{N-containing chemicals selectivity (\%)} \\ = \frac{\text{Moles of carbon in specific N-containing chemicals}}{\text{Total moles of carbon in all the N-containing chemicals}} \times 100\% \end{aligned} \quad (6)$$

2.4. Catalyst characterization

The BET surface area and pore volume of the samples were calculated from N₂ adsorption/desorption isotherms obtained at

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