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An experimental and kinetic modeling study including coke formation for catalytic pyrolysis of furfural

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ABSTRACT

Catalytic conversion of furfural to olefins and aromatics was conducted over ZSM-5 in a fixed-bed reactor. The effects of temperature, weight hourly space velocity and partial pressure on the yield and selectivity of products were investigated and the coked catalysts were characterized. The kinetics of furfural catalytic conversion including catalyst deactivation caused by coke deposition was built. The results showed that the main products of furfural catalytic conversion were aromatics, olefins, furan and coke. High temperature, high partial pressure and low WHSV promoted the formation of olefins and aromatics. The catalytic reaction pathway was speculated to be the decarboxylation of furfural to form furan, with further reactions to form olefins and aromatics. The amount of coke deposited on the catalyst increased with increasing reaction time. The surface area and acidity of catalysts declined as coke formed on the acid sites and blocked the pore channels, which led to the decrease of olefin and aromatic yields. Finally, a kinetic model considering coke deposition had been built based on the above reaction pathway to properly predict the product distribution.

1. Introduction

Owing to the depletion of fossil fuels as well as the increasing environmental threats like global warming and pollution of fog and haze caused by large-scale consumption of fossil fuels, it is imperative to increase the fractions of energy and chemicals supplied by renewable resources [1]. Lignocellulosic biomass is the most abundant renewable resource available for producing liquid fuels and chemicals [2–5]. Catalytic pyrolysis is regarded as one of the most effective technologies to convert solid biomass to high-valued fuels and chemicals directly in one single reactor [6–8]. The significant advantage of this technology is that the vapors derived from biomass pyrolysis undergo oxygen removal through a series of dehydration, decarbonylation and decarboxylation reactions by entering the pore of a catalyst in one reactor [9,10].

Catalyst plays an essential role in biomass catalytic pyrolysis. Many studies used ZSM-5 (zeolites, silica–alumina and molecular sieves) for catalytic conversion of different kinds of biomass and its derivatives, and ZSM-5 has been proved to be one of the most effective catalysts to produce aromatics and olefins because of its active sites and shape selectivity [11–14]. However, catalyst addition brings coke deposition, which results in rapid deactivation of the catalyst and the reduction of olefin and aromatic yields. Many researchers have focused on modification of ZSM-5 zeolite to decrease the coke yield and improve the hydrocarbon yield [15–19]. Gayubo et al. [20] found that furan compounds are strongly related to coke formation during the catalytic upgrading of biomass derivatives. Cheng et al. [21] investigated the conversion of furan over HZSM-5 and identified the influence of reaction conditions on the selectivity of olefins and aromatics. Graphite-type coke was found to be formed on the catalyst which caused its rapid deactivation with time on stream. Shao et al. [22] studied catalytic conversion of biomass derivatives with different structures and found furan produced the highest coke yield, which was more than 15%. Foster et al. [23] investigated the conversion of glucose, furan and maple wood over different types of ZSM-5, and obtained the maximum aromatic yield from glucose. Thus, the investigations for the reaction chemistry and mechanism of coking deactivation will help to find an efficient method to prevent coke deposition and enhance hydrocarbon yield.

Many papers about kinetic models of biomass pyrolysis have been published in recent years [24]. Lu et al. [25] proposed a model assuming that biomass first decomposes to gaseous product, tar and char via three competitive reactions and then tar go through a second cracking reaction to produce gas and char. It is acknowledged that coke deposition has a great influence on

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Table 1
Chemical composition of the catalyst.

Composition	Al_2O_3	SiO_2	Na_2O	K_2O	CaO	ZnO	Fe_2O_3	P_2O_5	TiO_2
Percent (%)	25.3	58.9	0	0.1	0.12	0.05	0.15	1.36	0.091

product distribution, and kinetic model must consider the effect of catalyst deactivation caused by coke [26–28]. Chen et al. [29,30] built a kinetic model including the deactivation by coke deposition. This model could be used to simulate the changes of olefin selectivity in methanol to olefins with SAPO-34 catalyst. Gayubo et al. [31] established a kinetic model for the transformation of bioethanol into hydrocarbons and it is suitable for quantifying product distribution. Froment et al. [32] proposed a deactivation function which combined catalyst activity with coke content in the coking kinetic model. The deactivation function mainly used in steam reforming of natural gas, ethylbenzene-to-styrene, catalytic cracking of heavy oil fractions, methanol-to-olefins and solid acid alkylation. However, the coking problem of biomass pyrolysis vapors is much more severe. The deactivation rate of catalyst in biomass catalytic pyrolysis is more than 10 times of that in methanol-to-olefins process [33]. The exciting models can not predict the product distribution exactly. New models need to be built for heave coking process in catalytic fast pyrolysis of biomass.

Lignocellulosic biomass is a complex natural material, and the complexity of the feedstocks limits the mechanism of catalytic reaction studies. Model compounds are useful to understand the complicated catalytic chemistry [34,35]. Cellulose and hemicellulose are two main components of biomass (60–70% by weight) [36]. The pyrolysis of cellulose first converts to sugars and then to furan compounds via dehydrogenation reaction, while hemicellulose directly produces furan compounds. Thus, furan compounds are major intermediates for catalytic pyrolysis of cellulose and hemicellulose, and furfural is the main component of furans [37,38]. In order to understand the reaction mechanism in depth, furfural is chosen as the model compound to study the coking kinetics of biomass catalytic pyrolysis in this study.

In this work, catalytic conversion characteristics of furfural to olefins and aromatics was investigated systematically, including reaction conditions, reaction chemistry, mechanism of catalyst deactivation and kinetic model of coke deposition. The effects of reaction conditions (reaction time, catalytic temperature, weight hourly space velocity and furfural partial pressure) on the carbon yield and selectivity of products were studied using a fixed bed reactor. A possible pathway of furfural catalytic conversion was proposed according to the experiments. To understand the mechanism of coke deposition on the catalyst, various techniques were used to characterize the fresh and spent catalysts at different reaction times. A kinetic model including the deactivation caused by coke deposition was developed.

2. Materials and methods

2.1. Materials

Furfural (AR, 99.0%, Aladdin Company, PR China) was used as the feedstock. ZSM-5 catalyst with SiO_2/Al_2O_3 molar ratio of 38 (The Catalyst Plant of Nankai University, PR China) was used in this study. The chemical composition of the catalyst was shown in Table 1. ZSM-5 catalyst was sieved to 80–100 mesh and calcined in the reactor at 600 °C with 100 mL/min oxygen flow for 6 h prior to all experiments.

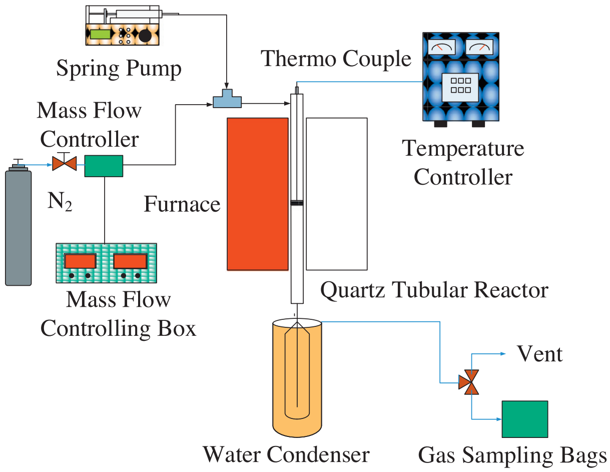

Fig. 1. The schematic diagram of the fixed bed for catalytic conversion of biomass derivates.

2.2. Catalytic conversion experiments

The catalytic conversion of furfural was conducted in a fixed bed shown in Fig. 1. The system includes quartz reactor, spring pump, ice bath cooling trap, mass flow controller and temperature controller. Sieved catalysts were held on the quartz bed. Furfural was injected into the reactor by a spring pump, then vaporized and flew across the catalyst bed by the carrier gas (N_2). The condensed liquids were trapped to be analyzed by GC/MS (Agilent, 7890A-5975C). The gas products were collected in the gas sampling bags and analyzed by GC-FID/TCD (Shimadzu 2014). After reaction, the reactor was flushed with nitrogen of 100 mL/min for 30 min at the reaction temperature. When the reactor was cooled to room temperature, the coked catalysts were taken out for different analyses. The furfural catalytic conversion was performed at the following operating conditions: temperature, between 400 and 650 °C; WHSV, ranging from 4 to 10.7 h^{-1}; furfural partial pressure, ranging from 0.98 to 3.12 kPa. The heating rate of furfural was between 480–1200 °C/s. The feeding rate of furfural was 1 g/h. Most of runs were conducted for 10 min, which means 167 mg furfural was fed to the reactor. For 45 min of coke testing run, the total amount of furfural fed to the reactor was 750 mg.

2.3. Characterizations

To understand the coking behavior of the catalyst, various characterization techniques were applied. Coke amount of the catalyst was analyzed by measuring the weight loss of deactivated catalyst using a thermogravimetric (TG) analyzer. The coked catalysts were heated from room temperature to 900 °C at a heating rate of 20 °C/min in an air stream. X-ray diffraction (XRD) analysis was recorded on a Rigaku Ultima IV diffractometer (Japan) with Cu KR radiation. Scans were taken at 5–40° 2θ range with a scanning rate of 5°/min. The surface areas and pore volumes of the catalyst were measured on a V-Sorb 2800P instrument (Gold APP Instruments, China) using nitrogen adsorption at 77 K. Ammonia temperature programmed desorption (NH_3-TPD) was applied to study the effect of coke deposition on catalyst acidity. The sample (50 mg) was