

Kinetics of n-butanol oxidation over Pt/ZSM-5 catalyst

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ABSTRACT

A kinetic study of n-butanol catalytic combustion over the Pt/ZSM-5 was performed in a fixed-bed combustor at ambient pressure and temperature range in 390–470 K. The Power Law model and Langmuir-Hinshelwood (L-H) model were constructed to characterize the n-butanol catalytic oxidation. The reaction orders of n-butanol and O₂ were −0.24 and 1, respectively. Five pathways rate expressions were selected to predict the reaction rate for L-H model. The sum of the squared differences between the experimental data and the fitted data indicated that surface reaction and oxygen adsorption were probably rate-determining steps. The reliability of the rate expressions was affirmed by comparing the experimental and the fitted rates.

1. Introduction

N-butanol is one of new renewable biofuels synthesized from biomass with many advantages such as high energy density, high calorific value, low ignition temperature, weak water absorption and low volatility [1–3]. Recently, n-butanol is considered as a very competitive alternative fuel for using in internal combustion engines, and it has attracted special attention of many scholars [4–8]. Pyrolysis, oxidation and combustion of n-butanol have been extensively studied in the fields of engine, shock tube, premixed flame and diffusion flame [9–15]. The combustion efficiency of n-butanol is a key problem for the future application, and catalytic combustion is usually carried out to realize fast low temperature ignition and enhance the combustion efficiency [16]. Consequently, catalytic oxidation of n-butanol has been investigated thoroughly.

Many catalysts such as iron oxide [17], Rh/Al₂O₃ [18], clay [19], Pt [20–22] and so on, have been found to promote the catalytic combustion of n-butanol effectively. Supported platinum is seem to be the most effective catalyst for the oxidation of alcohol fuel among these catalysts [23]. The total oxidation of n-butanol on Pt/-Al₂O₃ catalyst was observed by Yang et al. at only 373–593 K [21]. Pt/zeolites is another supported platinum catalyst that promotes the combustion of hydrocarbons substantially compared to Pt/Al₂O₃ according to the research [24–26]. Therefore, Pt/ZSM-5 is a well-performed catalyst for butanol combustion.

Although the above studies have achieved certain results in improving the combustion efficiency, the catalytic reaction mechanism is still need for further research. To well understand the reaction kinetics of the n-butanol catalytic combustion and predict the reaction rate

accurately, a kinetic study of butanol catalytic combustion over the Pt/ZSM-5 was investigated from 390 K to 470 K.

2. Experimental

2.1. Catalyst preparation and characterization

The Pt/ZSM-5 catalyst was prepared by the impregnation method and the loading of Pt was 5 wt%. ZSM-5 zeolite (Nankai University Catalyst Plant, China) was ground into powder, which was washed by deionized water and dried to obtain ZSM-5 powder (2–5 μm). Then the powder was impregnated into the aqueous solution of chloroplatinic acid with Pt concentration of 0.018 g/ml, stirred with a magnetic stirrer, dried at 363 K for completed evaporation and then weighed. The weight increase of the sample indicated the loading of Pt was 5 wt%. At last, the sample was reduced in the mixture gas of 4% hydrogen and 96% nitrogen at 773 K for 3 h.

Catalyst particles were characterized by transmission electron microscopy (TEM) images and X-ray photoelectron spectra (XPS). The detailed methods were described in Ref. [27]. The mean diameter of Pt particle was 3.96 ± 1.08 nm based on the statistical data from TEM images. XPS measurement indicated the ratios of Pt⁰, Pt²⁺ and Pt⁴⁺ were 31.66%, 60.84% and 7.5%, respectively. Similar Pt/ZSM-5 catalyst was proved efficient and stable [27].

2.2. Experimental setup

The combustion experiment was performed in a quartz packed bed reactor (inner diameter = 4 mm, Fig. 1) at atmospheric pressure.

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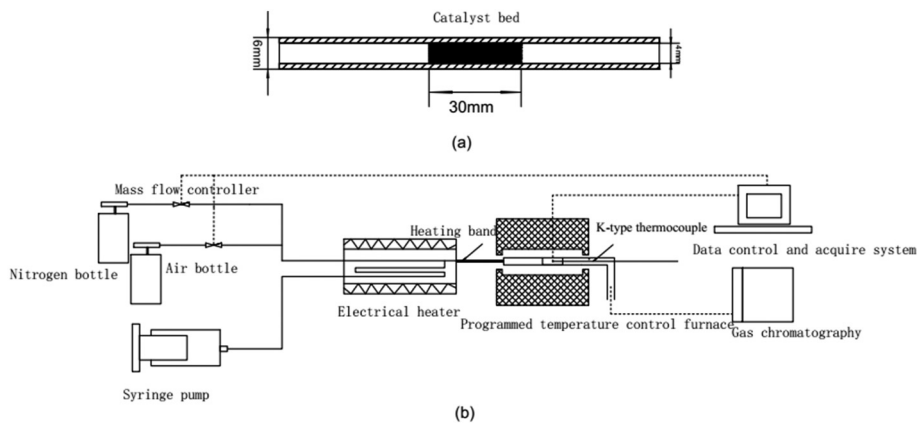


Fig. 1. Schematic of (a) the combustor and (b) the experiment system.

0.060 g catalysts were diluted with 0.060 g quartz particles to prevent temperature gradient. Previous experiments showed the temperature difference in the bed was less than 2 K. For the particle size of 2–5 μm , the effect of internal mass-transfer retardation is usually ignored according to Weisz-Prater criterion and the literature [28, 29]. Air and N_2 flow were controlled by the gas mass flow meters (CS200, China) with accuracies of $\pm 0.8\%$. The flow rate of n-butanol was determined by the syringe pump (LSP01-1BH, Longer pump), whose accuracy is 1.785 $\mu\text{l}/\text{min}$. The pipes from the electrical heater exit to the combustor inlet were wrapped with the heating band to ensure the complete gasification of n-butanol and preheat the mixture of air and n-butanol. The combustor was heated by a programmed temperature-controlling furnace at a heating-up rate of 2 K/min. K-type thermocouple (inner diameter = 50 μm) was fixed into the middle of catalyst bed to acquire the temperature of the catalyst. The exhaust gas was detected by a gas chromatography (Agilent 7890B, USA) with the measurement accuracy of $\pm 2\%$.

N-butanol, air (21% O_2 and 79% N_2) and N_2 were introduced to the combustor and their concentrations were presented in Table 1. The total flow rate was 160 ml/min (GHSV = 25,465 h^{-1}). The calculated linear velocity of the gas flow exceeds 0.2 m/s (exactly 0.212 m/s). According to the literature [30], it has been assumed that under such conditions the external diffusion doesn't influence the total process rate of the heterogenous catalytic reaction.

No partial oxidation products were detected except CH_4 , whose yield was 0–0.1% vol. Since CH_4 was not the objective product and its yield was low, the conversion of n-butanol was defined as the ratio of n-butanol converted to CO_2 only. The conversion of n-butanol was calculated by Eq. 1. The conversions were kept below 10% to guarantee the reaction rates were kinetically controlled [26, 31].

Table 1
n-Butanol conversion at different cases.

Conditions	$f_{n\text{-butanol}}(\text{ml}/\text{min})$	$f_{\text{air}}(\text{ml}/\text{min})$	$f_{\text{N}_2}(\text{ml}/\text{min})$	Φ^1	X(%)				
					393 K	398 K	403 K	408 K	413 K
Case 1	1.58	158.48	0	0.3	1.4	2.84	4.18	4.66	5.69
Case 2	1.58	118.83	39.59	0.4	1.12	1.67	2.89	3.62	4.99
Case 3	1.58	95.08	63.34	0.5	1	1.35	2.21	3.16	4.19
Case 4	1.58	79.09	79.32	0.6	0.77	1.18	1.84	2.75	3.76
Case 5	1.58	67.79	90.63	0.7	0.67	1.04	1.47	2.12	3.24
Case 6	1.98	118.83	39.19	0.5	0.88	1.26	2.25	2.62	3.42
Case 7	2.38	118.83	38.76	0.6	0.7	1.02	1.80	2.16	2.72
Case 8	2.77	118.83	38.38	0.7	0.59	0.84	1.47	1.81	2.22
Case 9	3.17	118.83	38.01	0.8	0.5	0.67	1.26	1.53	1.89

¹ Equivalence ratio, $\Phi = \frac{f_{n\text{-butanol}} / f_{\text{O}_2}}{(f_{n\text{-butanol}} / f_{\text{O}_2})_{\text{stoichiometric}}}$.

$$X_{n\text{-butanol}} = \frac{n_{\text{CO}_2, \text{out}}}{4n_{n\text{-butanol}, \text{in}}} \times 100\% \quad (1)$$

where $n_{\text{CO}_2, \text{out}}$ and $n_{n\text{-butanol}, \text{in}}$ are the outlet molarity of CO_2 and the inlet molarity of n-butanol, respectively.

According to the study [26, 31], the reaction rate ($-r$) can be expressed as Eq. (2):

$$-r = \frac{n_{n\text{-butanol}, \text{in}} X_{n\text{-butanol}}}{m_{\text{pt}}} \quad (2)$$

where m_{pt} is the weight of catalyst.

3. Results and discussions

3.1. Experimental results

Table 1 shows the conversions of n-butanol on Pt/ZSM-5 catalyst. Case 1–5 were used to study the effect of O_2 partial pressure on the reaction rate. Case 6–9 and Case 2 were used to study the effect of n-butanol partial pressure on the reaction rate. The fitting of the kinetics models in this paper were based on the experimental results in Table 1.

3.2. Power law model

The Power Law (P-L) model expression is universally applied to determine the reaction orders of the reactants, as shown in Eq. (3).

$$-r = k P_{n\text{-butanol}}^m P_{\text{O}_2}^n \quad (3)$$

where $P_{n\text{-butanol}}$ and P_{O_2} are the partial pressures of n-butanol and O_2 ; m and n are the reaction orders; k is the kinetic constant.

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