Fuel 150 (2015) 339–346

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Catalytic combustion of methane, methanol, and ethanol in microscale combustors with Pt/ZSM-5 packed beds

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ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 3 February 2015
Accepted 5 February 2015
Available online 20 February 2015

Keywords:
Micro combustion
Catalyst
Alcohols
Combustion stability
Combustion efficiency

ABSTRACT

Experiments on combustion of methane, methanol, and ethanol in packed bed combustors were performed with the ZSM-5 zeolite supported nanometer-sized Pt as the catalyst. Methane combustion was investigated in the combustors in which the lengths of catalyst beds were 40, 20, and 10 mm, respectively. The stabilization and conversion rate of methane combustion were both the highest in the combustor with a 20-mm-sized catalyst bed, thus this combustor was chosen to implement the comparative studies on combustion of methanol and ethanol. Methanol showed a wider equivalence ratio (Φ) range of stable combustion, lower conversion rates, higher CO_2 selectivity and higher energy release efficiencies compared to ethanol. As Φ increased from 0.8 to 1.4, the relative conversion rate of methanol increased whereas that of ethanol decreased. The mechanism of the combustion characteristics was interpreted from the aspects of fuel feature, adsorption on active sites and chemical reactions.

1. Introduction

Microscale combustion has attracted increasing attention owing to its potential utilization as an efficient and reusable energy supply system for portable electronic–mechanical devices. Fuels discussed in microscale combustors are usually produced in renewable routes [1,2]. Methane, methanol and ethanol can be easily obtained from biomass in industry-scale, which are considered as sustainable alternatives for fossil fuels. They are widely used owing to the convenient storage and transportation, satisfactory combustion performance and high heat value. However, the application of methane and alcohols in microscale combustors are still challenged by their instability and low energy conversion efficiency [3].

Catalysis is an effective way to enhance the combustion. Investigations have been performed to reveal the effects of combustor fabrications, operating conditions and catalyst or support type on combustion characteristics [4–12]. It was demonstrated that methanol–air could self-ignite at room temperature with catalyst of platinum nanoparticles [13]. The high surface energy of nanometer-sized catalysts contributed to their high catalyst activity [14–16]. Most reports on micro combustion of methanol and ethanol were focused on the integrated reforming process including a catalytic combustor [17–20]. The direct combustion of methanol and ethanol in catalytic combustors were less investigated [21–25]. Applegate et al. [23] performed methanol combustion in a catalyst reactor with square channels (0.85 mm × 0.05 mm). The impact factors on catalyst activity were investigated, but the estimated conversion efficiency was relative low. Yuan et al. [26] proved that a higher catalyst loading increased the methanol conversion rate. Leu et al. [27] performed comparative experiments of methanol combustion in packed bed and micro channel bed combustors. They evaluated the performances of combustors with different catalysts, but the efficiencies in the packed bed combustor were not analyzed in detail.

Catalytic micro combustion in packed bed is theoretically suitable for methane and alcohols. The characteristic size and external heat exchange surface of the packed bed combustor are smaller than those of micro channel combustor when the cross area and volume are the same. This means the combustion heat can be concentrated and surface heat loss can be inhibited in the packed bed combustor. In addition, the structure and fabrication of packed bed combustor are simpler. Therefore, the direct combustion of natural gas or alcohols in packed bed combustors is of great importance to the simplification of micro power supply device. In this paper, catalytic combustion of methane, methanol, and ethanol in packed bed combustors was conducted to investigate the effects of main factors (e.g., flow rate, equivalence ratio, length of the catalyst bed, and fuel properties) on combustion characteristics.

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http://dx.doi.org/10.1016/j.fuel.2015.02.018
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Nomenclature

Φ	the equivalence ratio, $(m_{H2}/m_{Air})/(m_{H2}/m_{Air})_{stoi}$
Φ_{lean}	the equivalence ratio limit of the fuel-lean stable combustion;
Φ_{rich}	the equivalence ratio limit of the fuel-rich stable combustion
f_{in}	the inlet flow rate of the mixture, ml/min
Q_{surf}	the release rate of the heat transferred to the ambience through the combustor surface, W
X_{fuel}	the conversion rate of the fuel—the proportion of the actually-reacted fuel to the total inputted fuel
$X_{R\text{-}fuel}$	the relative conversion rate of the fuel—the proportion of the actually-reacted fuel to the fuel that could be completely oxidized theoretically
ρ	density, kg/m^3
c_p	specific heat at constant pressure, kJ/(mol K)
HHV	high heating value of the fuel, kJ/mol
$(V_{air}/V_{fuel})_{stoi}$	volume basis stoichiometric air/fuel ratio
ΔH_{vap}	heat of vaporization, kJ/mol
T_{ig}	ignition temperature, °C
k	the reaction rate constant
$[O]_0$, $[fuel]_0$	the initial species concentration on the catalyst
α, β	reaction orders
m_{cata}	mass of the catalyst;
τ_{Pt}	mass fraction of Pt
$\overline{ds}$	the average surface diameter of Pt
$Y_{CO2\text{-}fuel}$	the selectivity of CO_2—the proportion of the fuel converted to CO_2 to the total reacted fuel
Q_{gen}	the total release rate of the combustion heat and the preheating heat, W
Q_{ex}	the enthalpy of the exhaust gas, W
Q_{in}	the input power through the fuel, W

2. Experimental

2.1. Catalyst preparation

Chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) was used as a precursor. ZSM-5 zeolite (Nankai University Catalyst Plant, China) and Al_2O_3 (Sinopharm Chemical Reagent, China) were the alternative supports. The zeolite and Al_2O_3 (both 200–300 mesh in diameter) were processed in the same method. Granules were washed with deionized water and dried in oven at 105 °C for 24 h. Then the granules of a certain weight were impregnated into the aqueous solution of chloroplatinic acid with Pt concentration of 0.018 g/ml. The catalyst slurry was dried at 90 °C for completely evaporation and then weighed. The weight increase of the sample indicated the load density of Pt was 23.8 wt.%. At last, the supported Pt samples were calcinated and reduced in the mixture gas of 4% hydrogen and 96% nitrogen at 500 °C for 3 h.

The BET results in Table 1 showed the surface changes of ZSM-5 zeolite and Al_2O_3 after loading Pt. ZSM-5 zeolite had about three times higher pore surface than Al_2O_3 before the loading. Marked reductions of the surface area and mesopore volume appeared on zeolite after the loading process. Pores with diameters greater than 2 nm almost disappeared on zeolite after the loading. The phenomenon could be reasonably attributed to the presence of Pt particles in zeolite pores. No notable surface changes on Al_2O_3 occurred after the loading. TEM images graphed with an acceleration voltage of 200 kV (2100F, JEOL, Japan) clearly showed the distribution patterns of Pt on the supports, as displayed in Fig. 1. The light grey bases represented the supports and the black spots represented Pt. Pt particles, whose diameters were about 5–10 nm, were distributed on the ZSM-5 zeolite uniformly. But Pt attached to the surface of Al_2O_3 with more agglomerations. Hence the ZSM-5 zeolite supported Pt was chosen as the combustion catalyst.

Table 1
BET results of the two supports.

Support material	Pore surface (m^2/g)		Pore volume (ml/g)		Main pore size (nm)	
	Before loading	After loading	Before loading	After loading	Before loading	After loading
ZSM-5 zeolite	483	79.91	0.285	0.095	2 and 5	<2
Al_2O_3	151	123	0.196	0.176	3–4	3–4.5

2.2. Experimental apparatus and method

Three quartz tubes filled with packed catalyst beds were used as the combustors, as displayed in Fig. 2(a). Their configurations were the same except for the length of the catalyst beds. The inner diameter and the length of each tube were 4 and 68 mm, respectively. The self-sealed packed beds, each containing 40 mg catalyst particles, were fixed into the tube with their heads positioned 20 mm away from the inlet. The cylindrical packed beds, whose frameworks were made up of stainless steel screen (400 mesh), had the same diameter of 4 mm. Considering the effective length of the combustor (60 mm) and the minimum volume of 40 mg catalyst, the bed length of 40, 20 and 10 mm were selected in our experiment. The combustors in which the lengths of the catalyst beds were 40, 20, and 10 mm were denoted as combustor A, B, and C, respectively. The catalyst density was defined as the mass of Pt per unit distribution volume. The catalyst densities in combustor A, B, and C were calculated as 0.017, 0.038 and 0.076 mg/m^3. Fresh catalyst was used for each combustion test. Since the catalyst usually remains active in the first few hours [28–31], the catalyst deactivation can be neglected in our experiments because each test lasted less than one hour.

An overview of the experimental setup was given in Fig. 2(b). Mass flow controllers (CS200, China) with the full-scale measurement accuracy of ±1%, were applied to control the flow rate of air (21% O_2, 79% N_2) and methane. A syringe pump (LSP01-1BH, Longer pump, China), whose accuracy was 1.785 μl/min, was used to control the flow rate of the liquid fuels. Air and the fuels were preheated separately in an electrical heater to 150 °C (higher enough for the complete evaporation of the fuels) before they were mixed and fed into the combustor in gas phase. The pipes from the electrical heater exit to the combustor inlet were wrapped up in the heating band to maintain the temperature of the gas mixture at 150 °C at the combustor inlet. K-type thermocouples were fixed at the inlet and outlet of the combustor to acquire the mixture temperature. An infrared camera (ThermaCam S65, FLIR, USA) was applied to acquire the temperature distribution on the combustor surface. The range of 0–500 °C was selected and the measurement accuracy of temperature was ±2%.

Hydrogen flame was used to preheat the combustor wall to 500 °C before the fuel was inputted. The hot wall ignited the mixture gas after feeding fuel. All the measurements were not carried out until the combustion was steady so that the influences of ignition process could be neglected. The combustion was considered to be steady when the temperature fluctuations of the wall and the