

Low Pressure Catalytic Combustion of Hydrogen on Palladium

Xi Wang¹, Yixiang Shi^{1*}, Ningsheng Cai¹, Xiaocheng Lv², Wei Yao²

¹Key laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing, China

²China Academy of Space Technology, Zhongguancun Nandajie, Beijing, China

Email: *shyx@tsinghua.edu.cn

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Abstract

Exhausts of airship fabric bag in the stratosphere such as hydrogen which can be used for fuels by using catalytic combustion method. This can save the extra fuels used in the power system. Pd/ γ -Al₂O₃ catalyst was prepared in this work by impregnation method and the H₂ catalytic combustion reaction kinetic was investigated between the pressure of 3.6 kPa and 101.3 kPa. The effects of temperature, pressure and gas composition ratio were studied in the paper. According to the experiment results, the increase of temperature increases the H₂ conversion. The parameter pressure has a positive effect on H₂ reaction kinetics and low concentration of H₂ in mixtures shows better performance. The dependence of temperature on H₂ reaction rate becomes more sensitive in high pressure.

Keywords

Airship, Hydrogen, Catalytic Combustion, Impregnation, Reaction Kinetic

1. Introduction

The airship fabric bag emissions of dilute hydrogen can be used in the power generation system by low temperature catalytic combustion technology. Due to the low pressure in the stratosphere, the application of catalytic combustion in stratospheric airship power generation system provides the advantages of low ignition temperature at lean combustion conditions, low pollution emissions, high combustion efficiency and stability [1]-[6] when compared with conventional combustion technology. Exothermic energy obtained from hydrogen catalytic combustion reaction can be provided to the power generation system as heat source which avoids carrying additional fuels into the stratosphere.

For the catalysts of the low temperature catalytic combustion of hydrogen, noble metal catalysts such as palladium and platinum have attracted large attention because of their high catalytic combustion activity and relative simple preparation method [7] [8]. Depending on the catalysts, different wash coats are adopted such as Al₂O₃, CeO₂ *et al.* The wash coats should have large specific surface area and high thermal stability [9] [10] to

*Corresponding author.

improve the dispersy of the active component and activity of the reactants.

While in the stratosphere the pressure is between 5.5 kPa and 1.2 kPa [11], the H_2 reaction kinetics in low pressure and atmospheric pressure are differed from each other. Consequently, it is important to find out the difference between each other. This study focused on experiment studies of low pressure hydrogen catalytic combustion on $Pd/\gamma-Al_2O_3$ catalyst with the tested pressure varying from 3.6 kPa to 101.3 kPa. In the experimental part, a fixed bed reactor experiment set-up was used, in which different pressures were tested between the reaction temperature of 100°C and 150°C. Additionally, different ratios of the fuel to oxidizer were applied to investigate the effect of H_2 concentration on the reaction kinetics.

2. Experiment

2.1. Experiment Set up

In the present work, the sketch of the fixed bed quartz reactor set-up is shown in **Figure 1**. The reactor is made up of quartz glass tube that has a diameter of 1.1 cm. Catalysts are filled into the tray in the middle of the reactor and thermocouple is attached to it to test the temperature. The furnace is used for ignition of the reaction if needed. All relevant products in the outlet are detected by mass spectroscopy (MS) measurement device. When the experiments are operated below the atmospheric pressure, the vacuum pump is used to make sure a low pressure atmosphere in the reactor. And the vacuum regulating valve is used to adjust the pressure to the testing pressure in the reactor.

2.2. Catalyst Preparation and Characterization

The $\gamma-Al_2O_3$ supported Pd catalyst was prepared by impregnation method. The substrate is alumina spherical grain that has a diameter of about 1 mm. Pd was incorporated in the substrate by impregnation from $Pd(NO_3)_2$

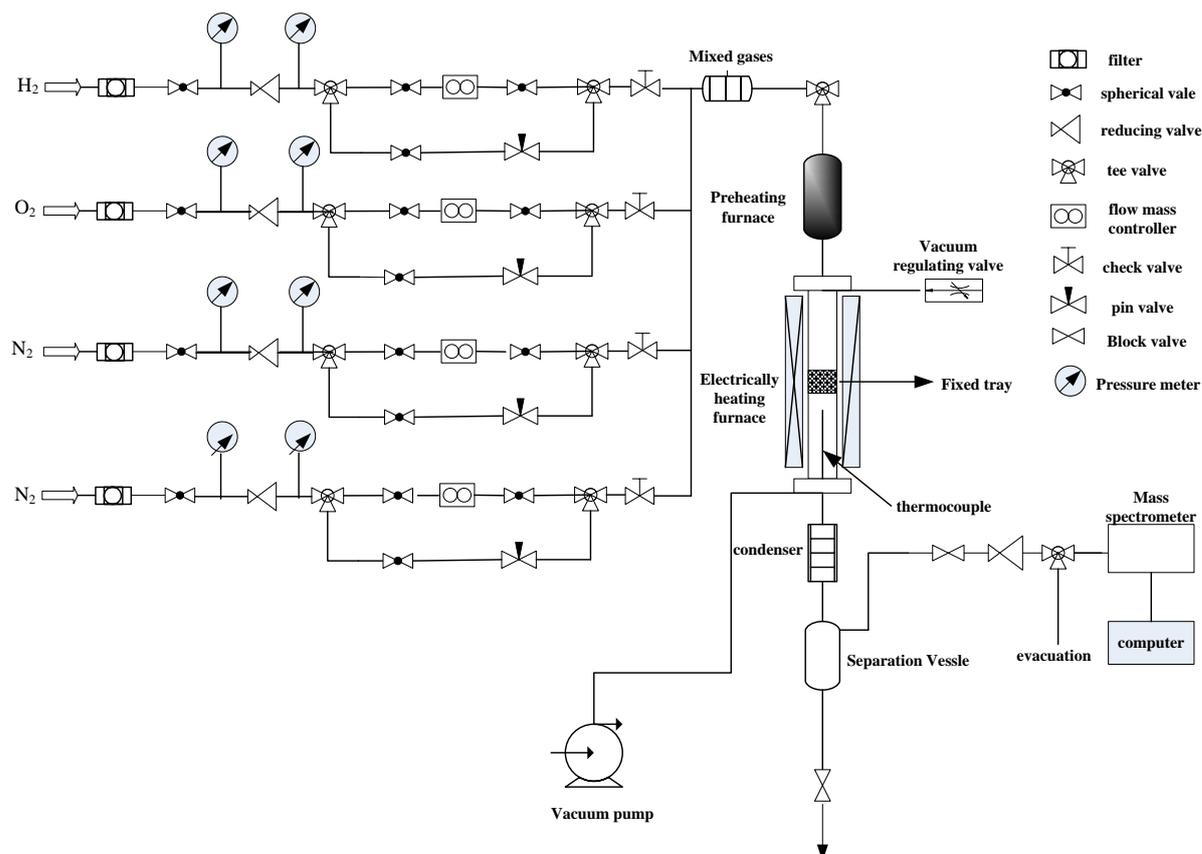


Figure 1. Schematic diagram of fixed bed reactor.

aqueous solution. The catalyst was heated by oil bath at 120°C for 2 h and dried at 120°C for 30 min. Subsequently it was calcined at 500°C for 10 h. The mass percent of Pd is 3.9wt%.

Specific surface area of the substrate was measured by the adsorption of N₂ using the Micromeritics ASAP-2000 specific surface area analyzer. According to the result, the specific surface area was 280.5 m²·g⁻¹ and it is large enough to be the catalyst supporter.

The prepared catalyst was characterized by powder X-ray diffraction (XRD), scans were performed over a 2 θ range from 10° to 90°. The materials are shown in **Figure 2**, indicating that the active catalyst phase is PdO. In the characterization, the diffraction peak of PdO exists in the diffraction angle of 35°, 55°, 60°. According to the microstructure characterization shown in **Figure 3**, the small PdO particles are distributed well on the surface of Al₂O₃ support and the aggregation of the PdO particles is not obvious. The EDS analysis in point 1 is shown in **Table 1** and the weight ratio of Al to Pd is close to 1.

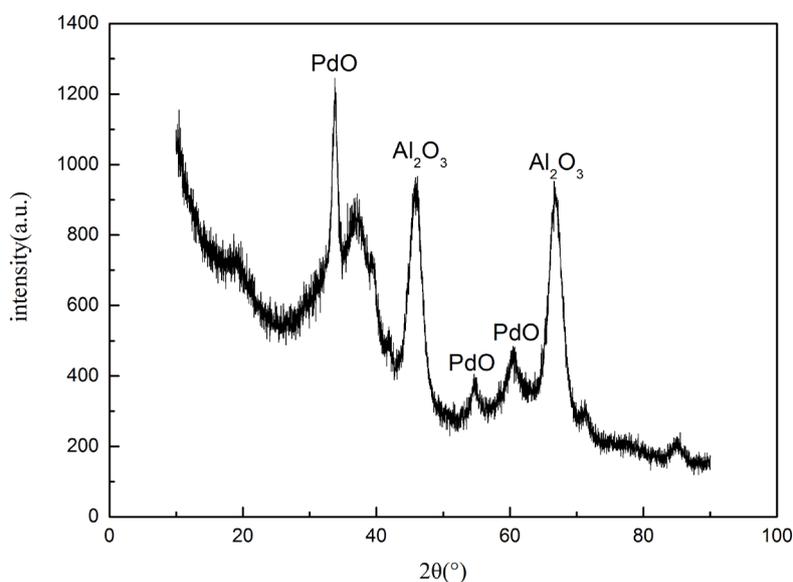


Figure 2. XRD of catalyst before testing.

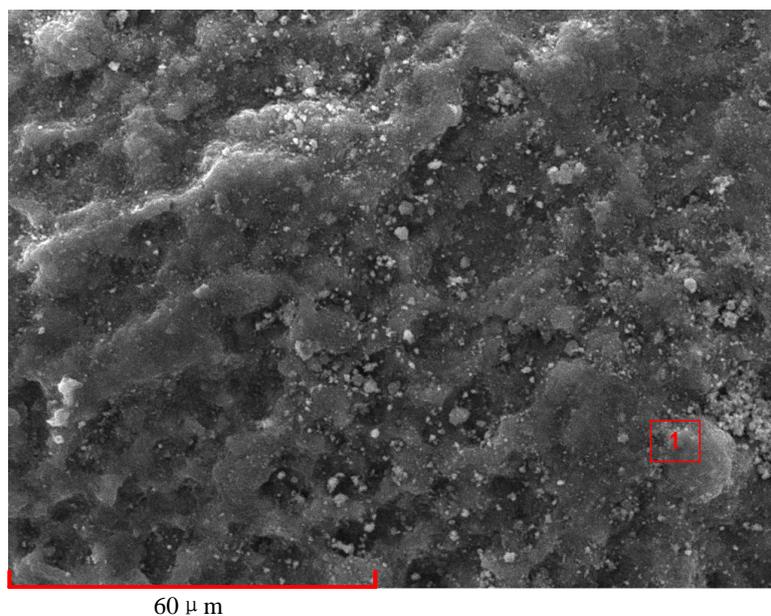


Figure 3. SEM image of Pd/ γ -Al₂O₃ catalyst before testing.

2.3. Measurement Conditions

To investigate the catalytic activity of H_2 on Pd/Al_2O_3 in atmospheric pressure and the vacuum pressure, a series of experiments were carried out at different operation conditions such as total reaction pressure, H_2/O_2 equivalence ratio, temperature. The hydrogen and oxygen mixtures were diluted by nitrogen at total flow rate of 0.056 standard liter per minute (slpm). The furnace was used to ignite the reaction by heating up the reactor until light off occurs. The mass of the catalyst was 0.02 g. In addition, more Al_2O_3 sphere particles without impregnating active component Pd were filled in the reactor.

3. Results and Discussion

3.1. Effect of Total Reaction Pressure on the Catalytic Combustion Performance

Reaction pressure is an important parameter of H_2 catalytic combustion reaction kinetics. In this paper three different pressures were adopted to study the influence of pressure on catalytic activity. Experiment operating conditions are listed in **Table 2**. The molar ratio of H_2 to O_2 is 0.6 which means equivalence ratio is 0.3. As can be observed in **Figure 4**, results show that the conversion of H_2 increases with increasing pressure. The slow decrease of conversion is seen from atmospheric pressure of 101.3 kPa to low pressure 3.6 kPa indicating that pressure has a gentle influence on H_2 conversion performance. At 125 °C, the conversions are 0.58 and 0.56 respectively. Though pressure decreases by 1/28 of atmospheric pressure, the conversion has decreased by 2% displayed by experiment results. This phenomena is similar to the experimental results conducted by Michael [12]. In the experiments, the reaction rate of methane catalytic combustion on Pt/Al_2O_3 catalyst increases with increasing pressure above atmospheric pressure. The study of the effect of pressure on H_2 conversion performance indicates that H_2 catalytic combustion in low pressure environment conditions is available and can achieve good performance as in atmospheric pressure.

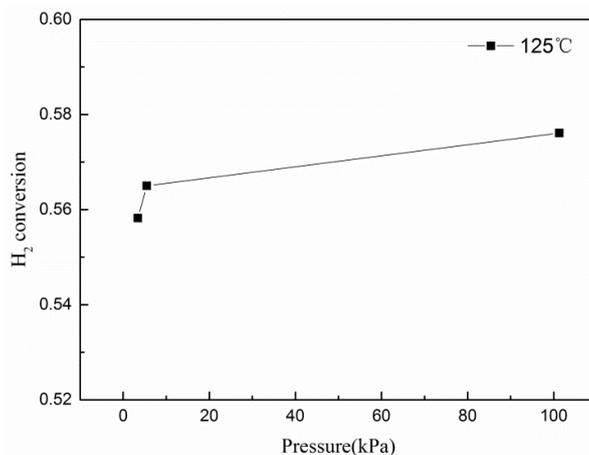


Figure 4. H_2 conversion in different pressures at 125 °C.

Table 1. The element contents in point 1.

Element	Weight ratio (%)	Atom ratio (%)
O	23.63	45.36
Al	38.38	43.68
Pd	37.99	10.96

Table 2. Main parameters of experiment study.

Reactants molar ratio	$H_2:O_2:N_2 = 0.6:1:4$		
Temperature (°C)	125		
Pressure (kPa)	101.3	5.5	3.6

3.2. Effect of Temperature on the Catalytic Activity

The effect of temperature on the lean burn hydrogen catalytic combustion at the equivalence ratio of 0.3 ($H_2/O_2 = 0.6$) are shown in **Figure 5**. It is observed that at the pressure of 3.6 kPa, hydrogen conversion increases by 5.6% from 100°C to 150°C, while at 5.5 kPa and 101.3 kPa the conversions increase by 6.4% and 6.5% respectively. The parameter temperature has a gentle positive influence on H_2 conversion. Theoretically, high temperature is beneficial for the improvement of H_2 reaction kinetics. Comparing the effects of pressure with temperature, the influence of temperature in improving reaction kinetics is a little larger than pressure.

3.3. Effect of Equivalence Ratio on the Catalytic Activity

The different inlet reactants ratios of H_2 to O_2 were investigated at different pressures on the H_2 catalytic activity. As shown in **Figure 6**, it is found that hydrogen conversion increases with decreasing equivalence ratio which indicates that the increase in the concentration of H_2 lead to the decrease of hydrogen conversion. This may be due to the reason that the diffusion of H_2 on the catalyst surface is inhibited in high H_2 concentration conditions. More active reaction sites are occupied by H_2 molecules through adsorption process. This in turn increases the reaction pathway between H_2 and O_2 molecules that leads to the decrease of H_2 conversion. Therefore, the equivalence ratio of 0.3 ($H_2/O_2 = 0.6$) is the optimal choice in whatever low pressure or atmospheric pressure.

3.4. The Dependence of Temperature on H_2 Reaction Rate at Different Pressures

Figure 7 gives the dependence of temperature on H_2 reaction rate with pressure varying from 3.6 kPa to 101.3 kPa with $H_2/O_2 = 0.6$. The reaction rate r represents the H_2 reaction moles per second. It can be seen that the reaction rate can be enhanced with increasing pressures. The increase of temperature also increases the reaction rate. With the increase of pressure, the improvement of temperature on reaction rate becomes more significant. **Table 3** gives the expressions of H_2 reaction rates in different pressures. Obviously, when the pressure gets higher, the dependence of temperature on H_2 reaction rate becomes larger. In the low pressure region, the reaction rate increases with temperature linearly.

4. Conclusion

The airship fabric bag emissions of dilute hydrogen can be used for fuels in the stratosphere. The $Pd/\gamma-Al_2O_3$ catalyst was prepared by impregnation method. The reaction kinetics of H_2 in atmospheric pressure and low pressure (of 5.5 kPa) were investigated. The parameter of pressure has a little positive effect on H_2 conversion performance with the pressure varying from 3.6 kPa to 101.3 kPa. The increase of temperature leads to the

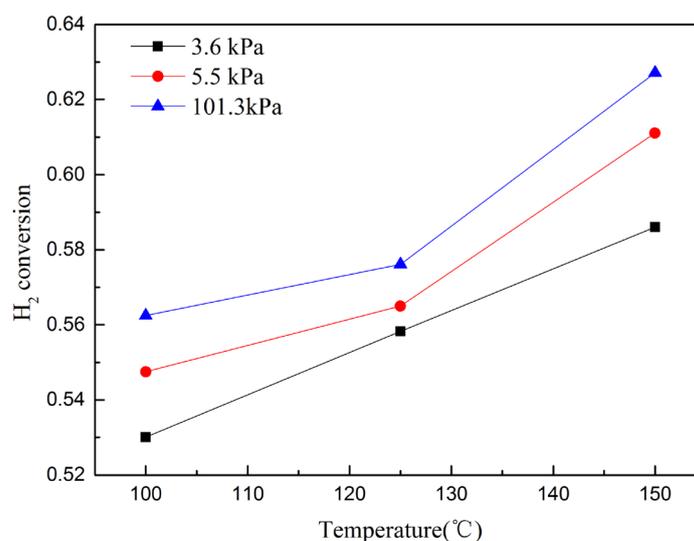


Figure 5. Hydrogen conversion of different temperatures at equivalence ratio of 0.3.

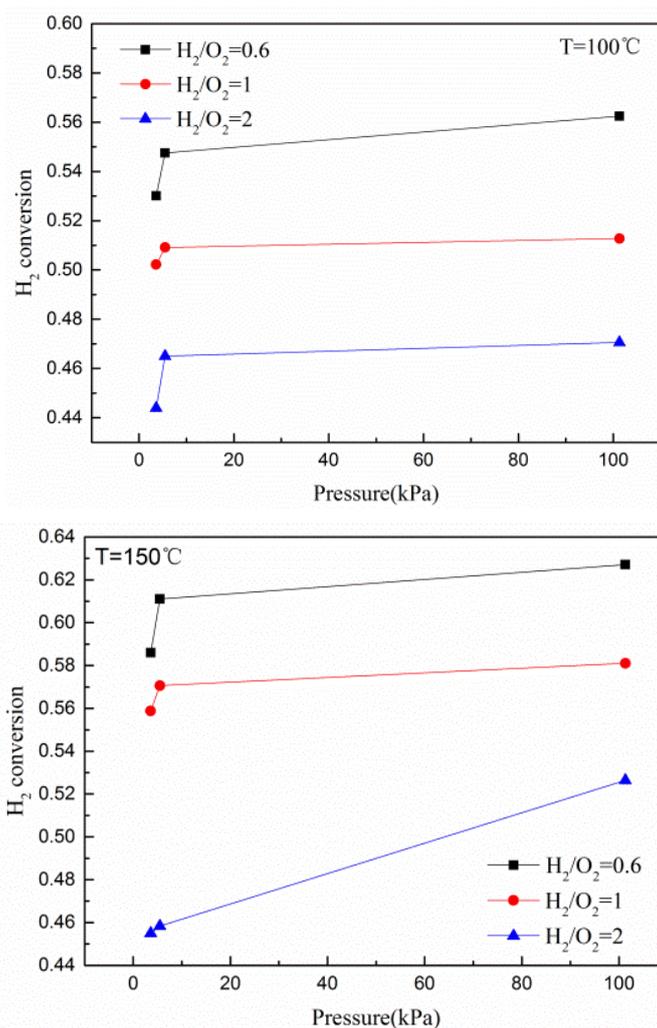


Figure 6. Hydrogen conversion of different H₂ to O₂ ratios at 100°C and 150°C.

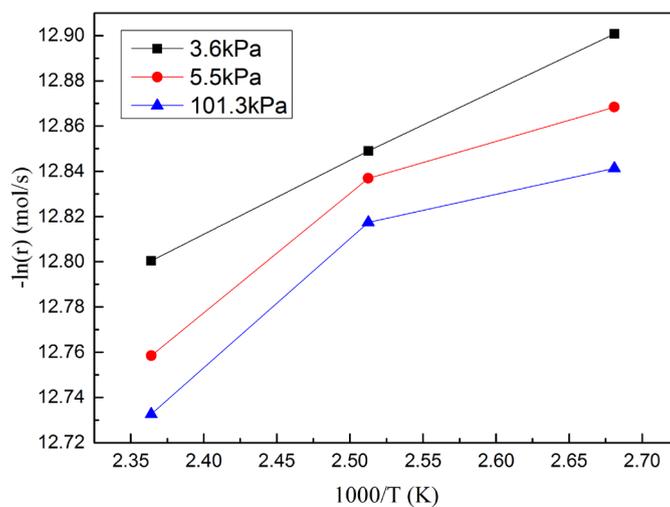


Figure 7. Reaction rates of H₂ between 100°C and 150°C at different pressures.

Table 3. Reaction rates of H₂ in different pressures.

p (kPa)	r (mol/s)
3.6	$r = \exp\left(-\frac{316.4}{T} - 12.053\right)$
5.5	$r = \exp\left(-\frac{343.2}{T} - 11.957\right)$
101.3	$r = \exp\left(-\frac{338.8}{T} - 11.944\right)$

increase of H₂ conversion. And low concentration of H₂ is beneficial for H₂ conversion performance due to the inhibited surface diffusion processes. The reaction rates of H₂ on the dependence of temperature at three pressures are given. Results suggest that the effect of temperature becomes more sensitive at high pressure. The reaction rate of H₂ is also higher in high pressure conditions.

Acknowledgements

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