

## Experimental Studies on Lean Premixed Catalytic Combustion of Natural Gas and Theoretical Analyses

Kao XU, Zhongliang LIU, Lizhen HAO, Weimin QIAN, Tianfang KANG, Hong HE, Chongfang MA

The Key Laboratory of Enhanced Heat Transfer and Energy Conservation of the Education Ministry, China  
The Beijing Municipal Key Laboratory of Heat Transfer and Energy Conversion  
College of Environmental and Energy Engineering, Beijing University of Technology, China [xukjs@emails.bjut.edu.cn](mailto:xukjs@emails.bjut.edu.cn)

**Abstract** Lean premixed catalytic combustion of natural gas was studied over the catalyst supports washcoated with palladium, lanthanum, strontium and manganese. The experimental results showed that the temperatures of the flameless catalytic combustion ranged from 600 to 900 and very low temperature led to extinguishment and very high temperature made the catalyst disabled. In the experiments, the natural gas-air ratios ranged from 4% to 12% by volume and in some given conditions, the good catalytic effect was fulfilled at the ratio of 8% and catalytic combustion would extend the range of the fuel-air ratio, which was not very strict with the fuel concentration. Meanwhile, the experiments proved that in the shorter monolith, catalytic combustion was in very good condition and the surface temperatures of monolith were relatively low. Oppositely, in the longer monolith, the surface temperatures increased and the lethal gas emissions were slightly increased, which will do much harm to the environment. Subsequently, the performances of heat and mass transfer in catalytic support were analyzed.

**Keywords:** Lean premixed catalytic combustion, Natural gas, Fuel-air ratio, Heat and mass transfer

### 1. Introduction

For the conventional natural gas burners, they operate at a nearly stoichiometric  $\text{CH}_4/\text{O}_2$  ratio to obtain a high combustion efficiency and output[1]. However, for lean methane-air mixtures such as gas let off from coal mine, especially for the mines with the high methane concentration where the methane concentration reaches 3%~5% by volume, how to make the best of the methane to decrease environmental pollution is maybe an urgent mission.

Following the initial demonstration of catalytically stabilized thermal combustion by Pfefferle[2,3] in 1970s, substantially theoretical and experimental work was undertaken in this field. Recent researches[4-7] show catalytic combustion is possible to settle these problems above. Catalytic combustors for gas turbines and domestic gas appliances have evolved from research level to field testing, claiming that lower  $\text{NO}_x$ , CO and unburned HC emissions. Because heterogeneous oxidation reactions of hydrocarbons on the surface of catalysts in the support have relatively lower activation than the homogenous counterpart, the mixtures of methane and air below homogenous concentration can burn, while still generate a high thermal output. Meanwhile, catalytic combustion has a relatively larger range of fuel-air ratios than homogeneous combustion.

Based on the reasons above, now the catalytic combustion is becoming the hotspot at home and abroad. Nowadays the more popular catalysts for catalytic combustion of natural gas are some noble metals such as platinum and palladium and so on[8,9]. However, because of their costs, it is difficult to afford and popularize them in applications. So developing cheaper

combustion catalysts has also been one important field of researches. For the different catalysts, there exist a different range of temperature application. Noble metals, as low temperature catalysts, are widely used in the low temperature section of catalytic gas turbine combustors or household appliances. Some cheap catalysts must be sought as the noble metal substitutes. Meanwhile, recently the most researches[10-12] were only involved in the field of chemistry to study the catalytic combustion emissions and the activation mechanism of catalysts. In this paper, many types of metal compounds were used as the catalysts to study the temperature and the concentration fields of premixed catalytic combustion and of the non-catalytic combustion of natural gas in honeycomb. In comparison between the two different styles of combustions (heterogeneous and homogeneous) and two same styles of combustion over catalyst honeycombs in different length, the best combustion effect and the best fuel-air ratio will be found. In the end, how the length of the catalyst honeycombs influences combustion emissions and the axial and surface radial temperatures were analyzed based on heat and mass transfer.

### 2. Catalyst specifications and experimental procedures

In the experiments, Pd0.1%-La0.8Sr0.2 Co0.6Mn0.4 as the catalysts were supported over ceramic honeycombs. The honeycomb was washcoated with  $\gamma\text{-Al}_2\text{O}_3$  of high surface areas. Catalysts were then added to washcoated honeycomb by impregnation. The catalysts were dried at 100 for about 10 hours and calcined at 500 for 6

hours. The loading of the catalyst Pd was 0.1 wt.% based on the weight of honeycomb. The washcoated honeycomb specification is 125mm(diameter) × 12mm or 25mm(height). The interface of a small-scale channel in the honeycomb is 1.1mm × 1.1mm square and the porosity of the whole honeycomb is 72%. The supports are shown in fig.1(A,B-catalyst support, C-non-catalyst support).

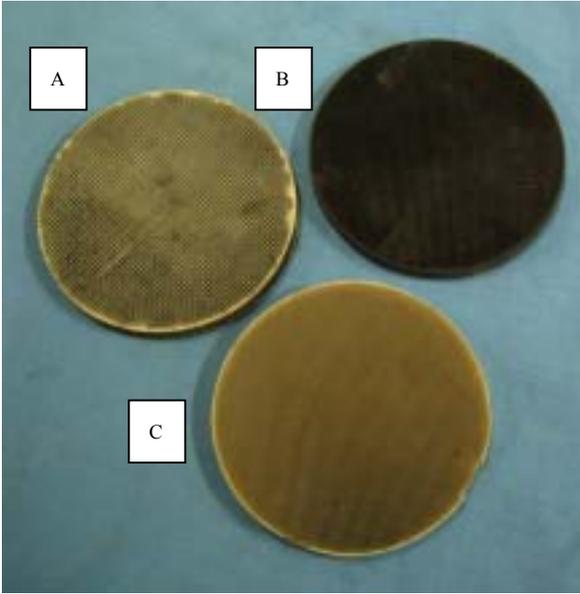


Fig. 1. The catalyst support structure

Fig.2,3 show an overall scheme of the test rig of premixed catalytic combustion of natural gas. The test system consisted of a natural gas bottle, a reductor, two valves, two mass flowmeters, a fan, a static mixer, a wire screen, the thermocouples and gas analyzer and so on. The natural gas at the high pressure passed through the first reductor and the second reductor, then the pressure reached 2000Pa. A adjustable valve and a mass flow meter were installed at the backward position to control and measure the volume of natural gas. The combusting



Fig. 2. The testing spot

air was supplied from a fan and controlled by adjustable valve and measured by a mass flowmeter. Subsequently the air and the natural gas converged in the pipeline. A static mixer was installed downstream so as to make the mixtures of fuel and air uniform prior to inlet of honeycomb. A wire screen consisting of a few layers of stainless steel mesh was mounted prior to the inlet of the honeycomb so as to minimize the radiation effects and to achieve plug flow conditions. The mixtures of natural gas and air flowed through the honeycomb in the laminar condition ( $Re < 100$ ). In the end, the mixtures were ignited by ignition set.

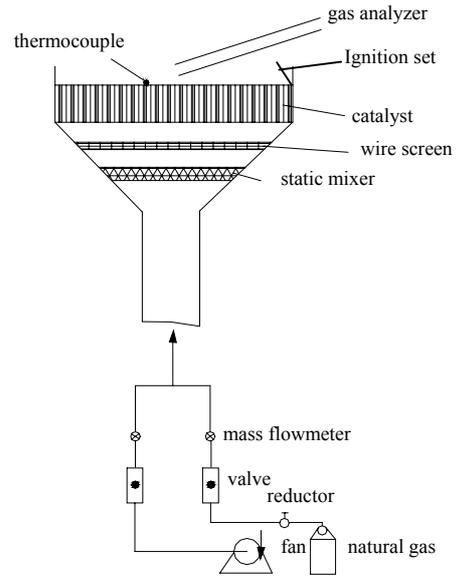


Fig. 3. The test rig

Natural gas in the experiment was from Shanganning areas and its Mole species are shown in the table 1.

Table 1. The Mole species of natural gas

species	Mole fraction(%)	thermal value ( $J/Nm^3$ )
CH <sub>4</sub>	95.9494	35906
C <sub>2</sub> H <sub>6</sub>	0.9075	64397
C <sub>3</sub> H <sub>8</sub>	0.1367	93244
H <sub>2</sub> S	0.0002	23383
CO <sub>2</sub>	3	
H <sub>2</sub> O	0.0062	

The surplus air coefficient is defined as follows.

$$\alpha = \frac{V}{V_0} \quad (1)$$

### 3. Results and Discussions

In the experiment, the three similar supports were used and they had the same porosity and the specific surface at height of 12mm, 12mm and 25mm, the two (12mm, 25 mm) of which were chosen as catalyst supports and another (12mm) was not washcoated with catalysts. The ambient temperature was about 30 centigrade degrees

and the temperature of natural gas was also 30 centigrade degrees. The precision of gas analyzer is between 1ppm and -1ppm and that of thermocouple is about 0.1 . The experimental results are shown in Fig. 4, 5, 6, 7 and 8. The fig. 4 shows the influence on the surface temperatures of the catalyst supports and combustion emissions at different fuel-air ratios. The results reveal when the fuel-air ratios are at the ranges between 6 and 12vol% (the air surplus coefficient ranges from 1.6 to 0.83), as the fuel-air ratio increases ( the air surplus coefficient minishes), the surface temperature goes up from 600 to around 880 and at the beginning , the CO production and the unburned HC rapidly decrease, then keep steady. Meanwhile, NOx mildly increases. Emissions are in the best condition until the fuel-air ratio reaches 8vol%.

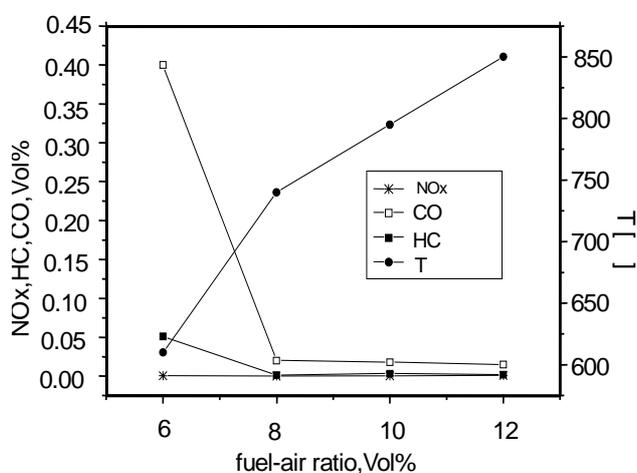


Fig.4. The influences of different fuel-air ratios on the temperatures of catalyst support in the length of 12mm and combustion emissions

The fig.5 shows the influence on surface temperatures of the non-catalyst support and combustion emissions at different fuel-air ratios. The curves in the fig.5 are similar as those shown in the fig. 4. According to the fig.4 and fig.5, some conclusions are found, namely, when the supports are not washcoated with catalysts , the CO production and the unburned HC are remarkably increased and the highest surface temperature of the support goes up by about 80 and NOx is slightly increased. On the other hand, the fig.5 still reveals the ranges of fuel-air ratios in the catalytic condition are wider than those in the non-catalytic condition. Seo et.al.[13]found that the ranges of fuel-air ratios were much wider in catalytic condition if the combusting air was heated. Consequently, the results above come to conclusions as follows, i.e., the noncatalytic combustion (homogeneous) combustion does harm to the environment, instead, the catalytic combustion (heterogeneous combustion) may aptly reduce the lethal gas products and fulfill complete combustion.

The fig.6 shows the influence on surface temperatures of

the catalyst support in length of 25 mm and combustion emissions at different fuel-air ratios. Comparing the fig.4 with the fig.6, we could find that in the same conditions, CO products and unburned HC are remarkably increased with the increase of the length of catalyst support and the surface temperatures are 100 higher than the former. Meanwhile, the NOx emissions are nearly 2 ppm higher shown in the fig.7. The comparisons above show the physical characteristics of catalyst supports such as the length and so on play important roles in the performances of catalytic combustion.

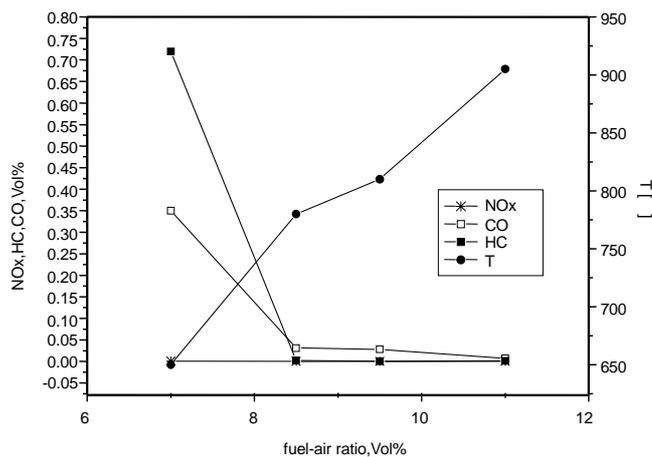


Fig.5. The influences of different fuel-air ratios on the temperatures of no catalyst support in the length of 12mm and combustion emissions

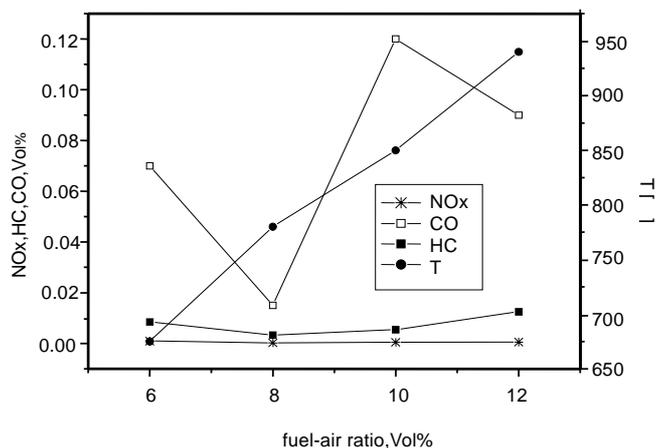


Fig.6. The influences of different fuel-air ratios on the temperatures of catalyst support in the length of 25mm and combustion emissions

The fig.7 shows the NOx emissions of three types of supports (catalyst supports in length of 12mm and 25mm and the non-catalyst support in length of 12 mm). It is evident that the NOx emissions of catalyst support in length of 12 mm are the least of the three. Posteriorly, the

emissions of catalyst support in length of 25 mm are less. The emissions of another are the most. According to the comparisons, it is evident that the length of the support plays a very important role in (catalytic) combustion emissions. The support in the proper length will be helpful to reduce lethal products.

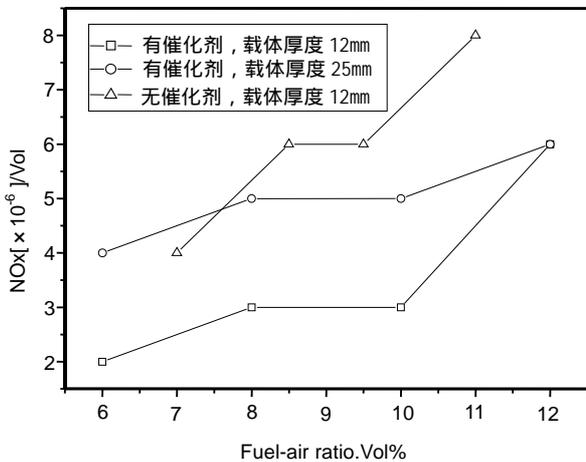


Fig.7. The NOx productions of the catalyst or no catalyst supports in the different length

The fig.8 shows the axial temperatures for the catalyst supports in length of 12mm and 25mm in the same combustion conditions. During the course of measuring the temperatures, the type K thermocouple was firstly fixed on the slidable bar with graduations, then was inserted in a centrally located channel when the fuel-air ratio was at 8 vol%. It is clear (shown in the fig.8) that for the catalyst support in the length of 25mm, its surface temperature is about 100 higher than that in length of 12mm, meanwhile, its bottom temperature is nearly 150 lower. Thus it can be seen the short catalytic support has the good performance of heat and mass transfer and the large capacity of heat radiation.

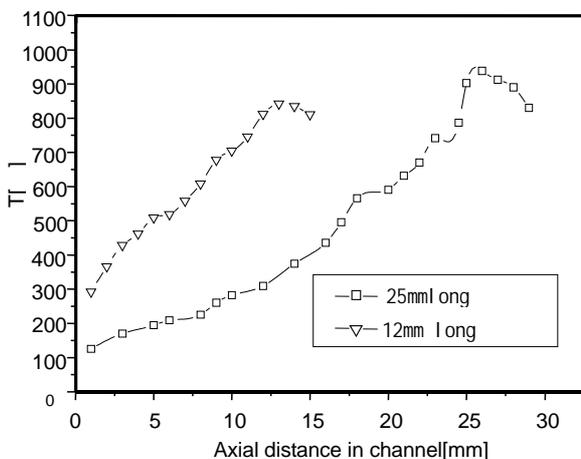


Fig.8. The axial temperatures for the catalyst supports in the length of 12mm and 25mm in the same combustion conditions.

In summary, according to the experimental results above, we come to the conclusions as follows.

- I. Catalytic combustion in the support with the suitable length may reduce thermal NOx and CO products, as well as HC, which is conducive to the environment.
- II. In the specific condition, catalytic combustion may extend the fuel-air ratio range and is not very strict with fuel concentration.
- III. Catalytic combustion in very good condition must be at the specific fuel-air ratio. If the fuel-air ratio is too small, heating the surplus air needs much heat energy so as to reduce the temperature in combustion areas and react slowly so that the hydrocarbon can not be consumed up. Meanwhile, in the same conditions, the physical characteristic of a support such as the length plays a very role in combustion emissions and heat mass transfer in the support.

#### 4. The theoretical analyses of catalytic combustion and heat mass transfer in catalyst supports

##### 4.1 The catalytic combustion mechanism of natural gas

According to the viewpoint on energy changes, the existence of catalysts only changes the approach to chemical reaction, but not the balance position of chemical reaction. The final energy change for some reaction system is independent on the existence of catalysts or not [14]. Even if some catalysts join the reaction, the reaction only passes by a shortcut and need not overcome the initial larger energy force shown in the fig.9. The debasement of the reactive activation energy, for the strong exothermic reaction, reduces the reactive temperature, one side, which makes the reaction head for thermal advantageous condition so as to increase the products of CO<sub>2</sub> and H<sub>2</sub>O and avoid the support sinter, on the other hand, which reduces the thermal NOx products.

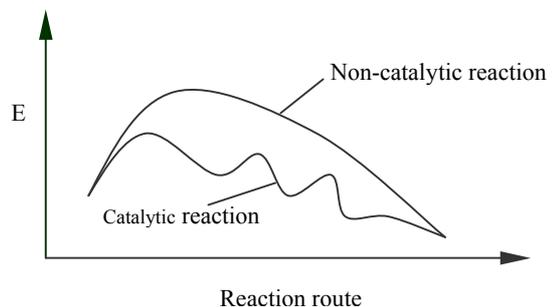


Fig. 9. The energy changes of two kinds of reaction (catalytic and non-catalytic reaction)

For the combustion of natural gas, the catalysts are used to reduce the activation energy in reactive system, which aptly reduces the reactive temperature so as to lessen the

thermal NO<sub>x</sub> just shown in the experiments. In the mean time, Oxygen is absorbed on the surfaces of the catalysts to promote oxidation of hydrocarbon so that hydrocarbon is almost consumed up.

### 3.2. Heat and mass transfer

Based on Prandtl's boundary layer theory[15], when the fluid flows into a pipeline at some uniform speed, because of viscosity, the flowing boundary layer forms on the internal surface of axial symmetry, and furthermore, the thickness of the boundary layer increases gradually along with axes.

In the same way, the mixtures of natural gas and air flow into the channels in the support with the steady speed. The boundary layers form in the channels and increase along with the axes shown in the fig.10. Generally, the reaction in the catalyst support is divided into three regions [16,17], namely, the kinetic region, the mass transfer region and the homogeneous gas-phase reaction region. The former two regions are respectively at low temperatures and at high temperatures and they locate on the surface of the channel. Meanwhile, the gas mixtures continuously transport to the surface so as to maintain the heterogeneous reaction. Exothermic reactions make temperatures of the fore surface increase, which leads to the homogeneous combustion in the rear of the channel. As a rule, the larger the diffusion coefficient is, the bigger is the heat transfer coefficient [18]. Because of the existence of boundary layer, the heat transfer coefficient and the diffusion coefficient of the mixtures of natural gas and air depend on the thickness of the boundary layer to a great extent. For the longer support channel, the fully developed boundary layer forms near the internal surface of the channel, which limits the diffusion of gas mixtures towards catalytic regions and the heat transportation produced by reactions. For the shorter channel, because of the thin boundary layer in the channel, heat mass transfer is not limited. Grounded on the explanations above, it is evident from the fig.8 that the surface temperatures of the 25mm long support are higher than those of the 12mm long support and the bottom temperatures are lower.

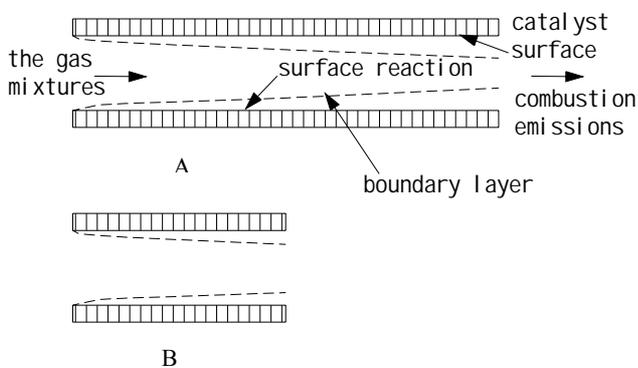


Fig.10. The catalytic reaction and heat mass transfer in the catalytic support channels in the different length

## 5. Prospect

The theories of catalytic combustion are very complicated, which is involved in flow, heat and mass transfer and chemical reactions. Until now, there exist many essential elements to further research.

## Acknowledgment

Financial support for this work was provided by the Beijing Municipal Key Lab Fund Project (No. 05005790200406).

## Notation

$V$  - The actual air volumes per unit volume fuel, Mol;  
 $V_0$  - The theoretical air volumes per unit volume fuel, Mol;  
 $a$  - surplus air coefficient.

## References

1. V.A. Sazonov, Z.R. Ismagilov and N.A. Prokudina. Catalytic Combustion of Lean methane-air Mixtures, *Catalysis Today*, Vol.47, pp.149-153, 1999.
2. R. Pfefferle. U.S. Patent 3, 928,961(1974).
3. W.C. Pfefferle Catalytic Method, *Applied Thermal Engineering*, Vol. 11, pp.27-29, 1997.
4. Dupont V, Zhang SH and Williams A, Experiments of Methane Oxidation on a Platinum Surface, *Chemical Engineering Science*. Vol.56, pp2659 – 2670, 2001.
5. Dupont V, Zhang SH and Bentley R, et al., Experimental and Modeling Studies of the Catalytic Combustion of Methane, *Fuel*, Vol. 81, pp. 799–810, 2002.
6. Forzatti P and Groppi G, Catalytic Combustion for The Production of Energy, *Catalysis Today*, Vol 54, pp.165-180, 1999.
7. Y.C. Chao, G.B. Chen and H.w. Hsu at.al., Catalytic combustion of gasified biomass in a platinum monolith honeycomb reactor, *Applied catalysis*, Vol.261, pp. 99-107, 2004.
8. H. Sadamori, Application concept and evaluation of small-scale catalytic combustors for natural gas, *Catalysis Today*, Vol. 47, pp. 325-338, 1999.
9. F. Moallemi, G. Batley and T.J. Foster et.al., Chemical modelling and measurements of the catalytic combustion of CH<sub>4</sub>/air mixtures on platinum and palladium catalysts, *Catalysis Today*, Vol.47, pp.235-244, 1999.
10. M. Bizzi, L. Basini, G. Saracco and V. Specchia, Short contact time catalytic partial oxidation of methane: analysis of transport phenomena effects, *Chemical Engineering Journal*, Vol. 90, pp. 97-106, 2002.
11. S. Tischer, C. Correa and O. Deutschmann, *Transient*

- Three-dimensions of Simulations of a Catalytic Combustion Monolith Using Detailed Models for Heterogeneous and Homogeneous Reaction and Transport Phenomena *Catalysis today*, Vol.69,pp. 57-62, 2001.
12. D. Urs, B. Peter and M. John, Two-dimensional Modelling for Catalytically Stabilized Combustion of a Lean Methane-air Mixture with Elementary Homogeneous and Heterogeneous Chemical Reactions, *Combustion and Flame*, Vol.116, pp.243-258, 1999.
  13. Y.S. Seo, S.J. Cho and S.K. Kang, Experimental studies on combustion characteristics of a catalytically stabilized combustor, *Catalysis Today*, Vol. 59, pp. 75-86,2000.
  14. H. X. Guo, *Applied chemical engineering kinetics*, chap. 1, The Chemical Industry Press, Beijing,2003.
  15. Z.P. Ren, *Convective Heat Transfer*, chap. 2, High Education Press, Beijing, 1995.
  16. W.J. John, C.Joep and G. Van, Monolith in catalytic oxidation, *Catalysis Today*, Vol. 47, pp. 169-180, 1999.
  17. D.Q. Zhao(translator), *The occurrence and control technology of combustion resultants*, chap. 3, Science Press, Bijing, 2001.
  18. M. yubovsky, W.C. Pfefferle and P. Menachoudhury at al., Complete and Partial Catalytic Oxidation of Methane over Substrates with Enhanced Transport Property. *Catalysis Today*, Vol. 83, pp. 197 – 183, 2003.