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Experimental Study on Emission Control of Premixed Catalytic Combustion of Natural Gas Using Preheated Air*

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Abstract In this paper the premixed catalytic combustion emissions such as CO, unburned hydrocarbon (UHC), NO_x and the temperature distribution in the catalytic monolith with ultra low concentration of Pd were studied. Three types of monoliths were used for experiments and the temperature of preheated air was respectively 50℃, 100℃ and 200℃. The results showed that preheated air made radial temperature in the catalytic monolith uniform which helped to avoid local hot spots so as to decrease NO_x emission. The experiment also proved that the shorter monolith showed much better catalytic combustion performance than longer one and the temperature at the exit of the shorter monolith was relatively lower. On the contrary, the temperature was higher in the longer monolith and the lethal NO_x emission was slightly increased.
Keywords catalytic combustion, preheated air, natural gas, emission

1 INTRODUCTION

During recent decades, natural gas has been widely used as a clean energy source to decrease environmental pollution, especially in large cities. Methane, the principal component of natural gas, is one of the most difficult hydrocarbons to be oxidized in spite of its high thermal value. Complete combustion of methane in homogeneous flame usually requires high temperature and it produces high level of NO_x, unburned hydrocarbon (UHC) and carbon monoxide (CO). Following the initial demonstration of catalytically stabilized thermal combustion by Pfefferle[1,2] in 1970s, theoretical and experimental work[3—14] has been undertaken in this field and led to the conclusion that catalytic combustion was possible to make methane completely combust in the whole range of concentration. Because heterogeneous oxidation of hydrocarbons on the surface of catalysts in the monolith has relatively lower activation energy than that of the homogenous counterpart. Even the mixtures of methane and air below the homogenous concentration limit can burn and generate high level of thermal output.

There is limited experimental work in the area of preheated air, temperature distribution and heat transfer associated with combustion emissions in catalytic monoliths. Dupont and Zhang[15] used catalytic monoliths of the diameter 101.6mm and the length of 50mm, which housed many square channels (1.27mm×1.27mm) washcoated with total 2.2g of Pd, and found fewer CO, NO_x emissions in their experiments. Weber *et al*.[16] used high temperature (above 1000℃) preheated air to study emissions from homogeneous combustion of natural gas and found preheated air helped to reduce emissions, especially NO_x in the furnace. Choi and Katsuki[17] showed that preheated air at high temperature was conducive to decreasing NO_x in homogeneous reaction. Seo *et al*.[18] studied the light-off temperature of different catalysts [50mm long monolith, catalysts loading of 2% (by mass) γ-Al_2O_3] and found that Pd was better in catalyst activity and had the lower light-off temperature than Pt. Sazonov *et al*.[19] studied non-adiabatic catalytic combustion of lean-air mixture on the monolith with supported iron oxide and 9.3% (by mass) γ-Al_2O_3 of Pt and found that complete combustion at fuel/air ratio of 4.5% (by volume) and a small quantity of emission was produced. From the above-mentioned literatures, it is known that so far, all the published experimental results were involved in high concentration of catalyst. However, because of high cost, it is difficult to be used in large scale engineering applications. So developing cheaper combustion catalysts has also gained much attention. In addition, Lyubovsky *et al*.[20] showed that microlith catalyst substrate (shorter monolith) helped to allow complete conversion of methane because of its enhanced transport property, but no experimental results were presented. It is possible to change the length of monolith and choose some appropriate concentration of catalyst to acquire better combustion performance. So it is necessary to find the appropriate length of monoliths for catalytic combustion and decrease the use of noble metal. In the mean time, preheated air maybe plays an important role in reducing catalytic emissions under the condition of low concentration of catalyst.

In this paper, catalytic combustion emission was studied experimentally over the honeycomb monoliths of different lengths with lower loading of Pd and using preheated air. In comparison between catalytic combustion over honeycomb monoliths with different

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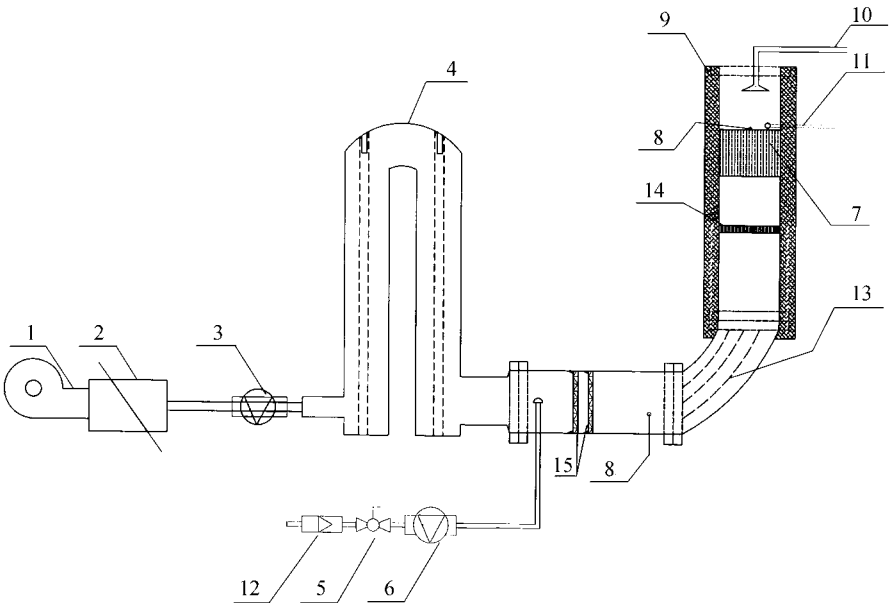

Figure 1 Experimental system of catalytic combustion with heating system
1—blower; 2—adjustable valve; 3—mass flow meter; 4—U type heater of air; 5—adjustable valve of natural gas; 6—mass flow meter of natural gas; 7—catalytic monolith; 8—thermocouple; 9—adiabatic layer; 10—emissions collection; 11—spark plug; 12—single direction valve; 13—metal flow guide; 14—mesh; 15—static mixer

lengths, the better combustion performance and the optimum fuel/air ratio (the ratio of fuel to air by volume) were found. The reason how the length of the catalyst honeycomb monolith influences combustion emission and the axial and radial temperature profiles were analyzed

2 EXPERIMENTAL

Figure 1 shows a detailed scheme of the catalytic combustion system used in the experiment. The air was supplied from a blower providing 200Pa pressure and controlled by a mass flow controller. Natural gas (96% CH_4, 3% CO_2 and 1% C_2H_6, by volume) was introduced by another mass flow controller. Two static mixers were installed in premixed chamber with the length of 300 mm to guarantee a perfect mixing of natural gas and air prior to entering the catalyst monolith. In order to conveniently collect combustion emissions, an elbow was installed behind the premixed chamber. In the elbow, three sets of metal flow guide were installed along the passage. The testing results for some cross-sections behind the catalytic monolith in Fig.2 show that the air flow is uniform in the tube with an elbow. The catalyst monolith was installed at the position of 300mm above the elbow. The emission collecting was at the position of 150mm above the monolith. A metal mesh with 2mm holes was set up at the upstream of catalytic monolith to make gas components well mixed before entering the monolith. The whole combustor was insulated by a 50mm thick layer of ceramic fiber.

At the beginning of an experimental run, the mixture of natural gas and air was ignited by a spark plug at the exit of the monolith. The combustion flame was stabilized in the downstream region of the monolith at first, but it spreaded gradually to the rearward of monolith. After about half an hour, the catalyst monolith turned red at its rear and the flameless catalytic combustion or little flame combustion started.

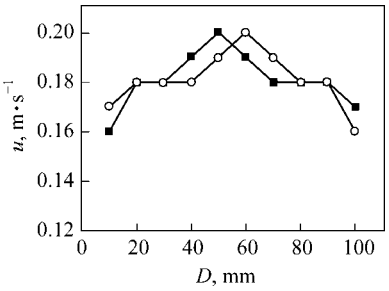

Figure 2 Velocity distribution on a cross-section of the tube with elbow (cross-sectional average velocity 0.186m·s^{-1})
■ survey perpendicular to the center line of the elbow;
○ survey from the direction outboard elbow to inboard

Gas samples of combustor exhaust were taken at the exit of the catalyst monolith and analyzed online as shown in Fig.3. The exhaust gas from the combustor was firstly imbibed in the bottle and cooled by mixture of ice and water, then sent to the exhaust (UHC, NO_x and CO) analyzers. 42 C NO_x analyzer by America Thermo Co. was used for measurement of NO_x with an accuracy of 1% (relative) and $\pm 0.1\times10^{-6}$ in mol fraction (part per million). The analyzers for UHC and CO were made by Testo, Germany with an accuracy of 10×10^{-6} in mol fraction. Pre-calibrated K type thermocouples (1mm and 0.5mm in diameter) were used to measure the surface (at the exit of the monolith) and the catalytic wall temperature. The average temperature of 5 locations of equal radial distance was termed as exit surface temperature. The first

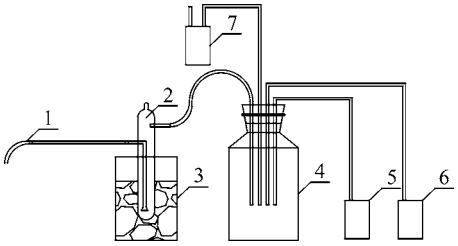

Figure 3 Exhaust testing scheme
1—sample pipe; 2—cooling bottle; 3—icy water; 4—jar; 5—CO, UCH analyzer; 6—NO_x analyzer; 7—sampling apparatus

measuring point was at the distance of 10mm of monolith brim and it was averagely 20mm's interval for the four other points.

In the experiments, the noble metal Pd was used as main catalyst and Ce, La and Ba were co-catalysts. Monolith was made of cordierite and was 100mm in diameter. Its internal channels have square cross sections with the dimension of 1.25mm. The interspace between the tub and the monolith was sealed by ceramic fibre. A conventional impregnation method was used to washcoat the honeycomb monoliths. The main procedures are: (1) pretreatment: wash up the monolith with nitric acid and bake; (2) catalyst support: weigh γ-Al_2O_3 powder (less than 10μm in diameter) corresponding to more than 10% of the monolith mass and mix it uniformly with some water to get a slurry in which water possesses 80% of the total slurry mass. Subsequently, mix the co-catalyst solution uniformly with the slurry. Each co-catalyst metal dosed in form of nitrate is about 1% (by mass) of γ-Al_2O_3; (3) Coating support: immerse the monolith in the support slurry, then bake and desiccate the monolith for 4 or 5h and weigh up the monolith. Repeat the procedure until γ-Al_2O_3 is 10% of monolith mass. In this way, the thickness of square channel side is increased by 50μm and on the interface of two sides, the thickness is increased by 150μm; (4) Impregnation of noble metal: immerse the monolith coated with γ-Al_2O_3 and co-catalyst in nitric acid solution with Pd dissolved, in which Pd weighs up a little more than 0.5% (by mass) of γ-Al_2O_3 , then bake and desiccate the monolith for 4 or 5h and weigh up the monolith. Repeat the procedure until Pd mass is 0.5% of γ-Al_2O_3 mass.

Monoliths of square channels used in the experiments and their lengths are shown in Table 1. They have the same pore number density of 400 cells per square inch (cpsi), and their actual pore dimension is 1.25mm×1.25mm.

Table 1 Catalyst monolith parameters

Monolith	Catalyst (by mass)	Length
monolith A	0.5% Pd (0.115g)	58mm
monolith B	0.5% Pd (0.085 g)	40mm
monolith C	0.5% Pd (0.04 g)	20mm

3 RESULTS AND DISCUSSION

In the following discussion, the fuel/air ratio is defined by volume on the normal condition. The largest fuel/air ratio is 10.5% of the stoichiometric CH_4/O_2 ratio. Because the catalyst and cordierite monolith can not bear high temperature, the fuel/air ratio was chosen below 10.5% in this work, with air in great excess. Air flow rate is 41L·min^{-1} in all experiments (superficial air velocity of 0.085m·s^{-1} based on the tube cross-section).

In order to find whether Pd influences combustion emissions, the experiment of catalytic combustion at the ordinary temperature (293K) was conducted over 20mm monolith shown in Figs.4 and 5. According to the two figures, we can find that not only CO, but also unburned hydrocarbon (UHC) from catalytic combustion is less than that from non-catalytic combustion. Meanwhile, the surface temperature at the catalytic monolith exit is distinctly lower than that of non-catalytic monolith because intense homogeneous reaction occurs for non-catalytic combustion at the tail of monolith. As a result, more NO_x emission comes from non-catalytic combustion. Thus, it can be seen that catalytic combustion at low concentration of Pd also helps to reduce combustion emissions, especially for NO_x. It is also found that CO and UHC emissions from catalytic combustion are the same as those from non-catalytic combustion at fuel/air ratio of 7%. Instead, the exit surface temperature of non-catalytic combustion is higher than that of catalytic combustion. It is not difficult to explain this by observing non-catalytic combustion phenomena. After non-catalytic combustion at the exit of monolith is ignited at the atmosphere pressure, the flame will propagate into the

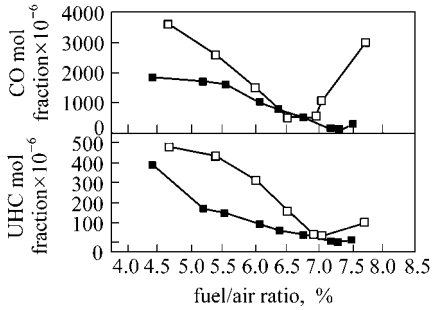

Figure 4 Content of UHC and CO in exhaust gas *versus* fuel/air ratio at the normal temperature (monolith C)
□ no catalyst; ■ catalyst

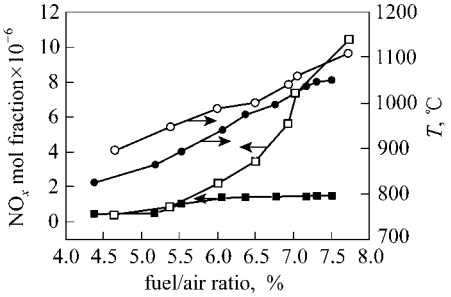

Figure 5 Exit surface temperature of monolith and content of NO_x at the normal temperature in exhaust gas *versus* fuel/air ratio (monolith C)
○,□ no catalyst; ●,■ catalyst

monolith and combustion occurs only at the tail of monolith. The exit surface of non-catalytic monolith is besieged by flame. So the exit surface temperature of non-catalytic monolith is influenced by the flame temperature of homogeneous combustion. However, no chemical reaction occurs on the foreside of non-catalytic monolith, which loses less heat there than catalytic monolith. On the contrary, little flame occurs at the exit surface of catalytic monolith.

In fact, NO_x emission and the surface temperature at the exit of monolith reach the peak value after the fuel/air ratio is increased to 9.8%. Because high temperature does harm to the catalyst, experimental data are not plentiful for these conditions and not presented here.

Because some CO emission is still produced and some hydrocarbon is not burned out, it is necessary to preheat air to explore whether emissions can be further reduced.

Figure 6 shows content of CO, UHC and NO_x in exhaust gas and the temperature of monolith exit with the length of 58mm *versus* fuel/air ratio at different preheated temperature of air. According to Figs.6(a) and 6(b), CO and UHC emissions decrease gradually to the minimum and then increase as fuel/air ratio further increases. Meanwhile, CO and UHC also decrease with increase of the temperature of preheated air. However, when air is preheated, the methane conversion is complete at the fuel/air ratio of 8% though CO emission subsequently starts to increase. Figs.6(c) and 6(d) show NO_x emission and the exit surface temperature of monolith. The NO_x emission is compatible with the exit temperature of the monolith and remarkably lower than that when air is at the normal temperature of 20℃. The NO_x emission and temperature increase slightly as the preheating temperature is increased above 50℃.

To study the effects of the catalysis level on combustion, monolith B (40 mm) was used and compared with monolith A. Figs.7(a)—7(d) present some of the experimental results, showing similar species and temperature variations with fuel/air ratio as those in Fig. 6. Though fuel/air ratio ranges from 5.5% to 6%, UHC emission from monolith A is less than that from monolith B. Generally speaking, the pollutants such as CO, UHC and NO_x from monolith B are less than those from monolith A, especially when the fuel/air ratio is after 6.5%. When the fuel/air ratio ranges from 7.5%—8%, CO and thermal NO_x are increased with increase of the surface temperature, but NO_x and surface temperature do not reach the peak.

Figure 8 depicts the measured emissions and the surface temperature at the exit of the shortest monolith (monolith C of 20mm). Comparing with the results for monoliths A and B, one can find that monolith C has the lowest NO_x emission regardless of inlet air temperature. In addition, the results in Figs.5, 6, 7 and 8 reveal that when air is preheated, NO_x emission is less than that when air is at the normal temperature and as the length of monolith decreases, fewer NO_x emission is produced under the same condition. The temperature at the exit of monolith and NO_x emission are only

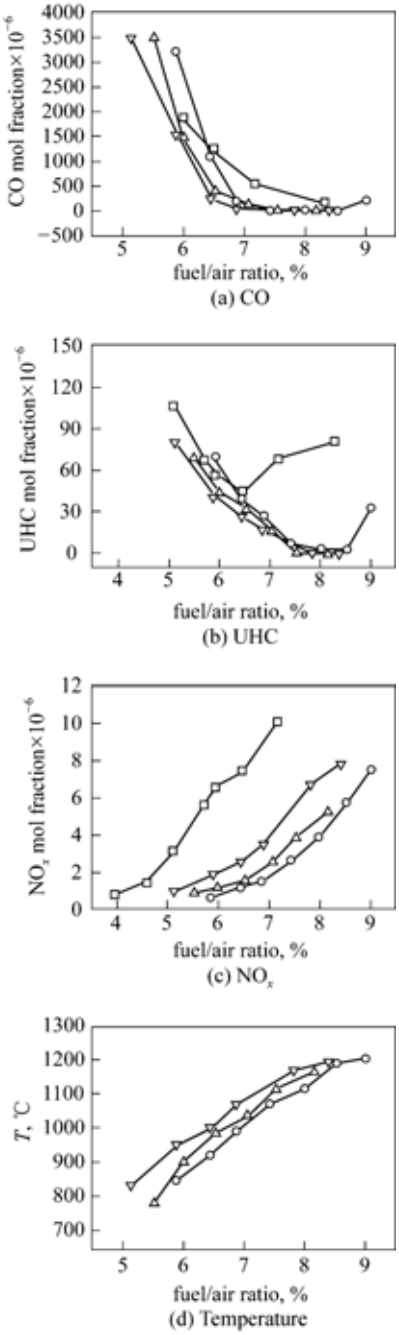

Figure 6 Content of CO, UHC and NO_x in exhaust gas and temperature of the exit of monolith *versus* fuel/air ratio at the different preheated temperatures of air (monolith A)
□ 20℃; ○ 50℃; △ 100℃; ▽ 200℃

increased slightly with the increase of the preheated air temperature.

In Fig.8, the optimal fuel/air ratio is 6.5% at the preheated temperature of 50℃ and its emissions of CO, UHC and NO_x are respectively 34×10^{-6}, 5×10^{-6} and 0.946×10^{-6}. Though the higher preheated temperature than 50℃ is conducive to CO and UHC emission control, more NO_x is produced and more thermal energy is consumed to heat air.

The axial wall temperature distribution of the catalyst monolith with the lengths of 20mm, 40mm

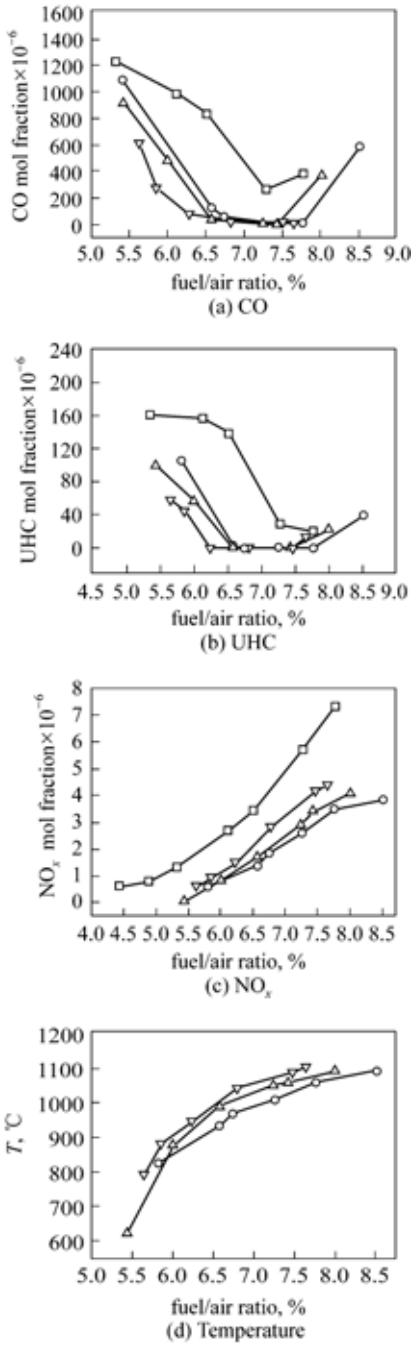

Figure 7 Content of CO, UHC and NO_x in exhaust gas and temperature of the exit of monolith *versus* fuel air ratio at the different preheated temperatures of air (monolith B)
□ 20℃; ○ 50℃; △ 100℃; ▽ 200℃

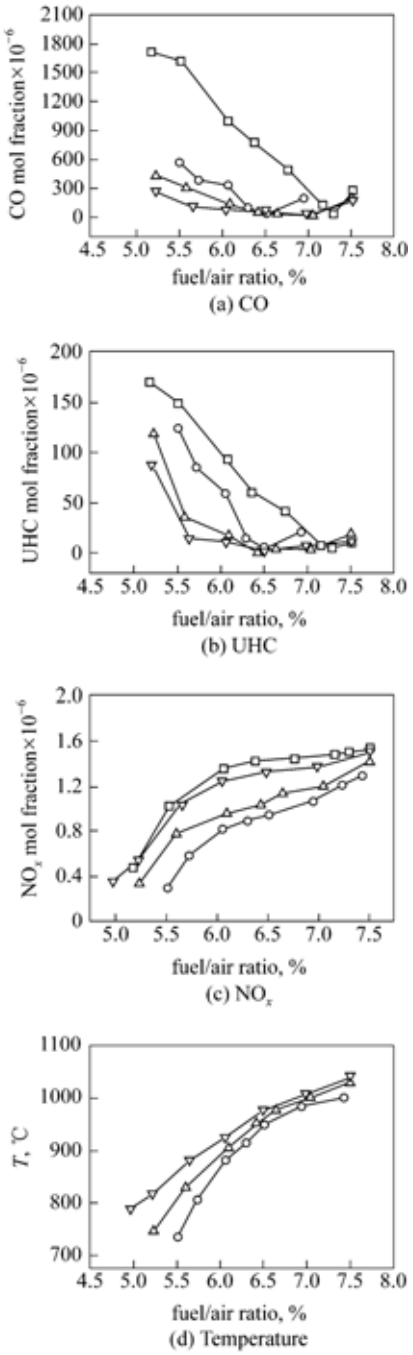

Figure 8 Content of CO, UHC and NO_x in exhaust gas and temperature of the exit of monolith *versus* fuel/air ratio at the different preheated temperatures of air (monolith C)
□ 20℃; ○ 50℃; △ 100℃; ▽ 200℃

and 58mm inside the same monolith pore channels are shown in Fig.9. These results were all obtained under the same experimental conditions (fuel/air ratio of 6.75%, air at the temperatures of 20℃ or 100℃, and flow rate of 41L·min^{-1}). For the measurement of the temperature, a K-type thermocouple was fixed on a sliding bar. Meanwhile, the measurement head was slightly bent and inserted into the channel on catalytic surface. It can be seen clearly from Fig.9 that for the monolith with the length of 58mm, its peak temperature is about 110℃ higher than that with the length of 20mm and about 50℃ higher than that with 40mm when the air temperature is 20℃. When air is preheated to 100℃, the similar temperature changes are shown. At the wall temperature of entrance (bottom) to monolith, the temperature in 20mm channel is the higher because the entrance to 20mm channel is very close to reaction area. The temperature reduces at the position of above monolith after reaching the summit due to radiation heat transfer loss. Furthermore, at the

same axial position, the wall temperature of the 20mm channel is higher than those in 40mm and 58mm channels shown in Fig.9, which means more intensive reaction occurs in 20mm channel. For 20mm catalytic monolith there is also a distinct difference between the preheated temperature of 20℃ and 100℃. The exit wall temperature at the air temperature of 100℃ is similar to that at the air temperature of 20℃. One side, higher temperature increases reaction rate on the wall of the channel. So, higher temperature will decrease hydrocarbon to attend homogeneous combustion at the rear of monolith and makes temperature uniform on monolith.

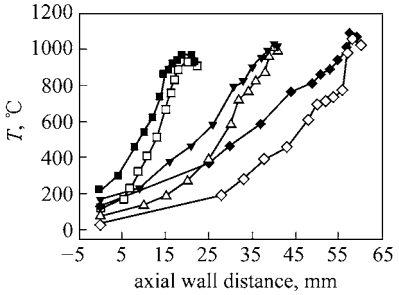

Figure 9 Temperature distribution along catalytic monolith wall
20℃: □ 20mm; △ 40mm; ◇ 58mm
100℃: ■ 20mm; ▼ 40mm; ◆ 58mm

According to Figs.6(d) and 8(d), the exit surface temperature of monolith C is obviously lower than that of monolith A. Meanwhile, NO_x emission from monolith C is less than that from monoliths A and B. NO_x is known to be produced by high temperature. The reason why the phenomenon above occurs is perhaps because of the axial heat conduction effect of the monolith. At the same fuel/air ratio in this work, the catalyst on the surface of the 20mm long monolith is enough for the catalytic combustion of the natural gas. Hereafter, even if the length of catalytic monolith (catalyst) is increased, the catalytic combustion will not be promoted further. So, compared to the 20mm long catalytic monolith, the longer catalytic monoliths can actually contribute few to the improvement of the catalytic combustion. The difference between the temperature distributions of the longer catalytic monolith and the 20mm long catalytic monolith is a direct result of the heat conduction in the monoliths with low thermal conductivity. Therefore, the temperature is low in the region near the entrance of the longer monolith, lower temperature results in lower catalyst activity and thus weak combustion compared with high temperature situation. Therefore, the combustion will not be completed within its entrance part of the longer monolith, and is shifted to its rear part. Meanwhile, because of the adiabatic characteristic of monolith, the heat loss due to the axial heat conduction of the longer monolith is greatly reduced compared with the 20mm long catalytic monolith. Hence, the temperature is higher at the rearward of the longer monolith than that the 20mm long catalytic monolith, and of course this results in a higher NO_x emission. To prove the above discussion, Fig.9 depicts the experimental axial temperature distribution of the monoliths with different length. From this figure, it can be seen that the temperature of the entrance part (the first 20mm) of the longer monoliths is indeed lower than the temperature of the 20mm long monolith.

Figure 10 shows the radial temperature distribution at the exit of 58mm long monolith at the same operating condition (fuel/air ratio of 6.75%, air flow rate of 41L·min^{-1}). When air is not preheated, the radial temperature is not uniform and a large temperature gradient occurs along the diameter. The difference of the center and the margin is 225℃. Instead, using preheated air makes the radial temperature profile uniform though the temperature of monolith appropriately increases due to preheated air. This is the reason why using preheated air decreases NO_x emission: local high temperature produces more NO_x. When air is preheated, higher temperature helps to speed up the reaction rate at the catalytic surface of the monolith (Fig.9) and makes less fuel left at the exit of catalytic monolith under the same fuel/air ratio. Instead, more unreacted fuel passes by at the exit of the monolith at air temperature of 20℃ and the unburned fuel is ignited. Thus, homogeneous reaction occurs at the rear end of the monolith, which makes the temperature higher. However, for preheated air only a little homogeneous reaction occurs at the rear of monolith. This is the reason why the temperature in the central area of the monolith at air temperature of 20℃ is much higher than those at preheated temperatures of 50, 100 and 200℃ as shown in Fig.10.

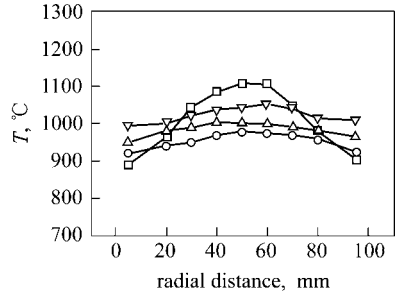

Figure 10 Radial temperature distribution at the exit of monolith with the length of 58 mm (monolith A)
□ 20℃; ○ 50℃; △ 100℃; ▽ 200℃

4 CONCLUSIONS

The characteristics of honeycomb monolith containing Pd of low concentration as natural gas–air fuelled catalytic combustor under steady-state were investigated. The pollutant emissions and axial and radial temperature distribution in the monolith were obtained under the same conditions.

Based on the experimental results, the following conclusions are obtained:

(1) A long catalytic monolith has less axial heat loss and high temperature at the rearward, which makes NO_x emission increase.

(2) Preheated air helps to reduce catalytic combustion emissions (CO, UHC and NO_x) and makes the

radial temperature profile in the monolith uniform so as to avoid more NO_x emission produced by local high temperature.

(3) The radial temperature profile is slightly raised as the preheated temperature increases.

(4) When air is preheated to 50℃, less combustion emissions (34×10^{-6} CO, 5×10^{-6} UHC and 0.946×10^{-6} NO_x) are achieved over the shortest catalytic monolith (20mm) at optimized fuel to air ratio of 6.5%.

In this work, although the target for noncontaminative combustion (less than 5×10^{-6} of emissions) is not achieved with using less noble metal, it is very possible to develop a true clean combustion technique by suitable configuration of catalytic monolith and preheated air.

REFERENCES

1 Pfefferle, W.C., "Catalytically supported thermal combustion", US Pat., 814752(1974).
2 Pfefferle, W.C., "Catalytic method", *Appl. Therm. Eng.*, **11**, 27—29(1997).
3 Burch, R., "Low NO_x options in catalytic combustion and emission control", *Catal. Today*, **35**, 27—36(1997).
4 Vaillant, S.R., Gastec, A.S., "Catalytic combustion in a domestic natural gas burner", *Catal. Today*, **47**, 415—420(1999).
5 Hayashi, S., Yamada, H., Shimadaira, K., "High-pressure reaction and emission characteristics of catalytic reactor for gas turbine combustors", *Catal., Today*, **26**, 319—327(1995).
6 Carroni, R., Schmidt,V., Grifin, T., "Catalytic combustion for power generation", *Catal. Today*, **75**, 287—295(2002).
7 Quick, L.M., Kamitomai, S., "Catalytic combustion reactor design and test results", *Catal. Today*, **26**, 303—308(1995).
8 Schlegel, A., Benz, P., "Catalytic stabilization of lean premixed combustion: Method for improving NO_x emissions", *Combust. Flame*, **105**, 332—340(1996).
9 Gelin, P., Primet, M., "Complete oxidation of methane at low temperature over noble metal based catalysts: A review", *Appl. Catal.*, **39**, 1—37(2002).
10 Sadamori, H., "Application concepts evaluation of small-scale catalytic combustors for natural gas", *Catal. Today*, **47**:325—338(1999).
11 Forzatti, P., Groppi, G., "Catalytic combustion for the production of energy", *Catal. Today*, **54**, 165—180(1999).
12 Petrović, S., Karanović, L., Plamen, K., "Catalytic combustion of methane over Pd containing perovskite type oxides", *Appl. Catal.*, **58**(1), 133—141(2005).
13 Persson, K., Ersson, A., Manrique, C.A., "Supported palladium-platinum catalyst for methane combustion at high pressure", *Catal. Today*, **100**(3), 479—483(2005).
14 Yeh, T.F., Lee, H.G., Chu, K.S., "Characterization and catalytic combustion of methane over hexaaluminates", *Mater. Sci. Eng.*, **384**(1), 324—330(2004).
15 Dupont, V., Zhang, S.H., "Experimental and modeling students of the catalytic combustion of methane", *Fuel*, **81**, 799—810(2002).
16 Weber, R., Smart, J.P., Kamp, W. , "On the (MILD) combustion of gaseous, liquid, and solid fuels in high temperature preheated air", In: Procceeding of Combustion Institute, Pennsylvania, U.S.A.(2005).
17 Choi, G.M., Katsuki, M., "Advanced low NO_x combustion using highly preheated air", *Ener. Conver. Manag.*, **42**, 639—652(2001).
18 Seo, Y.S., Cho, S.J., Kang, S.K., "Experimental and numerical study on combustion characteristics of a catalytically stabilized combustor", *Catal. Today*, **59**, 75—80(2000).
19 Sazonov, V.A., Ismagilov, Z.R., Prokudina, N.A., "Catalytic combustion of lean methane-air mixtures", *Catal. Today*, **47**,149—153(1999).
20 Lyubovsky, M., Pfefferle, W.C., Menachoudhury, P., "Complete and partial oxidation of methane over substrates with enhanced transport property", *Catal. Today*, **83**, 197—183(2003).