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Convective heat transfer of exothermic reactive gas flowing across a heating cylinder coated with platinum catalyst in a narrow duct

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Abstract

The effect of a catalytic surface reaction on the convective heat transfer is studied for a cross flow to a cylinder. Platinum catalyst is coated on the surface of the cylinder which is set horizontally in a rectangular duct. The fluid is a mixture of SO_2 and O_2 and the following exothermic reaction takes place on the surface of the cylinder: $SO_2 + 1/2O_2 = SO_3 + 99$ kJ/mol. The cylinder is uniformly heated electrically from the inside by the DC power supply, and the reactant gas flows through a small clearance between the cylinder and the duct wall. The heat transfer coefficient is determined based on the temperature difference between the inlet gas and the forward stagnant point of the cylinder. The heat transfer coefficient for the non-reacting gas is at least about two times higher than the conventional correlation because of the effect of natural convection and small clearance. When the reaction takes place, the heat transfer coefficient rises by 4–16%. The effect of the enhancement is proportional to the reaction rate. The same correlation of the convective heat transfer as the SO_2–O_2 reaction system is observed for the reaction system: $CH_4 + 2O_2 = CO_2 + 2H_2O$, which proceeds faster without volume change of the gas than the former reaction. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Convection; Cross flow; Heating cylinder; Exothermic reaction; Narrow duct; Platinum catalyst; Reactive gas flow

1. Introduction

The problems of convective heat transfer accompanied by homogeneous or heterogeneous chemical reactions are industrially significant for design of reactors. The reaction rate is usually sensitive to temperature of the reactant. The heat transfer in the reacting fluid or between the fluid and a surface is influenced by the reactions as well. Energy is transmitted in the form of the reaction enthalpy accompanied with the diffusion or migration of reactants as well as heat convection or conduction in the field of a temperature gradient. The contribution was representatively reported by Krieve and Mason [1], Schotee [2] and Oshima [3] that the overall heat transfer rates on the flow of N_2O_4–NO_2 in heating tubes or ducts can be several times as high as the ones obtained in the non-reacting flow. The heat transfer with a homogeneous chemical reaction was modeled by accounting the effect of both the conduction and the diffusion in the boundary layer on the heat transfer surface by Irving and Smith [4], Brian and Reid [5], Rothenberg and Smith [6] and so on.

The heat transfer problem on catalytic surface is significantly important in order to control the reaction rate or the temperature as well. The heat transfer is contributed not only by the convection but also by the enthalpy due to diffusion of reactants in the boundary layer on the surface, i.e. a reaction takes place on the catalytic surface and heat generates simultaneously there. There has been a paper by Rothenberg and Smith [7] on heat transfer with surface reaction. Usami

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Nomenclature

A	heat transfer area ($=0.0012$) (m^2)
C_0	inlet vol% of SO_2 (%)
h_0	local heat transfer coefficient without the reaction (W/m^2 K)
h	local heat transfer coefficient with the reaction (W/m^2 K)
ΔH	reaction enthalpy evaluated at the heat transfer surface temperature (J/mol)
q_{conv}	convective heat flux (W/m^2)
q^*_{conv}	convective heat flux with the reaction (W/m^2)
q_s	the electric power supplied to the heater (W/m^2)
q_{rad}	radiant heat flux between the heater surface and the duct wall (W/m^2)
r	reaction rate (mol/m^2 s)
T_s	heater surface temperature (K)
T_b	inlet gas temperature (K)
Nu	Nusselt number (–)
Re	Reynolds number (–)
Gr	Grashof number (–)

et al. [8] reported recently that the overall heat transfer coefficient in a plate-type reformer tube can be five times as large as that of non-reacting fluid flow. Most of catalytic reactions aim industrially at producing effectively functional materials or compounds by rising the synthesis rates, and are operated mostly by packing or fluidizing porous catalyst particles in the reactor to enlarge the specific surface area. In these reactors, heat exchanger is assembled to control the temperature, but the heat transfer resistance is generally large in packed beds. If the reaction takes place so rapidly, the system performance must be controlled by the overall heat transfer as it is difficult to maintain sufficient heat transfer rates in packed beds. Then catalyst wall reactors may be available for the appropriate temperature control. Fukuhara and Igarashi [9] analyzed the performance of reaction and heat transfer in a rectangular wall reactor with a catalyst wall which separates two channels of reactants and heat transfer working fluids in order to examine the improvement effect. Zeng et al. [10] applied catalytic reactions to heat transfer devices as a chemical heat pipe. They studied the performance of the chemical heat pipe in which catalyst was coated on the heat transfer surface and a reversible reaction and heat transfer took place simultaneously on the surface. In this type of the heat exchanger, a significant effect of heat transfer enhancement could be expected because the exothermic or endothermic reaction proceeds not in the bulk flow of reactant gas but on the heat transfer surface. Additionally several catalytic reactions involve a stoichiometric change, which causes a volume change of the reacting gas. This change can influence the flow pattern in the boundary layer on the surface and may result in enhancement of the heat transfer. In the past works, the heat transfer in the boundary layer over the heating catalyst plate with endothermic reaction or the cooling catalyst plate with exothermic reaction was given by the sum of the reaction heat and the convective heat transfer in the non-reacting flow for the contribution of the temperature gradient in the reacting system. However, it has not been known if the convective heat transfer between the surface and the fluid when exothermic reaction takes place on the heating surface coated by catalyst could be correlated by the one for the flow in the non-reacting system. On the other hand, if the heat exchanger system whose heat transfer surface is combined with catalytic reaction surface were introduced, reactant fluids may be usually operated so as to flow in a small clearance between multi tubes and/or sectional walls in a duct in order to ensure the specific surface area of catalyst as large as possible and to enhance effectively the reaction conversion. In these cases, the heat transfer in the boundary layer must be influenced by a several complicate factors.

In the present work, the effect of a catalytic reaction on the convective heat transfer is studied for a cross flow to a cylinder in a narrow duct assuming a small clearance between cylinders array. This system models a part of tubes sectioned by walls placed for a stabilization of flow and promotion of catalytic reaction and radiative heat transfer enhancement in a high temperature field. The fluid used is two types of two components mixture; SO_2–O_2 and CH_4–O_2. The exothermic reaction of these mixtures takes place on the heating surface of the cylinder coated by platinum catalyst with a constant heat flux. Then the convective heat flows to the reactants through the boundary layer on the heating catalyst surface. The heat transfer coefficient is experimentally determined based on the temperature difference between the inlet gas and the forward stagnant point of the cylinder, and compared with that in the non-reacting flow.

2. Experiments

Fig. 1 shows the schematic drawing of experimental apparatus. This apparatus is constructed with the parts of feed and preheat of reactant gas, test section and treatment of flue gas. The reactant gas flows into the test section through the preheater. The test section is a rectangular duct made of stainless steel. The cross-sec-

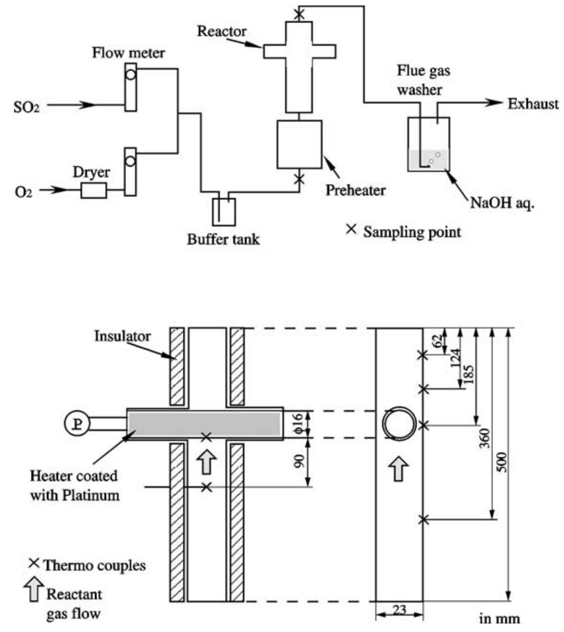

Fig. 1. Schematic drawing of experimental apparatus.

tion of the duct inside is 23 mm × 23 mm and the length 500 mm. A cylindrical heater of 16 mm∅ is set horizontally at the height 290 mm from the bottom of the duct. The surface of the heater is coated with catalyst and uniformly heated electrically with a constant heat flux from the inside by the DC power supply. The clearance between the duct wall and the cylinder is as small as 3.5 mm. The surface temperature of the heater is measured by attaching a K-type (CA) thermocouple of 0.1 mm∅ at the forward stagnation point. The temperature measurements of the inlet gas and the duct wall are done by traversing the thermocouple and by inserting thermocouples into sheaths welded at each point, respectively.

The heat transfer experiments are performed for three sorts of the working fluids: oxygen as a reference of the non-reacting system, a mixture of SO_2 and O_2 and a mixture of CH_4 and O_2 as examples of reacting systems. Both the reacting systems are active for platinum catalyst. Hence the cylindrical heater coated by platinum as catalyst is used here for all runs. In these reacting systems, the reactions take place, respectively, on the surface of the catalyst as follows:

$$SO_2 + 1/2O_2 = SO_3 + 99\ \text{kJ/mole} \tag{R1}$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 800\ \text{kJ/mole} \tag{R2}$$

While the former reaction changes stoichiometrically the volume, i.e. the reaction of 1 molar SO_2 and a half molar O_2 produces only 1 molar SO_3, the latter proceeds with no volume change.

The acid gas of the residue SO_2 and the product SO_3 is neutralized by NaOHaq in the system of the reaction (R1) and then only oxygen is exhausted to the outside.

The experimental procedure is as follows: Firstly O_2 is fed to the duct at a fixed flow rate and the electric power is supplied to the heater. When the system reaches the steady state, each temperature and the amount of the electric power are measured. After SO_2 or CH_4 is added so as to maintain a fixed concentration, electric power and temperatures are determined at steady state. The concentration of each component in the gas sampled at both the inlet and the outlet of the duct is analyzed by the gas-chromatograph to determine the reaction rate. The heat transfer coefficient is defined by Eq. (1) based on the temperature difference between the inlet gas and the surface of the cylinder:

$$h = \frac{q_{\text{conv}}}{A(T_s - T_b)}, \tag{1}$$

where q_{conv} is the apparent convective heat flux determined from Eq. (2) to eliminate the contribution of the radiant heat flux because of high temperature of the heater surface:

$$q_{\text{conv}} = q_s - q_{\text{rad}}, \tag{2}$$

where q_s is the electric power supplied to the heater and q_{rad} is the radiant heat flux which is estimated from the temperatures of the cylinder surface and the duct wall. When the reaction takes place, q^*_{conv} defined by Eq. (3) is applied replacing q_{conv} in Eq. (1):

$$q^*_{\text{conv}} = q_{\text{conv}} + q_{\text{react}}, \tag{3}$$

where q_{react} is the exothermic enthalpy due to the reaction given by $r\Delta H$.

3. Results and discussion

Fig. 2 shows the relation between the Reynolds number, *Re* and the Nusselt number, *Nu* observed experimentally for the flow of the non-reacting gas, i.e. O_2. The heat transfer coefficient on the forward stagnation point for the cross flow around the cylinder in an infinite space can be correlated as [12]

$$Nu = 1.14Pr^{0.4}Re^{0.5}. \tag{4}$$

The empirical correlation is drawn by a broken line for the comparison. The present data is remarkably greater than expected by the correlation. This difference can be caused because the experiment is carried out in the cross flow in small clearance between the cylinder and the duct wall. When the correlation involving the effect of the clearance by Robinson and Han [13] is plotted by a solid line, the line shifts toward the experimental data, but the deviation is still large. While the present experiment was

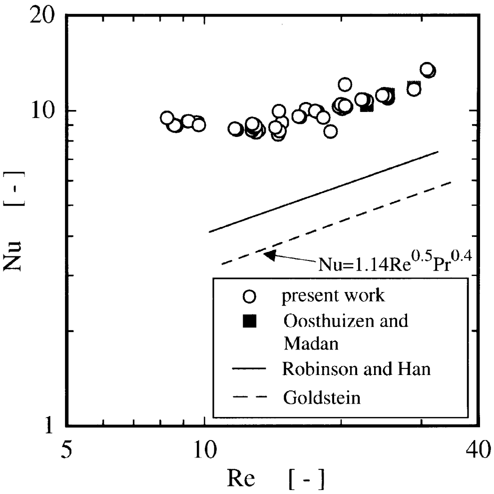

Fig. 2. Comparison of Nusselt number between measured data for non-reacting system and result estimated from empirical correlations.

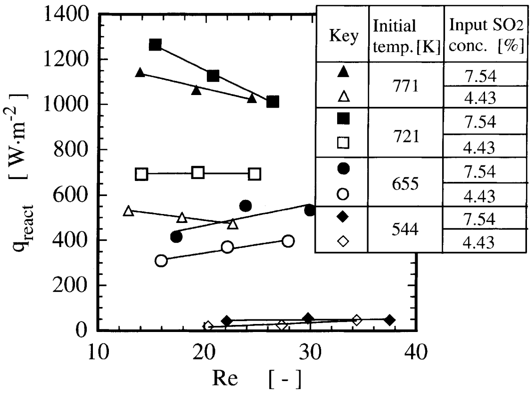

Fig. 3. Heat generation by the exothermic reaction of various mixtures of SO_2 and O_2 on the heating surface coated by catalyst.

done in lower Reynolds number region than 40, the temperature difference between the heating surface and the gas stream was significantly larger than 150 K for all runs. Under these conditions, the effect of natural convection could not be neglected. Hence the correction for predicting the combined forced and natural convection by Oosthuizen and Madan [11] is added furthermore to *Nu* of the solid line. The fitness is improved as far as it is applied in the region of *Re* over 20 as their correction is beyond the applicable limit of this correlation in lower *Re* than 20. In such a low region of the Reynolds number, the ratio of the Grashof number to the Reynolds number ($= Gr/Re^2$), which represents the effect of natural convection, becomes 30 and more, but there is no way available to the empirical prediction. This trend implies at least that the heat transfer around the cylinder is influenced by various factors including buoyancy and a close wall, and the mechanism is complex phenomena. However, the present paper aims to study the contribution of a catalytic reaction to the heat transfer on a combined catalyst and heat transfer surface, and the effect of natural convection will not be described furthermore here.

The exothermic reaction rate of SO_2 and O_2 is shown against the Reynolds number in the form of the heat generation rate per unit surface area of the cylinder in Fig. 3. The rate is influenced remarkably by the surface temperature and the composition in the reactant gas fed to the test section. The reaction rate is negligibly small at the lower temperature than 544 K. This reaction becomes a maximum rate at 721 K in the initial surface temperature, which is defined by the temperature under the reaction free in the flow of only O_2, and slows down beyond the temperature as the equilibrium of the reversible reaction shifts toward the direction reducing the formation of SO_3 above the temperature. The larger concentration of SO_2 lifts the reaction rate in the present experimental conditions. The reaction must be generally enhanced with increasing *Re* if the rate is controlled by diffusion of the reactants in the boundary layer around the cylinder. However, the overall rate is noticed to slightly fall against Reynolds number when the temperature is higher than 721 K. The reaction rate is correlated by the reaction kinetics, that is dependent on activity of catalysis, temperature and composition of reactants on the surface of catalysis. In particular, reversible reactions take place by competition of the forward and backward reactions. The composition on the surface is determined by the generation and the dissipation rate of components due to the reaction as well as mass transfer in the boundary layer on the catalytic surface. In the present system, the mass transfer behavior is significantly complex to evaluate quantitatively due to an interaction of the flow through the small clearance around the cylinder and natural convection. The measured data of the reaction rate also include somewhat inaccuracy of the composition analysis since much small difference of the composition must be detected in the analysis of chemical species. The integration of these factors resulted in showing the reaction behavior in Fig. 3. More discussion on this kinetics will not be done here since it is beyond the objective of the present study.

Fig. 4 shows the convective heat flux determined from the sum of the chemical enthalpy and the electric power supplied to the cylinder. But the flux excludes the radiative heat transfer emitted from the surface as the energy of the sum of the chemical enthalpy and electric power is transferred by both convection and radiation to the surrounding from the surface of the cylinder. The flux increases slightly against the Reynolds number.

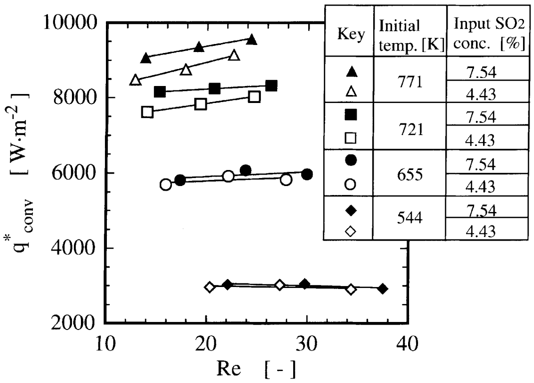

Fig. 4. Total convective heat flux on the heating and reacting surface in the SO_2–O_2 reaction system.

Based on these data, the convective heat transfer coefficient is plotted in Figs. 5(a)–(c). The heat transfer coefficient rises larger than that in non-reacting system at any initial surface temperature when the reaction takes place at least. Particularly, the effect of the heat transfer enhancement due to the reaction is apparently most significant at 721 K, where the reaction rate is expected to be maximum as far as the experiments were carried out in this range of the SO_2 concentration by using the present catalyst whose effect may not be so significant thermodynamically.

The effect of the heat transfer enhancement is plotted by the form of the ratio of the heat transfer coefficient in the reacting system to that in the non-reacting system, h/h_0 in Fig. 6. The convective heat transfer accompanied with the reaction is improved by 4–16% depending on the operating conditions carried out in the present work. The fact implies that the catalytic reaction influences positively the heat transfer behavior in the boundary layer on the surface of the cylinder. The ratio h/h_0 falls somewhat with an increase of Re in the region of $12 < Re < 30$ except for the initial surface temperature 655 K. The influence of the SO_2 concentration appears remarkably as well. These behaviors show a similar trend to the reaction heat in Fig. 3.

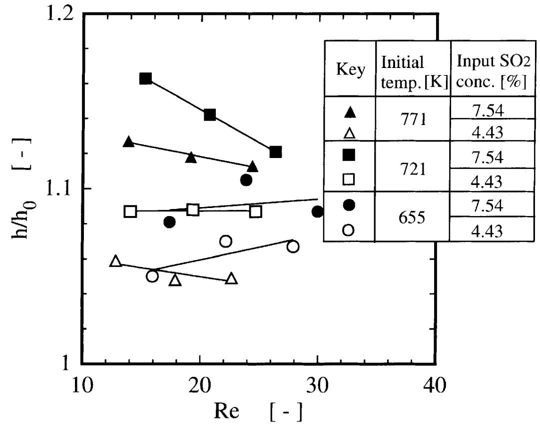

Fig. 6. The effect of the SO_2–O_2 reaction on the convective heat transfer on the catalytic surface.

In order to correlate all these data, the ratio h/h_0 is plotted as a function of the ratio of the convective heat flux accompanied with reaction to the flux in non-reacting system in Fig. 7. All data results are collected successively on a line which is proportional to $q^*_{\mathrm{conv}}/q_{\mathrm{conv}}$, where q_{conv} is the heat flux in the non-reacting system. This fact implies that the convective heat transfer is enhanced by the magnitude corresponding to the enthalpy generated by the exothermic reaction on the surface. It should be noted that this behavior must be substantially different from the effect seen in the heat transfer on the cooling catalytic surface with the exothermic reaction as reported in the past work by Rothenberg and Smith [7]. While energy is transported through the boundary layer on the surface by the two

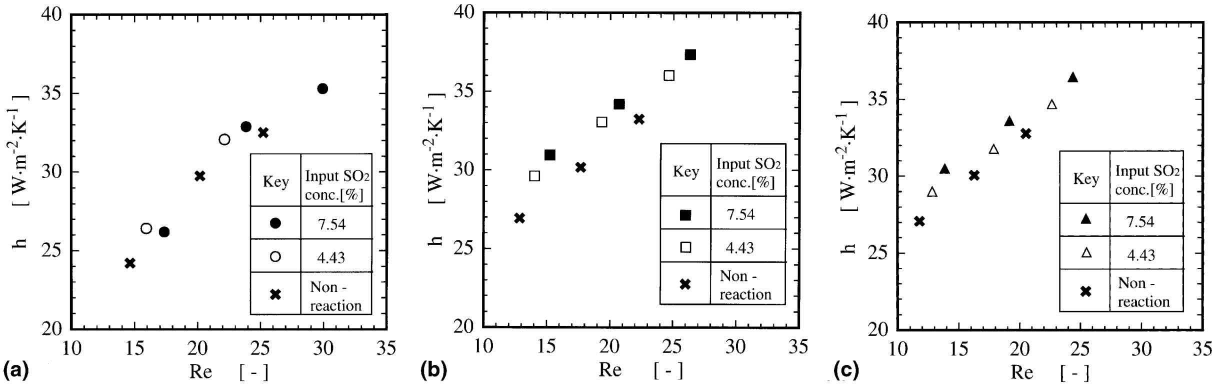

Fig. 5. Heat transfer coefficients on the surface of the cylinder against Reynolds number in the SO_2–O_2 reaction system: (a) surface temperature 655 K, (b) 721 K, (c) 771 K.

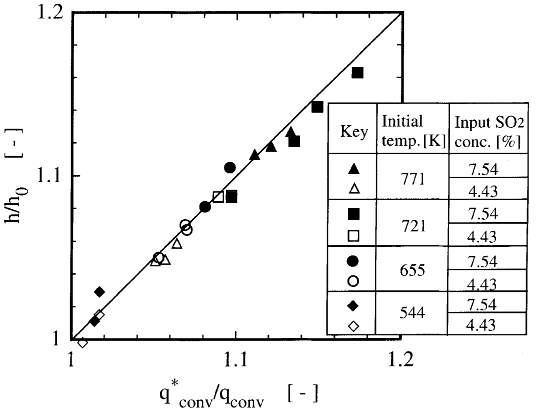

Fig. 7. Correlation between the heat transfer coefficients and reaction heat generation in the SO_2–O_2 reaction system.

modes of heat convection and chemical enthalpy transfer caused apparently by diffusion or movement of reactants involving internally the reaction enthalpy in their system, total heat excluding radiation must be conveyed only by convection or sensitive heat to the fluid from the heating surface in the present system. Hence these results reveal that the heat transfer in the boundary layer may be influenced by such interactions as the diffusion of the reaction species and/or the stoichiometric change of the chemical reaction. Finally the contribution of the surface catalytic reaction to convective heat transfer can be empirically expressed as a function of the reaction rate and the convective heat transfer rate in the non-reacting system:

$$h/h_0 = q^*_{\mathrm{conv}}/q_{\mathrm{conv}} = (q_{\mathrm{conv}} + r\Delta H/)/q_{\mathrm{conv}}. \tag{5}$$

The correlation can be applicable in the following range: $12 < Re < 30$, $655\ \mathrm{K} < T_s < 771\ \mathrm{K}$ and $4\ \mathrm{vol\%} < C_0 < 8\ \mathrm{vol\%}$ at least.

The above correlation involves the influence of the reaction with the stoichiometric change on the convective heat transfer. In order to examine what interaction dominates the effect of heat transfer enhancement due to the reaction, a similar experiment is carried out for the reaction system of CH_4–O_2/CO_2–H_2O as well. In this reaction system, one mole of methane and two moles of oxygen produce one mole of carbon dioxide and two moles of water, and the volume of the gas does not change finally between before and after the reaction. The relationship between h/h_0 and $q^*_{\mathrm{conv}}/q_{\mathrm{conv}}$ is drawn in Fig. 8. The result shows the same behavior as seen in Fig. 7 even if this reaction system belongs not only to volumetric change but also proceeds more rapidly than the SO_2–O_2/SO_3 system.

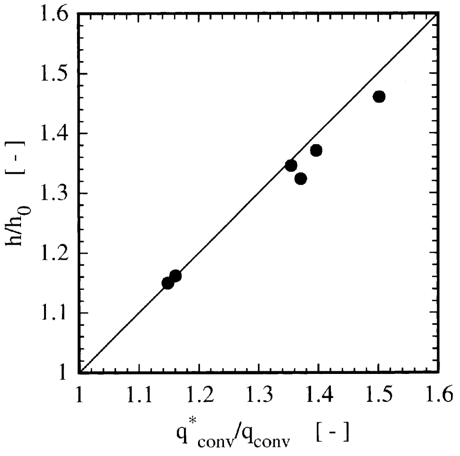

Fig. 8. Correlation between the heat transfer coefficients and reaction heat generation in the CH_4–O_2 reaction system.

If those results are summarized, it can be concluded that the convective heat transfer is enhanced rather by the following combined factors than by the stoichiometric change of reactions in this heat transfer system: (1) promoting the transportation of the sensible heat accompanied with diffusion of the reactants and (2) affecting the flow pattern, microscopic motion of molecules and/or energy transmission mechanism between molecules on the catalytic surface due to an interaction of activation states of reactants in the progress of the reaction. The quantitative evaluation should be proven by more accurate microscopic experiment in the future works.

4. Conclusion

The convective heat transfer was studied for the reactive gas flow across the cylinder coated by catalysis and placed horizontally in a narrow duct. The heat transfer coefficients on the heating surface were enlarged by coexistence of the catalytic exothermic reaction, and the maximum degree of enhancement was about 16% in the present experimental range. The effect of the heat transfer enhancement rises almost in proportional to the increase of the reaction rate relating to the equilibrium and the mass transfer. It is also implied that the heat transfer in which the exothermic reaction takes place on the heating surface is influenced rather by combined factors including diffusion of the chemical species and microscopic phenomena during the reaction than by the change of the flow pattern in the boundary layer caused by reaction.

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