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Experimental study of CH_4 catalytic combustion on various catalysts

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Abstract

The objective of this paper is to experimentally study the reaction performance of methane catalytic combustion and hydrogen assisted combustion in a monolith honeycomb reactor with various promoters. The characteristics of catalytic ignition and reaction with various promoters are investigated with a view to developing more efficient technology and improving the use of precious metal catalysts. This paper presents experimental results on CH_4 and H_2 assisted catalytic combustion performance of 3 cordierite-based honeycomb monolith reactors. The experimental results show that the honeycomb with Pd catalyst and various promoters show different reaction activities, the required combustor inlet temperature can be lower as the catalyst temperature can be increased by the heat release due to catalytic hydrogen oxidation at lower temperatures, the addition of hydrogen ensures light-off of ultra low heat value fuel.

Keywords: Catalytic combustion, Cordierite-based honeycomb catalyst, Catalytic ignition

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1. Introduction

Catalytic combustion of methane and other hydrocarbons is a promising technology for the reduction of pollution emissions, especially nitrogen oxides. Considerable efforts have been devoted to research and development of catalytic combustors for gas turbine application. Lean-burn gas turbines have been developed worldwide [1, 2]. The recuperative gas turbine of Energy Development Limited (EDL) is designed to operate when the methane concentration in air is above 1.6%, which leads to the air being preheated to 973 K. The Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia and Ingersoll Rand (IR) in USA are also trying to develop a microturbine with a catalytic combustor powered by 1% methane in air. Catalytic combustor development is the key technology for the lean-burn gas turbine. The noble metal catalyst is considered more effective for methane oxidation, but there are some issues for noble metal catalysts such as high temperature thermal stability, low temperature reactivity and high price [3]. Considering the problems, it would be highly desirable to design high thermal stability and a cheaper system.

The catalytic monolith combustor utilizes a honeycomb-type monolithic reactor, and is known for its outstanding characteristics of very low pressure drop at high mass flows, high surface area and high mechanical strength [4–6]. Therefore, the catalytic monolith combustor is appropriate for the lean-burn gas turbine since a low pressure drop is a prerequisite with a gas turbine.

Some work has been done by researchers into the reaction activation of various catalysts. Lee, Trimm

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Email address: `liuaiguo119@yahoo.com.cn` (Aiguo Liu*) and Ledwich drew some valuable conclusions: Pt and Pd are generally found to be the most active catalysts for low temperature oxidation. Pd especially is considered the most active catalyst compared with the others [7, 8].

For applications in gas turbines there is an urgent need for thermal stability catalysts to be developed since the noble metal catalyst will sinter at high temperature. Due to its thermal stability CeO_2-ZrO_2 is a promising candidate for use as an active phase in catalytic combustion, but CeO_2-ZrO_2 has poor low temperature activity, lower specific area and hole volume, which can affect the light-off and reaction characteristics [9–11]. A convenient light-off mechanism is the key point of a catalytic combustor applied in a gas turbine [12]. The addition of hydrogen to the initial mixture may help to reduce the ignition temperature, because catalytic ignition of hydrogen occurs at almost room temperature [13–15].

In the present work, the honeycomb monolith catalytic combustor with various promoters in washcoat and lower Pd content was studied experimentally to analyze the performance of the monolith reactor. The reaction condition was closer to actual engineering for the commercial applications of the catalytic combustion technique. Various washcoats were suggested, the reaction characteristics of CH_4 and the H_2 assisted catalytic ignition of lean methane/air mixtures were studied experimentally. This paper sets out the test results of the catalytic combustor under traditional gas turbine operation conditions.

2. Experimental rig and catalysts

Use of Pd as the active component for the oxidation of CH_4 is the most promising because Pd has a high specific activity in this reaction and a relatively low volatility compared to other noble metals [16]. These properties of Pd attract researchers' interest to its behavior in the methane oxidation reaction. Alumina has a reasonable match thermal expansion with cordierite, which can ensure the catalyst adheres firmly to the substrate. Supporting Pd on a substrate using γ-Al_2O_3 or modified with other element oxides can increase the surface area and thermal stability of the catalyst through an increase in the degree of dispersion of the active component and its aggregation stability [17–21].

Table 1: Catalyst characteristics

NO.	catalyst
NO.1	0.5%Pd/CeO_2 /γ-Al_2O_3
NO.2	0.5%Pd/ZrO_2 /γ-Al_2O_3
NO.3	0.5%Pd/Ce/ZrO_2 /γ-Al_2O_3

The substrate of the honeycomb monolith is the cordierite, which has the desired properties of a low thermal expansion coefficient and high temperature stability. The honeycomb monolith used in the experiment is 200 cells per square inch with an approximate 1.8 mm diameter and 0.4 mm wall thickness for each channel. The blockage ratio is 20% and the maximum working temperature is less than 1173 K. For the preparation of honeycomb samples one can refer to [22].

The honeycomb monolith was washcoated with γ-Al_2O_3 loading 6 wt% of the monolith weight in the solution and calcinated at 620 K for 2 hours. Then the active phase CeO_2 and ZrO_2 was deposited by dipcoating. The monoliths were dipped into the $Ce(NO_3)_3$ and $ZrO(NO_3)_2$ solution for 20 minutes for the monoliths with CeO_2 and ZrO_2 washcoats. The monoliths were calcinated at 620 K for 2 hours and 1120 K for 8 hours. The resulting CeO_2, ZrO_2 and Ce/ZrO_2 loading was 6 wt% of the total weight of the structured catalyst, which can be checked by X-ray fluorescence. Pd impregnation was achieved by saturating the monolith several times with an ammonia aqueous solution of $Pd(NO_3)_2 \cdot 2H_2O$ followed by 4 hours of calcination at 720 K. The analytical composition was determined by ICP (inductively coupled plasma) analysis and corresponds to a total Pd loading of 0.5 wt% of the monolith weight. Energy dispersive X-ray spectroscopy measurements showed that no other compounds were left on the catalyst surface after the impregnation process. As a result, 3 Pd based catalysts were prepared with varied substrate, i.e. with γ-Al_2O_3 modified with CeO_2 and ZrO_2. A solid solution of CeO_2 and ZrO_2 with the composition of $Ce_{0.63}Zr_{0.37}O_2$ was also prepared, because this support has a relatively high BET area and preservation of oxygen mobility in methane combustion [23]. A summary of catalyst samples is given in Table 1.

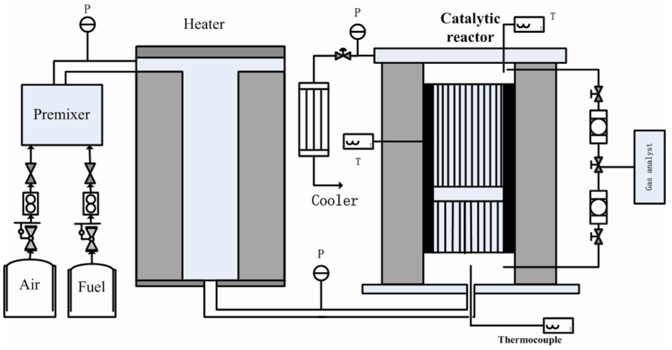

Figure 1: Schematic diagram of catalytic combustion experimental rig

A sketch of the experimental setup is shown in Fig. 1. The catalytic combustion reacts on the monolith honeycomb reactor with a premixer and a preheater. The premixer is designed to give good premixing of fuels and air to produce a uniform concentration profile at the inlet. Mass flow meters are used to control the fuel and air flow rates, fuels and air are premixed in the pre-mixer to achieve the desired fuel concentration. The premixed gas flow is preheated by an electrical heater to the desired temperature to activate the catalyst. The honeycomb monoliths with the cordierite substrate, Pd catalyst and various washcoats are placed within a cylindrical reactor with a diameter of 92 mm and the wall is insulated to minimize heat loss. 3 honeycomb monoliths are placed in the cylindrical reactor in line, each with the length 127 mm. One unloaded monolith is placed in front of the others in order to preheat and stabilize the gas flow.

3 K-type thermocouples are placed in the inlet, center and exit of the monolith respectively. The inlet one is placed below the monolith to monitor the preheater temperature and this value is termed the preheated temperature. The center and exit thermal couples are used to analyze the reaction characteristics. Species concentrations of the inlet and exit are measured using gas analyzers through quartz-sampling probe to calculate the fuel conversion ratio. During the reaction, some CO is formed at the catalytic surface and diffuses into the gas phase, but almost all the CO can be consumed by the surface reaction again, so the CO is not detected by the analyzer. The refrigerative dehumidifier and desiccants are used before sample gas enters the gas analyzer.

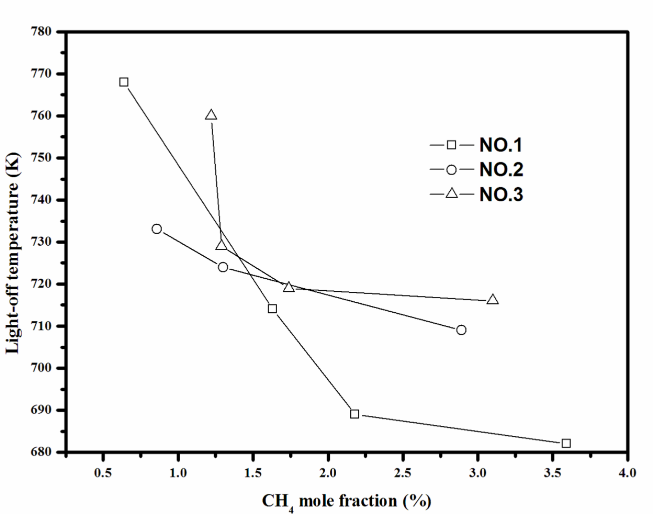

Figure 2: Experimental light-off temperature

3. Experimental result and discussion

3.1. Catalytic combustion of CH_4

Ce is widely used in the three-way automotive catalyst and its main function is to act as an oxygen storage component. But its thermal stability seems to be insufficient for high temperature. Zr appears to be the best additive to increase thermal stability, and the solid solution of Zr and Ce can improve oxygen storage capacity and oxygen mobility [24, 25]. The light-off performance and fuel conversion rate are key points for the use of Pd catalyst with Zr, Ce promoters.

Each experimental run starts with preheating the monolith to 500 K with constant air flow. In all the experiments, the GHSV was set at a realistic value of 100,000 h^{-1} before the preheater. The fuel and preheater temperature are slowly increased until the temperature of monolith center changes in a notable fashion. The temperatures are measured in front and behind the monolith in the gas phase. The point at which the monolith exit temperature is higher than the inlet temperature is called the light-off temperature. The measured light-off temperature is less than the adiabatic temperature due to heat loss from the monolith to the ambient room temperature and a decrease between the thermocouple and monolith. Fig. 2 shows the light-off temperature for methane oxidation as a function of fuel concentration for different catalysts. As expected, the light-off temperature decreases as the fuel concentration increases.

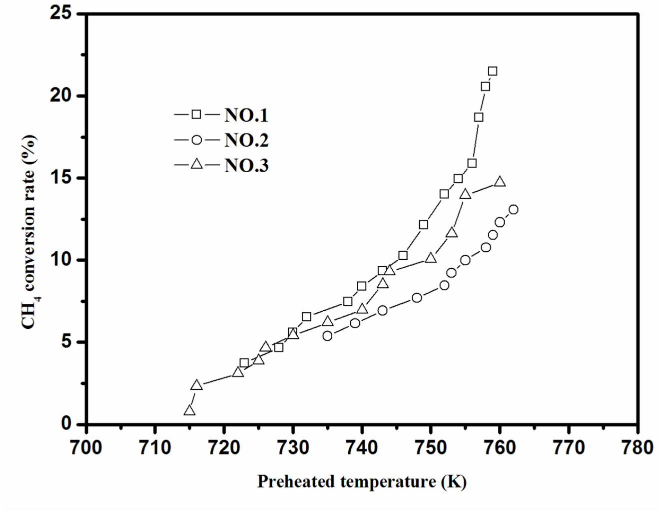

Figure 3: Fuel conversion ratio as a function of preheated temperature

But the light-off temperature was relatively higher than the other result [26]. This is caused by the lower Pd content and the non-adiabatic conditions of the reactor.

The light-off temperature decreases as the methane concentration is gently increased for catalyst NO.2. For NO.1 and NO.3, there is a turnover point. The light-off temperature changes markedly after the turnover point. For catalyst NO.1, the methane concentration at the turnover point is 2.25%, while for NO.3 it is 1.2%. The light-off performance of catalyst NO.2 is better than NO.1 when the fuel concentration is lower than 1%, while over this value the performances change in the opposite direction.

The effect of preheated temperature on the methane conversion rate was tested using various catalysts at the methane concentration 1.3%, as shown in Fig. 3. It is evident that at the same space velocity, pressure and fuel concentration, the conversion rate dramatically increases when the preheated temperature increases. This is due to the higher preheated temperature increasing the combustion intensity and particularly the reaction rate. The trends remain the same for different catalysts.

Different catalysts are shown to have different light-off and reaction properties, and this is because they contain different promoters. The catalyst with promoter CeO_2 performs better than ZrO_2 and Ce/ZrO_2 solid solution.

The reaction of fuel on the catalyst surface is a process of adsorption-reaction-desorption. The fuel and oxygen absorb on the active base through different absorption activity and decompose to response elements. The response elements combine with each other to generate new material from the surface to complete the surface reaction. The rule of γ-Al_2O_3 is to increase the reaction surface. The promoter CeO_2 is used as an oxygen storage component and ZrO_2 is used as an additive to CeO_2 to increase thermal stability. Promoters can improve some defects of precious metal catalysts, but this can also reduce the reaction energy of catalysts due to the formation of the reduction agent being covered with adsorption centers, the formation of metal complexes, the charge-transfer effect of oxygen adsorption, reaction area and the reduction of activation energy [27–29]. The additive ZrO_2 introduces Zr^{4+} ions into the CeO_2 lattice, which as the experimental results show affects catalytic activity.

3.2. H_2 assisted catalytic combustion

Methane is the least reactive of the hydrocarbons and therefore the most difficult to oxidize. All the hydrogen can be consumed by heterogeneous reactions on the catalyst at room temperature. However, there are some problems with using hydrogen at lower temperatures: easy explosion, storage and transportation difficulty. The methane can light-off at lower temperature using hydrogen as assisted fuel. The hydrogen assisted catalytic combustion of methane on Pt has been studied experimentally [15]. In this study the hydrogen assisted catalytic combustion of methane on Pd with various promoters using the same experimental rig was completed.

The H_2 assisted catalytic light-off of CH_4 is primarily determined by the catalyst temperature. The catalyst temperature is a consolidated result of preheated temperature and the heat release due to catalytic H_2 oxidation. Fig. 4 shows the methane conversion rate as a function of preheated temperature and hydrogen concentration for 3 different catalysts. The required preheated temperature for the light-off of methane decreases with increasing hydrogen content as shown, while the reaction performances are different for different catalysts and hydrogen concentrations.

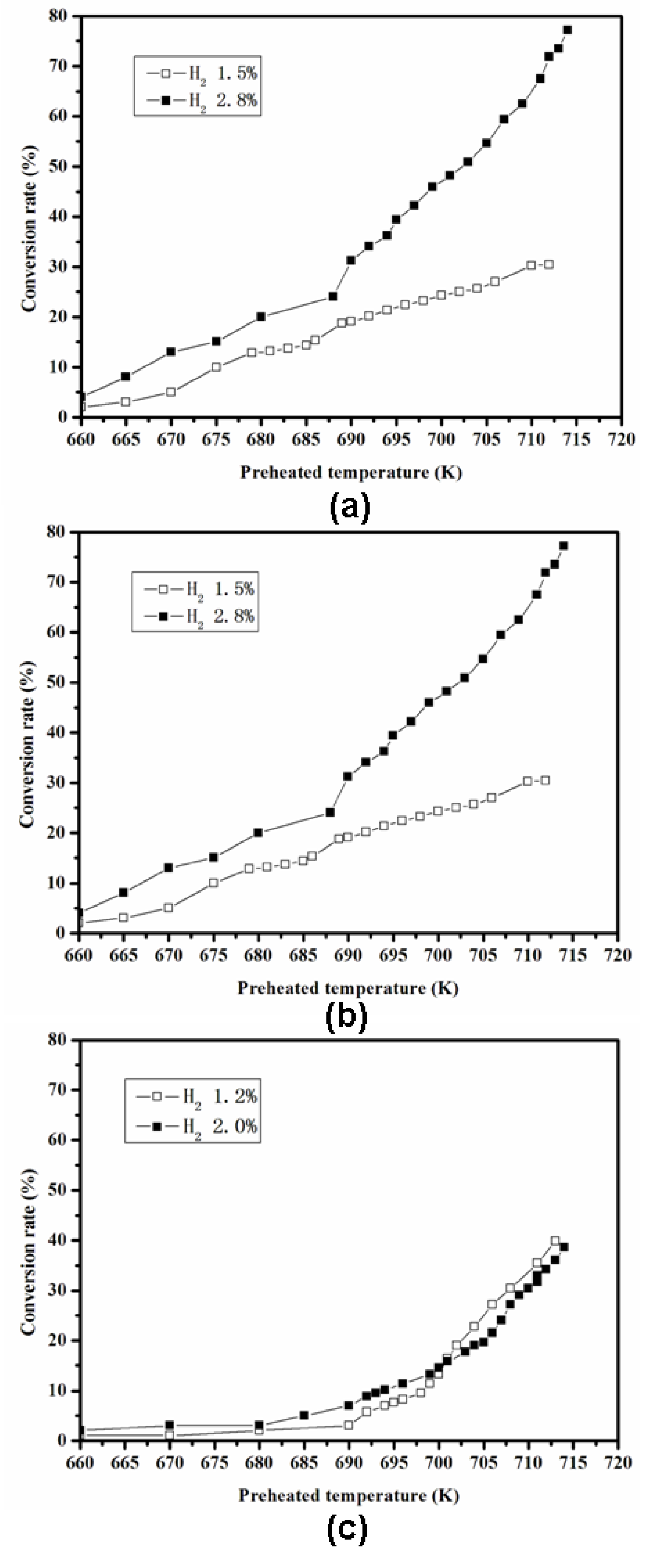

Figure 4: Performance of CH_4 conversion rate with preheated temperature and H_2 concentration for 3 catalysts

The light-off temperature decreases as the H_2 concentration increase. This can be explained as follows: the oxygen is in excess for the mixture, the surface of the catalyst is mainly covered with oxygen, which inhibits methane adsorption and subsequent oxidation. The sticking coefficient of hydrogen is about four times larger than that of methane. Hence, almost all the uncovered surface sites available will be used for hydrogen adsorption and hydrogen is completely depleted. The H_2 oxidation can lead to a temperature at which CH_4 oxidation starts in the H_2 assisted catalytic light-off. With the increase of addition H_2, the CH_4 conversion rate increases at the same preheated temperature.

Fig. 4(a) and (b) show the reaction performances for NO.1 and NO.2 monolith with the different hydrogen addition for the 3.2% methane concentration. The addition of hydrogen into the initial mixture helps to reduce the light-off temperature due to the hydrogen light-off properties at lower temperatures on the catalyst. The catalyst temperature can be increased due to the heat release of catalytic hydrogen oxidation, and then realize the conversion of methane. The increasing methane conversion rate is evident when the addition hydrogen concentration increases from 1.5% to 2.8%. The methane conversion rate increases 30% as the hydrogen addition increases from 1.5% to 2.8% with the 700 K preheated temperature.

Fig. 4(c) shows the reaction performances for catalyst NO.3 with a methane concentration of 1.58%. The effect of H_2 concentration increasing from 1.2% to 2.0% is not evident in the methane conversion rate. The preheated temperature has a different effect on the conversion rate after 700 K. The methane conversion rate with lower hydrogen addition is higher than the higher hydrogen addition. This performance may be caused by the addition of promoters and the adsorption performance of a different composition on the catalyst surface. This phenomenon should be studied in various aspects including reaction kinetics, effects of promoter on catalyst activities and so on. This paper does not enter into a detailed discussion of these matters.

4. Conclusions

The effects of various promoters and hydrogen addition on the light-off and reaction performance of methane were studied. Some defects of precious metal catalysts can be improved by the addition of a promoter, but the reaction activity of the precious metal catalyst decreases as the effect of the promoter and interaction between the precious metal catalyst and promoter increase. The light-off temperature can be decreased with the hydrogen addition, the reaction performance increases with the increase of addition hydrogen. The addition of ZrO_2 can increase the thermal stability of CeO_2, and the introduction of Zr^{4+} ions in the CeO_2 lattice does not affect the Pd catalytic activity to CH_4 markedly.

Acknowledgments

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References

[1] S. Su, A. Beath, H. Guo, C. Mallett, An assessment of mine methane mitigation and utilisation technologies, Prog Energy Combust Sci 31 (2) (2005) 123–170.

[2] S. Su, A. C. Beath, C. W. Mallett, A method and system for combustion of methane (2002).

[3] E. M. Johansson, K. M. J. Danielsson, Catalytic combustion of gasified biomass over hexaaluminate catalysts: influence of palladium loading and ageing, Applied catalysis A: General 182 (1999) 199–208.

[4] S. Cimino, R. Pirone, G. Russo, Thermal stability of perpvskite-based monolithic reactors in the catalytic combustion of methane, Ind Eng Chem Res 40 (2001) 80–85.

[5] R. M. Heck, S. Gulati, R. J. Farrauto, The application of monoliths for gas phase catalytic reactions, Chem Eng J 82 (2001) 149–156.

[6] P. Marin, M. A. G. Hevia, S. Ordonez, F. V. Diez, Combustion of methane lean mixtures in reverse flow reactors: comparison between packed and structured catalyst beds, Catal Today 105 (3–4) (2005) 701–708.

[7] J. H. Lee, D. L. Trimm, Catalytic combustion of methane, Fuel Process Technol 42 (1995) 339–359.

[8] J. Ledwich, S. Bhatia, S. Su., Catalytic combustion of coal mine ventilation air: literature review and experimental preparation, in: CSIRO Exploration and Mining, 2001.

[9] S. Morel, The afterburning of carbon monoxide in natural gas combustion gases in the presence of catalytic ceramic coatings, Journal of Power Technologies 92 (2) (2012) 109–114.

[10] L.-H. Xiao, Y.-X. Yang, K.-P. Sun, Study of ch_4 low temperature catalytic combustion on pd/ceo_2 catalyst-effect of preparations on catalyst performance, Petrochemical 15 (2004) 192–193.

[11] L.-P. Gao, J.-Z. Liu, J. Wu, Characterization of reactivity and activation energy for catalytic combustion of methane on pd-m/al_2o_3, Journal of China University of Mining & Technology 39 (2010) 859–864.

[12] Z. R. Ismagilov, N. V. Shikina, S. A. Yashnik, Development and testing of granular catalysts for combustors of regenerative gas turbine plants, Kinetics and Catalysis 49 (6) (2008) 873–885.

[13] Y.-C. Chao, G.-B. Chen, H.-W. Hsu, Catalytic combustion of gasified biomass in a platinum monolith honeycomb reactor, Applied Catalysis A: General 261 (1) (2004) 99–107.

[14] S. Su, J. Agnew, Catalytic combustion of coal mine ventilation air methane, Fuel 85 (6) (2006) 1201–1210.

[15] O. Deutschmann, L. I. Maier, U. Riedel, A. H. Stroemman, R. W. Dibble, Hydrogen assisted catalytic combustion of methane on platinum, Catalysis Today 59 (1–2) (2000) 141–150.

[16] H. Arai, T. Yamada, K. Equchi, T. Seigama, Catalytic combustion of methane over various perovskyte-type catalysts, Applied Catalysis A 26 (1986) 265–279.

[17] T. R. Baldwin, R. Burch, Remarkable activity enhancement in the catalytic combustion of methane on supported palladium catalysts, Appl. Catal. 6 (1) (1990) 131–138.

[18] Y. F. Chang, J. G. McCarty, E. D. Wachsman, V. L. Wong, Catalytic decomposition of nitrous oxide over ru-exchanged zeolites, Applied Catalysis B: Environmental 4 (4) (1994) 283–299.

[19] G. Groppi, C. Cristiani, L. Lietti, C. Ramella, M. Valentini, P. Forzatti, Effect of ceria on palladium supported catalysts for high temperature combustion of ch_4 under lean conditions, Catal. Today 50 (2) (1999) 399–412.

[20] Z. R. Ismagilov, M. A. Kerzhentsev, V. A. Sazonov, L. T. Tsykoza, N. V. Shikina, V. V. Kuznetsov, V. A. Ushakov, S. V. Mishanin, N. G. Kozhukhar, G. Russo, O. Deutschmann, Study of catalysts for catalytic burners for fuel cell power plant reformers, Korean J. Chem. Eng. 20 (3) (2003) 461–467.

[21] Y. Ozawa, Y. Tochihara, M. Nagai, S. Omib, Pdo/al_2o_3 in catalytic combustion of methane: stabilization and deactivation, Chem. Eng. Sci. 58 (3–6) (2003) 671–677.

[22] L. Liotta, G. D. Carlo, G. Pantaleo, A. Venezia, G. Deganello, E. M. Borla, M. Pidria, Supported $co_3o_4 - ceo_2$ monoliths: Effect of preparation method and $pd - pt$ promotion on the co/ch_4 oxidation activity, in: D. D. V. S. H. P. J. J. M. E.M. Gaigneaux, M. Devillers, P. Ruiz (Eds.), Scientific Bases for the Preparation of Heterogeneous Catalysts Proceedings of the 9th International Sym-

posium, Vol. 162 of Studies in Surface Science and Catalysis, Elsevier, 2006, pp. 657–664.

[23] C. Bozo, N. Guilhaume, E. Garbowski, M. Primet, Combustion of methane on ceo_2-zro_2 based catalysts, Catalysis Today 59 (1–2) (2000) 33–45.

[24] P. Fornasiero, G. Balducci, R. Di Monte, J. Kaspar, V. Sergo, G. Gubitosa, A. Ferrero, M. Graziani, Modification of the redox behaviour of ceo_2 induced by structural doping with zro_2, Journal of Catalysis 164 (1) (1996) 173–183.

[25] C. E. Hori, H. Permana, K. Ng, A. Brenner, K. More, K. M. Rahmoeller, D. Belton, Thermal stability of oxygen storage properties in a mixed ceo_2-zro_2 system, Applied Catalysis B: Environmental 16 (2) (1998) 105–117.

[26] A. Cybulski, J. A. Moulin, Structured catalysts and reactors, 2nd Edition, Boca Raton, London, New York, 2006.

[27] P. Meriaudeau, O. H. Ellestad, M. Dufaux, et al., Metal-support interaction. catalytic properties of tio_2-supported platinum, iridium and rhodium, Journal of Catalysis 75 (2) (1982) 243–250.

[28] S. J. Tauster, S. C. Fung, R. L. Garten, Strong metal-support interactions. group 8 noble metals supported on titanium dioxide, Journal of American Chemistry society 100 (1) (1978) 170–175.

[29] K. S. Sim, L. Hilaire, F. Le Normand, R. Touroude, V. Paul-Boncour, A. Percheron-Guegan, Catalysis by palladium-rare-earth-metal(repd) intermetallic compounds: hydrogenation of but-1-ene, buta-1, 3-diene and but-1-yne, Chem Soc Faraday Trans 87 (9) (1991) 1453–1460.