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The development of novel metal-based combustion catalysts

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Abstract

The performance of a newly developed metal-based combustion reactor is discussed. The heat transfer properties under combustion conditions of a so-called sintered-metal reactor covered with a palladium oxide on silica catalyst have been studied up to 550°C. Also enhancement of the thermal stability of the silica by means of addition of aluminium was investigated. With mixed oxides of silicon and aluminium combustion catalysts have been prepared and they have been shown to exhibit good activity in the combustion of methane. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic combustion of natural gas is a powerful tool in reducing the emissions of NO_x, CO and unburned hydrocarbons. With catalytic combustion complete conversion to CO_2 can be attained at low temperatures, due to which NO_x formation is minimised. Application of combustion catalysts in gas turbines has received much attention, and other applications of catalysts, like for example in (radiant) heaters, (compact) reformers and domestic boilers, are presently under consideration.

Recently, a novel type of combustion reactor, the sintered metal reactor, has been developed [1–3]. This reactor exhibits a high thermal conductivity due to the good contact between the metal spheres and between the metal spheres and the reactor wall. A schematic drawing of a sintered metal reactor is given in Fig. 1. On the left-hand side of Fig. 1 a traditional fixed bed reactor filled with metal spheres is presented.

Since there is hardly any contact either between the spheres, or between the spheres and the reactor wall, the heat conductivity of a fixed bed is quite low. In Table 1 it is demonstrated that, although the heat conductivity of the individual metal particles is quite high, the heat conductivity of a bed of metal spheres is comparable to the heat conductivity of a bed of alumina extrudates.

On the right-hand side of Fig. 1 a sintered-metal reactor is presented. The metal spheres are sintered to each other and to the wall, resulting in an intimate and more extended contact. It is demonstrated in Table 1 that, as a consequence of the improved contact, the heat conductivity of a sintered metal is much higher than for a fixed bed of metal spheres, which have not been sintered. This makes a sintered metal reactor preeminently useful for strongly exothermic, or strongly endothermic processes.

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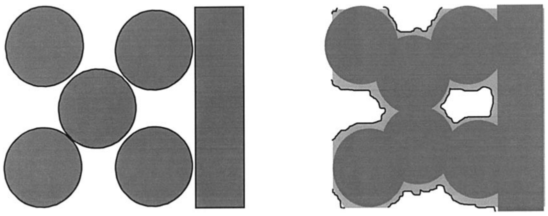

Fig. 1. Reactor in which metal spheres have not been sintered (left) and a reactor in which metal spheres have been sintered to each other and to the wall (right).

Table 1
Heat conductivity for different reactor fillings [2]

Material	Heat conductivity (W/mK)
Alumina extrudates	0.32
Metal powder (316L)	0.55
Sintered 316L powder	3–8

A problem to be encountered in the application of (sintered) metal reactors, is the low specific surface area of the (porous) metal. A highly porous layer containing the catalytically active component must therefore be deposited on the metal surface in order to obtain a sufficiently high catalytic surface area. Difficulties are met, however, in applying such porous layers on these supports. Since metal surfaces are both smooth and hydrophobic, adhesion of catalysts/oxides presents a severe problem, especially when the active component, or its precursor, has to be deposited from an aqueous solution or suspension. Consequently, traditional (dip) coating techniques are not satisfactory.

Recently, a method has been developed for deposition of thin layers of highly porous silica on sintered-metal bodies for application in gas separation. This method consists of two steps, notably application of a silicone elastomer on a metal surface and subsequent decomposition of the elastomer in air at 450°C [4]. According to this procedure a homogeneous, well adhering silica layer was deposited onto the metal surface of a sintered-metal body. This silica coated sintered-metal body was impregnated with a platinum precursor and the resulting platinum-on-silica on sintered-metal catalyst was tested in the oxidation of hydrogen [1]. Whereas the performance of the resulting catalyst was comparable to that of a fixed bed platinum-on-silica catalyst, the tube did not exhibit a significant temperature gradient, in contrast with the fixed bed.

This paper deals with the (further) development of sintered-metal reactors toward application in catalytic combustion processes. For this purpose three aspects have been studied more closely. Firstly, in order to increase the low thermal stability of the silica at temperatures exceeding 700°C, the effect of addition of aluminium sec-butoxide to the silicone rubber solution during the preparation was studied. The stability of mixed oxides of silicon and aluminium thus obtained has been investigated up to 900°C for a variety of silicon:aluminium ratios. Secondly, the most suitable silicon:aluminium mixed oxide was selected for the preparation of a supported palladium and a platinum combustion catalyst. Their activity was tested in the catalytic combustion of methane. Finally, a silica-coated sintered-metal reactor, on which palladium oxide had been deposited, was tested under combustion conditions up to 550°C. The development of temperature gradients during methane combustion experiments over the reactor length was studied.

2. Experimental

2.1. Preparation and ageing of the mixed oxides

To a solution of silicone elastomer (PDMS) in diethylether (6 wt%) a solution of aluminium sec-butoxide in diethylether was added. The solution was poured out into a glass plate, after which the solvent was allowed to evaporate under ambient conditions. The rubber was vulcanised in air at room temperature for 24 h. Next, the rubber was pyrolised in air by heating the rubber from room temperature to 600°C with a heating rate of 5°C/min, kept at this temperature for three hours and, finally, cooled down to room temperature with a rate of 5°C/min. With this procedure mixed oxides with Si:Al ratios of 80:20, 65:35, 50:50 and 35:65 were prepared.

To gain information about the thermostability of the mixed oxides the pyrolised samples were heated in stagnant air with a rate of 5°C/min up to 600, 700, 800 or 900°C, kept at this temperature for 3 h, and cooled down to room temperature with a rate of 5°C/min. Another ageing procedure was performed in which the samples were held at 800°C for prolonged periods of time. Again, the heating rate and the cooling rate were 5°C/min.

Specific surface areas and pore volumes were obtained from nitrogen adsorption–desorption isotherms measured at −196°C using a Micromeretics ASAP 2400. Prior to the measurements, all powdered samples were degassed at 100°C under vacuum. The total surface area of all samples was calculated using the BET equation.

2.2. *Catalyst preparation and activity tests*

A 6.5 wt% palladium oxide on alumina–silica catalyst was prepared by means of incipient wetness impregnation of a silicon–aluminium 80:20 mixed oxide powdered support with a $Pd(NH_3)_4(NO_3)_2$ solution (Johnson Matthey). The catalyst was dried overnight at 60°C and calcined in air for three hours at 450°C. A sample of 0.16 g of this catalyst was tested in a feed consisting of 1 vol% methane, 4 vol% oxygen and 2 vol% water in balance nitrogen at atmospheric pressure with a flow rate was 100 ml/min (STP), corresponding to a GHSV of 15 000 h^{-1}. A description of the apparatus and the procedure has been given elsewhere [5].

Also a 1 wt% Pt on silica–alumina catalyst was prepared by means of incipient wetness impregnation of a silica–alumina 80:20 powder support with a $Pt(NH_3)_4(OH)_2$ solution (Johnson Matthey). The catalyst was dried overnight at room temperature and calcined overnight in air at 500°C. A sample of 0.93 g of this catalyst was tested for its activity in methane combustion in a feed consisting of 1.5% CH_4 and 10% O_2 in nitrogen with a flow rate of 473 ml/min (STP) corresponding with a GHSV of 20 000 h^{-1}.

2.3. *Sintered-metal reactor*

A sintered-metal tube, which has been described in detail elsewhere [3], was coated with a layer of silicone rubber. After decomposition of the rubber in air by keeping the tube during 24 h at 600°C, a silica loading of 170 g/l was obtained. The catalytically active phase was applied onto the silica coating, by impregnating a $Pd(NH_3)_4(NO_3)_2$ solution (Johnson Matthey) into the metal tube, using the capillary forces of the system. In three impregnation steps, with intermediate calcination (500°C, stagnant air), 4 g of palladium was applied. A total palladium loading of 0.75 wt% based on the weight of the sintered metal and, consequently, 10.4 wt% based on the silica coating, was obtained. This reactor was tested for varying inlet gas temperatures with a feed of 1% CH_4 in air with a flow rate varying from 200 to 400 Nl/min. More details about the test procedure have been given elsewhere [3].

3. Results

3.1. *Thermal stability of silica–aluminas*

The main drawback of using silica layers prepared from silicone rubbers is their insufficient thermal stability. Mulder has shown that after pyrolysis at 800°C a surface area smaller than 10 m^2/g is obtained [6]. This decrease of surface area with increasing temperature is presented in Fig. 2. According to Mulder an enormous enhancement of the thermal stability was observed after addition of titanium, while the microporous nature of silica was preserved. For fast catalytic reactions, however, large pores are preferred over micropores. For this purpose another additive, aluminium, was selected. The results obtained with mixed oxides of silicon and aluminium are presented in Figs. 2 and 3. In Fig. 2 the effect of ageing temperature is presented, in Fig. 3 the effect of prolonged ageing periods at 800°C.

The addition of aluminium enhances the thermal stability with respect to pure silica. Moreover, higher specific surface areas are obtained with decreasing silicon:aluminium ratio at all temperatures. With the silicon–aluminium oxide with a ratio 35:65 a surface area larger than 350 m^2/g was obtained, even after ageing at 900°C.

Another property that determines the quality of the coating is its "sticking efficiency". The "sticking efficiency" of the pure silicone rubber is very high, resulting in layers that are well attached to the metal surface. The "sticking" properties of the silicone rubber mixed with aluminium sec-butoxide tend to decrease with decreasing silicon:aluminium ratios. Consequently, unsatisfactory results were obtained with rubbers with silicon:aluminium ratios of 50:50 and 35:65. The silicon–aluminium oxide with a ratio of 80:20 is favoured, since it exhibits the optimum

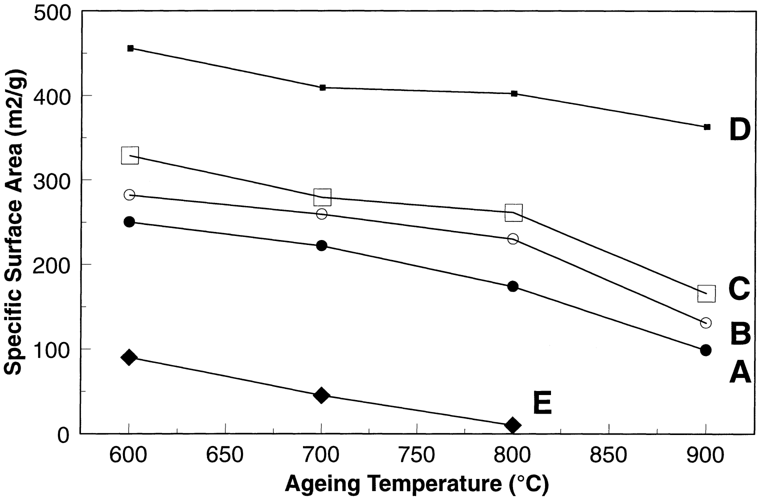

Fig. 2. Thermal stability of mixed oxides of silicon and aluminium in the ratios 80:20 (A,●), 65:35 (B,○), 50:50 (C,□) and 35:65 (D,■), and of pure silica (E,◆) as a function of ageing temperature. At each temperature an ageing time of 3 h was chosen.

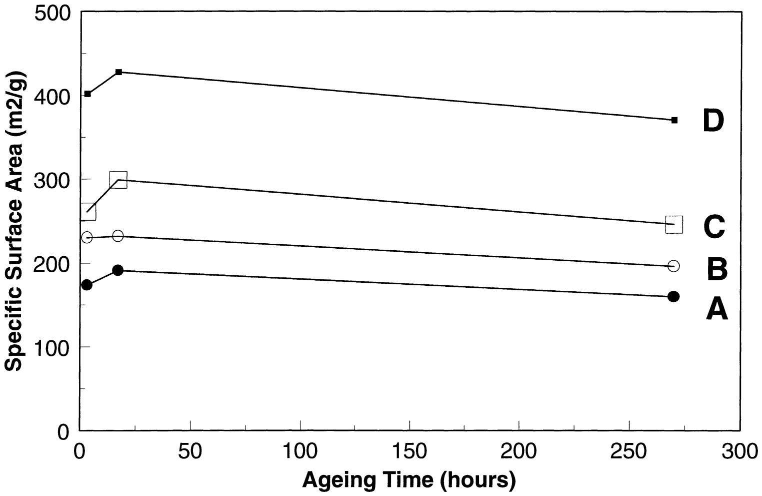

Fig. 3. Thermal stability of mixed oxides of silicon and aluminium in the ratios 80:20 (A,●), 65:35 (B,○), 50:50 (C,□), and 35:65 (D,■) as a function of ageing time at 800°C.

combination of thermal stability and costability. The lowest surface areas are observed for this material, but it is expected that a surface area of 100 m^2/g, which is obtained after the severest ageing conditions, is still sufficient for application as a support material in catalytic combustion processes. In the next paragraph the performance of palladium oxide and platinum catalysts prepared with the silicon:aluminium 80:20 supports is presented. For this purpose powdered catalysts have been prepared and tested in the oxidation of methane.

3.2. *Catalyst activity tests*

The activity of the palladium oxide on silicon–aluminium 80:20 oxide catalyst is presented in Fig. 4. The activity of this catalyst, characterised by the low ignition temperature and by the low tempera-

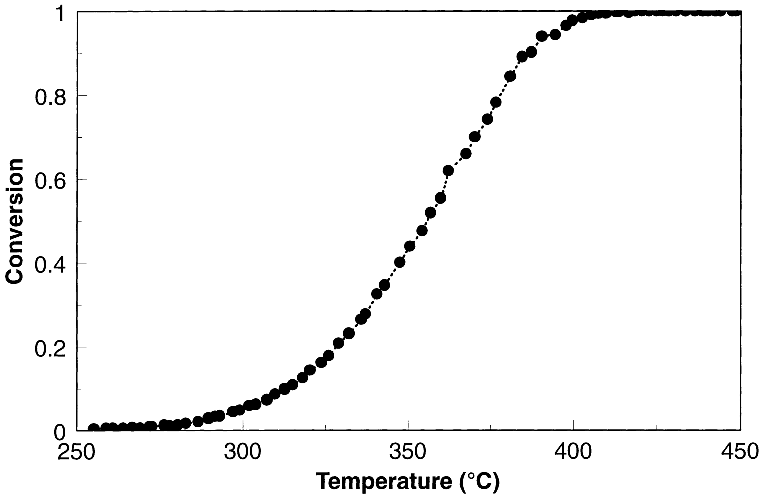

Fig. 4. Activity of a PdO on silica–alumina catalyst with a feed consisting of 1% CH_4, 4% O_2 and 2% H_2O in nitrogen (GHSV: 15 000 h^{-1}).

ture of complete conversion, is comparable to the activity observed for other supported palladium oxide catalysts. From this experiment, which was executed with a wet feed, consisting of 1% CH_4, 4% O_2 and 2% H_2O in nitrogen, an apparent activation energy of 150 kJ/mol was calculated. This activation energy, as well as the other kinetic parameters, are in very good agreement with the kinetic parameters found with other supported palladium oxide catalysts [5], which demonstrates that the silicon–aluminium oxide exhibits similar properties as common catalyst supports.

Another metal that is frequently used for catalytic combustion is platinum. In Fig. 5, the performance of a platinum on alumina–silica catalyst is presented. Again, an active combustion catalyst was obtained, thus demonstrating that indeed the mixed oxides are very suitable for application in catalytic combustion.

3.3. *Sintered-metal reactor tests*

Finally, the performance of a sintered metal reactor coated with a palladium oxide on silica catalyst was studied. The temperature profiles over the axial direction of the 10 cm tube that were observed when a feed of 1% CH_4 in air was passed through the sintered-metal reactor with a flow rate of 200 Nl/min, corresponding to a maximum heat production of 1 kW (when 100% conversion of methane is obtained), and with a flow rate of 400 Nl/min, corresponding to a maximum heat production of 2 kW, are presented in Figs. 6 and 7. The inner part of the tube was cooled with air. The flow rate of the cooling air was kept constant at 600 Nl/min, resulting in a maximum cooling capacity of ±1 kW. With the 200 Nl/min (1 kW heat production capacity) experiments a typical pressure drop of 600–850 mbar was observed. A maximum conversion of 93% was obtained.

In Figs. 6 and 7 the reactor wall temperatures measured at different axial positions along the tube (reactor length=2, 4, 6 and 8 cm), the inlet gas temperature ("reactor length"=−0.5 cm), and the outlet gas temperature ("reactor length"=10.5 cm) are presented for varying gas inlet temperatures. At low gas inlet temperatures a gradual decrease of the temperature along the length of the reactor is observed. Under these conditions low conversion of methane is observed (10–20%). Consequently, the heat production is insufficient to avoid cooling of the tube downstream. When the inlet temperature was 425°C or higher, high conversions were observed (>50%). Still, rather flat temperature profiles were. Apparently, the oxidation of methane proceeded gradually over the reactor, which is confirmed by the lack of a significant cooling effect towards the end of the reactor. This would be expected if the reaction proceeds merely in the beginning of the tube, resulting in a very localised heat production. With the 1 kW experiment, all the heat produced during the reaction had been transferred to the cooling air, since the gas inlet and the gas outlet temperature did not show a

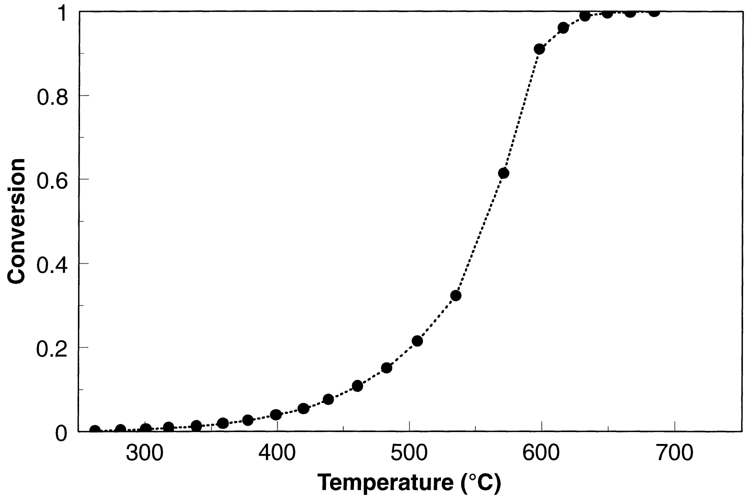

Fig. 5. Activity of a Pt on silica–alumina catalyst with a feed consisting of 1.5% CH_4 and 10% O_2 in nitrogen (GHSV: 20 000 h^{-1}).

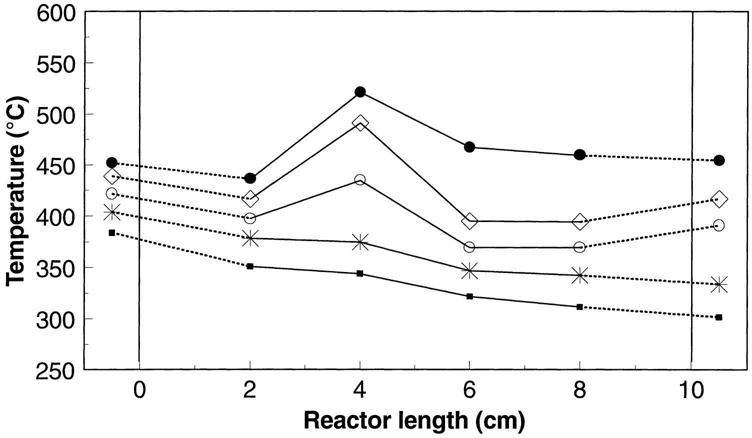

Fig. 6. Temperature profiles within the sintered-metal tube (1% CH_4, 1 kW).

significant difference. At a higher flow rate, a considerable amount of heat had been transferred to the reaction gas. This can be explained by considering that the heat production capacity exceeds the cooling capacity, when the conversion of methane becomes higher than ±50%. During all experiments the maximum temperature rise in the reactor was ±75°C, which is considerably smaller than the adiabatic temperature rise. It can be concluded that, indeed, sintered metal reactors are very efficient in minimising the development of temperature gradients. Moreover, no NO_x or CO could be detected during the combustion experiments, even when the conversion and the temperature were high. The detection limits for both are of the order of 0.1 ppm.

4. Conclusions

The ability of sintered-metal combustion catalysts to effectively transfer the heat produced during the combustion of methane has been demonstrated up to a temperature of 550°C. Application of these reactors at higher temperatures is within reach. It has been demonstrated that the thermal stability of the silica layer, which is deposited onto the metal surface, can be improved by means of addition of aluminium.

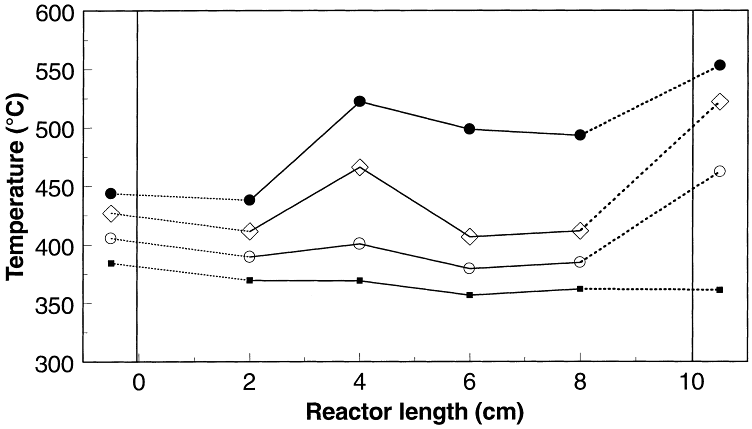

Fig. 7. Temperature profiles within the sintered-metal tube (1% CH_4, 2 kW).

Moreover, it was observed that the surface area increases with decreasing silicon:aluminium ratios. The best coating results, however, are obtained with a high silicon–aluminium ratio. Two powder catalysts consisting of palladium oxide and platinum on a silicon–aluminium 80:20 mixed oxide were tested for their activity in the combustion of methane and the performance was satisfactory.

Acknowledgements

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