Low temperature catalytic combustion of propane over Pt-based catalyst with inverse opal microstructure in a microchannel reactor†

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A novel Pt-based catalyst with highly regular, periodic inverse opal microstructure was fabricated in a microchannel reactor, and catalytic testing revealed excellent conversion and stable activity for propane combustion at low temperatures.

In order to control hydrocarbon emissions from propane-driven fuel processor/fuel cell systems, the development of an efficient catalyst for complete catalytic combustion of propane at low temperatures is essential. This combustion reaction is applied to supply energy to an evaporator, which in turn provides the fuel processor with the steam required for the steam reforming reaction similar to other submillimetre combustors.[1] A number of studies have been reported on the catalytic combustion of propane over different precious metals.[2–6] It was found that the catalytic activity varied much with both the support materials and the additives. The catalyst on the more acidic support showed higher activity, which could be remarkably enhanced by the additives with high electronegativity such as molybdenum and tungsten. However, catalytic tests are always performed using fixed-bed flow reaction systems. As is well established, fixed-bed reactors generally suffer from excessive and unsustainable pressure drops across the catalyst bed. This results in large parasitic losses by conveying fluid transportation and possible mechanical failure of the conveying devices in the application. In recent years, micro-structured reactors have shown significant advantages over conventional reactors due to their enhanced mass and heat transport and compactness.[7] However, when this new type of reactor was used for heterogeneously catalysed gas phase reactions such as propane combustion, any maldistributed coating of catalysts still results in the formation of hot spots and negate the advantages of uniform temperature and concentration profiles in the microchannels. Therefore, an even distribution of catalyst coating in the microchannel would further contribute to enhancing the process intensification by microstructured reactors. To date, various coating techniques, such as washcoating, anodic oxidation, CVD and dip-coating with sols, have been reported for various heterogeneously catalysed processes in microchannels.[7–9] However, these techniques do not generate enough surface area or the homogeneous dispersion of active elements that are required in most cases to achieve sufficient reactor productivity. Recently, Kenis *et al.* have reported on the fabrication of catalyst supports with inverse opal structure composed of silicon carbide (SiC),[10,11] or silicon carbonitride (SiCN),[10] or carbon,[12] in microchannels and characterized these catalytic monoliths by applying the decomposition of ammonia into hydrogen and nitrogen as the test reaction.[10,11] It was found that this inverted beaded bed structure has a high surface area per unit volume and the pressure drop was approximately two orders of magnitude lower than that of a packed beaded structure with the same geometric surface area. This kind of structure also avoided cracking and channeling of reactants commonly encountered with packed beds of loose catalyst particles. Herein, the preparation of Al_2O_3 inverse opals in the microchannels, and verification of their capability as catalyst support for low-temperature catalytic combustion of propane will be reported.

Before the preparation of the Al_2O_3 inverse opals, a stable aluminium sol was synthesised as stated in the ESI.† The microreactor applied was composed of two stainless steel plates with microchannels. The microchannels were formed on the stainless steel using a photoetching technique based on wet chemical etching with aqueous iron trichloride solution.[7] Each plate has 14 microchannels, and each channel has a dimension of 500 μm × 250 μm × 25 mm (width × depth × length). Before the preparation of the inverse opals coatings in the microchannels, the plates were cleaned and thermally treated at 800 °C in air for 2 h.

PMMA (Polymethylmetacrylate) monodispersed colloids with particle size of 370 nm were synthesised using the "surfactant-free emulsion polymerization" method.[13] 0.35 mL of the suspension containing 10 wt% of such kind of PMMA nanospheres was allowed to flow slowly into the microchannels from one end *via* the effect of capillary forces. Once the solution reached the other end of the channel, the nanospheres began to pack and the self-arrangement proceeded towards the inlet side with the evaporation of the solvent. Growth of ordered domains of packed nanospheres occurred when the suspension flowed to the nucleation sites to replace the evaporated solvent at the outlet end.[14] As shown in Fig. 1, this process resulted in tightly filled microchannels (Fig. 1(a)) with highly regular, periodic artificial PMMA opals (Fig. 1(c)). Then, the prepared opals were treated at 90 °C for 24 h to ensure good contact between the PMMA particles. Infiltration of the

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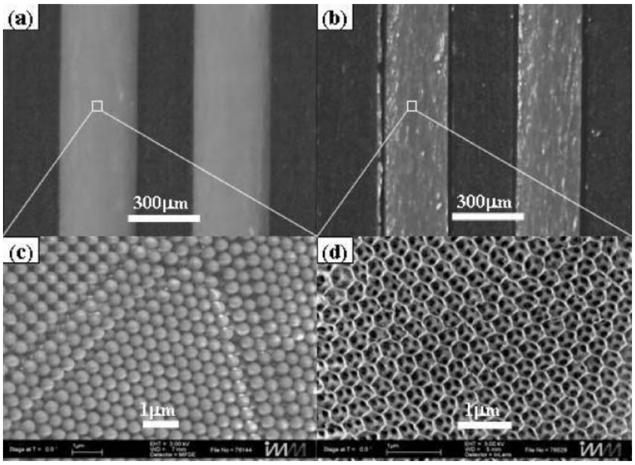

Fig. 1 Optical micrographs of PMMA opals (a) and corresponding Al_2O_3 inverse opals (b) in the microchannels, and their SEM images: (c) for PMMA opals and (d) for Al_2O_3 inverse opals.

interstitial void in the opals with the prepared alumina sol was performed inside a nitrogen-purged glove box. The sol entered the void by capillary forces. After infiltration, the plates were kept in the glove box to let the sol dry for 24 h at room temperature. Because the concentration of the sol was low, the infiltration process was repeated 10 times. After this infiltration process, the temperature for calcination of the plates was then increased to 500 °C at a ramping rate of 1 °C min^{-1} and held for 5 h in air. As a result, the Al_2O_3 support (Fig. 1(b)) with highly regular, periodic inverse opal microstructure (Fig. 1(d)) was obtained in the microchannels. The prepared inverse opals have ∼300 nm uniform pores interconnected by ∼100 nm windows between adjacent layers. Shrinkage of about 19% occurred during the calcination compared with the used 370 nm PMMA nanospheres as templates, which is attributed to the shrinkage of Al_2O_3 gel during pyrolysis. PMMA opals may serve as structural support during the early stages of the pyrolysis of Al_2O_3 gel by partly absorbing shrinkage stresses and preventing the collapse of the pore structure. Obviously, the high void fraction (ε = 0.74) is a main advantage for the use of this inverse opal structure as a catalyst support. Furthermore, as seen in Fig. 1(b), this shrinkage also reduced the overall dimensions of the inverse opal structure in the microchannel, always leaving a small gap present between the walls of the microchannels and the Al_2O_3 inverse opals. These voids should be carefully filled with a small amount of the Al_2O_3 suspension composed of Al_2O_3 powder, polyvinyl alcohol and water, used for the wash-coating of Al_2O_3 layers onto the microchannels.[7] It is found that this filling process also enhanced the adhesion of the inverse opals onto the microchannels. The weight of the Al_2O_3 inverse opals was determined by the weight difference of the stainless steel plates before and after the coating.

In order to impregnate the catalysts on the Al_2O_3 inverse opals, the calculated amount of aqueous solution of $Pt(NO_2)_2(NH_3)_2$ based on the weight of the coating (inverse opals) was dropped into the coated microchannels, followed by drying at 110 °C for 12 h, and then by the impregnation of an aqueous solution of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$). After the plates were dried at 110 °C for 12 h and calcined at 400 °C for 3 h, the MoO_3-promoted Pt catalyst loaded on Al_2O_3 inverse opals coated in the microchannels was obtained. X-Ray fluorescence analysis showed that 2.1 wt% of Pt and 14.9 wt% of Mo were precipitated on the support. For comparison, a sole Pt(2.1 wt%) catalyst loaded on Al_2O_3 inverse opals in the microchannels was also prepared. The micropore properties of the prepared original and catalyst-loaded Al_2O_3 powders with inverse opal microstructure are shown in Table 1 of the ESI.†

Two plates with the catalyst coating were first laser welded face-to-face and then stainless steel tubes for gas transport were also laser attached on both sides to yield the microreactor for catalytic activity measurements. The microreactor was heated in a steel housing using heating cartridges. The reaction temperature was monitored by a thermocouple placed near the outer surface of the microreactor. The reactant gas stream consisted of propane and synthetic air (composition: 80% of N_2 and 20% of O_2) with a molar ratio of propane : O_2 of 1 : 5.6, which is an optimum ratio for a series of tests between 1 : 5.0 and 1 : 10 and is closer to the realistic and practical applications. Catalytic reactions were first conducted at temperatures in the range of 250–375 °C and at a total flow rate in the range of 50–200 $cm^3\ min^{-1}$ (STP) (WHSV = 150–600 $dm^3\ h^{-1}\ g_{cat}{}^{-1}$) under atmospheric pressure, and then, kept at 300 °C and WHSV = 300 $dm^3\ h^{-1}\ g_{cat}{}^{-1}$ for 170 h for the catalytic stability test. Thereafter, a catalyst stability test at 275 °C for 50 h was also performed. The pressure drop across the microreactor was about 1350 Pa.

The effluent gases were analysized by an on-line ThermoFinnigan trace gas chromatograph equipped with two thermal conductivity detectors. The separation of the components was achieved by a precolumn Porapak N for delaying any organic molecules and water and allowing the other species to enter first, a Hayesep Q for water and carbon dioxide separation, a Molecular Sieve 5A for separation of carbon monoxide, and a combined Hayesep and Molsieve for hydrogen separation. The nitrogen carrier gas flow and two-helium gas flows were set to a pressure at the gas chromatograph inlet of 100, 150 and 100 kPa, respectively. No partial combustion product such as CO was detected in the propane combustion over all catalysts in this communication.

Fig. 2 shows the catalytic activity of the prepared MoO_3-promoted Pt/Al_2O_3-inverse opal as a function of the reaction temperature in propane combustion. The results are compared

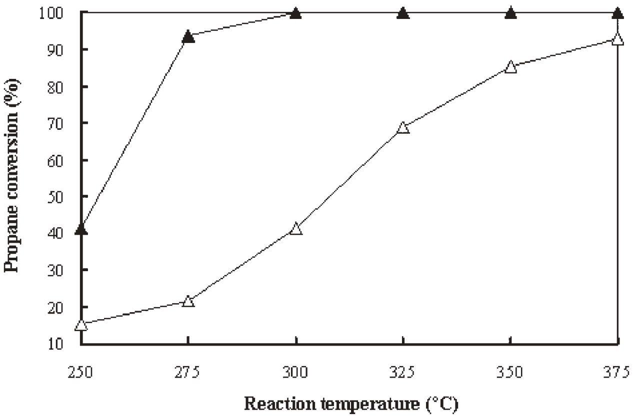

Fig. 2 Comparison of the propane conversion over the prepared Mo-promoted Pt catalysts loaded on Al_2O_3-inverse-opals (closed triangles) with that over Pt/Al_2O_3 inverse opals (open triangles) (WHSV = 300 $dm^3\ h^{-1}\ g_{cat}{}^{-1}$).

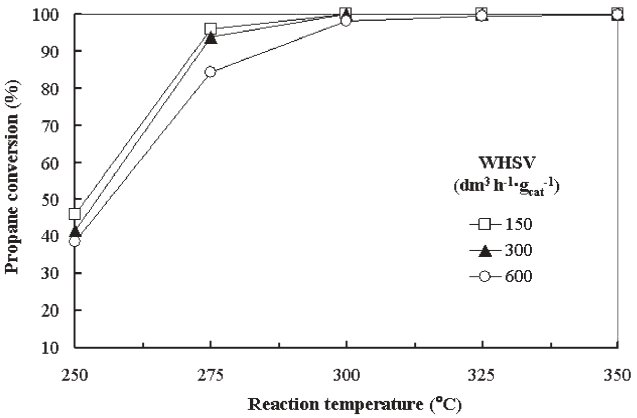

Fig. 3 The propane conversion over the prepared catalyst of Mo-promoted Pt/Al_2O_3 inverse opals as a function of the reaction temperature at various space velocities.

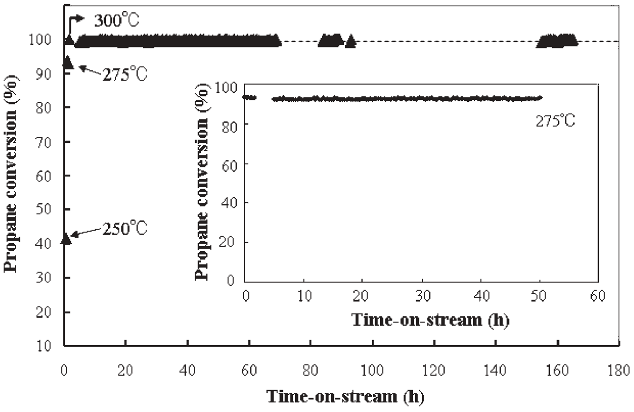

Fig. 4 Catalyst long term operation over the prepared catalyst of Mo-promoted Pt/Al_2O_3 inverse opals at 300 °C and 275 °C.

with the catalytic activity of pure Pt catalyst loaded onto Al_2O_3-inverse opals in microchannels. The propane conversion increased with an increase in the operating temperature. Interestingly, it is found that the propane can be completely converted at a temperature as low as 300 °C for the Mo-promoted Pt catalyst loaded on the Al_2O_3 support with inverse opal microstructure. However, without addition of Mo to the Pt catalyst loaded on Al_2O_3-inverse opals, even when the reaction temperature was increased to 375 °C, propane could not be completely converted, suggesting that the addition of Mo much effectively enhanced the catalyst activity. Yoshida *et al.* investigated the effect of additives on the catalytic activity of the Pt catalyst in propane combustion in conventional fixed-bed reactors, and suggested that the activity of Pt catalyst is mainly determined by the oxidation state of platinum under the oxidising atmosphere.[2–6] In their studies, compared with Pt/Al_2O_3, addition of molybdenum with high electronegativity (2.96) led to lower oxidation state of platinum and, as a result, the catalytic activity in the propane combustion was enhanced. In our case, when we fabricated the support material with sponge-like inverse opal structure in the microchannel, the tailored macroporous structure allowed both the platinum particles and the additives to disperse on the support much more homogeneously. As a consequence, the noble metal, the additive and the support could be mutually adjacent at a smaller scale with more pronounced interplay. It was then expected that the total electrophilic property of Mo additive and Al_2O_3 would lead to a large improvement in the oxidation-resistance of Pt which results in higher catalytic activity.

Fig. 3 shows the catalytic activity of the prepared MoO_3-promoted Pt/Al_2O_3 catalyst with inverse opal microstructure as a function of the reaction temperature at various space velocities in propane combustion. When the space velocity, *i.e.*, WHSV was smaller than or equal to 300 $dm^3\ h^{-1}\ g_{cat}{}^{-1}$, complete conversion of propane was observed at 300 °C. When the WHSV was increased to 600 $dm^3\ h^{-1}\ g_{cat}{}^{-1}$, the temperature of propane complete conversion increased to 325 °C. This temperature is about 100 °C lower than that for the Mo-promoted Pt/Al_2O_3 catalyst with no inverse opal structure used in the fixed bed.[2] Fig. 4 shows a long term testing of the catalyst at temperatures of 300 °C and 275 °C with WHSV = 300 $dm^3\ h^{-1}\ g_{cat}{}^{-1}$. The prepared catalyst exhibited high catalytic activity and stable behaviour for at least 170 h at a low temperature of 300 °C. Moreover, even at a lower temperature of 275 °C, the reaction also proceeded in a stable manner.

To summarize, a novel catalyst support with well-defined inverse opal microstructure has been fabricated in a microchannel reactor. The activity testing of Mo-promoted Pt catalyst supported on it revealed excellent reactivity and long term stability performance for propane combustion at low temperatures. This kind of catalyst support could be also used for other fuel processing applications such as preferential CO oxidation, steam reforming and water–gas-shift.

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