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Design and operation of an ammonia-fueled microchannel reactor for autothermal hydrogen production

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ABSTRACT

The present work describes the design and operation of an autothermal microchannel reactor for portable and distributed hydrogen production via ammonia decomposition. The microreactor consists of an array of alternating catalytic plate channels where the heat for the endothermic ammonia decomposition reaction is supplied in adjacent microchannels via exothermic oxy-fuel combustion of ammonia. The reactor performance was investigated under various operating conditions, such as ammonia flow rate in the decomposition channel, combustible feed flow rate, and fuel equivalence ratios. The best operating conditions were obtained at ammonia flow rate of 0.4 NLPM, combustible feed flow rate of 0.8 NLPM, and fuel-rich operation corresponding to fuel equivalence ratio of 1.2. At these conditions, > 99% NH_3 conversion was obtained, and the reactor could generate enough hydrogen for a 45 W_e fuel cell system at an equivalent reactor power density of 1.5 kW_e/L. Overall, the work reported here successfully demonstrated the feasibility of ammonia decomposition for distributed hydrogen generation and delineated the attainable operating region, results of which could be used further to advance and scale-up autothermal ammonia-fueled microchannel reactors in the kW-range.

1. Introduction

Polymer Electrolyte Membrane (PEM) fuel-cell power systems are rapidly gaining consideration for transportation, portable and distributed applications owing to high power densities and inherent ability to operate quietly at near-zero pollution levels [1–5]. In spite of the growing interest, expansive commercial breakthrough however remains elusive owing to the present lack of a sustainable (easy, safe, and cheap) infrastructure to deliver hydrogen (H_2) fuel (preferred feed) to the PEM fuel cell [6,7]. Without a doubt, the extremely low volumetric energy density of H_2 is widely considered the primary constraint causing its storage and transportation difficulties. The on-demand generation of H_2 via fuel processing of liquid H_2 carriers already having an existing infrastructure promises substantial market penetration of PEM fuel cell power systems [3,4,7,8]. Among the various H_2 carriers, ammonia (NH_3) has continuously been suggested for CO_x-free hydrogen production via ammonia decomposition [9–14].

Chiuta et al. [7] reviewed the state-of-the-art reactor technologies for NH_3 decomposition and revealed microchannel reactors to be integral parts of ammonia fuel processors for portable and distributed fuel cell applications. Indeed, their small characteristic length scale (sub-millimetre range) greatly increases the surface area-to-volume ratio, which leads to enhanced heat and mass transfer characteristics [15–18]. As a result, some fundamental experimental studies have been performed using microchannel reactors for ammonia decomposition [19–26]. More recently, Chiuta et al. [26] demonstrated the successful operation of a high-throughput ammonia-fuelled microchannel reactor. Almost without exception, electrical heating was typically used in reported experiments to provide heat required for the endothermic ammonia decomposition. The use of electrical heat source however, severely reduced the reformer efficiency [25,26] and is therefore not suitable for practical miniaturised hydrogen production.

Yet, another option is to design and operate multifunctional reactors where exothermic combustion and endothermic reactions are thermally-coupled in a single device where the reactions are separated by a heat-conducting wall [27–29]. Until now, Arana et al. [19] reported the only experimental microchannel reactor-exchanger, in which catalytic butane combustion supplied the heat to sustain NH_3 decomposition on a washcoated Ir/Al_2O_3 catalyst. Yet, Chellappa et al. [30] patented an autothermal ammonia-based hydrogen generation apparatus in which their preferred embodiment constituted of inserted porous substrates into meso-scale fluid flow channels. In this study, we limit ourselves to microchannel reactors having washcoated catalysts, and so the design by Chellappa et al. is fundamentally different from the intended scope. Other experimental work considering coupled microreactors for ammonia decomposition have been reported by the Kwon research group

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[31–33]. These are however not of particular interest to this paper since they considered annular-type packed-bed microreactors moreover coupled to homogenous combustion. Incidentally, homogenous combustion presents operational challenges when extended to microchannels vis-à-vis flame stability issues arising from large heat losses [34–39]. Several simulation studies on the subject of the catalytic combustion of propane to provide reaction heat for ammonia decomposition have been reported [40–44]. However, these micro-devices were hardly ever realized.

All the same, the various studies considered a combustion fuel (hydrocarbon) for the burner different to the primary fuel (ammonia). In a practical system, this may present logistic challenges and other complexities associated to handling a second fuel such as decrease in system efficiency [45]. Our focus on ammonia as a common fuel for both combustion and decomposition has been motivated in part by the fact it is of little or no worth to the general public compared to logistic fuels (e.g. hydrocarbon fuels). And so, there is a low possibility of fuel theft particularly from fuel cell power systems located in remote, off-the-grid areas. The catalytic ammonia combustion (oxidation) has largely been associated to the industrial manufacture of nitric acid via the Ostwald process [46–49]. Most recently, ammonia oxidation is however gaining popularity in the now-commercialized selective catalytic reduction of NO_x emissions from diesel engines [50]. Outside of these application frontiers, there is a limited scope in open literature where ammonia oxidation has been used particularly as a heat source for autothermal hydrogen production. Interestingly, Rebrov et al. [51–54] experimentally investigated the thermal behaviour of various microchannel reactor geometries using ammonia oxidation as an example of a highly-exothermic reaction. Their studies however did not extend to thermal coupling for the purposes of hydrogen production, but rather revealed the potential of using ammonia combustion as a useful heat source.

In this paper, experimental results on the operation and performance of a coupled ammonia-fueled microchannel reactor/combustor were presented for the first time where catalytic oxy-fuel ammonia combustion provides heat to ammonia decomposition through a heat-conducting wall within the same device. The principal aim of this study was to demonstrate feasibility of the thermally self-sustaining hydrogen production system. In particular, the micro-device performance was evaluated by investigating the effect of operating parameters (ammonia flow rate, combustible feed flow rate and fuel equivalence ratio) on key performance parameters (NH_3 conversion, residual NH_3 concentration, H_2 production rate, and reformer efficiency). Particular attention was devoted to delineating the optimal autothermal operating point with reference to the ammonia flow rate and combustor operating conditions for sustained ammonia decomposition. This work supports the on-going stage-wise development (initial work reported in Refs. [26] and [55]) towards the realization of an ammonia-fueled microchannel fuel processor for portable and distributed fuel cell applications.

2. Experimental

2.1. Reaction analysis: thermal effects

The microchannel reactor/combustor considers thermal coupling of ruthenium-catalyzed ammonia decomposition with platinum-catalyzed oxy-fuel combustion of ammonia according to the following reactions;

R1: $2NH_3 \rightarrow N_2 + 3H_2 \quad \Delta H^0 = +46\,kJ/mol$

R2: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad \Delta H^0 = -226\,kJ/mol$

R3: $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad \Delta H^0 = -317\,kJ/mol$

R4: $2NH_3 + 2O_2 \rightarrow N_2\,O + 3H_2O \quad \Delta H^0 = -276\,kJ/mol$

The ammonia combustion occurs through the reactions R2 to R4 [46–50], which all have different thermal effects with the potential to release about 273 kJ of heat per mole of ammonia. On the other hand, ammonia decomposition requires approximately 46 kJ of heat per mole of ammonia. At the least, combusting 1 mol of ammonia releases sufficient heat to decompose 6 mol of ammonia assuming adiabatic operation. Heat losses are however expected to decrease the number of moles of ammonia that can be decomposed per mole of ammonia combusted. The analysis of the heat of reactions gives a preliminary indication as to the feasibility of coupling reactions R1 to R4 in a multifunctional micro-device for autothermal hydrogen generation.

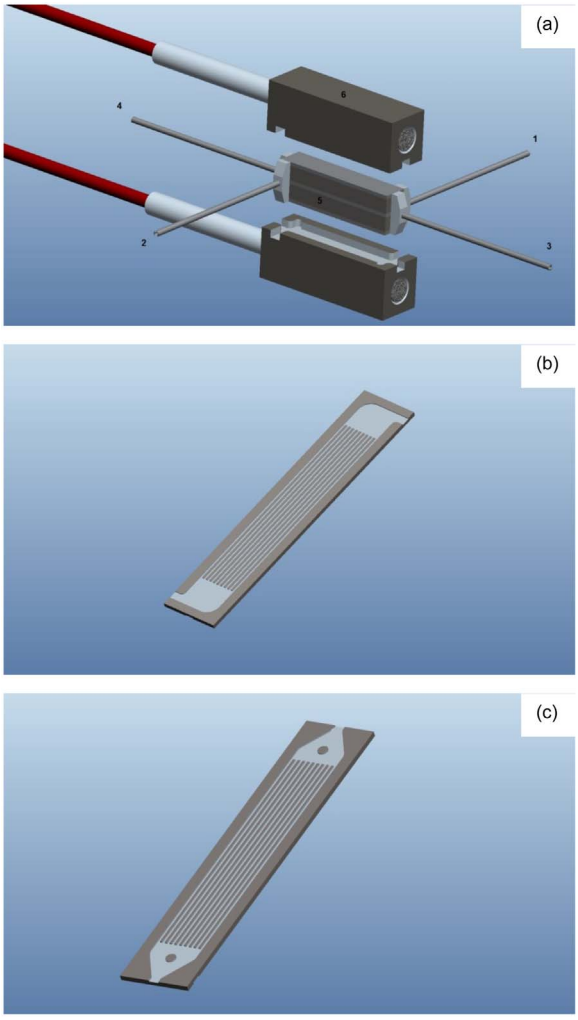

Fig. 1. 3D CAD geometry for (a) microchannel reactor/combustor with laser-welded inlet/outlet tubes; (1) Inlet: ammonia decomposition (2) Outlet: ammonia decomposition (3) Inlet: ammonia combustion (4) Outlet: ammonia combustion (5) Reactor stack with 16 units of single microchannel platelets (6) Heating block with inserted heating rods (b) double-sided microstructured platelet showing decomposition channels on the top side and (c) combustor channels on the bottom side of the same platelet [58].

2.2. Reactor design and development

The multifunctional reactor (Fig. 1a) was designed and constructed in collaboration with Fraunhofer-ICT-IMM (Mainz, Germany), on the basis of promising results obtained from the 1st generation reactor testing reported in our previous studies [26,55]. In contrast to the 1st generation reactor, the multifunctional reactor consists of a compact stack of 16 double-sided microstructured plates (Fig. 1b–c) each comprising of 10 channels apiece on the decomposition and combustion sides, respectively. The microchannels were engraved on a 1-mm-thick stainless steel substrate (German steel classification 1.4841) using wet