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Ceramic microreactors for on-site hydrogen production

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Abstract

This paper describes the synthesis and characterization of ceramic microreactors composed of inverted beaded silicon carbide (SiC) monoliths with interconnected 0.75-, 2.2-, or 7.2-µm pores as catalyst supports, integrated within high-density alumina reactor housings obtained via an optimized gel-casting procedure. Structural characterization revealed that these tailored macroporous SiC porous monoliths are stable at temperatures up to at least 1200 °C, and have surface areas and porosities as high as 7.4×10^7 m^2/m^3 and 74%, respectively. Further characterization of the ceramic microreactors using the decomposition of ammonia with Ru as the catalyst at temperatures between 450 and 1000 °C showed that as much as 54 sccm of hydrogen, or 9.8×10^4 sccm H_2 per cm^3 of monolith volume, could be obtained from a 36-sccm entering stream of NH_3 at $>99.9\%$ conversion at temperatures above 700 °C. Moreover, using SiC as a catalyst support appears to increase the catalytic activity of the Ru catalyst, as evidenced by high turnover frequencies.

Keywords: Ceramic microreactor; Silicon carbide; Hydrogen production; Ammonia decomposition; Fuel reforming

1. Introduction

The continuous operation of electronic devices lacking access to wired electrical power, such as vehicles and electrical equipment in remote locations (e.g., construction sites, military fields), requires electrical power sources of high specific energy. Rechargeable lithium ion batteries are presently used for many of these applications, but they have energy densities of only up to ~200 W-h/l and thus must be recharged frequently [1]. Higher energy densities can be obtained by using hydrogen gas in polymer electrolyte membrane (PEM) fuel cells [2–4]. The transport and storage of compressed hydrogen entails safety issues, however. By producing H_2 on-site [5,6] by, for example, decomposition of ammonia (energy density of ~4 kW-h/l) or steam reforming of liquid hydrocarbons such as gasoline (energy density of ~9 kW-h/l), fuel cells can provide electrical power for longer periods and have a higher specific energy than rechargeable batteries [2].

The decomposition of NH_3 within a microreactor is a direct route to producing H_2 for PEM fuel cells. The only products are H_2 and N_2, and this microreactor can be integrated with a microscale heat source, such as a microburner [7] or a catalytic combustor [8], making it advantageous for portable power applications due to the small overall volume. Compared to steam reforming of liquid hydrocarbons, the decomposition of NH_3 has fewer issues. Steam generation is not necessary, and no CO is produced; therefore, additional water–gas shift reactors and preferential oxidation reactors are not needed to avoid CO poisoning of the fuel cell catalyst [9]. Furthermore, the potential for sulfur poisoning of the reforming catalyst is avoided, eliminating the need for sulfur removal units or sulfur-tolerant catalysts [9]. A limitation still exists because NH_3 can poison the catalyst used in PEM fuel cells; however, an NH_3 adsorbent can be used to reduce the ammonia concentration to ppb levels on entering a PEM fuel cell [10].

Several microreactors for on-site production of H_2 have been reported [1,2,11–15]. Channel and posted reactors fabricated from anodized aluminum have been used for the decomposition of NH_3 up to 650 °C [11–13]. Integrated reformer systems consisting of burner, vaporizer, and reformer units have

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been fabricated of stainless steel for the steam reforming of methanol between 260 and 450 °C [1,2,14]. In addition, MEMS fabrication methods have been used to produce silicon-based microreactors for methanol reforming [15]. Although these microreactor systems have achieved high conversion of NH_3 and methanol into hydrogen, they are often not stable for continuous operation above 800 °C, the minimum temperature required to eliminate coking of the catalyst during the steam reforming of higher hydrocarbons, such as propane and gasoline [16]. Aluminum melts at 660 °C, and silicon and stainless steel oxidize in the presence of steam above 800 °C and can corrode to a significant extent. Jensen et al. recently reported the more promising solution of a microreactor composed of suspended silicon nitride tubes with wash coats of catalyst to enable ammonia decomposition up to 825 °C [8].

To date, the development of high-surface area catalyst support structures that are stable above 800 °C has been a challenge, especially when the pressure drop across the support must be low enough to both reduce parasitic losses due to pumping of fluids and prevent mechanical failure of the structures. Recently, we have reported on the fabrication of inverted beaded monoliths with 7.2-μm interconnected pores, composed of silicon carbide (SiC) or silicon carbonitride (SiCN) [17], which are stable up to 1200 °C in air and have a $\sim$2 order of magnitude lower pressure drop than a packed beaded structure with the same geometric surface area. These monoliths also avoid the issues of cracking and channeling of the reactants, problems commonly encountered with wash coat-based catalyst layers and packed beds of loose catalyst particles.

In this paper, we describe the synthesis and characterization of ceramic microreactors composed of SiC catalytic monoliths with 0.75-, 2.2-, and 7.2-μm pores integrated in high-density alumina microreactor housings that we obtained using an optimized gel-casting procedure. We report a detailed analysis of the structural properties of the SiC catalyst supports (surface area, porosity, thermal stability) and of the deposited Ru metal on these supports (catalyst loading, dispersion, surface area of active sites). We further characterize these catalytic monoliths using the decomposition of ammonia into hydrogen and nitrogen at temperatures as high as 1000 °C, to show their promise in on-site hydrogen production for PEM fuel cells.

2. Experimental

2.1. Catalyst preparation

2.1.1. High-surface area porous monoliths (catalyst supports) preparation

Poly(dimethylsiloxane) (PDMS) molds with microchannel patterns were prepared for fabrication of porous monoliths and for molding of the high-density alumina housings (Section 2.3) by replica molding of a master obtained through photolithography [18]. For the preparation of SiC porous monoliths, we adopted the micromolding-in-capillaries (MIMIC) method used previously for the synthesis of porous oxide materials [19]. Solutions of polystyrene (PS) spheres (1.1, 3.2, and 10 μm diameter; Polysciences) were centrifuged three times at 10,000 rpm for 10 min (centrifuge 5415D, Eppendorf), with decanting of the water and addition of DI water after each centrifugation to remove surfactant. The final concentrated solution was obtained by removing half of the water after settling of the solution for 12 h. About 5–50 μL of the concentrated PS sphere solution was then placed at one end of a microchannel (500 μm wide, 150 μm high, 5–7 mm long) and left for 12 h for the completion of the packing process, followed by drying under vacuum at 70 °C for 48 h.

SiC porous monoliths were prepared by infiltration of the resulting packed beds of PS spheres in PDMS microchannels with a mixture of allylhydridopolycarbosilane (SP matrix, Starfire Systems) and 3–5 wt% of the thermal initiator 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (92%, Aldrich), followed by curing of the precursor mixture at 70 °C for 12 h. All of these steps were carried out in a glove box under an argon atmosphere. After the PDMS mold was removed, pyrolysis was performed at 1200 °C for 2 h under an argon atmosphere, as described previously [17], to yield SiC porous monoliths typically 350 μm wide, 100 μm high, and 3 mm long after shrinkage, as shown in Fig. 1.

2.1.2. Catalyst deposition

Ruthenium (Ru) catalyst was deposited on the SiC porous monoliths by wet impregnation with 14.72 wt% (0.67 M) $RuCl_3$ (Aldrich) in a mixture of 10 vol% DI water in acetone, similar to a method described previously [11]. The structures were then dried in a conventional oven at 60 °C for 48 h to remove the remaining water and acetone, followed by calcination in air at 580 °C for 5 h using a tube furnace (HTF5500 series, Lindberg/Blue M). Finally, the catalyst was reduced in the tube furnace under an atmosphere of 5% H_2 in argon at 550 °C for 6 h.

2.2. Characterization of the porous catalytic monoliths

The morphology of the pores in the SiC porous monoliths was studied using either a Hitachi S-4700 or a JEOL 6060-LV scanning electron microscope. The surface areas of the SiC porous monoliths were determined by N_2 adsorption–desorption at 77 K using a BET apparatus (Micromeritics ChemiSorb 2705). Before the BET analysis, the samples were degassed under vacuum at 100 °C for 24 h to remove any moisture. Mercury intrusion porosimetry (MIP) analysis was carried out using a Micromeritics AutoPore II 9220 to determine the porosities of the SiC porous monoliths.

The dispersion of active metal phase of the Ru catalyst in the SiC porous monoliths was measured using pulsed CO chemisorption and H_2 chemisorption at room temperature using a Micromeritics ChemiSorb 2705, assuming a 1:1 ratio of CO or a 1:2 ratio of H_2 chemisorbed to exposed Ru metal. The Ru loading was determined using inductively coupled plasma spectrometry (OES Optima 2000 DV, Perkin–Elmer).