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Disk-shaped packed bed micro-reactor for butane-to-syngas processing

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ABSTRACT

A novel disk-shaped packed bed micro-reactor containing Rh/ceria/zirconia nanoparticles is investigated with respect to catalytic butane-to-syngas processing at moderate temperatures of 550 °C. The main goal of this study is the development of an efficient butane processor which can be integrated into a micro solid oxide fuel cell system due to its small size, easily packaged geometry in layered microdevices, high compactness, low pressure drop, and low reaction temperature. It is shown that Rh/ceria/zirconia has an excellent long-term stability and achieves very high C_4H_{10} conversion and syngas selectivity, considering the relatively low operating temperature. The yields of H_2 and CO can be increased up to 71% and 57%, respectively, by optimizing operational parameters such as the C/O ratio and the total inlet flow rate. The introduced disk-shaped packed bed reactor shows significant advantages in catalytic behavior, at a 6.5 times lower pressure drop compared to an equivalent tubular packed bed reactor. This increased catalytic performance is pursued extensively by investigating possible reaction pathways in three regions of the radial-flow reactor, leading to the significant discovery of a threefold pathway of syngas production on a single catalyst. To this end, it is shown that the excellent selectivities to H_2 and CO for high flow rates are due to the combination of partial oxidation, steam reforming, and dry reforming of C_4H_{10}, indicating one direct and two indirect reaction paths.

1. Introduction

Micro fuel cell systems generating electric power of the order of a few watts are seen to have promising potential to compete with conventional battery systems for small portable electronic devices due to their higher power density both per volume and per mass. Small fuel cell systems fed by hydrocarbons combine the high energetic efficiency of fuel cells with the high availability and easy storage of hydrocarbon fuels (Hotz et al., 2006). Modern materials for solid oxide fuel cells (SOFCs) lead to higher efficiencies compared to other types of fuel cells at intermediate operating temperatures in the range of 500 and 600 °C (Bieberle-Hütter et al., 2008) using syngas as fuel. An interesting hydrocarbon fuel widely available for this application is butane, allowing the production of a H_2- and CO-rich syngas with high efficiency and relatively easy storage in liquid phase at room temperature and low pressure.

The catalytic partial oxidation (POX) of butane was investigated in the past and the characteristics of different catalysts for this purpose were tested (e.g., Acharya et al., 2006; Hotz et al., 2007; Huff et al., 1994; Laosiripojana and Assabumrungrat, 2006; Wang and Gorte, 2001, 2002). However, these studies do not account for many typical requirements of a fuel processor operated as part of an entire micro fuel cell system.

The novelty of this study is to introduce an easy-to-pack, disk-shaped packed bed micro-reactor for high-temperature fuel processors with a design feasible for practical applications such as micro SOFC systems presented previously (Bieberle-Hütter et al., 2008). Crucial requirements for the integration of a fuel processor into an entire micro SOFC system are easily integrated into a layered device, a small reactor volume, a highly compact design, low pressure drop, and low reaction temperature. Since the geometry of planar SOFC membranes leads to disk-shaped fuel cell designs, a likewise disk-shaped reactor for the fuel processing increases the compactness of the entire system. The main goal of this study is to show the feasibility of a disk-shaped packed bed micro-reactor for butane-to-syngas processing as part of a micro SOFC system, achieving excellent catalytic activity and high long-term stability at a relatively low operating temperature and pressure drop within a compact and small reactor.

As a noble metal, rhodium was chosen for its excellent performance in butane-to-syngas conversion (Hotz et al., 2007). The advantageous use of ceria/zirconia as a catalyst support for

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high-temperature reactions was demonstrated earlier (Stark et al., 2003a, 2005).

A desirable reaction path for syngas production from hydrocarbons is POX, written as

$$C_4H_{10} + 2O_2 \rightarrow 5H_2 + 4CO, \quad (1)$$

which achieves high yields of H_2 and CO. POX has been identified as the ideal reaction path for hydrocarbon processing to syngas and investigated experimentally and numerically for different hydrocarbon fuels, e.g., methane (Neumann and Veser, 2005; Stutz et al., 2006; Stutz and Poulikakos, 2005) and higher alkanes (Panuccio et al., 2006; Williams and Schmidt, 2006).

Another effective reaction for hydrocarbon processing is steam reforming (SR), where butane reacts with water:

$$C_4H_{10} + 4H_2O \rightarrow 9H_2 + 4CO. \quad (2)$$

A second water consuming reaction which might take place in a micro-reactor besides SR is water gas shift (WGS):

$$CO + H_2O \rightarrow H_2 + CO_2. \quad (3)$$

Syngas can be produced from hydrocarbons by CO_2 or dry reforming (DR):

$$C_4H_{10} + 4CO_2 \rightarrow 5H_2 + 8CO. \quad (4)$$

A well performing butane processor should show high selectivity towards H_2 and CO instead of total oxidation (TOX) products of butane, which is written as

$$C_4H_{10} + 6.5O_2 \rightarrow 5H_2O + 4CO_2, \quad (5)$$

and low methane production by decomposition of C_4H_{10} or methanation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O. \quad (6)$$

2. Experiments

2.1. Catalyst preparation

$Ce_{0.5}Zr_{0.5}O_2$ nanoparticles with optional rhodium doping were prepared in a one-step process by flame spray synthesis described in previous studies (Hotz et al., 2007; Stark et al., 2003a,b, 2005). For the ceria/zirconia precursor, cerium(III) 2-ethylhexanoate (12 wt% Ce, Shepherd Chemical Company) and zirconium(IV) 2-ethylhexanoate (18 wt% Zr, Borchers GmbH) were mixed to result in a metal molar ratio Ce/Zr of 1:1 and diluted with xylene to a total metal concentration of 0.8 mol/L. Rhodium(III) 2-ethylhexanoate (UMICORE AG & Co.) was added to the Ce/Zr-precursor such that the calculated rhodium content in the ternary system Rh/ceria/zirconia ($Rh/Ce_{0.5}Zr_{0.5}O_2$) was 2.0 wt%.

2.2. Catalyst characterization

The specific surface area of the catalyst was measured using nitrogen adsorption on a Tristar (Micromeritics Instruments) at 77 K with the BET method and used to calculate the mean particle diameter. The phase composition and formation of ceria/zirconia mixed oxides was determined by X-ray powder diffraction on a Stowe STADI-P2 (Ge monochromator, Cu $K\alpha_1$, PSD detector). The catalytic nanoparticles were analyzed by flame atomic absorption spectrometry (AAS) on a Varian SpectrAA 220FS. The chemisorption of the Rh surface was measured using an ASAP 2010 (Micromeritics Instruments). The samples were reduced at 400 °C for 90 min using pure hydrogen and cooled down to 40 °C under helium atmosphere. From the results of hydrogen chemisorption measurements, the metal dispersion was calculated as molecular hydrogen adsorbed dissociatively on Rh metal (H/Rh = 1) (Montini et al., 2007). Transmission electron micrographs (TEM) of fresh and spent catalyst particles were recorded on a CM30 ST (Philips, 300 kV voltage, point to point resolution 0.19 nm) equipped with an energy dispersive X-ray spectrometer (EDX) to analyze the chemical composition of the particles qualitatively. For the TEM and EDX analysis, all samples were dispersed in ethanol, prepared in an ultrasonic bath, and deposited onto a carbon-coated TEM grid. Additionally, the material used in the reactors consisting of spent catalyst and silica sand was dispersed in ethanol and manually ground with a mortar and pestle before being treated in an ultrasonic bath. This was necessary to properly separate catalytic Rh/ceria/zirconia nanoparticles from larger silica particles used in the reactors.

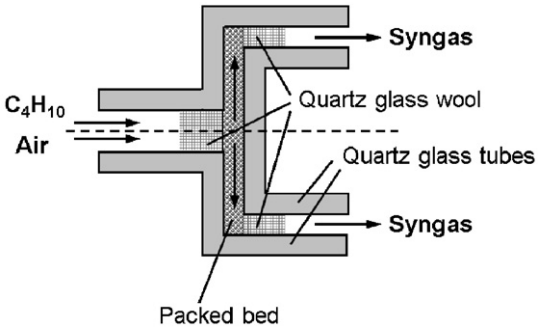

Fig. 1. Schematic of the disk-shaped packed bed reactor.

2.3. Reactor

It has been previously shown that the catalyst described above can be used for the production of syngas from butane in small tubular reactors (i.d. 2 mm) (Hotz et al., 2007). However, the geometry of tubular reactors contradicts to the requirement of compact design in micro fuel cell systems, especially in context with disk-shaped SOFC membranes. Therefore, we used a disk-shaped design for the micro-reactor with a catalytically active volume of 10 mm diameter and 0.5 mm height. In addition to the compactness of the geometry, this design led to lower pressure drop due to the increasing flow cross-section along the reaction path, as it has been shown for low-temperature fuel processors (Pattekar and Kothare, 2005), and higher catalytic activity.

The air/butane mixture entered the reactor from the left side of the center of the reactor and flowed radially outwards through the catalytically active packed bed consisting of Rh/ceria/zirconia nanoparticles and SiO_2 sand, as shown in Fig. 1. The reactor walls consisted of quartz glass and the packed bed was fixed on both sides by quartz glass wool.

The packed bed consisted of nanoparticles and SiO_2 sand (average diameter: 200 μm) of different mass ratios: for the standard configuration, 10 mg Rh/ceria/zirconia nanoparticles with an Rh loading of 2.0 wt% were mixed with 30 mg SiO_2 sand. To investigate the different reactions taking place along the radial flow direction, disk-shaped packed bed reactors with 6 and 8 mm diameter were tested. Since all the three reactors contained catalyst with identical volumetric density, the reactors of 6, 8, and 10 mm diameter were identical except for their radial path length. By subtraction of the molar gas flow of these three reactors, the molar production rate of different gas species within three regions could be calculated: region 1 up to 3 mm radial path length, region 2 between 3 and 4 mm, and region 3 between 4 and 5 mm radius.