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Zinc-copper oxide coated monolithic reactors for high capacity hydrogen sulphide removal from gaseous streams

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ARTICLE INFO

Article history:

Received 6 June 2016

Received in revised form

26 July 2016

Accepted 4 August 2016

Available online xxx

Keywords:

Desulphurisation

Metal oxide sorbent

Monolithic reactor

Fuel processing

Fuel cell

ABSTRACT

Production of fuel-cell grade hydrogen via reforming of gaseous hydrocarbon fuels requires the design and implementation of efficient formulations, which incorporate high performance materials for the removal of undesired impurities; notably H₂S. To this respect, the present study relates to the preparation and parametric evaluation of small-scale honeycomb structured flow-through reactors, coated with an in-house synthesized ZnO/CuO, 50%mol/50%mol, sorbent. Experimental tests involved quantification of the H₂S trapping capacity and efficiency of the coated monoliths by monitoring the evolution of H₂S concentration at the reactor outlet for known H₂S feeds at the reactor inlet. The de-H₂S performance of the coated monoliths was examined at reactor temperatures ranging from 160 °C to 400 °C, under two different synthetic mixtures containing a) 30% vol H₂, 32%vol H₂O, N₂ balance and b) 30%vol H₂, 32%vol H₂O, 6.5%vol CO₂, 4.5%vol CO, N₂ balance. Space velocities at the reactor ranged from 20,000 to 60,000 h⁻¹ for the experiments designed to examine trapping capacity and from 10,000 to 90,000 h⁻¹ for the experiments designed to examine trapping efficiency. The breakthrough curves obtained proved that the particular formulation can provide a very efficient solution, particularly for the case of decentralized applications, for which system compactness is of prime importance. Total capture capacities up to a targeted H₂S breakthrough value of 0.1 ppmv at the reactor outlet varied between 5 and 25 (g_{sulphur}/100 × g_{sorbent}). This value depended on reactor temperature and flow conditions, gas composition, monolith loading and monolith cell density.

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<http://dx.doi.org/10.1016/j.ijhydene.2016.08.033>

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Introduction

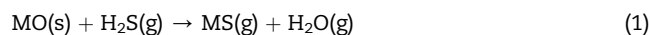
Hydrogen fuel cells (HFCs) development has been increasingly active over the past two decades [1–5]. Coupled with appropriate technologies, their use as auxiliary, small-scale, power generators in transport [6–10], residential and industrial heating [11–13] and electronics [14,15] applications is widening. The findings reported here relate to the development of a zinc-copper oxide coated monolithic reactor for high capacity H₂S removal from gaseous streams and are part of a larger project dealing with the creation of an integral HFC system fuelled by propane/liquefied petroleum gas (LPG) for the eventual delivery of electric power to cover the hotel energy demands of a small boat. Details for the project, entitled as PURE and funded by the Fuel Cell and Hydrogen Joint Undertaking (FCH-JU), Grant Agreement No. 3034572013, can be found in Ref. [16].

In the absence of an efficient hydrogen market of adequate infrastructure, hydrogen fuel cells still typically rely on fuel reforming processes for the conversion of hydrocarbons (HCs) to hydrogen. Gaseous hydrocarbons such as natural gas (NG) and liquefied petroleum gas (LPG) [17] are attractive candidates for reforming as they benefit from a wide infrastructure for storage and transport and have relatively low sulphur compound content. For reasons of safety, LPG is odorized by ethyl mercaptan (C₂H₆S) at levels up to 150 ppmv for domestic use and up to 50 ppmv for transportation [18]; tetrahydrothiophene (THT, C₄H₈S) is a commonly used odorant for NG with total S concentrations in NG being as high as 20 ppmv [19]. However, even at such relatively low concentrations, sulphur compounds are poisons for the fuel cell anode catalysts, hence their removal down to 0.1–1 ppmv level [17] at some stage upstream the fuel cell is essential.

A common practice is to remove sulphur compounds before the reforming process. In principle, this would allow usage of standard reforming catalytic materials, without particular design measures to achieve tolerance to sulphur (e.g. abundant and cost-effective oxides of transition metals). Desulphurisation of NG or LPG upstream the reformer is a mature technology. Methods such as amine scrubbing [20,21] or hydrodesulphurisation (HDS) of petroleum derivatives [22,23] are customarily employed at the industrial scale. Sulphur removal upstream the reformer can also be achieved via less complex configurations, by utilising solid sorbent materials such as zeolites [24,25] and activated carbon [26,27] or alumina [28,29] at room temperatures. Nevertheless, the sulphur trapping capacity of such sorbents is relatively low (typically < 1 mg S/ml sorbent) and, as a result, system compactness is inhibited. Moreover, their sulphur removal efficiency is not high enough for HFC requirements. Sulphur presence at the reformer outlet, mainly in the form of hydrogen sulphide (i.e. H₂S > 0.1 ppmv), leads to the necessity for an additional sulphur removal polishing step downstream the fuel reformer, which is again at the expense of hardware space efficiency.

For applications that require extreme compactness, as in the case for the system introduced in the Pure project [16], the usage of a sulphur tolerant reforming catalyst based on precious metals [30], albeit with an additional cost, is more

suitable as it allows for a single desulphurisation step taking place downstream the reformer. An important consideration is that for temperatures typical to those at the reformer outlet, almost all sulphur in the gaseous stream exists as H₂S [17]. The use of solid metal oxide adsorption is an established technology [31], where removal of H₂S takes place at moderately high temperatures (typically > 200 °C) and follows the solid–gas sulphidation reaction,



where MO(s) is the metal oxide in the solid phase, and MS(s) is the metal sulphide in the solid phase. Past studies have evaluated the H₂S trapping capacity and/or efficiency of various metal oxides, with typical examples of proven performance being ZnO [32], CuO [33], Fe₂O₃ [34], MnO₂ [35], V₂O₅ [36] and CeO₂ based [37] sorbents. The vast majority of such studies have investigated the use of sorbents in the form of powder or pellet, suitable for large scale applications with relatively low space velocity, SV (h⁻¹). However, for small-scale portable fuel cell applications, the use of sorbent coated on monolithic structures is a better option. Although published data on such monolithic structures is very sparse, utilisation of honeycomb coated monoliths has been shown to reduce pressure drop [38,39], and thus eliminate challenges related to it, and increase trapping capacity cf. respective powder formulations by more than an order of magnitude [38].

The current study builds on previous knowledge at APTL, acquired during examination of a series of zinc based metal oxides under moderate temperatures for synthetic reformat gas streams [40]. Reported here are recent findings from work performed to examine the H₂S trapping efficiency and capacity of the in-house synthesized ZnO/CuO sorbent coated on monolithic reactors with two different cell densities of 400 and 600 cells per square inch (cpsi) and various active loading ratios, expressed in terms of $100 \times g_{\text{sorbent}}/g_{\text{monolith}}$.

Most of the experiments addressed the trapping capacity of the monoliths with respect to space velocity, active material loading, reactor temperature and monolith cpsi. Space velocity ranged from ~20,000–60,000 h⁻¹ and active loading varied from ~25% to 70%, resulting to specific space velocities of ~70 to ~350 m³/kg_{sorbent}/h. The effect of reactor temperature was examined in the range of 240 °C–400 °C. Tests to obtain the trapping capacity of the monoliths were also performed for two different synthetic gas atmospheres of a) 30%vol H₂, 32%vol H₂O, N₂ balance and b) 30%vol H₂, 32%vol H₂O, 6.5%vol CO₂, 4.5%vol CO, N₂ balance. It should be highlighted that for experiments addressing the trapping capacity of the monolith, hydrogen sulphide inlet feed was set at 25.0 ppmv throughout the study. This choice was a compromise between the estimated H₂S concentration at the outlet of the reformer of the PEM fuel cell system under design for the Pure project [16] and the lowest possible concentration that would allow realistic experimental duration of circa 5–50 h per experiment.

Two additional experiments were performed in order to address the trapping efficiency of the monoliths, at various reactor temperatures, space velocities and H₂S feeds, as those are shown later in Table 1. Note that trapping efficiency was defined as,

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