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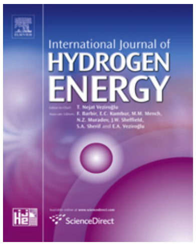

Hydrogen production via sulfur-based thermochemical cycles: Part 2: Performance evaluation of Fe_2O_3-based catalysts for the sulfuric acid decomposition step

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ABSTRACT

The sulfuric acid dissociation reaction, via which the production of SO_2 and O_2 is achieved, is the most energy intensive step of the so-called sulfur-based thermochemical cycles for the production of hydrogen. Efforts are focused on the feasibility and effectiveness of performing this reaction with the aid of a high-temperature energy/heat source like the sun. Such coupling can be achieved either directly in a solar reactor by concentrated solar radiation, or indirectly by means of a heat-exchanger/decomposer reactor using a suitable heat transfer fluid. Since a very limited amount of work regarding the potential formulations and sizing of such suitable reactors has been performed so far, the present work addresses further steps necessary for the efficient design, manufacture and operation of such reactors for sulfuric acid decomposition. In this respect, parametric studies on the SO_3 decomposition with iron(III) oxide-based catalysts were performed investigating the effect of temperature, pressure and space velocity on SO_3 conversion. Based on these results, an empirical kinetic law suitable for the reactor design was developed. In parallel, siliconised silicon carbide honeycombs coated with iron(III) oxide were prepared and tested in structured laboratory-scale reactors to evaluate their durability (i.e. activity vs. time) during SO_3 decomposition, with the result of satisfactory and stable performance for up to 100 h of operation. The results in combination with characterization results of "aged" materials can provide valuable input for the design of prototype reactors for sulfuric acid decomposition.

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1. Introduction

Thermochemical water-splitting cycles (TWSCs) represent an appealing carbon-free option for hydrogen production powered by alternative (carbon-free) energy sources. Until today, hundreds of TWSCs have been conceived and evaluated, but only a limited number reached higher development and demonstration level. These include the hybrid sulfur [1,2] and the sulfur–iodine (SI) cycles [3,4], belonging to the so-called "sulfur family" because they involve the vaporization of liquid and concentrated sulfuric acid and subsequent decomposition to sulfur dioxide and oxygen:

$$H_2SO_4 \rightarrow H_2O + SO_3 \ (H_2SO_4 \text{ vaporization}, \ {\sim}400\,^{\circ}C) \quad (1)$$

$$SO_3 \rightarrow SO_2 + ½O_2 \ (SO_3 \text{ splitting}, >750\,^{\circ}C) \quad (2)$$

The feasibility of both processes has been demonstrated by bench-scale closed cycle operation [5,6]. Hence, current actions are mainly focused on the technological advancement, including the selection and development of scalable materials and key components needed for large scale demonstration.

The endothermic catalytic reduction of sulfur trioxide into sulfur dioxide and oxygen is the high-temperature step common to all sulfur-based thermochemical cycles. Its coupling with a C-free heat source, either solar or nuclear, can be directly achieved in a solar reactor fed by concentrated solar radiation, or indirectly by means of a heat-exchanger/decomposer reactor using a suitable heat transfer fluid. Different concepts to bring in either high-temperature solar or nuclear heat into the endothermic chemical process above have been conceived and comparatively evaluated [7]. Those concepts differ with respect to the way the chemical process is coupled with the energy source. The concepts of a volumetric receiver–reactor for the solar process and a heat-exchanger reactor for nuclear heat have been identified as the only two that are feasible for the high-temperature decomposition of sulfuric acid.

However, these two kinds of reactors have different operating conditions in terms of pressure (the solar reactor operates at atmospheric pressure, whereas the heat-exchanger reactor requires pressures as high as 9 bar mainly to minimize reactor volume) and employ the catalyst structure in different forms (coated on honeycombs and in the form of pellets, respectively). Moreover, when the process is powered by a high-temperature gas cooled nuclear reactor decomposition temperatures must be limited below the helium coolant temperature of ca. 900 °C. Also in the solar case it is reasonable to reduce the SO_3 splitting temperatures, if one takes into consideration that the solar receiver efficiency increases at lower temperatures due to reduced reradiation [8] and that photolytic effect by direct solar radiation can be considered negligible in comparison to thermal decomposition; this last statement can be noticed, for instance, by comparing some relevant published results [9,10].

The major challenges of sulfur-based thermochemical cycles are the high temperatures and corrosive environments present in their key steps. The conditions require not only advanced materials for the key components but also special components design and fabrication methods. The relevant materials for decomposition of H_2SO_4 should maintain appropriate conditions for the chemical reaction at temperatures higher than 850 °C, be corrosion and thermal shock resistant, exhibit high fracture and creep strength maintained in this temperature range and last but not least be inexpensive and preferably fabricated in net-shape design. Promising material candidates for the decomposition section cover nickel-based alloys, high-temperature ferritic steels, as well as carbon and SiC composites (disregarding very expensive noble metals). Studies in the US [11–13] identified the SiC family as one of the most promising candidates for this application. SiC obtains its corrosion stability through the formation of a stable surface silica layer. Indeed, its exceptional thermal conductivity (170 W/m/K at room temperature), its refractoriness (up to 1600 °C under air) and its resistance to corrosive environment contribute to the consideration of this material as a favored candidate for high-temperature heat-exchanger concepts. In fact, several of the authors of the present work have introduced the concept of solar honeycomb monolithic reactors with the catalytic material coated on the walls of multi-channeled honeycomb ceramic supports made of SiC capable of absorbing concentrated solar irradiation [14], to perform successfully solar-aided endothermic reactions such as water splitting for the production of hydrogen [15,16]. Similarly, SiC was found perfectly suitable as the material of choice for a solar absorber/receiver/reactor for the performance of H_2SO_4 decomposition [7]. This is due to the combination of the above mentioned chemical resistance and thermo-mechanical properties plus its excellent optical properties (high absorbance for radiation).

In order to minimize materials cost, a satisfactory reaction rate in the sulfur trioxide splitting is needed. This can be ensured only by the use of dedicated catalyst systems featured by a high catalytic activity, high stability, immobility of catalyst materials under the harsh conditions applied, and an acceptable price. Hence, for an effective design and operation of a sulfuric acid decomposition reactor, it is necessary to assess the stability and endurance of the catalyst structures under the harsh reaction environment as well as to derive reliable SO_3 decomposition kinetic models under realistic operation conditions. The use of suitable catalysts (i.e. active, stable, and cost effective) will allow for lower operating temperatures: in fact, in absence of suitable catalysts, high SO_3 conversion and satisfactory reaction rates can be detected only at temperatures above 900 °C [10,17]. As a result, smaller reactor sizes and lower material costs can be reached using suitable catalysts.

Literature data on catalytic SO_3 decomposition [18–22] show that iron(III) oxide and mixed oxides based on that can be considered among the best catalyst options at temperatures equal or above 850 °C, because of its catalytic activity, stability and low cost. In contrast, at temperatures below 850 °C more complex/expensive materials must be used, such as supported platinum [20,22]. Part 1 of this work [23] addresses exactly the synthesis and evaluation of such iron oxide-based alternative catalytic materials such as spinels (AB_2O_4) or perovskites (ABO_3). It is also reported that chromium(III) oxide shows satisfactory activity, but it is also mentioned that material leaching is observed during its exposure to the reaction