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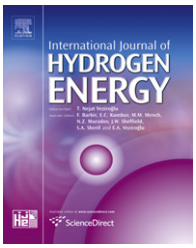

Catalytic activities of cobalt, nickel and copper ferrospinels for sulfuric acid decomposition: The high temperature step in the sulfur based thermochemical water splitting cycles

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ABSTRACT

The catalytic decomposition of sulfuric acid is the most endothermic step of the sulfur based water splitting thermochemical cycles, which are promising technologies for large scale hydrogen production in future. In the present study the catalytic activities of three ferrospinels AFe_2O_4 (A = Co, Ni, Cu) were evaluated for high temperature sulfuric acid decomposition reaction. Catalyst characterization by Mössbauer spectroscopy confirmed the occupancy of octahedral and tetrahedral sites by Fe^{3+} ions in all three inverse spinels. The temperature programmed reduction studies revealed that the reducibility of Fe^{3+} was greatly enhanced in $CuFe_2O_4$ as compared to other ferrites. Copper ferrite was found to be the most active catalyst for the reaction with ~78% conversion at 800 °C. Presence of sulfate species on the spent catalysts was revealed by an *ex situ* analysis of the spent catalyst samples by FTIR, SEM and evolved gas analysis (EGA). FTIR spectra of all the three spent catalyst samples exhibit four prominent peaks in the region 950–1200 cm^{-1}, which is an indicative of C_{2v} symmetry and bidentate sulfate coordination. A plausible mechanism for the sulfuric acid decomposition over spinel ferrites was proposed via the metal sulfate formation and then decomposition followed with an oxygen evolution step with the sulfate decomposition being the rate determining step at higher temperatures. EGA showed evolution of SO_2 as a decomposition product from existed sulfate of spent catalysts at high temperatures, with the rate of SO_2 evolution following the order: $CuFe_2O_4 > NiFe_2O_4 > CoFe_2O_4$. The enhanced rate of decomposition of the sulfates of copper ferrite can be attributed to the higher electronegativity of Cu^{2+} as compared to Ni^{2+} and Co^{2+}, which renders the S–O bond in the mixed metal sulfate weaker than others and thus more susceptible to dissociation. The lower thermal stability of sulfate and better reducibility are responsible for the improved catalytic properties of copper ferrite among the three ferrospinels investigated for sulfuric acid decomposition.

1. Introduction

The catalytic decomposition of sulfuric acid to produce sulfur dioxide, oxygen and water is a topic currently gaining enormous importance as it can serve as thermal to chemical energy conversion step in all the sulfur based thermochemical cycles such as the sulfur–iodine thermochemical cycle [1], the hybrid sulfur cycle [2], and the sulfur–bromine hybrid cycle

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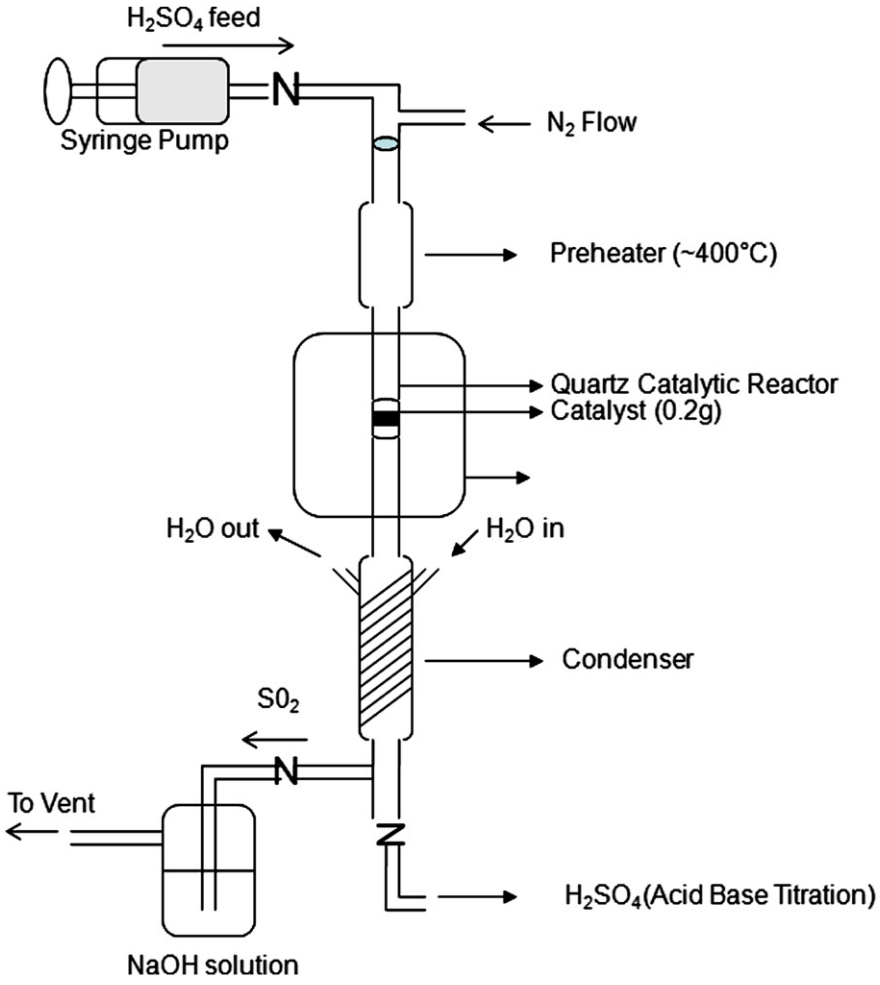

Fig. 1 – Block diagram of the experimental set up for carrying out sulfuric acid decomposition reaction.

[3], for successful massive hydrogen production by water splitting. Thermochemical cycles consist of a series of chemical reactions to produce hydrogen from water at much lower temperatures than required for the direct thermal decomposition of water [4]. Water splitting into hydrogen and oxygen is achieved via chemical reactions using intermediate elements which are recycled. The sum of all the reactions is equivalent to the dissociation of the water molecule. The primary energy source to drive the cycle could be a renewable energy source such as nuclear [4,5] or solar heat [6] and hydrogen can be produced without the need of any fossil fuels and also not releasing any green house gases considered being responsible for global warming. The efficiency of these sulfur based thermochemical cycles is potentially high and thus hydrogen production costs potentially low. The reactions involved in these sulfur based cycles are as follows:

Sulfur–Iodine Cycle:

$$I_2\,(l) + SO_2\,(g) + 2H_2O\,(l) \rightarrow 2HI\,(l) + H_2SO_4\,(l)\ (70–120\ ^\circ C) \quad (1.1)$$

$$2HI\,(l) \rightarrow I_2\,(g) + H_2\,(g)\ (300–450\ ^\circ C) \quad (1.2)$$

$$H_2SO_4\,(l) \rightarrow H_2O(l) + SO_2(g) + 1/2O_2(g)\ (800–900\ ^\circ C) \quad (1.3)$$

Hybrid-Sulfur Cycle:

$$SO_2\,(aq) + 2H_2O\,(l) \rightarrow H_2SO_4\,(aq) + H_2\,(g)\ (70–120\ ^\circ C, \text{electrolysis}) \quad (1.4)$$

$$H_2SO_4\,(l) \rightarrow H_2O\,(l) + SO_2\,(g) + 1/2O_2\,(g)\ (800–900\ ^\circ C) \quad (1.5)$$

The sulfur–iodine thermochemical cycle, comprising mainly of three chemical reactions - Bunsen reaction (Eq. (1.1)), Hydriodic acid decomposition (Eq. (1.2)) and sulfuric acid decomposition (Eq. (1.3)), was originally proposed by General Atomics (GA) [1] and is currently considered as one of the most promising technologies for large scale hydrogen production in future due to its high efficiency [7,8]. Also the cost analysis shows that the hydrogen production cost by sulfur–iodine cycle is lower than steam-methane reforming, and conventional and high temperature electrolysis, due to less use of electricity, no carbon related charges and no methane requirement [9,10]. Closed loop lab and bench scale testing of