Investigation of the Solar Hybrid Photo-Thermochemical Sulfur-Ammonia Water Splitting Cycle for Hydrogen Production

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Hydrogen is currently being used in many industries, from chemical and refining to metallurgical, glass and electronics, while being at the same time a promising energy carrier. Therefore the need for hydrogen is experiencing a very rapid growth. At the same time, the traditional hydrogen production methods (e.g., steam methane reforming, water electrolysis) are energy and resources intensive. Thus, research focus is on sustainable technologies that can produce hydrogen in an economic and environmental friendly way. Hydrogen production via a solar driven hybrid sulfur-ammonia water splitting cycle (HySA) developed at Florida Solar Energy Center is such a promising technology. For this reason, it is important to design and study, beyond the conceptual level, an efficient and realizable production process. Based on extensive preliminary works a state-of-the-art process has been proposed that integrates a solar-photocatalytic hydrogen production step (driven by the photonic portion of solar irradiance) with a high-temperature solar thermochemical oxygen evolution step (driven from the thermal portion) and efficient thermal energy storage as part of the cycle operation. Present work investigates the theoretical and engineering aspects of the proposed HySA process. It also provides an updated assessment and discussion of the related cycles and developments, of the photocatalysts, and analyzes the thermodynamics and implications of the reactions involved.

1. Introduction

To date, three pathways and their combinations for hydrogen production namely electrochemical, photochemical, and thermochemical have been developed with solar energy (Steinfeld, 2005). Thermochemical water splitting cycles (TCWSCs) have been shown to achieve high overall heat-to-hydrogen energy conversion efficiencies (Funk, 2001). The Westinghouse hybrid cycle still remains as one of the most studied TCWSCs conceived for the production of hydrogen from water. There are several issues involving the Westinghouse cycle. They include the use of high process temperatures, electrical input, relatively low solubility of SO_2, and the existence of pH effects during electrolysis of sulfur dioxide in aqueous solutions. In order to mitigate these problems, T-Raissi et al. (2006) developed a novel family of hybrid sulfur thermochemical water splitting, based on a sulfur–ammonia cycle (HySA), by introducing ammonia as working reagent to attain more efficient solar interface and less problematic chemical separation steps. Two approaches were considered for the hydrogen production step of the HySA cycle, photocatalytic and electrolytic oxidation of ammonium sulfite to ammonium sulfate in aqueous solutions. For the oxygen evolution step, two sub-cycles were also proposed, with zinc sulfate/zinc oxide and potassium sulfate/potassium pyrosulfate. The first version of the HySA cycle employed a photocatalytic
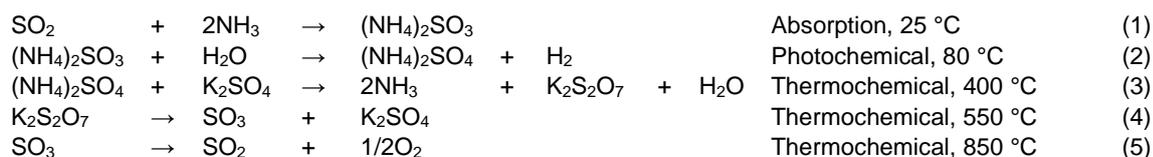
reaction step for generating hydrogen and a zinc sulfate/zinc oxide sub-cycle for oxygen generation (T-Raissi et al 2005). The second version, was examined by Taylor (2010), applying electrolytic oxidation for the hydrogen production step and a molten salt potassium sulfate/potassium pyrosulfate sub-cycle for oxygen evolution step.

Present work focuses on the most recent version of this cycle (Huang, 2014) where the above mentioned cycles are combined. Aims are to i) examine and clarify the reaction pathways of both sub-cycles ii) present the recent developments on the photocatalyst, and iii) improve the thermodynamic calculations using literature sources, experiments results, and advanced thermodynamic databases and tools.

2. Methodology

2.1 Description of the cycle

Eqs(1)-(5) describe the main steps, which involve a photocatalytic step for the hydrogen production and a thermochemical molten salt step for the oxygen production. The main advantage of the proposed cycle is the utilization of a wider fraction of solar spectrum, spanning from the UV-Visible (photochemical step) to the infrared wavelengths. This allows the cycle to reach potentially a higher overall efficiency than is possible with the purely photochemical or thermochemical water splitting cycles of the past (Huang et al., 2006). With reference to Eq(2), water splitting is achieved via a photochemical oxidation of ammonium sulfite with a simultaneous release of hydrogen (hydrogen-subcycle). Then, ammonium sulfate decomposes to ammonia, sulfur dioxide and oxygen via three thermochemical steps with successive temperature increases, Eqs(3)-(5) (oxygen-subcycle). At the first step (Eq(3)) potassium sulfate is employed to restrain the release of sulfur trioxide and separate it from ammonia and the remaining water. At a higher temperature (Eq(4)) the formed pyrosulfate decomposes back to the sulfate. Finally, sulfur trioxide decomposes to sulfur dioxide and oxygen (Eq(5)), while later both gases are separated using an ammonia absorber (Eq(1)). All cited temperatures originate from the corresponding literature.

$$SO_2 + 2NH_3 \rightarrow (NH_4)_2SO_3 \qquad\qquad \text{Absorption, 25 °C} \qquad (1)$$
$$(NH_4)_2SO_3 + H_2O \rightarrow (NH_4)_2SO_4 + H_2 \qquad \text{Photochemical, 80 °C} \qquad (2)$$
$$(NH_4)_2SO_4 + K_2SO_4 \rightarrow 2NH_3 + K_2S_2O_7 + H_2O \quad \text{Thermochemical, 400 °C} \qquad (3)$$
$$K_2S_2O_7 \rightarrow SO_3 + K_2SO_4 \qquad\qquad \text{Thermochemical, 550 °C} \qquad (4)$$
$$SO_3 \rightarrow SO_2 + 1/2O_2 \qquad\qquad \text{Thermochemical, 850 °C} \qquad (5)$$

Concerning the hydrogen subcycle, past studies focused mainly on the photocatalysts development. Cadmium sulfide (CdS) is the primary material examined. Muradov et al. (1981) proposed CdS as an ideal photocatalyst for conducting the hydrogen generation step. Over the years, a series of complex photocatalysts have been prepared and tested for high efficiency hydrogen production from sulfide and sulfite solutions. Although, many mechanisms have been proposed (Buhlet et al., 1984) and further developed (Tsuji et al. 2004), a detailed and comprehensive analysis, both numerical and experimental, is still missing. On the other hand, the oxygen subcycle is mainly based on the experimental thermal analysis of the employed materials and the related process simulation. The molten salt thermochemical part was experimentally examined by Wang (2012). Following, Littlefield (2012) simulated an integrated process using Aspen Plus and literature for properties of the sulfates/pyrosulfates (Lindberg 2006). In this case, generalized and simplified thermodynamic approximations have been used, which might have resulted to inaccurate estimation of process conditions and balances.

2.2 Numerical tools

Several issues have been identified, in previous works (Littlefield et al 2012) which require further investigation. The present work is based on extensive literature research, the use of advanced thermodynamic numerical tools (like Aspen Plus and FactSAGE) and comprehensive thermodynamic databases (e.g. FACT and DIPPR project 801). Later, these tools will facilitate the incorporation of new materials and processes into the existing ones.

2.3 Experimental tools

Photocatalytic hydrogen production experiments were conducted in a simple bench scale configuration involving a glass container (photoreactor), a water bath for temperature control, and a solar simulator (Newport/Oriel Corp., 300-1,000W output, model 9119X with an air mass (AM) 1.5 global filter). The synthesized photocatalyst combined with co-catalyst were added to the aqueous solution containing 1 M $(NH_4)_2SO_3$ placed inside the photoreactor. Before each experiment, the photoreactor was purged with ultra-pure argon gas (Linde, 99.999 %) for about 1 h to remove dissolved oxygen from the solution. The evolved hydrogen gas was collected over the water using an inverted graduated burette.
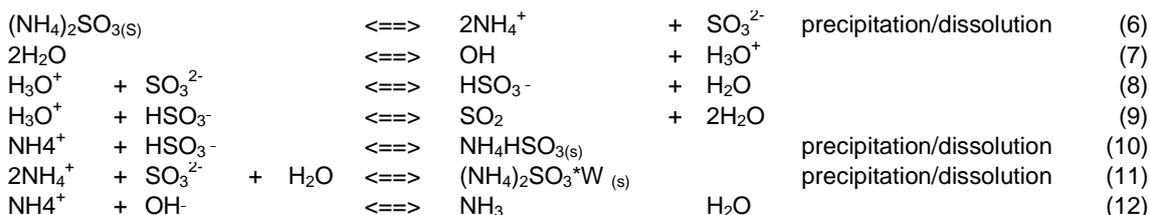
3. Results and discussion

This section first describes the mechanism investigation of the hydrogen production sub-cycle – ammonium sulfite oxidation and the recent developments concerning the employed photocatalyst. Then, it discusses the thermodynamic analysis of the oxygen sub-cycle using a specific sulfate/ pyrosulfate.

3.1 Investigation of the photochemical hydrogen sub-cycle mechanism

Photochemical water splitting using ammonium sulfite solution is a very promising route for the production of hydrogen. According to the thermodynamic analysis, the reactants can be fully converted into products following the overall Eq(2). However, in practice kinetic plays an important role in complete oxidation of ammonium sulfite. In order to understand the photochemical sub-cycle we have to focus on the intermediate reactions that take place behind the profound main one. Thus, the focus of this section is the preliminary theoretical investigation of the hydrogen sub-cycle mechanism.

The photochemical reaction Eq(2) occurs between the soluble salt ammonium sulfite $(NH_4)_2SO_{3(aq)}$ and water, producing ammonium sulfate $(NH_4)_2SO_4$ and H_2. Both $(NH_4)_2SO_3$ and $(NH_4)_2SO_4$ are very soluble in water (about 6 M at 30 °C) and thus good electrolytes for hydrogen production (Huang et al., 2006). Ammonium sulfite $(NH_4)_2SO_{3(aq)}$ separates into ions in water solution, according to the equilibrium reaction Eq(6). Ammonium sulfite compound does not exist inside the solution except in the form of salt/solid phase. This means that reactions occur between ions-aqueous species like NH_4^+ and SO_3^{-2}. The dissociation of water is also an equilibrium reaction. The use of hydronium H_3O^+ is recommended, because the presence of H_3O^+ in the solution chemistry is better able to represent the phase and chemical equilibrium of an electrolyte system. Hydronium and hydroxide ions are formed in all aqueous solutions by a proton transfer reaction between two water molecules. The water self-dissociation in Eq(7) is significant because it is omnipresent in aqueous solution, which means that it applies to all solutions, regardless of other solutes that may affect the concentrations of hydrogen and hydroxide ions.

$(NH_4)_2SO_{3(S)}$		<==>	$2NH_4^+$	+	SO_3^{2-}	precipitation/dissolution	(6)
$2H_2O$		<==>	OH^-	+	H_3O^+		(7)
H_3O^+ + SO_3^{2-}		<==>	HSO_3^-	+	H_2O		(8)
H_3O^+ + HSO_3^-		<==>	SO_2	+	$2H_2O$		(9)
$NH4^+$ + HSO_3^-		<==>	$NH_4HSO_{3(s)}$			precipitation/dissolution	(10)
$2NH_4^+$ + SO_3^{2-} + H_2O		<==>	$(NH_4)_2SO_3*W_{(s)}$			precipitation/dissolution	(11)
$NH4^+$ + OH^-		<==>	NH_3		H_2O		(12)

Thermodynamic calculations of Eq(2) and Eq(6)-(12), and experimental results show that the formation of ammonium sulfate and hydrogen occurs at ambient conditions. However, the above mentioned reactions are mainly phenomenological. This means that we have to focus on the oxidation of SO_3^{-2} ($S^{(IV)}$) reaction that can lead to the formation of SO_4^{-2} ions ($S^{(VI)}$). Guo et al. (2014) examined the mechanism and the parameters that affect the ammonium sulfite oxidation. He reported that the ammonium sulfite oxidation may include two steps: an intrinsic reaction of sulfite in the solution and diffusion of oxygen from air bubbles into the solution and considered that the diffusion of oxygen is the controlling step of the oxidation of ammonium sulfite. The main difference is that in our case water has to be the oxidizing agent. Therefore the change of sulfur valence using water is very important in order to produce sulfate ions.

$$\text{Photocatalyst} \quad + \quad hv \quad \rightarrow \quad h^+ \quad + \quad e^- \tag{13}$$

Atmospheric chemistry literature (Seinfeld and Pandis, 2006) provides information about the spontaneous reactions taking place between the existing ions, HSO_3^-, SO_3^{-2}, OH^-, H_3O^+. As long as hydroxyl radicals are formed, a chain reaction is taking place in the presence of dissolved oxygen. Instead, and in the absence of oxygen, photo-catalysts (e.g. semiconductors) are used for reduction (electron supply) and oxidation (extraction of oxygen) reactions. Bao (2008) and later developed by Wang et al (2012) explain that when a photo is absorbed by the catalyst, an e^- / h^+ pair is generated as in Eq(13). The e^- and h^+ may migrate to the surface and react with the adsorbed reactants in the desired process. The photo-generated electrons in the conductive band reduce the water to form hydrogen. In the meanwhile, the photo-generated holes in the valence band can oxidize SO_3^{-2} to form SO_4^{-2} directly, according to Eq(13) or indirectly. Thus, the hydrogen sub-cycle mechanism lies to a series of intermediate reactions involving ions, which come from the dissociation of the reactants, ammonium sulfate and water; according to literature and in combination with experimental results and our preliminary thermodynamic results, further investigation, should follow to confirm the determining steps of the hydrogen sub-cycle mechanism.

3.2 Photocatalytic hydrogen production

Earlier, we reported CdS-photocatalyzed H_2 production from aqueous ammonium sulfite $(NH4)_2SO_3$ solutions (Huang et al., 2014). More recently we examined the catalytic effect of transition metals, including, Pt, Pd, Ru, Ni and Co, added to the photocatalytic system in the form of fine polymer-stabilized colloidal particles, on the kinetics of H_2 photogeneration (Muradov et al., 2015). The photocatalyst was synthesized in situ where ZnS is deposited on CdS particles following by the loading of the transition metal. Pt cocatalyst showed the highest activity, therefore here we examined the effect of the Pt quantity to the hydrogen production rate. Figure 1 summarizes the preliminary results compared to the baseline of around 1 % to the amount (~0.3 g) of a photocatalyst (~1.8 mL $H_2.min^{-1}$). It also demonstrates the impact of the amount of the photocatalyst itself to the production of hydrogen.
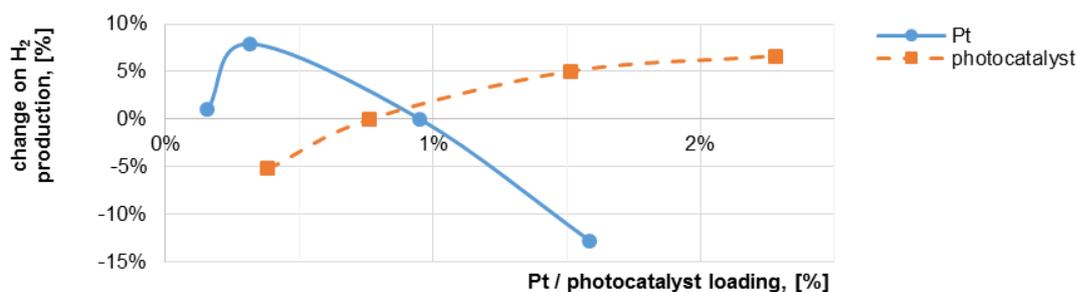
Figure 1: Effect of Pt cocatalyst and photocatalyst loading compared to baseline (~1 %Pt to 0.3 g of CdS)

3.3 Thermodynamic analysis of the thermochemical oxygen sub-cycle

In the past Littlefield (2012) studied a molten salt potassium sulfate/ pyrosulfate pair sub-cycle for oxygen evolution step. As it has been described earlier, the use of a sulfate is critical for the separation of SO_3 and NH_3 (see Eq(3)). The sulfate captures SO_3 and transforms to pyrosulfate which later decomposes back to the sulfate and releases the SO_3. An important aspect is the state (phase) of the mixture. Potassium sulfate and the like (i.e. sodium) have a melting point of close to 1,000 °C, which is an inhibiting factor for most chemical processes. Extensive experimental studies have shown that they form binary and reciprocal mixtures with quite lower melting points. Previous studies used Aspen Plus process simulation software to analyze the oxygen-subcycle. However, instead of using directly the experimentally derived thermodynamic properties (Lindberg, 2006), they applied a series of hardcoded specifications to constrain the mixture composition within the liquid phase (melt). Result of these studies is also the operating temperature ranges of each step of the subcycle. Instead, we incorporated into Aspen Plus the proper thermodynamic properties. We also used FactSage equilibrium calculator to check the Aspen Plus calculations and perform a detailed thermodynamic analysis. The available thermodynamic data were transformed into the appropriate formats following Lindberg (2006) experimental work and Fact database. It should be noted that phase transformation (solid to solid and solid to liquid) in Aspen Plus is rather weak, but most of these can be included in the form of a chemistry block.
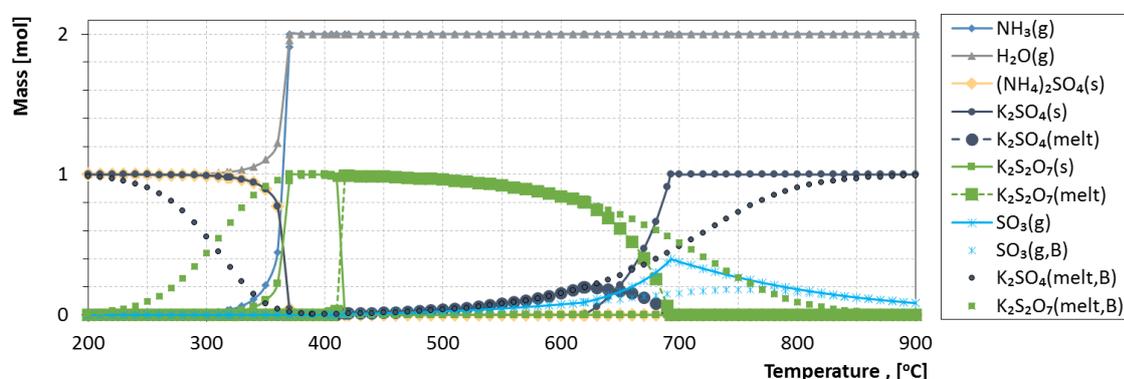

Figure 2: Temperature dependent thermodynamic equilibrium of .Eq(3)-(5) with initial stoichiometric ratios. [lines and symbols: the expected compounds and states; plain symbols: melts only are forced]

On the other hand, addition of more control blocks can lead to over-definition of the system with surprising results. This is why we recommend the conduction of an exploratory and non-constrained thermodynamic analysis with more specialized tools, as a first step. Figure 2 illustrates the temperature dependent thermodynamic equilibrium of an equimolar aqueous mixture of $(NH_4)_2SO_4$ and K_2SO_4 (plots with lines and symbols). We observe the evolution of Eq(3)-(5), and in addition the phase change of $K_2S_2O_7$ (~417 °C) and K_2SO_4 (~620 °C). For a more representative description of the equilibrium at temperatures lower than 400 °C we need to add ammonium bisulfate as an intermediate product and the aqueous solution of ammonium sulfate. Both have been omitted because it is not of primary interest here. To demonstrate the importance of including the phase change and state of the solid compounds, we have performed the same thermodynamic analysis by enforcing only the melt state and added in the same figure the plots (plain symbols) for K_2SO_4, $K_2S_2O_7$ and SO_3. In this case the conclusions are different for both the efficiency of the sulfate regeneration and appropriate temperature range for Eq(4).
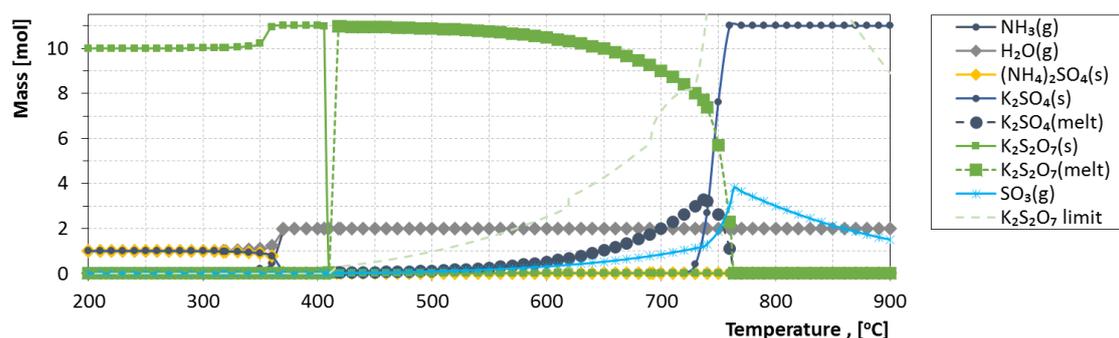

Figure 3: Same as in Figure 1 but with an initial ratio of K_2SO_4 to $K_2S_2O_7$ equal to 1:10. [lines and symbols: expected compounds and states; dashed line: necessary quantity of $K_2S_2O_7$ to maintain a liquid state]

Nevertheless, another way (Littlefield et al 2012) to increase the efficiency of this step is to reduce the K_2SO_4 to $K_2S_2O_7$ ratio, which also maintains a liquid reciprocal mixture at higher temperatures. This analysis is presented in Figure 3. Using a ratio of 1:10, we achieve a 100 % regeneration of K_2SO_4 at around 650 °C, while the maximum regeneration in the equimolar case (ratio 1:1) is around 20 %. At the same temperature, we also observer an increase to the released SO_3. A future combined thermodynamic-sensitivity analysis can reveal exactly the theorectical operational conditions and efficiencies.

4. Conclusions

The hybrid photo-thermochemical sulfur ammonia cycle can be one viable means for producing hydrogen using solar energy. In this work the most important aspects of the hydrogen and oxygen subcycles have been discussed. The consideration on the photocatalytic mechanism shows that the most probable path for the sulfur oxidation and thus water splitting is in all likelihood similar to the described in the literature for sodium sulfite solutions (Buhler et al 1984). We also demonstrated the optimum loading of Pt (% on the catalyst) and of the catalyst (% in the system) around 0.5 % and 1.5 %. The dependency of these values on other design parameters (i.e. reactor size, exposed area, mixing) is important (Ampelli et al 2014) but has not been investigated here. In the future a series of experimental and numerical studies will reveal the mechanism and controlling steps, and will lead to the selection and development of the most appropriate photocatalyst. Similarly, the thermodynamic analysis of the thermochemical steps demonstrates the importance of using specialized thermodynamic tools to screen the selected materials and optimize the operating conditions. As it is illustrated, lack of comprehensive thermodynamic properties could lead to the wrong conclusions. Nevertheless, the analysis confirmed the increase in efficiency with the use of higher than 1 ratio of pyrosulfate to sulfate. Further analysis (numerical and experimental) and improvements are needed in order to optimize the integrated cycle configuration.

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