

Material screening for two-step thermochemical splitting of H₂S using metal sulfide

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Abstract. Associated with the rise in energy demand is the increase in the amount of H₂S evolved to the environment. H₂S is toxic and dangerous to life and the environment, thus, the need to develop efficient and cost-effective ways of disposing of the H₂S gas has become all-important. To this end, a two-step thermochemical H₂S splitting cycle is proposed in this work which does more than just getting rid of the toxic gas but has the potential to produce valuable H₂ gas as well as store the solar heat energy. Studies have proved that the type of material used, such as metal sulfides, is critical to the efficiency of this thermochemical splitting process. As follows, this study focuses on establishing a criterion to aid in selecting favorable metal sulfides for application and further development in the H₂S thermochemical decomposition sphere. Using a computational approach, via the HSC Chemistry 8®, evaluations such as the equilibrium yield from the sulfurization and decomposition reaction steps, the temperature required for reaction spontaneity, and the Reversibility Index were determined. Investigations proved that sulfides of Zirconium, Niobium, and Nickel were auspicious candidates for the thermochemical decomposition.

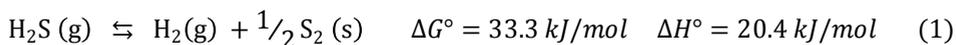
Introduction

Hydrogen sulfide, which is naturally present in crude oil and natural gas, is toxic and considered as a contaminant to the environment. Hydrogen sulfide is usually removed from petroleum products through the refining of crude oil and sweetening of sour natural gas. The rise in the global energy demand thereby poses a challenge because meeting this demand would require increased use of fossil fuels [1], ultimately leading to a rise in the amount of H₂S evolved to the environment [2].

Researchers and corporations have put in a lot of work to bring about ways to reduce these H₂S emissions. The Claus Process, which is the state of the art approach for disposing of noxious H₂S, involves the thermal decomposition of H₂S by partial oxidation to produce

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sulfur and water. This process releases a great deal of energy in the form of low-grade steam, which has relatively low economic value. However, the thermolysis of the noxious H₂S provides a realizable means of deriving higher economic benefits, as hydrogen is simultaneously generated during this process [3]. This reaction is endothermic having a potential for improving energy efficiency through storage of heat in the form of Hydrogen production. The H₂ produced can be used in the synthesis of new products, hydrodesulfurization and hydrocracking processes, and as a fuel source. The reaction for the thermal splitting is shown below [4]:



The technical challenge with producing H₂ from H₂S is that the direct reaction of H₂S decomposition to elemental sulfur is endergonic, thus its equilibrium for the reaction is unfavourable at all temperatures. Therefore, this process will require free-energy input, e.g. from heat recovery systems or from the sun, to drive the overall reaction.

To attain higher conversions using realistic reactor sizes and residence times, catalysts are generally applied to accelerate this kinetically limited process [5-11]. However, the thermodynamic forces of the thermolysis process are unaffected by the catalysts and strongly limits the overall process. The equilibrium H₂S conversion is about 6 % at 800°C under atmospheric pressure [12], which is too low for an economically viable process. To overcome this thermodynamic limitation, studies were carried out using catalytic membrane reactors [13-14]. Despite the fact that very high conversions were obtained using these membrane reactors, the high cost of implementation accompanying this method, via the application of metallic hydrogen-permeable membranes, makes it unfavorable.

In the pursuit to establish a comparatively cheap means of attaining high conversions of H₂, a two-step thermochemical closed cycle using metal sulfides was adopted in this work. The thermochemical approach was used to devise a sequence of easier reaction steps to accomplish the overall reaction of H₂S decomposition. The first step of the H₂S decomposition cycle involves a metal sulfide (MeS_{low}) sulfurization under H₂S atmosphere. This reaction is usually exothermic and takes place at lower temperatures. While the second step involves a regeneration of the metal sulfide (MeS_{low}) under high-temperature conditions. The cyclic reaction is derived from the Kiuchi-type 1 reaction as shown in the figure below [15]:

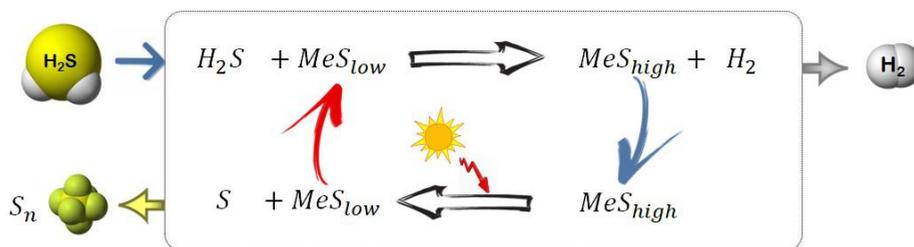


Fig. 1. Two-step thermochemical H₂S splitting cycle

The type of metal sulfides used for the H₂S splitting cycle is very crucial to process' efficiency [15-20]. A lot of work has been carried out on the direct thermal splitting of H₂S. However, just a few metal sulfides have been done using the two-step thermochemical splitting approach of H₂S and without any nomination basis for these metal sulfides used for the experimental studies. As such, the objective of this study is to identify the most promising candidates (metal sulfides) for the two-step thermochemical H₂S splitting cycle, which can aid in the provision of data and insight for further research and application.

Methodology

A systematic approach has been developed to achieve a successful material screening process regarding the thermochemical splitting of H₂S. This activity was broken down into a series of steps:

A) Identification of stable/predominant metal sulfides

First, identification of predominant and stable metal sulfides which exists at the specified operating conditions was carried out. In addition to acquiring information on the lower metal sulfides and higher metal sulfides that can be used for further analysis, knowledge on the metal sulfide reaction systems which have only one stable phase is obtained. These single-stable phase sulfides are not suitable for the two-step thermochemical cycle. Thus, this process helped in sieving out unsuitable metals prior to any further investigations.

A quick estimate of the phase stability of these metal sulfides was determined computationally using the Temperature-Partial Pressure (TPP) module of the HSC Chemistry 8.0®. Since thermodynamic stability occurs when a system is in its lowest energy state, the module aided in determining the phase stability based on the minimum Gibbs energy.

Identification of the stable higher sulfide phase was executed under isothermal conditions (25°C), with the partial pressures of H₂ and H₂S ranging from 0.1 to 1 bar. During the regeneration step, H₂S and H₂ are not present, thus, the assumption that the partial pressures of these components tend to zero. Identification of the stable lower sulfide phase was carried out under isothermal conditions (800°C), with the partial pressures of S₂ ranging from 0.1 to 1 bar.

B) Thermodynamic parameters determination

The predominant lower and higher metal sulfide phases recognized in the previous step was then applied in the Reaction Equation module of the HSC Chemistry 8.0® to determine thermodynamic properties describing the state of the heterogeneous reaction systems. The Enthalpy, Entropy, and Gibbs free energy were determined, providing more insight into the nature of the two-step cycle. The required input is the stoichiometric reaction equation for the sulfurization and regeneration reactions of the thermochemical H₂S splitting cycle at the appropriate operating conditions.

C) Equilibrium amount of reaction products

The multi-component equilibrium compositions for the reaction system were determined using the Equilibrium module of the HSC Chemistry 8.0®. The GIBBS solver, which makes use of the Gibbs energy minimization method, was applied via the Equilibrium module to calculate equilibrium amounts of reaction products using previously determined thermodynamic parameters. This was used to determine the equilibrium amount of the H₂ evolved and higher metal sulfide produced in the first sulfurization step, and the equilibrium amount of sulfur evolved and lower metal sulfide regenerated in the second step of the thermochemical H₂S splitting cycle.

To achieve accurate equilibrium results, the potentially stable phases for the heterogeneous system must be considered. This was achieved in the first step using the Phase Stability Diagram module. The appropriate number of moles of raw materials for the reaction was considered, estimated stoichiometrically, using a basis of 1 kmol. The

temperature for the two-step reaction of the thermochemical cycle was set at 25°C for the sulfurization step, and 800°C for the regeneration step, under isobaric conditions of 1 bar.

Aided by the three steps above, key parameters, as shown in Fig. 2, were determined to serve as performance yardsticks to guide in the selection of metal sulfides for the H₂S thermochemical splitting cycle:

- Phase stability at operating conditions.
- The yield of Hydrogen and higher metal sulfide produced.
- The yield of Sulfur and lower metal sulfide produced.

$$\text{Percent Yield}(\%) = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100 \quad (2)$$

- Temperature requirement for reaction spontaneity
- Reversibility Index (RI)

$$\text{RI} = \frac{\text{moles of } \text{MeS}_{\text{low}} \text{ produced in regeneration reaction}}{\text{Initial moles of } \text{MeS}_{\text{low}} \text{ reacting in sulfurization reaction}} \quad (3)$$

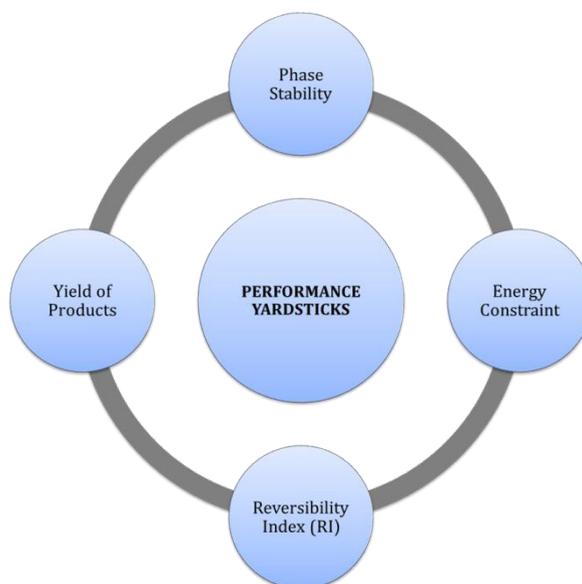


Fig. 2. Evaluation criteria for selection of metal sulfides

Results and discussion

Table 1 displays a list of the stable lower and higher metal sulfides at the reaction operating conditions. A total of 27 metals were tested, however, only the sulfides listed were used for performance analysis. Most of the metals tested were transition metals due to the favorable bonding interactions that exist between their d-orbitals and the p-orbitals of sulfur, along with their potential to form multiple oxidation states. Among the 27 metals tested, the following displayed a single-phase metal sulfide stability under the cyclic reaction conditions and did not qualify for any further inquiry: MoS₂, Cu₂S, ZnS, MnS, Li₂S, RuS₂,

CdS, MgS, Rb₂S, Cs₂S, and Al₂S₃. The bonding interactions, such as the metal-sulfur bond strength, is a major factor that brings about the single stable phase occurrence. For example, metal sulfides like ZnS have very low adsorption bonding with the sulfur atoms from H₂S, which prevents the progress of the sulfurization reaction.

Table 2. Stable Higher and Lower Metal Sulfides at Operating Conditions.

Metal	Higher Metal Sulfide (MeS_{high}) at 25°C	Lower Metal Sulfide (MeS_{low}) at 800°C
Sc	ScS ₃	ScS
Ti	TiS ₂	TiS
V	V ₂ S ₃	VS _{1.043}
Cr	Cr ₂ S ₃	CrS _{1.17}
Fe	FeS ₂	FeS
Co	CoS ₂	CoS
Ni	NiS ₂	NiS
Zr	ZrS ₃	ZrS ₂
Nb	NbS ₂	NbS _{1.65}
Tc	Tc ₂ S ₇	TcS ₂
Rh	Rh ₂ S ₃	Rh ₃ S ₄
Pd	PdS	Pd ₄ S
Ir	IrS ₂	Ir ₂ S ₃
Hf	HfS ₃	HfS ₂
Na	Na ₂ S ₂	Na ₂ S
K	K ₂ S ₂	K ₂ S

It is important to note that some of the metal sulfides listed in Table 1 have more than one stable sulfide that exists at a given state for both the sulfurization and regeneration operating conditions. As a case in point is the Ni-S binary reaction system. These sulfides exist in several thermodynamically stable sulfide states that are potentially functional for the cyclic H₂S splitting reaction. Some of the nickel sulfide phases include Ni₃S₂, Ni₇S₈, Ni₉S₈, NiS, Ni₃S₄, NiS₂. In this thermodynamic study, NiS and NiS₂ were applied as shown in Table 1. NiS₂ was used as the higher metal sulfide state existing after the sulfurization reaction, because of the tendency for it to be easily regenerated as compared to other nickel sulfides with lower sulfur content. This does not necessarily mean that these nickel sulfide

phases (NiS-NiS₂), as seen in Table 1, are the most favorable pair of nickel sulfide states that can be applied for the H₂S splitting cycle.

As shown in the Fig. 3, most of the metal sulfide reaction systems generated a high yield of hydrogen due to the exergonic nature of the sulfurization reaction which takes place at 25°C and at 1 bar. Thus, the sulfurization of the metal sulfides occurs spontaneously in most cases. Only the Hf-H-S reaction system revealed to be endergonic under the specified operating conditions, attributing to the relatively low yield achieved when reacting 1 kmol of Hafnium Sulfide with H₂S. The sulfurization reaction of HfS₂ has ΔG of 1.486 kJ. In all cases, the sulfurization reaction of the lower metal sulfides was exothermic, thereby increasing the temperature would cause a decrease in the equilibrium conversion and yield of hydrogen.

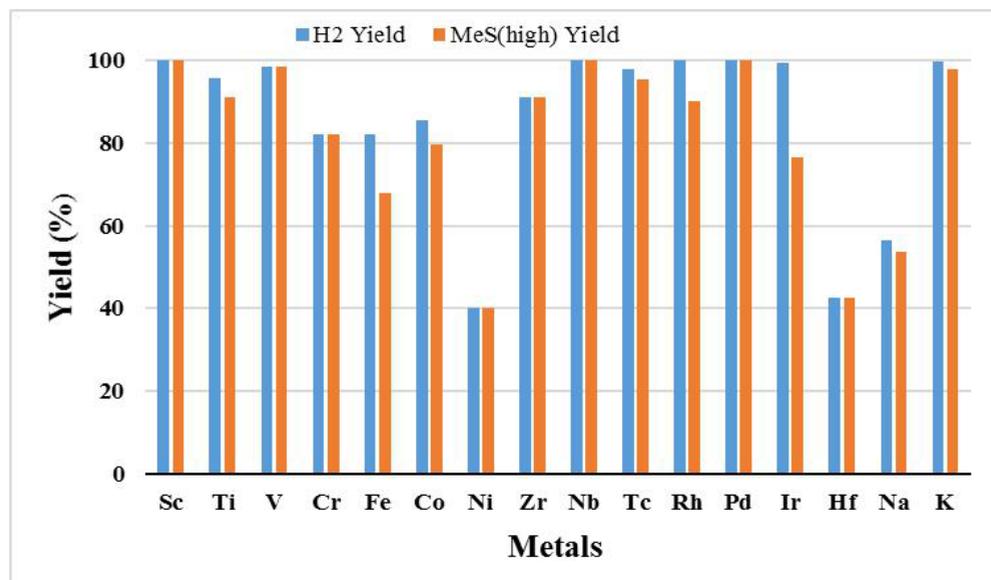


Fig. 3. The yield of hydrogen and higher metal sulfide generated at 25°C for 1 kmol of H₂S

Studies in literature corroborate the findings presented in Table 1. Even though some of these metal sulfides are not suitable for the two-step thermochemical cycle, the nature of their stable existence in one-phase enables them to function as catalysts for the direct thermal dissociation of H₂S. A couple of sulfides in our study which fit the bill are Molybdenum sulfide and Lithium Sulfide. Investigations conducted by several researchers [5-7] revealed that the reaction of MoS₂ with H₂S doesn't generate its trisulfide under X-ray diffraction analysis. MoS₂ seems to be inert at temperatures below 500°C but catalyzes the decomposition reaction at higher temperatures. At 500°C, the H₂ yield for the H₂S thermal decomposition reaction increased from 6% to 8.5% when MoS₂ was introduced. Li₂S also proved to be a poor candidate for the two-step thermochemical cycle but a good catalyst for the direct thermal splitting of H₂S. After thermally splitting the H₂S over Li₂S at 550°C, the metal sulfide remained unchanged, and there was an increase in H₂ yield from about 1% to 3% when compared to a non-catalytic thermolysis of H₂S [21].

On the other hand, more favorable candidates for two-step thermochemical cycles such as the monosulfides of Fe, Co, Ni, K, and Na have been verified in literature to show poor catalytic activity but rapidly reacts with H₂S to produce higher metal sulfides—disulfides specifically. Investigations by Chivers et al. [5] using Na₂S and K₂S for the sulfurization reaction were similar to Table 1, reacting with H₂S to produce Na₂S₂ and K₂S₂. At 600°C, the H₂ yield for Na₂S and K₂S was 14% and 18% respectively.

In the regeneration step, the higher metal sulfide is thermally decomposed at 800°C and 1 bar to produce its lower metal sulfide and elemental sulfur. The thermal decomposition efficiency is represented by the yield of the sulfur produced as well as the yield of the lower metal sulfide as shown in Fig. 4. For most reaction systems, the regeneration reaction is endergonic and endothermic at the 800°C and 1 bar, hence, the operating conditions are not favorable for many metal sulfides. However, for the Zr-H-S, Hf-H-S, and Nb-H-S reaction systems, the thermal decomposition occurs spontaneously with ΔG of -35.87 kJ, -49.81 kJ, and -2.396 kJ respectively. Higher sulfides of Zirconium and Hafnium decomposed to produce a 100% yield of sulfur and their lower metal sulfides, while Niobium produced a yield of about 80%. Sulfides of Chromium and Technetium also showed relatively great results for the decomposition reaction. However, the use of Technetium isn't favorable due to its radioactive nature.

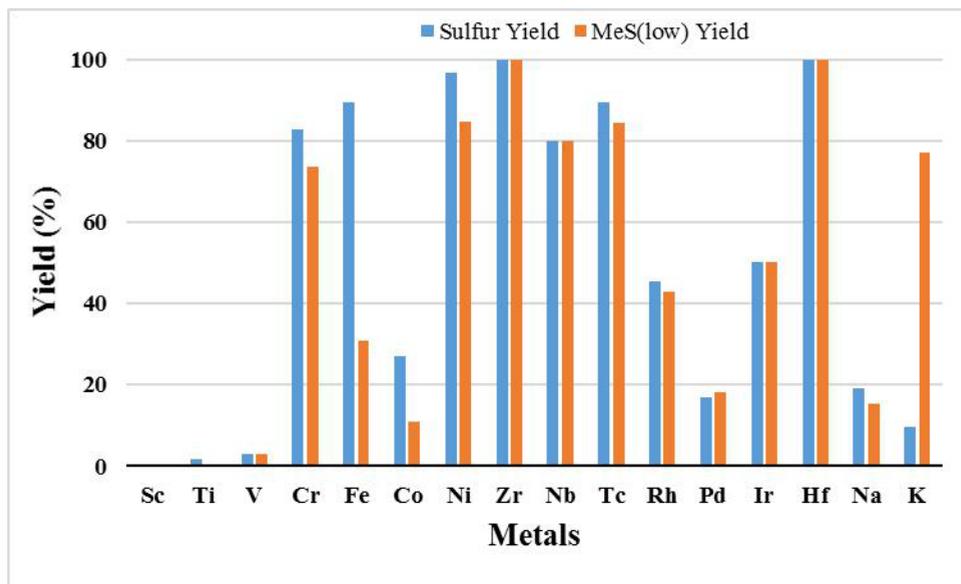


Fig. 4. The yield of sulfur and lower metal sulfide generated at 800°C

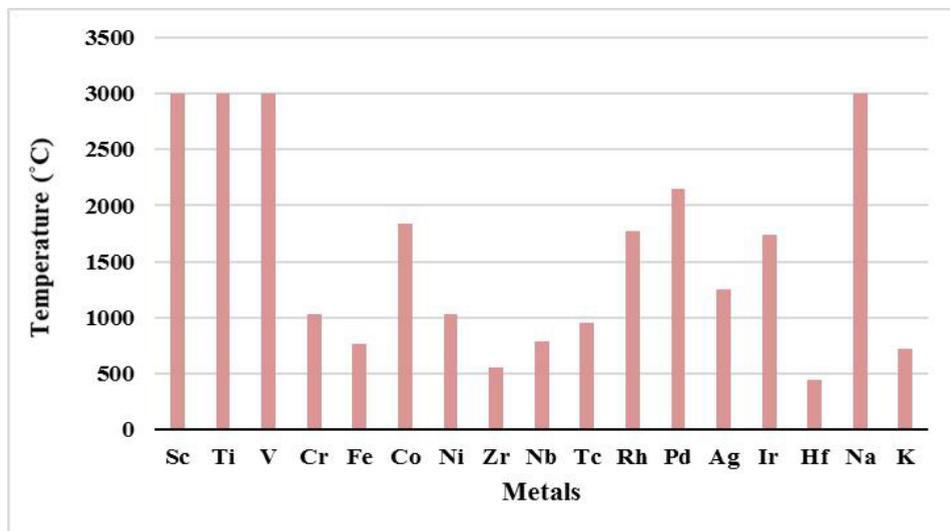


Fig. 5. Temperature requirement for reaction spontaneity

Figure 5 shows the temperature levels needed to attain reaction spontaneity in the regeneration process. When the temperature of the reaction is increased, the regeneration reaction, usually endothermic, can be transformed from an endergonic reaction to a spontaneous reaction. Sulfides of Zirconium, Hafnium, Niobium, Potassium, and Iron proved to have spontaneous regeneration reactions at temperatures below 800°C, ultimately resulting in a relatively higher yield of sulfur and lower metal sulfide shown in Fig. 4. Additionally, these sulfides are more energy efficient as relatively lower temperatures can be operated successfully for the regeneration reaction.

The amount of sulfur and lower metal sulfide presented in Fig. 4 was estimated based on the assumption that a yield of 100% was derived for the generated higher metal sulfide in the sulfurization step, thereby rendering the maximum possible yield for the sulfur and lower metal sulfide in the regeneration step. However, a more accurate depiction of the Reversibility Index for the H₂S splitting thermochemical cycle would require the latter thermal decomposition reaction to be a function of the yield of the higher metal sulfide derived in the sulfurization reaction. A key parameter considered in evaluating the performance of a catalyst is the Regeneration performance. Likewise, the Reversibility Index measures the degree to which one can recover the material used for the H₂S decomposition reaction. As clearly shown in Fig. 6, the Zr-H-S reaction system displayed the best RI with a value of about 0.91. Sulfides of Technetium and Niobium showed good results with RI of about 0.8.

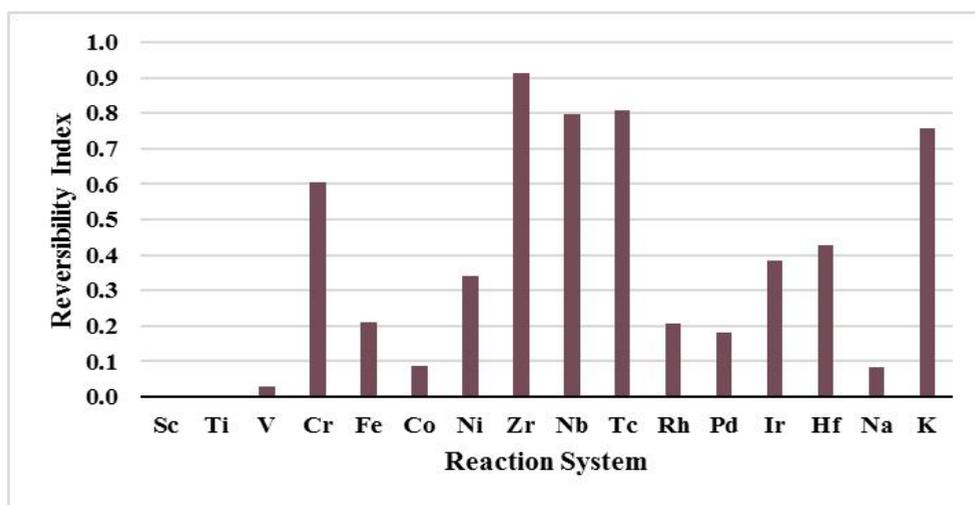


Fig. 6. Reversibility Index of Metal Sulfides

Conclusion

Following the computational activity executed in this study, some promising metal sulfides and relevant data have been identified, such as sulfides of Zirconium and Niobium, which can be applied and improved upon in the thermochemical H₂S decomposition field of study. These sulfides have a lot of potential for further research and development as they haven't been experimentally investigated for the H₂S decomposition process.

Sulfides of Nickel are uniquely promising because of the existence of several thermodynamically stable states that are functional for the H₂S splitting cycle. So, there's the possibility that even more favorable nickel sulfide pairs, than what was tested during the

material screening activity in this work, exists for the cyclic reaction. Moreover, nickel sulfides are relatively cheap and accessible, making it a good candidate for experimental investigations that would be carried in the future.

It is important to note that the yield for the products derived in this study is in the equilibrium state and doesn't truly reflect the actual conversions achieved in real reactors, which are dependent on the reaction kinetics and transport phenomena of the reactants. However, the equilibrium study in this work renders the maximum achievable amount, serving as a guide for the selection of materials, and a target for actual processes.

Finally, the experimental studies, using the favorable metal sulfides identified in this work, have begun to achieve a better understanding of the interplay between the thermodynamics and kinetics interactions associated with the two-step thermochemical decomposition of H₂S into Hydrogen production. Accomplishing this objective would also render some insights necessary for favorable process modifications and optimization in future projects.

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