

# A HIGHLY SUSTAINABLE PROCESS FOR THE PRODUCTION OF H<sub>2</sub> FROM H<sub>2</sub>S

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## **Summary:**

A new source of hydrogen obtained by processing H<sub>2</sub>S from waste gases can represent huge savings of natural gas resources (sustainability) as well as improved economics compared to the conventional route for obtaining H<sub>2</sub> by energy-intensive reforming of methane. A new catalytic process designed to oxidize CS<sub>2</sub> and COS, coupled with the well-known process to convert H<sub>2</sub>S and CO to H<sub>2</sub> (and COS), is documented. The SO<sub>2</sub> by-product has low moisture and results in a favorable feedstock for Claus reactors and sulfuric acid plants. This technology portends significant savings in capital cost and operating costs for H<sub>2</sub> consumers.

## **Keywords:**

Hydrogen production, sustainability, rational design of catalysts, green CRE

## **Introduction**

A new process for the production of hydrogen from hydrogen sulfide is described wherein carbon monoxide is reacted with hydrogen sulfide to produce hydrogen and carbonyl sulfide. The carbonyl sulfide is then reacted with oxygen to produce carbon monoxide and sulfur dioxide. The carbon monoxide is recycled back to the hydrogen sulfide reaction step.

Previous investigators have explored this basic chemistry but conversion and selectivities of desired products have been low. Recently, investigators under Prof. Israel Wachs at Lehigh University, have designed a class of catalysts that dramatically improve conversion and selectivities to the point where the economics of this technology can be a cost effective method of producing hydrogen.

Carbonyl sulfide (COS) is found in many industrial process streams such as those associated with natural gas production, petroleum refineries and coal gasification plants. COS is often catalytically converted by hydrogenation to methane (CH<sub>4</sub>), hydrogen sulfide (H<sub>2</sub>S), and water; by hydrolysis to carbon dioxide (CO<sub>2</sub>) and H<sub>2</sub>S, or by oxidation to CO<sub>2</sub> and SO<sub>2</sub>. Hydrogenation is an expensive waste of increasingly valuable hydrogen (H<sub>2</sub>) while hydrolysis and total oxidation produces CO<sub>2</sub>, considered by many to be an environmental threat due to its alleged impact on global warming.

H<sub>2</sub>S is encountered in refineries where hydrodesulfurization is widely used to remove sulfur from gasoline. Also natural gas geologic

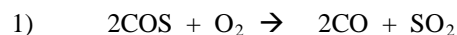
formations may contain as much as 10-30% . The H<sub>2</sub>S is typically separated from the methane and the latter is distributed for consumer and industrial use. The H<sub>2</sub>S is usually converted to elemental sulfur via the Claus process. In the Claus process, a first portion of the separated H<sub>2</sub>S is oxidized by combustion to SO<sub>2</sub> and water. The remaining portion of the H<sub>2</sub>S is reacted with water-laden sulfur dioxide in the presence of a suitable catalyst to produce additional water and elemental sulfur. Thus all of the potentially valuable hydrogen is lost to the atmosphere as water (The elemental sulfur is sold as a low priced commodity product).

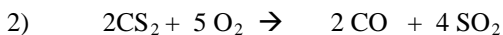
The Wachs process (1) would significantly improve the economies of sour gas recovery and would greatly benefit the operation of petroleum refinery operations. In addition, it would significantly reduce the amount of methane needed for H<sub>2</sub> production, thus sustaining this natural resource in part.

## **Experimental**

A series of experiments using selected metal oxides supported on oxides of different metals resulted in the choice of V<sub>2</sub>O<sub>5</sub> on various metal oxides as a family of most effective catalysts for the oxidation of COS and CS<sub>2</sub> to CO and SO<sub>2</sub>.

The CO thus generated could then be coupled with the known equilibrium reaction to reduce H<sub>2</sub>S with CO, thus producing valuable H<sub>2</sub> and relatively "dry" SO<sub>2</sub>.





The oxidation reaction (1), is very efficient over catalysts comprising a monolayer of vanadium ( $\text{V}_2\text{O}_5$ ) on various metal oxide supports. For the metal oxide supports examined, the Turnover Frequency trend (TOF) is:  $\text{CeO}_2 > \text{ZrO}_2 > \text{TiO}_2 > \text{NbO}_2 > \text{Al}_2\text{O}_3 \sim \text{SiO}_2$ .

$\text{COS}$  and  $\text{CS}_2$  are selectively oxidized to  $\text{CO}$  at yields between 90-100% (Table 1).

The "dry"  $\text{SO}_2$  thus produced (due to the  $\text{H}_2$  being formed instead of  $\text{H}_2\text{O}$ ) is advantageous to a Claus reactor because it favorably shifts the reaction towards the desired elemental sulfur product. Alternately, if used as a feed to a sulfuric acid plant, the moisture load and impurities to the  $\text{SO}_2$  driers are greatly reduced, particularly in comparison to feedstocks obtained from smelters and other industrial sources.

**Table 1: Oxidation of  $\text{COS}$  and  $\text{CS}_2$  to  $\text{CO}$  Over  $\text{V}_2\text{O}_5$  Supported Catalyst**

<u>Reactant</u>	<u>Temperature</u> °C	<u>TOF</u> $10^{-1} \times \text{s}^{-1}$	<u>Yield</u> %
$\text{COS}$	330 max	0.3-2.0	90-100
$\text{CS}_2$	270 max	0.2-1.6	90

The  $\text{CO}$  thus produced from the reaction in Table 1 is used to reduce the  $\text{H}_2\text{S}$  waste stream to hydrogen and co-product  $\text{COS}$  (equation (3) above). This  $\text{COS}$  is recycled to the process along with unreacted  $\text{COS}$ .

## Results

The foregoing chemistry can be used to design a process that yields valuable hydrogen from  $\text{H}_2\text{S}$  streams which now have only the value of their sulfur content. The hydrogen thus represents a value-added factor to  $\text{H}_2\text{S}$  streams.

In reference (1) a process outline describes the major steps as narrated below.

$\text{CO}$  may be obtained by oxidizing  $\text{COS}$  and/or  $\text{CS}_2$  from industrial streams or by the steam reforming of methane. A  $\text{COS}/\text{CS}_2$  oxidation reactor may operate at temperatures ranging from  $220^\circ \text{C}$  to  $350^\circ \text{C}$  and a pressure ranging from atmospheric to 500 psig. The reactants are fed in the vapor phase and contacted with a supported vanadium catalyst. The catalyst may be in the form of pellets or rings in a fixed bed or powder in a fluidized bed. Contact time in a fixed bed, wherein the catalyst pellets or rings are

packed into the tubes of a shell-and-tube reactor, is in the order of 2-10 seconds. The effluent from this reactor contains the desired  $\text{CO}$  as well as unreacted  $\text{COS}/\text{CS}_2$ ,  $\text{O}_2$ , and byproduct  $\text{SO}_2$ . The components are separated in unit operations known to those skilled in the art. This oxidation reactor is shown again in Figure 2 where an additional fresh stream of  $\text{COS}$  and or  $\text{CS}_2$  may also be introduced

The desired hydrogen is generated by reacting  $\text{H}_2\text{S}$  and  $\text{CO}$  utilizing the known vapor phase equilibrium reaction described by Fukada, et. al., (2) (3). Temperatures in the range of  $250^\circ \text{C}$  to  $400^\circ \text{C}$  and pressures from atmospheric to 500 psig. are employed. A downstream series of separations is required to separate unreacted  $\text{H}_2\text{S}$  and  $\text{CO}$  for recycle. The  $\text{H}_2\text{S}$  can, for example, be absorbed in amine solutions and thermally desorbed for recycle. Other processing steps can be used to separate the hydrogen from  $\text{COS}$ .

The hydrogen product is collected and utilized for hydrogenation purposes or as a reactant in hydrodesulfurization operations in a refinery, or, ultimately, as an automotive fuel. The  $\text{COS}$  is recycled to the oxidation reactor (Fig 1) to regenerate  $\text{CO}$  for the hydrogen reactor.

The  $\text{SO}_2$  from these operations is a desirable feedstock for a sulfuric acid plant or a Claus plant (producing elemental sulfur) because of its low moisture content. The efficiency of both of these operations is enhanced by low moisture.

## Conclusions

A catalytic process has been invented which permits the coupling of the known equilibrium reaction to produce hydrogen and a by-product,  $\text{COS}$ , with a new oxidation process for utilization of the  $\text{COS}$ . This is accomplished by oxidizing  $\text{COS}$  over supported vanadium catalyst(s) which results in high yields of  $\text{CO}$ . The  $\text{COS}$  becomes a useful recycle component, being alternately oxidized (by  $\text{O}_2$ ) and reduced by the  $\text{H}_2\text{S}$ , thus yielding valuable hydrogen.

## References

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- (3) Fukada, et. al., *Bulletin of Chemistry for Japan*, 51, 150 (1978)