

A HIGHLY SUSTAINABLE PROCESS FOR THE PRODUCTION OF H₂ FROM H₂S

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Summary:

A new source of hydrogen obtained by processing H₂S from waste gases can represent huge savings of natural gas resources (sustainability) as well as improved economics compared to the conventional route for obtaining H₂ by energy-intensive reforming of methane. A new catalytic process designed to oxidize CS₂ and COS, coupled with the well-known process to convert H₂S and CO to H₂ (and COS), is documented. The SO₂ 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 H₂ 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 (CH₄), hydrogen sulfide (H₂S), and water; by hydrolysis to carbon dioxide (CO₂) and H₂S, or by oxidation to CO₂ and SO₂. Hydrogenation is an expensive waste of increasingly valuable hydrogen (H₂) while hydrolysis and total oxidation produces CO₂, considered by many to be an environmental threat due to its alleged impact on global warming.

H₂S is encountered in refineries where hydrodesulfurization is widely used to remove sulfur from gasoline. Also natural gas geologic

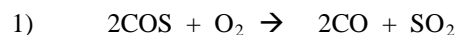
formations may contain as much as 10-30% . The H₂S is typically separated from the methane and the latter is distributed for consumer and industrial use. The H₂S is usually converted to elemental sulfur via the Claus process. In the Claus process, a first portion of the separated H₂S is oxidized by combustion to SO₂ and water. The remaining portion of the H₂S 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).

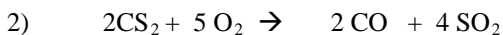
The Wachs process (1) would significantly improve the economies of sour gas recovery and would greatly benefit the operation of petroleum refinery operations. In addition, it would significantly reduce the amount of methane needed for H₂ production, thus sustaining this natural resource in part.

Experimental

A series of experiments using selected metal oxides supported on oxides of different metals resulted in the choice of V₂O₅ on various metal oxides as a family of most effective catalysts for the oxidation of COS and CS₂ to CO and SO₂.

The CO thus generated could then be coupled with the known equilibrium reaction to reduce H₂S with CO, thus producing valuable H₂ and relatively "dry" SO₂.





The oxidation reaction (1), is very efficient over catalysts comprising a monolayer of vanadium (V_2O_5) on various metal oxide supports. For the metal oxide supports examined, the Turnover Frequency trend (TOF) is: $\text{CeO}_2 > \text{ZrO}_2 > \text{TiO}_2 > \text{NbO}_2 > \text{Al}_2\text{O}_3 \sim \text{SiO}_2$.

COS and CS_2 are selectively oxidized to CO at yields between 90-100% (Table 1).

The "dry" SO_2 thus produced (due to the H_2 being formed instead of H_2O) 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 SO_2 driers are greatly reduced, particularly in comparison to feedstocks obtained from smelters and other industrial sources.

Table 1: Oxidation of COS and CS_2 to CO Over V_2O_5 Supported Catalyst

<u>Reactant</u>	<u>Temperature</u> °C	<u>TOF</u> $10^{-1} \times \text{s}^{-1}$	<u>Yield</u> %
COS	330 max	0.3-2.0	90-100
CS_2	270 max	0.2-1.6	90

The CO thus produced from the reaction in Table 1 is used to reduce the H_2S waste stream to hydrogen and co-product COS (equation (3) above). This COS is recycled to the process along with unreacted COS .

Results

The foregoing chemistry can be used to design a process that yields valuable hydrogen from H_2S streams which now have only the value of their sulfur content. The hydrogen thus represents a value-added factor to H_2S streams.

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

CO may be obtained by oxidizing COS and/or CS_2 from industrial streams or by the steam reforming of methane. A COS/CS_2 oxidation reactor may operate at temperatures ranging from 220°C to 350°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 CO as well as unreacted COS/CS_2 , O_2 , and byproduct 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 COS and or CS_2 may also be introduced

The desired hydrogen is generated by reacting H_2S and CO utilizing the known vapor phase equilibrium reaction described by Fukada, et. al., (2) (3). Temperatures in the range of 250°C to 400°C and pressures from atmospheric to 500 psig. are employed. A downstream series of separations is required to separate unreacted H_2S and CO for recycle. The H_2S can, for example, be absorbed in amine solutions and thermally desorbed for recycle. Other processing steps can be used to separate the hydrogen from 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 COS is recycled to the oxidation reactor (Fig 1) to regenerate CO for the hydrogen reactor.

The 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, COS , with a new oxidation process for utilization of the COS . This is accomplished by oxidizing COS over supported vanadium catalyst(s) which results in high yields of CO . The COS becomes a useful recycle component, being alternately oxidized (by O_2) and reduced by the H_2S , thus yielding valuable hydrogen.

References

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- (2) Fukada, et. al., *Journal of Catalysis*, 49 3 79 (1977)
- (3) Fukada, et. al., *Bulletin of Chemistry for Japan*, 51, 150 (1978)