



Simultaneous recovery of carbon and sulfur resources from reduction of CO₂ with H₂S using catalysts

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ABSTRACT

An approach to the simultaneous reclamation of carbon and sulfur resources from CO₂ and H₂S has been proposed and effectively implemented with the aid of catalysts. A brief thermodynamic study reveals the potential of direct reduction of CO₂ with H₂S (15:15 mol% balanced with N₂) for selective production of CO and elemental sulfur. The experiments carried out in a fixed-bed flow reactor over the temperature range of 400–800 °C give evidence of the importance of the employment of catalysts. Both the conversions of the reactants and the selectivities of the target products can be substantially promoted over most catalysts studied. Nevertheless, little difference appears among their catalytic performance. The results also prove that the presence of CO₂ can remarkably enhance H₂S conversion and the sulfur yield in comparison with H₂S direct decomposition. A longtime reaction test on MgO catalyst manifests its superior durability at high temperature (700 °C) and huge gas hourly space velocity (100,000 h⁻¹). Free radicals initiated by catalysts are supposed to dominate the reactions between CO₂ and H₂S.

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1. Introduction

CO₂ and H₂S, often co-existing in crude natural gas, shale gas, biogas, coal gas, refinery gas, etc., are two unpleasant and intractable substances. A variety of endangerments can arise out of CO₂ and H₂S not only on industrial applications of aforesaid gases but also on creature health. For removal of CO₂ and H₂S separately or simultaneously, various technologies and processes have been developed, which are mainly based on absorption and adsorption strategies [1–5]. Most of these separation technologies are industrially mature, but still suffer from such disadvantages as the necessity of frequent regeneration of liquid absorbents or solid adsorbents, the loss of solvents due to evaporation, the adsorbent decay in quality after recycling, the discharge of wastes during disposal causing second pollution, and the complexity of the specified multi-staged processes. Extremely high investment and operating cost and huge energy consumption are consequently inevitable. In order to compensate the economic loss incurred and also from the standpoint of the social sustainable development, recovery of carbon and sulfur resources from CO₂ and H₂S is absolutely necessary. Therefore, the scenarios for the reclamation of CO₂ and H₂S released from absorbents or adsorbents during regeneration have attracted worldwide attention. As a matter of fact, a num-

ber of methods for extracting elemental sulfur from H₂S have been developed and followed already since the establishment of Claus process in industry [6,7]. Concerning CO₂, however, its efficient conversion into valuable products such as fuels and chemicals is so far a global challenge [8–11]. Diverse approaches including catalysis have been resorted to overcome the barriers to the activation and transformation of CO₂ [9,12,13].

On the other hand, the occurrence of the reactions between CO₂ and H₂S was discovered under Claus furnace conditions. As early as 1990s, Tower et al. [14,15] perceived that the presence of CO₂ could promote the thermal decomposition of H₂S to elemental sulfur above 600 °C. The primary investigation on the use of MoS₂ as catalyst proved the feasibility of catalysis in the CO₂/H₂S system. But no more information about catalytic reactions was supplied. Clark et al. [6] studied the reaction pathways during the processing of CO₂ and H₂S in the partially oxidizing conditions of the Claus furnace, and put forward a synopsis of CO₂/H₂S chemistry. The homogeneous formation mechanisms of COS at the temperatures above 900 °C were focused on, while less attention was paid to catalytic reactions. In recent years, Gupta et al. [7,16] researched the effect of CO₂ on H₂S combustion in acid gas stream. They stated that the presence of CO₂ up to 30% mole fraction decreased the amount of sulfur captured. The consequence seems contradictory to the observation of Tower et al. [14,15]. Nevertheless, no further work is available in the literature on pursuing the interplay between CO₂ and H₂S especially the conversion of CO₂. Moreover, there is little effort devoted to the

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research of the effect of catalysis on the simultaneous conversion of CO₂ and H₂S.

In the present study, we will describe a novel process of direct reduction of CO₂ with H₂S in a catalytic fixed-bed reactor to simultaneously produce CO and sulfur and even hydrogen. Because of rare theoretical study reported before on CO₂ and H₂S reaction system, a thermodynamic equilibrium analysis will be made firstly to clarify the probability and the extent of the formation of CO and sulfur [6,16]. Different kinds of catalysts will be examined on their activity and selectivity. The purpose of the study is to disclose a new approach to the simultaneous utilization of CO₂ and H₂S by catalysis, which might open a new window into the applied chemistry of CO₂ and H₂S.

2. Experimental

2.1. Catalyst preparation

The powdery materials of SiO₂, CaO, MgO and γ -Al₂O₃ with chemical purity were purchased from Shanghai Sinopharm Chemical Reagent Company. A method of incipient wetness impregnation was adopted to synthesize the supported catalysts of NiO on MgO and γ -Al₂O₃. In brief, a Ni(NO₃)₂ solution was imposed to impregnate the supports of MgO and γ -Al₂O₃ at room temperature. NiO with a set weight ratio of 20 wt% was then formed on the supports after calcination in furnace at 600 °C for 6 h. All the materials used as the catalysts were heat-treated at 600 °C prior to their catalytic performance examination.

2.2. Reaction test

The examination of the reactions between CO₂ and H₂S was carried out in a fix-bed tubular flow quartz reactor under atmospheric pressure. In a typical procedure for reaction test, 0.8 mL catalyst powdery particles (40–80 mesh) were filled in the reactor. There was a porous plate made of fused quartz sealed in the middle zone of the reactor to hold up the powdery catalysts. A gas flow of N₂ was purged through the reactor until the temperature of the reactor reached a set value. After that, a mixture gas composed of 15 mol% CO₂ and 15 mol% H₂S balanced with 70 mol% N₂ at a total pressure of 0.1 MPa was introduced to attain the assigned gas space velocity. The compositions of the mixture gas fore-and-aft the reactor were monitored constantly, including CO₂, H₂O, H₂S, COS, O₂, N₂, CH₄, CO, CS₂ and H₂. Two gas chromatographic (GC) instruments both with thermal conductive detectors (Clause 680, PerkinElmer Instruments, USA) were used for routine composition analysis. One GC was mounted in series with PQ and 5A columns using H₂ as carrier gas to separate in succession CO₂, H₂O, H₂S, COS, O₂, N₂, CH₄, CO and CS₂ in case all existing; another one was equipped with a 5A column and adopted N₂ as carrier gas for H₂ detection. An additional GC with flame photometric detector was ready for SO₂ detection, which was fixed with a PQs column using H₂ as the carrier gas. The elemental sulfur formed in the catalyst bed blew with the stream and condensed on the wall of glass vessel which was connected with the reactor outlet and immersed in an ice-bath. The sulfur was captured to the utmost so as to prevent jamming up the downstream. The product water was also removed by cooling before the stream entering into the GC.

The conversions of CO₂ and H₂S were derived from the changes in the concentration of CO₂ and H₂S, respectively, fore-and-aft the reactor. The selectivity to CO was defined as the production of CO from the conversion of CO₂. The selectivity to sulfur (in the form of S₂) was the sulfur amount reckoned from the sulfur compounds including COS, CS₂ and SO₂ (if existing) instead of directly from the solid sulfur itself considering that all of the sulfur compounds are transformed from H₂S. The selectivity to H₂ was the ratio of the amount of H₂ produced to the amount of H₂S converted. The mole yield of each product was

the mole quantity of the product divided by the mole quantity of the corresponding feed, e.g., the yield of CO was based on CO₂, while that of sulfur was on H₂S. The calculation formulae of reactant conversion and product selectivity are as follows,

$$X_{\text{CO}_2}(\%) = \frac{n(\text{CO}_2)_{\text{in}} - n(\text{CO}_2)_{\text{out}}}{n(\text{CO}_2)_{\text{in}}} \times 100\% \quad (1)$$

$$X_{\text{H}_2\text{S}}(\%) = \frac{n(\text{H}_2\text{S})_{\text{in}} - n(\text{H}_2\text{S})_{\text{out}}}{n(\text{H}_2\text{S})_{\text{in}}} \times 100\% \quad (2)$$

$$S_{\text{CO}}(\%) = \frac{n(\text{CO})_{\text{out}}}{n(\text{CO}_2)_{\text{in}} - n(\text{CO}_2)_{\text{out}}} \times 100\% \quad (3)$$

$$S_{\text{S}_2}(\%) = 100\% - \frac{n(\text{COS})_{\text{out}} + \frac{1}{2} \times n(\text{CS}_2)_{\text{out}} + n(\text{SO}_2)_{\text{out}}}{n(\text{H}_2\text{S})_{\text{in}} - n(\text{H}_2\text{S})_{\text{out}}} \times 100\% \quad (4)$$

$$S_{\text{H}_2}(\%) = \frac{n(\text{H}_2)_{\text{out}}}{n(\text{H}_2\text{S})_{\text{in}} - n(\text{H}_2\text{S})_{\text{out}}} \times 100\% \quad (5)$$

where, X_{CO_2} , $X_{\text{H}_2\text{S}}$, S_{CO} , S_{S_2} and S_{H_2} refer to the CO₂ conversion, the H₂S conversion, the CO selectivity, the S₂ selectivity and the H₂ selectivity, respectively; n refers to the mole flow of gas composed of CO₂, H₂S, CO, COS, CS₂, SO₂, or H₂ in the feed or in the effluent from the reactor.

2.3. Material characterization

N₂ physisorption measurement on sample which had in advance been degassed in vacuum at 200 °C for 6 h was performed at -196 °C on a Micromeritics ASAP 2020 apparatus. Specific surface area was calculated with Brunauer–Emmet–Teller equation, and pore volume of pores between 1.7 and 300.0 nm in diameter was determined from the N₂ desorption isotherm using the Barrett–Joyner–Halenda method. The powder X-ray diffraction (XRD) pattern was recorded between 10° and 80° (2 θ) using a Bruker D8 advance A25 polycrystalline diffractometer equipped with a Cu K α radiation source ($\lambda = 0.154056$ nm), and operated at a voltage of 40 kV and a current of 40 mA. Temperature-programmed desorption (TPD) profile of CO₂ and H₂S was obtained on an ASAP2010 apparatus equipped with a thermal conductive detector. The sample was first treated in a 30 mL/min He flow at 200 °C for 1 h, and then cooled to room temperature. Adsorption of CO₂ or H₂S was carried out under a gas flow of 30 mol% CO₂/N₂ or H₂S/N₂ (30 mL/min) at room temperature for 2 h. The gas flow was switched subsequently to a 30 mL/min He flow and afterwards kept the He flow until the TCD signals returned to the baseline. The sample was heated again from room temperature to 800 °C in the He flow at a rate of 5 °C/min while the detector monitored the gas desorption signals all the time.

3. Results and discussion

3.1. Thermodynamic equilibrium analysis

Ten products including H₂, H₂O, CH₄, C, CO, COS, CS₂, S₂, S₈ and SO₂ all in gas state excepting C (solid) are supposed to present in consideration of the potential of the reactions involved with CO₂ and H₂S individually or mutually [6,14–21]. The equilibrium mole yield of every product and the conversions of CO₂ and H₂S in a Gibbs equilibrium reactor under isothermal and isotonic condition have been calculated according to the principle of Gibbs free energy minimization using Aspen Plus simulation software for chemical engineering processes. The equilibrium mole yield of each product is referred to the atomic percentage of product which can be formed from the corresponding reactant under equilibrium state. Fig. 1(a–c) depicts the equilibrium conversions of CO₂ and H₂S and the equilibrium mole yields of ten products changing with temperature over a range

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