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SELECTIVE CATALYTIC REDUCTION OF SULFUR DIOXIDE TO ELEMENTAL SULFUR

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DISCLAIMER

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ABSTRACT

Elemental sulfur recovery from SO_2-containing gas streams is highly attractive as it produces a saleable product and no waste to dispose of. However, commercially available schemes are complex and involve multi-stage reactors, such as, most notably in the Resox(reduction of SO_2 with coke) and Claus plants(reaction of SO_2 with H_2S over catalyst). This project will investigate a cerium oxide catalyst for the single-stage selective reduction of SO_2 to elemental sulfur by a reductant , such as carbon monoxide. Cerium oxide has been identified in recent work at MIT as a superior catalyst for SO_2 reduction by CO to elemental sulfur because of its high activity and high selectivity to sulfur over COS over a wide temperature range(400-650 °C). The detailed kinetic and parametric studies of SO_2 reduction planned in this work over various CeO_2-formulations will provide the necessary basis for development of a very simplified process, namely that of a single-stage elemental sulfur recovery scheme from variable concentration gas streams. The potential cost- and energy-efficiency benefits from this approach can not be overstated. A first apparent application is treatment of regenerator off-gases in power plants using regenerative flue gas desulfurization. Such a simple catalytic converter may offer the long-sought “Claus-alternative” for coal-fired power plant applications.

1 Introduction

Table 1 lists the reactions involved in the SO_2 reduction with CO together with available thermodynamic data at 700K. The reactions listed in Table 1 are thermodynamically favorable under typical reaction conditions. Specifically, reducing SO_2 to elemental sulfur, e.q. 1, is the desired reaction. But, the produced sulfur may react with the CO to form COS (e.q.2). COS is a more toxic compound than SO_2 and its production has to be minimized in the sulfur recovery process. Water vapor, commonly considered as one potential component or impurity in the feed streams, may both affect the properties of a catalyst and take part in reactions. For example, H_2O may react with CO through e.q. 3 (Water-Gas Shift reaction) to produce hydrogen that can be a reductant of SO_2(e.q.4). The H_2O can also hydrolyze the COS into hydrogen sulfide and carbon dioxide(e.q.6). The hydrogen sulfide can react with the SO_2 to form elemental sulfur according to Claus reaction(5). The introduction of the H_2O makes the reaction scheme for sulfur recovery complicated. However, the effect of H_2O on the catalytic activity and selectivity is of great interest, because all of the catalysts disclosed in the literature to-date are poisoned by the presence of H_2O.

Table 1.

Reactions		ΔG°(kcal)	K	ΔH°(kcal)
(1)	$SO_2 + 2CO = 2CO_2 + 1/x\ S_x$			
	x=2	-31.5	$7.4*10^9$	-48.9
	x=8	-34.1	$4.8*10^9$	-61.3
(2)	$1/x S_x + CO = COS$			
	x=2	-8.65	$5.13*10^2$	-44
	x=8	-6.2	87.6	-9.6
(3)	$H_2O + CO = H_2 + CO_2$	-3.1	9.4	-9.0
(4)	$SO_2 + 3H_2 = H_2S + 2H_2O$	-38.7	$1.34*10^2$	-52.0
(5)	$SO_2 + 2H_2S = 2H_2O + 3/x\ S_x$			
	x=2	-4.4	23.9	12.6
	x=8	-11.8	$4.98*10^3$	-24.5
(6)	$COS + H_2O = H_2S + CO_2$	-7.7	$2.58*10^2$	-8.3

2 Experimental Section

2.1 Reactor Setup

Figure 1 is a schematic of the reactor system. Stainless steel or Teflon tubes are used for all the connections. The reactor is a 10 cm I.D.by 50 cm length quartz tube with a porous quartz frit placed at the middle for supporting the catalyst. The tube reactor is heated with a Lindberg oven. The reaction temperature is monitored with a K-type thermocouple and controlled by an OMEGA one-point temperature controller. A HP5880A Gas Chromatograph(GC) with Thermal

Conductivity Detection(TCD) is used for the gas analysis. Helium is used as carrier gas and reference gas with flowrates of 31 cc/min and 25 cc/min, respectively. The detector and oven temperatures are set at 200 °C and 60 °C, respectively. The 1/4" O.D.x 2' long packed column of Chromosil 310 well separates CO, CO_2, COS, H_2S, CS_2, and SO_2 under the specified conditions. The TCD shows linear response to all the compounds mentioned above and has a detection limit of about one hundred parts per million.

Each gas stream, measured and controlled by a rotameter, mixes with the other gases prior to the reactor inlet. The resulting gas mixture passes through the packed catalyst bed downward. A cold trap attached at the outlet of the reactor is used to collect the elemental sulfur from the product gas stream. The product stream, free of sulfur, goes through a particulate filter and then enters a GC sampling loop for on-line analysis. The water vapor is introduced with helium bubbling through a water bath. The water content is controlled by the water bath temperature.

The pressure drop of the gas flow through the assembly is small. Thus, all the reactions hereafter proceed under nearly atmospheric pressure.

2.2 Catalyst Preparation

The cerium oxide used in this study is prepared by the well-known amorphous citrate method(ref.1), as outlined in Figure 2. The cerium nitrate and citric acid of molar ratio one are dissolved in de-ionized water, respectively. The citric acid solution is added into the nitrate solution dropwise and with constant magnetic stirring. The resulting solutions mixture is concentrated into a viscous fluid in a Rotavapor apparatus under the highest rotation speed and about 70 °C. The viscous fluid is then transfered on a pyrex dish in a vacuum oven, where a solid foam is formed during over-night drying in a vacuum oven at about 70 °C and 15 KPa. The solid foam is calcined several hours under flow air at a temperature over 500 °C in a muffle furnace so that all the citric acid is burnt out, and that the cerium nitrate is decomposed and oxidized into highly porous CeO_2. The CeO_2 phase is identified by X-Ray Diffraction. The catalyst surface area, measured with the single-point BET method, is typically about 30 m^2/g to 45 m^2/g. The packed density and void volume are typically 0.05 g/cc and 4.6 cc/g, respectively. Therefore, the CeO_2 prepared in this way has predominantly macropores which render the pore diffusion resistance negligible. The reaction rate will depend only on the intrinsic kinetics if the gas phase mass transfer can also be eliminated by using high gas flow velocity through the packed bed.

3 Experimental Results

In this section, we present results from using CeO_2 as a catalyst for the main reaction(1), reduction of SO_2 with CO to elemental sulfur, as well as for the secondary reactions (3) through (6).

3.1 Reduction of SO_2 with CO

Typical product distribution at various temperatures from reactions (1) and (2) using the bulk CeO_2 catalyst prepared in this work is shown in Fig. 3. A dry feed gas of stoichiometric $[CO]/[SO_2]$ ratio of 2 was used in these tests. The amount of the sulfur product is derived from the material balance of either sulfur or carbon. More than 90% of selectivity to elemental sulfur is obtained over the temperature range from 510 to 660 °C. Complete conversion of SO_2, with less than 10% COS by-product, takes place under these conditions. The small amount of H2S comes from the H_2O impurity in the feed streams.

Figure 4 shows the variation of the sulfur product with temperature when the inlet SO_2 concentration is held constant and the CO concentration is varied. In the presence of excess CO, COS becomes a dominant product. The more CO over the stoichiometric amount, the more COS and, thus, the less sulfur is produced. The sulfur yield increases with the temperature monotonically. Complete SO_2 conversion can be obtained at lower temperature when a feed gas of $[CO]/[SO_2]$ ratio higher than the stoichiometric is used.

3.2 Water-Gas Shift Reaction on CeO_2 Catalyst

Figure 5 shows the experimental results of using the same CeO_2 as a catalyst for the water gas shift reaction. The excess water is used to study the effect of catalyst surface hydroxylation on the catalytic activity. Little CO conversion is observed under low reaction temperature, though the reaction is thermodynamically favorable. The conversion significantly increases as temperature is raised from 600 to 650 °C. But, beyond 650 °C chemical equilibrium becomes a major factor. This indicates that the H_2O strongly deactivates the catalyst and its inhibition effect is decreased as the reaction temperature is increased.

3.3 Claus Reaction

The Claus reaction on the CeO_2 catalyst and the water vapor effect on it were investigated. As shown in Figure 6, more than 80% of the inlet SO_2 is converted into elemental sulfur around 230 °C in the absence of H_2O in the feed streams. Upon addition of 13% H_2O, the SO_2 increases by 65% of its inlet concentration while 90% of the inlet H_2S disappears. The excess SO_2 is postulated to come from following reactions,

$$H_2S_{ads} + 2H_2O \rightarrow SO_2 + 3H_2$$

$$S_{ads} + 2H_2O \rightarrow SO_2 + 3H_2$$

where the sulfur was produced by previous Claus reaction and adsorbed on the catalyst. The catalyst loses its activity very quickly when exposed to H_2O. Its activity can not be recovered by stopping the H_2O alone. The catalyst becomes re-activated only when the temperature is raised over 500 °C. There is a burst of SO_2 around 500 °C during the temperature rise, where twice the inlet SO_2 amount is produced with the consumption of 78% of the inlet H_2S. This may be explained by the adsorbed H_2O oxidizing the H_2S. It seems that the previously adsorbed H_2O on the catalyst desorbs only at high temperatures(>500 °C). The catalyst is completely re-activated after removal of the adsorbed H_2O.

3.4 Hydrolysis of COS on the CeO_2

As shown in Figure 7, COS can be completely hydrolyzed into H_2S and CO_2 over the temperature range of 250 °C to 670 °C.

3.5 Reduction of SO_2 with H_2

To test if H_2 can reduce all the SO_2 into elemental sulfur, the $[H_2]/[SO_2]$ ratio and reaction temperature were varied from 0 to 8 and 500 to 615 °C, respectively. The unreacted SO_2 and produced elemental sulfur versus produced H_2S are plotted in Figure 8. The unreacted SO_2 decreases monotonically with H_2S production. It seems that there is no way for SO_2 to reduce to elemental sulfur exclusively. Out of 10000 ppm of inlet SO_2, the maximum sulfur product obtained by modulating both the [H_2]/[SO_2] ratio and the temperature is 6500ppm, while 1600 ppm of H_2S is produced and 1900 ppm of SO_2 leave unreacted.

3.6 Activation of CeO_2 catalyst

The fresh or used CeO_2 catalyst needs to be activated before it can be used for the SO_2 reduction with CO The activation can be done by heating the catalyst at a temperature greater than 550 °C in the reducing atmosphere of either CO or H_2. The fresh or deactivated CeO_2 catalyst looks pale yellow. The activated one appears dark grey/blue. Figure 9 shows a typical regeneration profile of a used catalyst in 5% CO/He at 620 °C. A CO_2 peak appears during activation, concomitant with small amounts of COS and H_2S. The sulfur compounds result from residual sulfur on a used catalyst, because no sulfur compound appears during the activation of fresh CeO_2. The CO_2 may result from either the reaction of CO with adsorbed H_2O on the catalyst surface or the surface reduction of the CeO_2, because the CO disproportionation reaction was found to be negligible under the present conditions. It seems that to initiate the reduction reaction, the catalyst surface has to be free of H_2O or reduced.

4 Conclusion and Future Work

The bulk CeO_2 material prepared in this work is an active catalyst for the SO_2 reduction with CO as well as for the Claus reaction and COS hydrolysis. More than 90% sulfur yield can be obtained from a dry feed gas of stoichiometric compositions of SO_2 and CO. Excess CO favors the formation of COS. The CeO_2 catalyst has also shown good stability during long-time(about three weeks) repeated use in the same packed bed.

The effect of water vapor on the CeO_2 catalytic activity will be studied in detail next quarter. Modification of the CeO_2 catalyst with other metal oxide additives is also planned.

Reference

1 P. Courty and C. Marcilly, “A Scientific Approach to the Preparation of Bulk Mixed Catalysts", in Preparation of Catalysts III edited by G. Poncelet, P.Grange and P.A. Jacobs, Elsevier Science Publishers, Amsterdam, pp.485-519, 1983.

Figure 1. Schematic of the Experimental Reactor Set-up

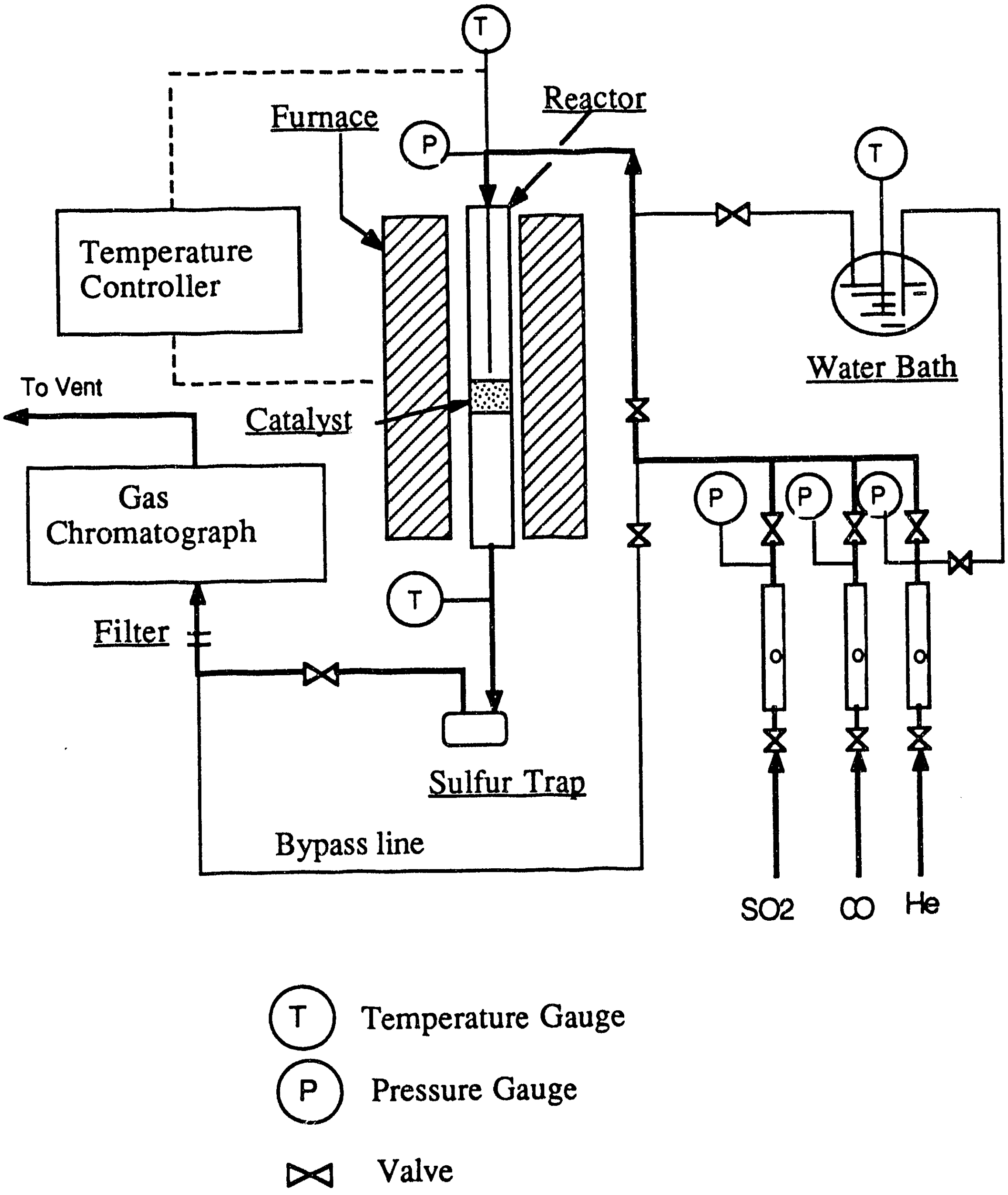
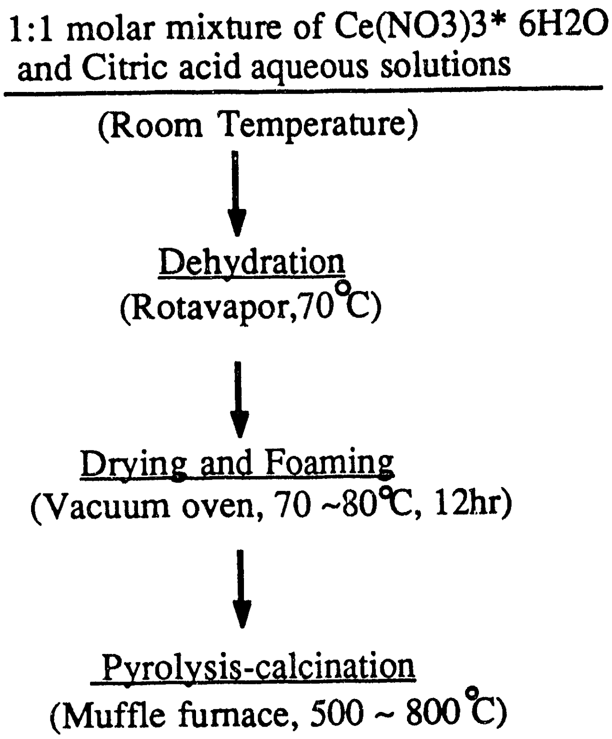


Figure 2. Outline of Catalyst Preparation



Calcination:	530°C 3hr
Surface Area, m2/g:	46. .
Bulk density, g/cc:	0.0493
Pore Volume, cc/g:	4.67

Figure 3. Product Distribution in Reduction of SO2 by CO

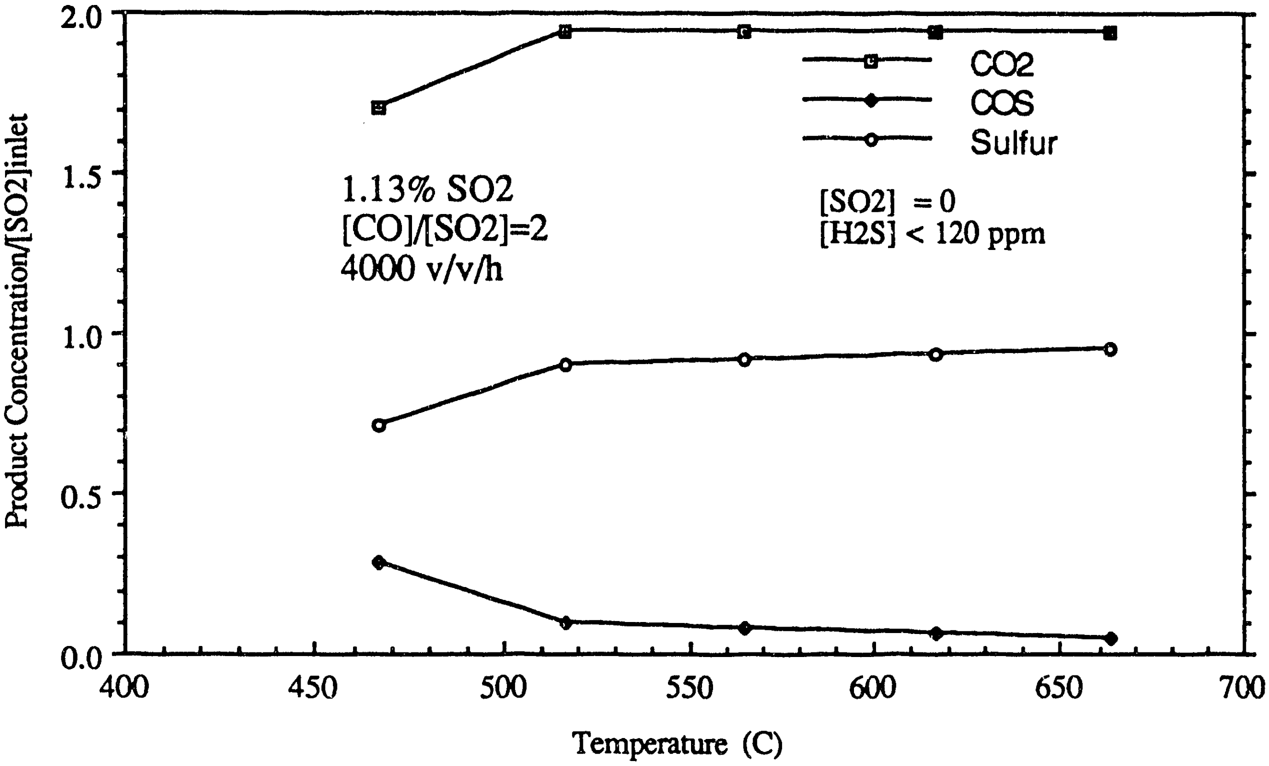


Figure 4. Temperature and [CO]/[SO2] ratio Effects on Elemental Sulfur Yield

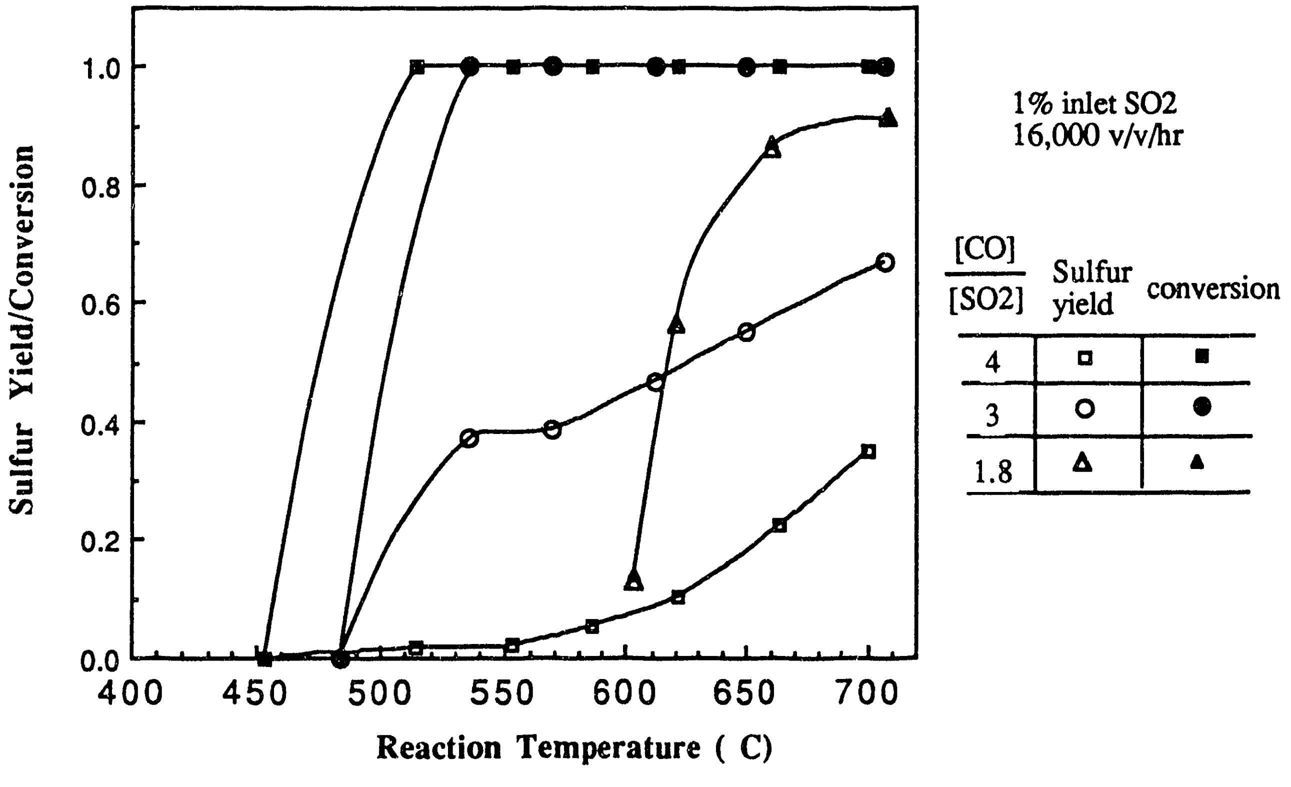


Figure 5. Water-Gas Shift Reaction on the CeO2 Catalyst

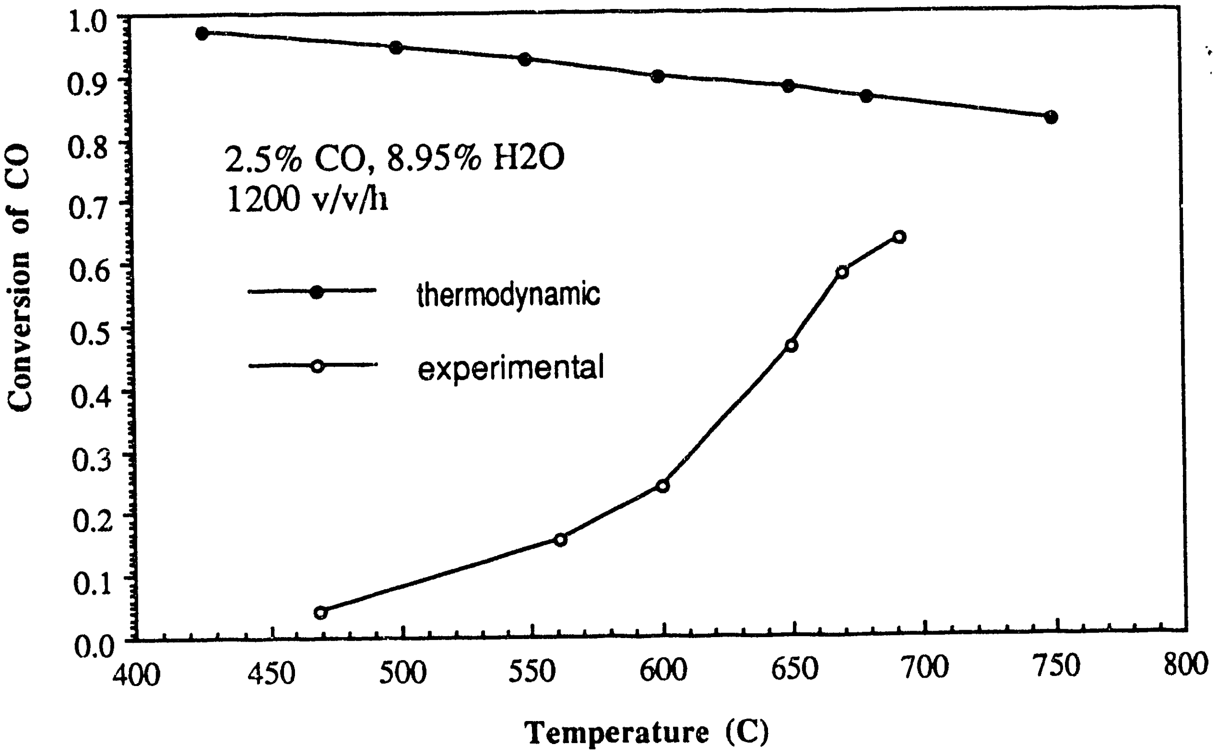


Figure 6. Claus Reaction on the CeO2 Catalyst
(1200 v/v/hr)

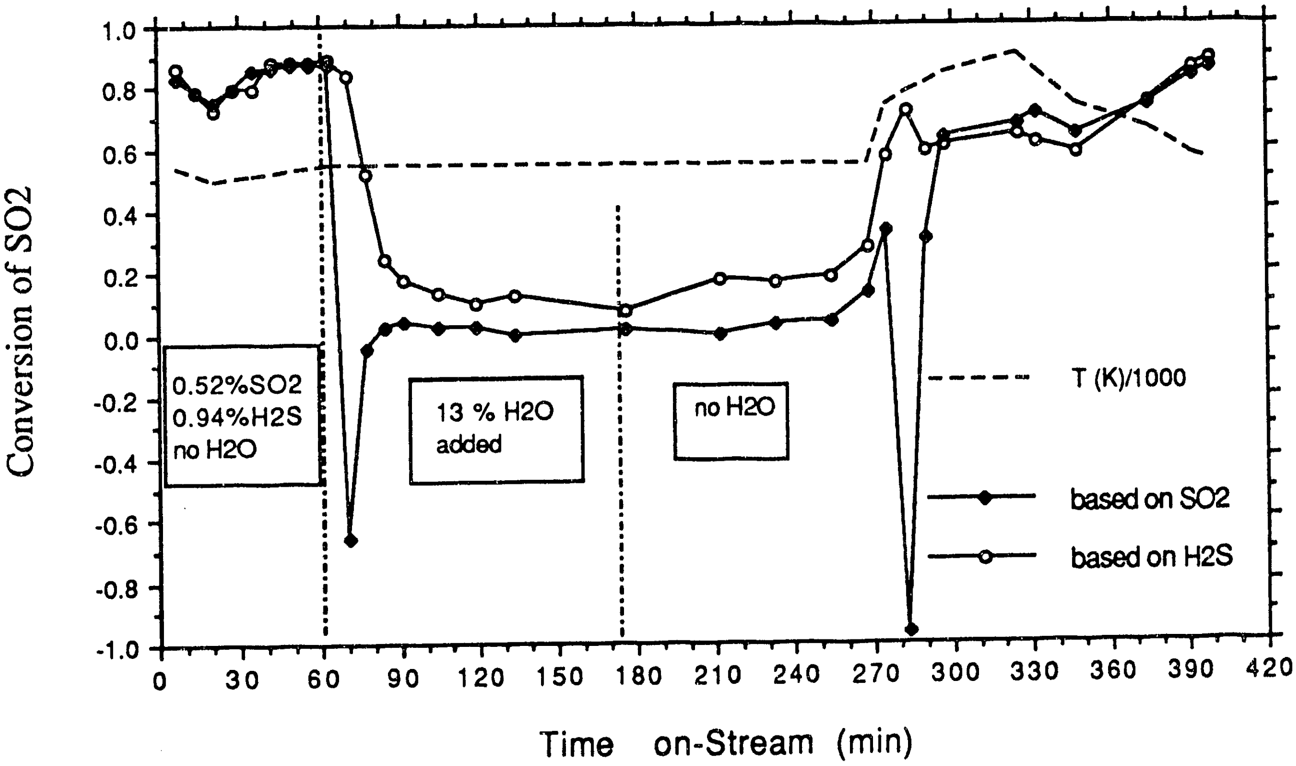


Figure 7. Hydrolysis of COS on the CeO2 Catalyst

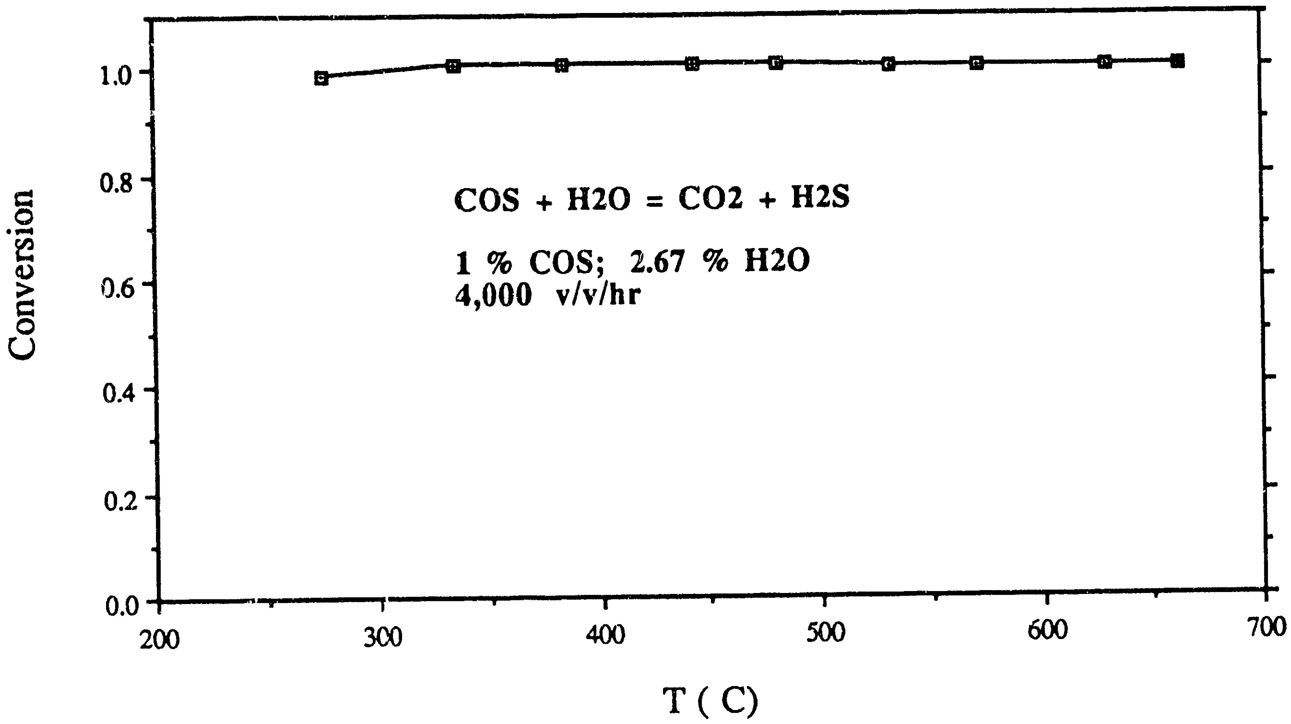


Figure 8. Product Distribution in the SO2 reduction with H2 on CeO2 Catalyst

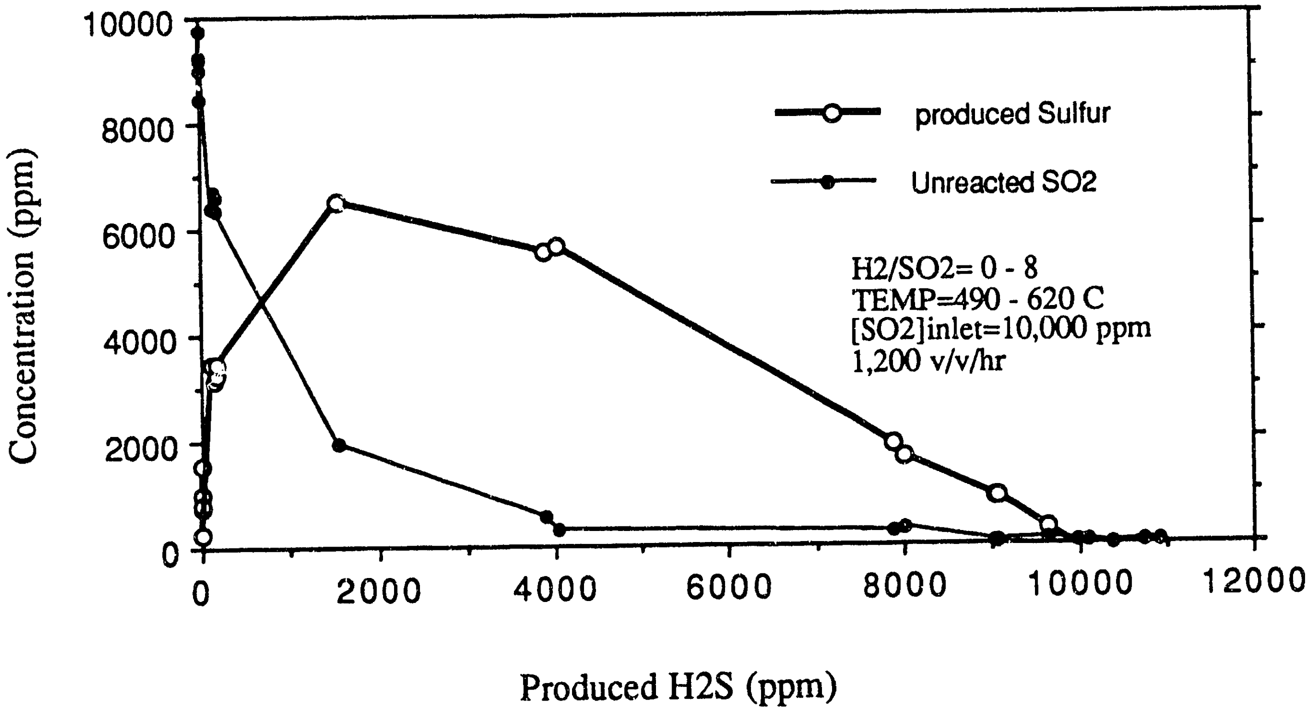
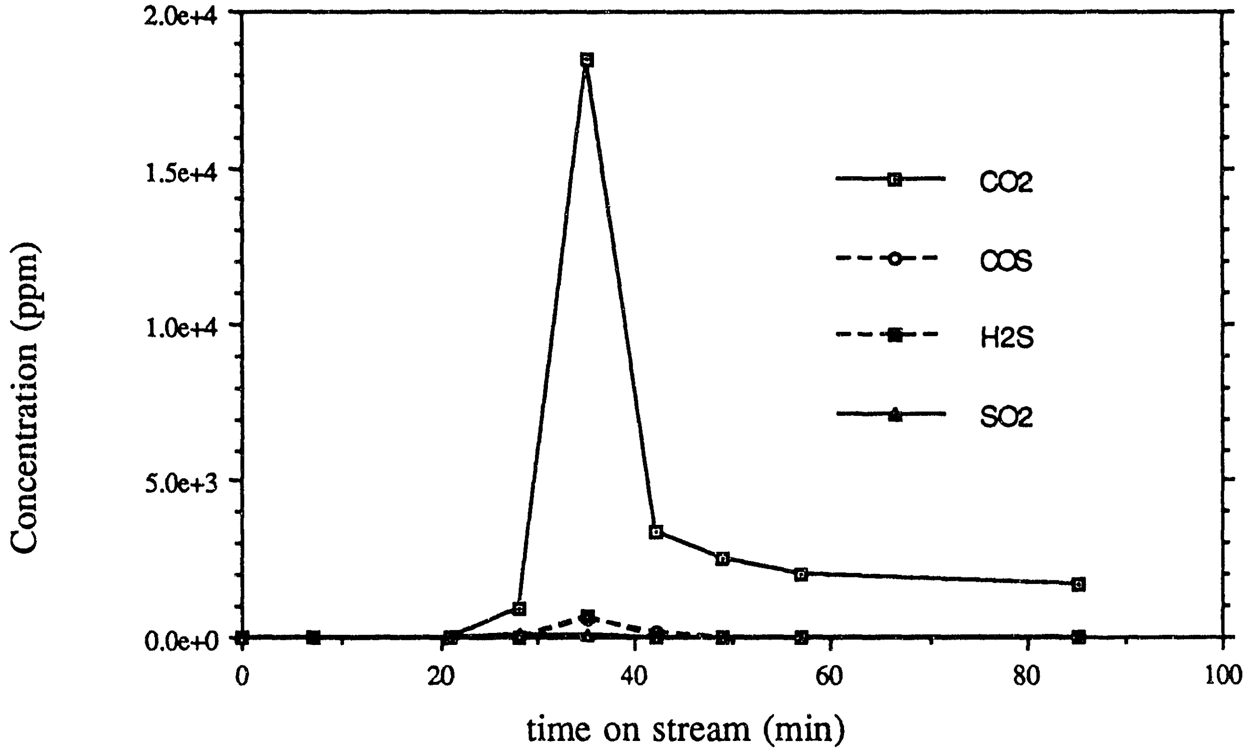


Figure 9. Activation Profile of a Used CeO2 Catalyst With 5% CO in N2 (T=620 °C)



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