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Removing Sulfur Dioxide by Carbon Monoxide Reduction

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REMOVING SULFUR DIOXIDE BY CARBON MONOXIDE REDUCTION

by

L. A. Haas,[1] T. H. McCormick,[2] and S. E. Khalafalla[3]

ABSTRACT

The feasibility of removing sulfur dioxide by carbon monoxide reduction in a fixed-bed catalytic reactor was investigated by the Bureau of Mines. The reduction rate of sulfur dioxide with carbon monoxide was significantly dependent upon the iron and alumina content of the mixed catalyst. Maximum catalytic activity was obtained with about 40 percent iron-alumina mixture with a nominal gas mixture of 10 percent carbon monoxide, 5 percent sulfur dioxide, and the balance nitrogen. The synergistic effect of this catalyst mixture was explained by a dual reaction site mechanism, with both iron and alumina augmenting their specific sites at their interparticle contacts. The catalytic activity also increased with decreasing catalyst pellet size. With 0.7-mm pellets, the entire pellet appeared to be catalytically active in a 2-gram catalyst bed. The apparent activation energy of the reaction was 18.3 kcal per mole in the temperature range of 350° to 600° C. Carbonyl sulfide (COS) was produced by the interaction of carbon monoxide and sulfur. The amount decreased with decreasing CO concentration. The ratio of COS formed per SO_2 removed reached a maximum at about 400° C. The reaction rate appeared to be independent of SO_2 concentration in the range of 0.2 to 16 percent. The rate, however, increased directly with the CO concentration in the range of 5 to 20 percent. The presence of CO_2 (<15 percent) had no appreciable effect on the rate. However, not over 0.5 percent oxygen could be tolerated. This method appears feasible for removing SO_2 from waste gas if the oxygen is removed prior to the catalytic SO_2 reduction process.

INTRODUCTION

Emission of SO_2 into the atmosphere by combustion-furnace powerplants and smelters is increasingly becoming a national concern. Because sulfur is an important industrial commodity and because the supply is limited, methods are being devised to recover sulfur from SO_2, an undesirable air pollutant.

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[1] Research chemist.

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Ryason and Harkins[4] studied the reduction of synthetic SO_2 combustion-furnace waste gas with carbon monoxide. The combustion furnace must be operated on a slightly rich fuel-to-air ratio to insure the presence of small quantities of CO in the stack gas for the SO_2 reduction process. Smelter SO_2 offgases were also reduced with CO in Canada,[5] but few catalytic kinetic data are available, especially for smelter gases that are too dilute for sulfuric acid production. Presently, the Princeton Chemical Research Center is studying the catalytic reduction of SO_2 from stack gases, but no details are available.[6] A kinetic study was therefore undertaken at the Twin Cities Metallurgy Research Center, Bureau of Mines, to determine the influence of various parameters on the catalytic SO_2-CO reaction.

EXPERIMENTAL METHOD

The apparatus arrangement is shown in figure 1. Chemically pure (>99.5+) gases were premixed by metering through capillary flowmeters which were calibrated to ±2 percent of maximum flow with an oil wet-test meter. Impurities in the gases, such as H_2O and CO_2, were removed with dry absorbers. Gas pressures in the reactor were measured with mercury manometers and controlled by two-stage regulators. The reactor pressure was held at 83 cm of mercury.

The Vycor[7] reactor consisted of three parts. The large inlet tube (5-cm bore) permitted the incoming gas to reach operating temperature before contacting the catalyst. Adequate gas preheating was verified when a nonporous Al_2O_3 pebble preheater was used and essentially the same results were obtained. The middle catalyst section consisted of a 1-cm bore, 5 cm long. A perforated porcelain disk was used to hold the catalyst in this section. The exhaust section consisted of smaller diameter tubing (0.6-cm bore), which reduced the residence time of the products in the hot zone. Sulfur was filtered and condensed from the exhaust gases with a glass wool ice trap.

The catalyst temperature was measured with an Alumel versus Chromel thermocouple and maintained within ±2° C of the desired temperature using an electronic controller. The unreduced catalyst was prepared from minus 10-micron hematite (>98.0 percent) and minus 0.05-micron gamma alumina (99.98 percent). Various ratios of these powders were mixed, pelletized to minus 16 plus 20 mesh, and indurated at 1,200° C for 2 hours. A portion of this mixture (quantity needed to obtain 1.936 grams of reduced catalyst) was then inserted into the reactor, heated in 0.5-standard-liter-per-minute (SLM) nitrogen, and reduced at the same flow in hydrogen for 1 hour at 600° C. This treatment resulted in complete reduction of the hematite. The reactor was again flushed

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[4] Ryason, P. R., and J. Harkins. Studies on a New Method of Simultaneously Removing Sulfur Dioxide and Oxides of Nitrogen From Combustion Gases. J. Air Pollution Control Assoc., v. 17, No. 12, 1967, pp. 796-799.

[5] Lepsoe, R. Chemistry of Sulfur Dioxide Reduction. Ind. and Eng. Chem., v. 32, No. 7, 1940, pp. 910-918.

[6] Cortelyou, C. G. Commercial Processes for SO_2 Removal. Chem. Eng. Prog., v. 65, No. 9, 1969, pp. 69-77.

[7] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

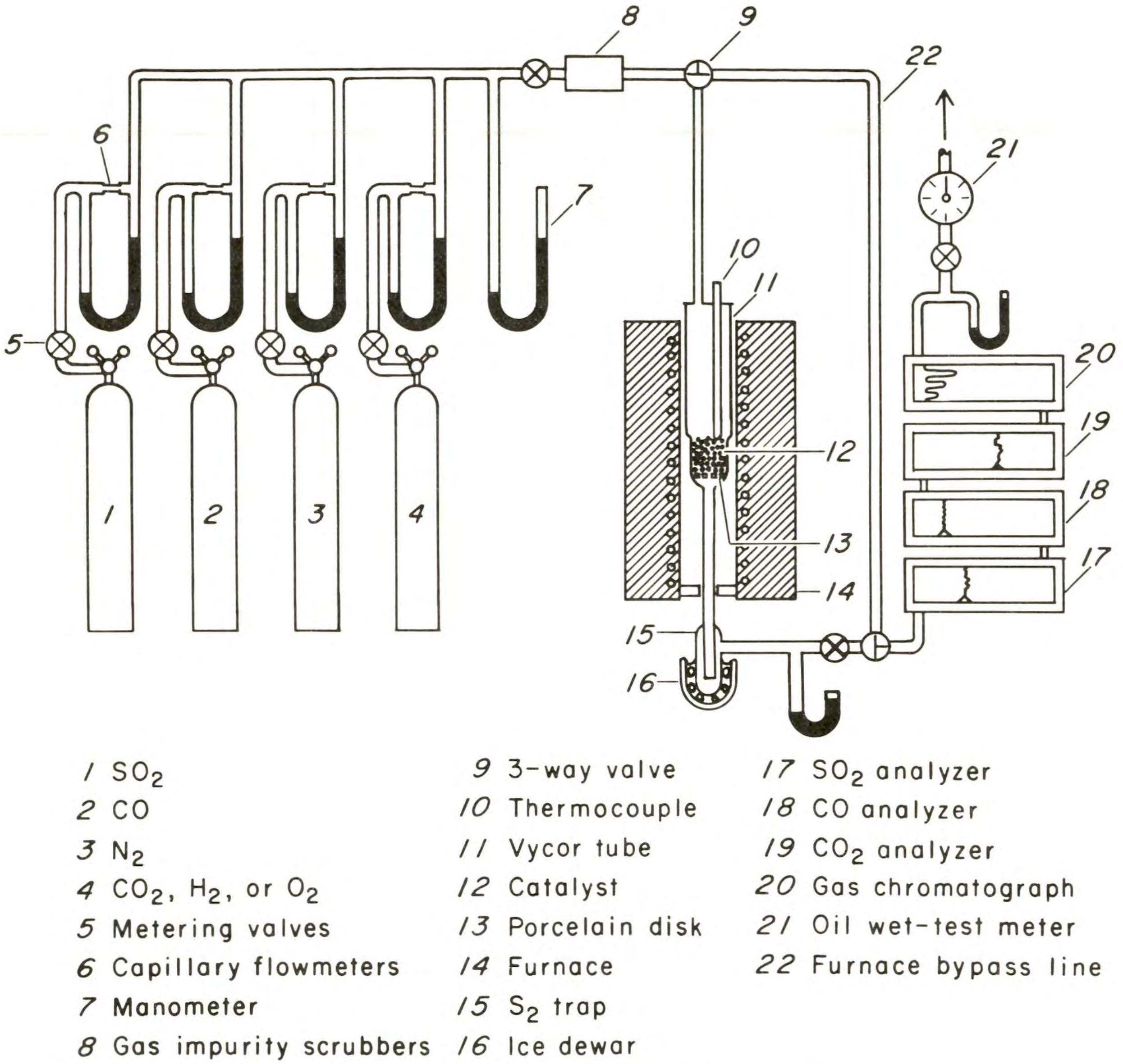

FIGURE 1. - Sketch of Laboratory Equipment for Sulfur Dioxide Removal Experiments.

with nitrogen while the furnace was adjusted to the desired operating temperature. The reactant gases (5 percent SO_2, 10 percent CO, and the balance N_2 unless otherwise stipulated) were then passed through the catalyst and the exhaust gases were continuously analyzed. When a steady state was obtained, the percent SO_2 conversion and the reaction rate were calculated. Infrared analyzers were used to determine the SO_2, CO, and CO_2 concentrations. A gas chromatograph was used to analyze for COS and also for the above-mentioned gases. This doublecheck, using different analytical detecting methods, eliminated error due to interfering gaseous species, etc. The analyzers were calibrated with commercial gas mixtures and were accurate to ±1 percent of the quantity of the constituent present.

The surface area of the catalyst pellets was determined by the classic low-temperature gas adsorption BET (Brunauer-Emmett-Teller) volumetric technique after the pellets were degassed for 10 hours at 200° C. Nitrogen was used as the adsorbate. The surface areas determined with this process agreed within 5 percent with several commercial samples. The repeatability with the same sample was about ±1 percent.

The reaction rate, $\Re$, was calculated by the flow balance method given by Anderson[8] and is shown by the following equation:

$$\Re = \frac{dx}{d(w/q)} = \frac{dx}{d\tau},$$

where x is the fraction of SO_2 reacted and τ is the space-time. Space-time was determined by dividing the catalyst weight (w) by the SO_2 mass feed rate (q). The SO_2 removal rate $\left(\frac{dx}{d\tau}\right)$, therefore, possesses these dimensions: mass of SO_2 converted per unit mass of catalyst per minute. The $dx/d\tau$ values were obtained from the initial slopes of the x-τ plots.

The SO_2 removal rate will be used in this study, as it is of main concern; however, the reaction rate can also be expressed either as CO removal or CO_2 formation. The following sequence of reactions would have to be considered (thermodynamic values were calculated using JANAF tables):

$$SO_2 + 2CO \rightarrow 2CO_2 + \tfrac{1}{2}S_2; \quad \Delta H^\circ_{773} = -48.84 \text{ kcal}; \quad \Delta F^\circ_{773} = -29.98 \text{ kcal}. \tag{1}$$

$$\tfrac{1}{2}S_2 + CO \rightarrow COS; \quad \Delta H^\circ_{773} = -21.91 \text{ kcal}; \quad \Delta F^\circ_{773} = -7.27 \text{ kcal}. \tag{2}$$

$$COS + \tfrac{1}{2}SO_2 \rightarrow CO_2 + \tfrac{3}{4}S_2; \quad \Delta H^\circ_{773} = -2.51 \text{ kcal}; \quad \Delta F^\circ_{773} = -7.72 \text{ kcal}. \tag{3}$$

$$COS \rightarrow \tfrac{1}{2}CO_2 + \tfrac{1}{2}CS_2; \quad \Delta H^\circ_{773} = -0.01 \text{ kcal}; \quad \Delta F^\circ_{773} = +1.13 \text{ kcal}. \tag{4}$$

Because 1 mole of SO_2 consumes 2 moles of COS in reaction 3, and because 2 moles of COS are generated from 2 moles of CO by reaction 2, the net effect is that 1 mole of SO_2 is consumed by 2 moles of CO, which is identical with reaction 1. Hence the change in concentration of SO can give an indication of the kinetics of reaction 1 regardless of postcatalytic reactions 2, 3, and 4. For similar reasons, the fraction of CO_2 in the exhaust gas could be used to calculate the reaction rate were it not for the possible occurrence of reaction 4 in the exhaust-hot parts of the reactor. In this investigation, the fractions of SO_2 in the inlet and exit gases were determined at various feed rates and the differential reaction rate was based on these quantities.

RESULTS AND DISCUSSION

Among the variables that influenced the reduction of SO_2 by CO were the catalyst composition, pellet size, temperature, and the partial pressures of

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[8] Anderson, R. B. (ed.). Experimental Methods in Catalytic Research. Academic Press, New York, 1968, 498 pp.

SO_2, CO, CO_2, and O_2. In over 150 experiments, these parameters were varied independently of each other to determine their respective effects.

Catalyst Composition

The rate of reaction of 5 percent SO_2 with 10 percent CO in the presence of nitrogen was first investigated with no catalyst. It was found that no measurable SO_2 removal was obtained even up to temperatures of 950° C at a total flow rate of 0.5 SLM. No detectable SO_2 removal with either pure iron or alumina was obtained at 500° C, but in the presence of iron and alumina mixtures, considerable SO_2 conversion was obtained. Table 1 and figure 2 give specific data about SO_2 conversion. These data show that the fractional conversion increases linearly with space-time up to a fraction of about 0.25. Taylor[9] found this relationship to be valid up to 8 percent. With very active catalysts (curve c in fig. 2), it was extremely difficult to determine the precise value of $dx/d\tau$ when x approaches zero. Attempts were made with the aid of a computer to determine the initial rate by representing the data in the form of a polynomial equation.[10] However, graphical differentiation of the initial slopes (dashed lines) of the x-τ plots was found satisfactory and taken as the rate ($\Re_{SO_2}$). These values, along with some additional rates ($\Re'_{SO_2}$), are shown in table 2.

From these data and figure 3 (curve a), it can be seen that a mixture containing about 40 percent iron exhibits a very sharp peak in its catalytic activity at 500° C when compared to other catalyst compositions. The catalyst activity increased slowly with additions of iron to alumina up to about 30 percent iron, after which the activity rose very sharply to reach a maximum at about 40 percent iron, and then dropped, also sharply, to very low activities when the iron content exceeded 60 percent. This behavior excludes interpretations based primarily on the antisintering effect of alumina on iron, as the beneficial effects of alumina would then increase with increasing alumina content or remain constant, but would not drop sharply.

To qualify this statement, the reaction rate data were normalized per gram of iron instead of per gram of total catalyst; that is, assuming that iron is the only catalyst and that alumina provides a continuum whose only effect is to prevent sintering. This normalization process will tend to increase the very small reaction rates observed with small weight-fractions of iron in the catalyst. The normalized reaction rate with respect to the iron component is calculated in the last column of table 2. When the normalized reaction rate was replotted against the weight-fraction of iron, curve b of figure 3 resulted. This curve still portrayed a sharp maximum at about 40 percent iron; also, the rate per gram iron is less with 80 percent alumina than with 60 percent. These two observations disqualify any interpretation based solely on the antisintering effects of alumina. The data in table 2

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[9] Taylor, W. F., D. J. C. Yates, and J. H. Sinfelt. Catalysis Over Supported Metals. II. Effect of Support on the Activity of Nickel for Ethane Hydrogenolysis. J. Phys. Chem., v. 68, No. 10, 1964, p. 2962.

[10] Kittrell, J. R., and R. Mezaki. Obtaining Rates From Integral Reactors Data. Brit. Chem. Eng., v. 11, 1960, pp. 1538-1539.

show that the surface area change was not large enough to account for the large change in catalytic activity.

TABLE 1. - Sulfur dioxide conversion at various feed rates and compositions of catalyst at 500° C with 10.0 percent carbon monoxide

Iron in catalyst, percent	Total inlet flow, std cm^3/min	Space-time (τ), min	SO_2 analysis, percent			Fractional conversion, x
			Inlet	Exhaust	Removed	
0.0..............	461	30.7	4.79	4.79	0.00	0.000
7.2..............	515	27.8	4.73	3.60	1.13	.239
	726	19.8		3.90	.83	.175
	945	15.2		4.07	.66	.140
	1,363	10.5		4.29	.44	.093
	1,638	8.7		4.38	.35	.074
	1,717	8.3		4.33	.40	.085
	2,381	6.0		4.55	.18	.038
23.1..............	432	32.7	4.80	2.86	1.94	.404
	599	23.5		3.23	1.57	.327
	779	18.1		3.60	1.20	.250
	983	14.4		3.70	1.10	.229
	1,503	9.4		4.15	.65	.135
	1,967	7.2		4.25	.55	.114
41.2..............	552	25.9	4.74	1.03	3.71	.783
	994	14.4		1.45	3.29	.694
	1,977	7.2		1.90	2.84	.599
62.0..............	455	31.4	4.74	2.15	2.59	.546
	581	24.6		2.44	2.30	.485
	788	18.1		2.87	1.87	.394
	988	14.5		3.13	1.61	.340
	1,497	9.5		3.64	1.10	.232
	1,993	7.2		3.84	.90	.190
86.3..............	591	24.1	4.76	4.11	.65	.136
	799	17.8		4.28	.48	.101
	1,018	14.0		4.42	.34	.071
100.0..............	500	28.8	4.70	4.70	.00	.000

Experiments with mixtures of iron and silica did not reveal substantial conversions of SO_2 at 500° C (last row in table 2). The reaction rate ($\Re_{SO_2}$) with alumina-iron catalysts was 74 times greater than that with silica-iron catalysts. Because silica alone does not catalyze the reaction at high or low concentration levels of the reactants and at temperatures as high as 950° C, it is concluded that silica acts only as a catalyst support for iron. Table 2 indicates that the surface area for silica-iron and alumina-iron catalysts were about the same. By contrast, alumina not only assumes the function of iron support, but also contributes to the catalytic activity.

TABLE 2. - Effect of catalyst composition on SO_2 conversion rate at 500° C with inlet gas of 10.0 percent CO and 4.7 percent SO_2

Iron in catalyst, percent	BET surface area, meters²/g	Rate ($\mathcal{R}_{SO_2}$), mg SO_2 removed / min X g catalyst	Normalized rate ($\mathcal{R}'_{SO_2}$), mg SO_2 removed / min X g iron
IRON-ALUMINA CATALYST			
0.0	7.8	0.0	0.0
7.2	2.6	8.7 [1]9.2	121.0 [1]128.3
23.1	4.3	15.4 [1]13.6	66.5 [1]59.0
31.9	7.0	36.4 [1]35.0	114.2 [1]109.6
36.4	4.8	66.4	182.4
41.2	([2])	218.9	531.0
50.0	5.7	148.5	297.0
56.6	4.0	75.3	133.0
62.0	4.8	23.0	37.1
86.3	6.5	5.1	5.9
100.0	1.2	.0	.0
IRON-SILICA CATALYST			
0.0	46.7	0.0	0.0
41.2	3.8	3.0	7.2

[1] Duplicate run to indicate reproducibility.
[2] Not available.

The significant synergistic effect observed with mixtures of iron and alumina, in the sense that they exhibit a catalytic activity for reaction 1 far in excess of the sum of the contributions made by the individual constituents, can best be explained by a change in reaction mechanism. With iron or alumina alone functioning as the catalyst, only one of the reactants is adsorbed, while the other reacts by collision from the gas phase with the adsorbed species according to the Langmuir-Rideal mechanism.[11] At relatively low reactant pressures, the catalytic activity of alumina on reaction 1 would decrease because of the rareness of collisions made by the nonadsorbed reactant.

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[11] Rideal, E. K. A Note on a Simple Molecular Mechanism for Heterogeneous Catalytic Reactions. Proc. Cambridge Phil. Soc., v. 35, 1949, p. 130.

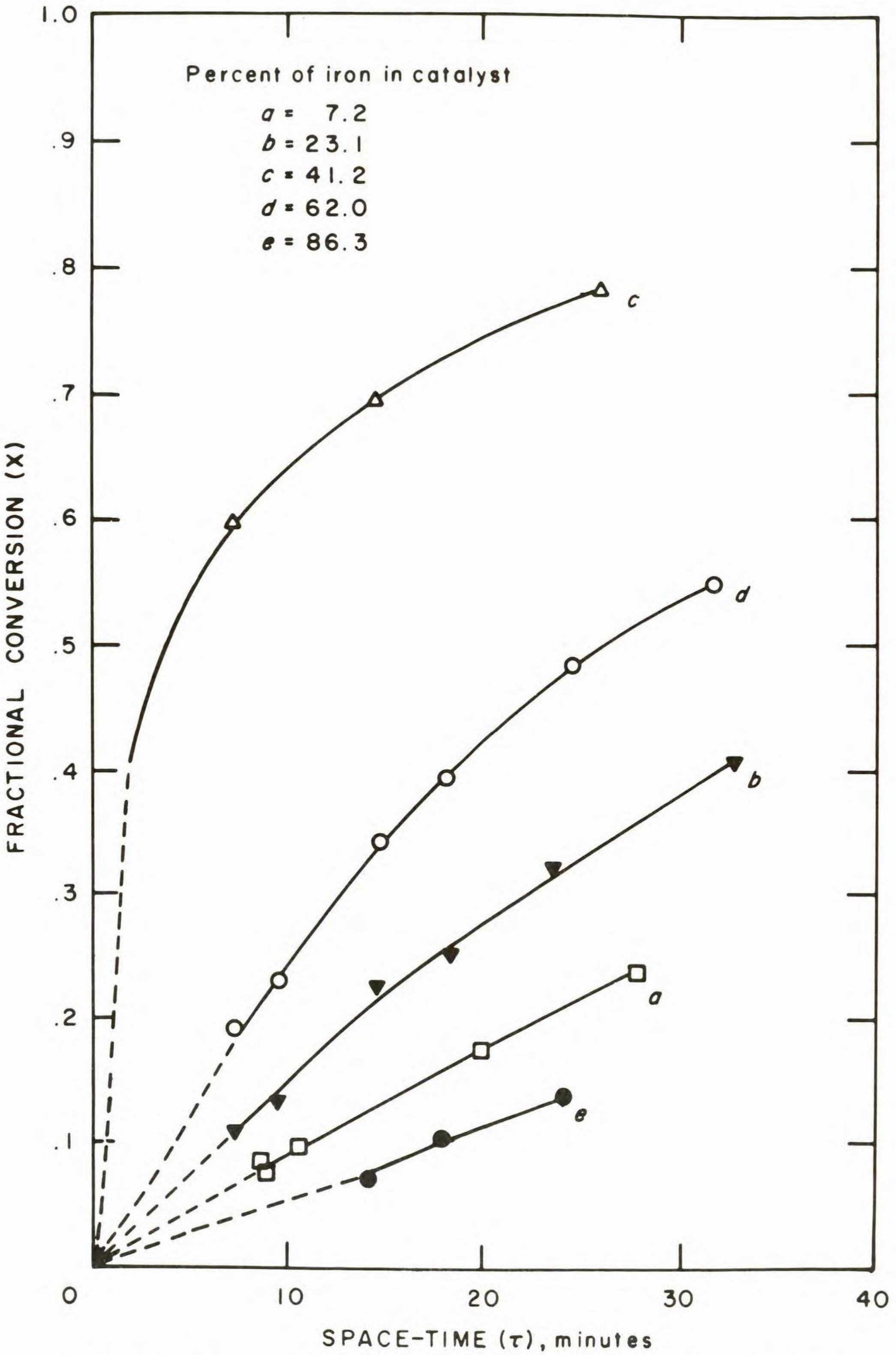

FIGURE 2. - Effect of Catalyst Composition on SO_2 Conversion at Various Space-Times at 500° C.

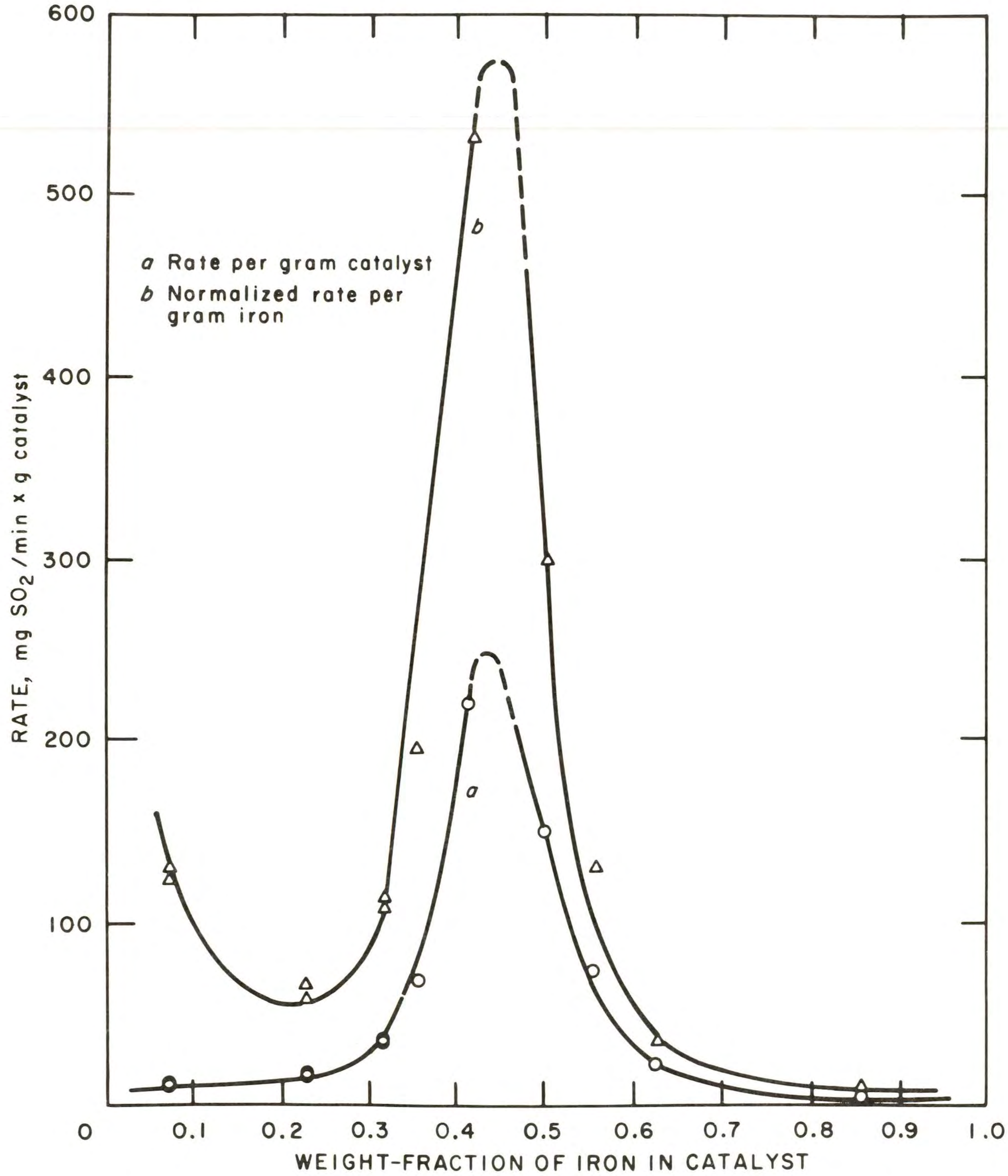

FIGURE 3. - Dependence of SO_2 Removal Rate at 500° C on Iron-Alumina Catalyst Composition.

Sinfelt and Lucchesi[12] explained the action of bifunctional catalysts by postulating the migration of intermediates from one of the catalyst components to the other. However, they did not present data to indicate the effect of composition on their bifunctional catalyst activity. For the hydrogenation of ethylene on a platinum-alumina catalyst, hydrogen atom intermediates (activated by dissociative adsorption of molecular hydrogen on platinum sites) migrate to alumina centers to react with chemisorbed ethylene. Likewise, the surface migration of activated carbon monoxide or elemental carbon from their chemisorbed state on the iron sites to nearby sites in alumina where SO_2 is adsorbed would undoubtedly account for the increased activity of the bifunctional catalyst.

Another type of dual-site mechanism can arise when iron and alumina share specific sites at interparticle contact areas. The conversion of the reaction from a Langmuir-Rideal mechanism to a Langmuir-Hinshelwood mechanism,[13] where both reactants are adsorbed on nearby sites, could account for the tremendous increase in reaction rate when alumina and iron are mixed in the right proportions. Alumina alone can act as a catalyst for the reaction of large concentrations of CO and SO_2. However, the present work indicates that at low concentrations iron or alumina alone is a poor catalyst, but that a proper mixture of iron and alumina surpasses by far the individual components in catalytic activity.

Catalyst Pellet Size

The influence of the catalyst pellet size on the reaction rate was studied because the pressure drop across the reactor is of definite concern to the process engineer. The pressure drop varies approximately to the minus 1.5 power of the catalyst diameter. The catalyst size can also influence the reaction rate when mass transfer of the reactants or products becomes rate controlling. This hypothesis was checked at 470° C by varying the pellet diameters from 0.69 to 1.54 mm using a catalyst containing 40 percent iron in alumina. It is apparent from table 3 that the SO_2 reaction rate was greatest with the smallest pellets. The depth of the catalyst pores is less for small pellets, thereby permitting better mass transfer of the reactants and products. The reaction rates were plotted against the reciprocal pellet diameters (fig. 4). The reciprocal pellet diameter is proportional to the external surface area of the pellet per unit mass. At pellet diameters less than 1 mm, the activity becomes less dependent on the pellet size, which means the pellet was almost entirely effective. With larger pellets, the effective depth or active layer thickness was much less than the pellet diameter and an inactive core existed in the pellet.

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[12] Sinfelt, J. H., and P. J. Lucchesi. Kinetic Evidence for Migration of Reactive Intermediates of Surface Catalysis. J. Am. Chem. Soc., v. 85, 1963, pp. 3365-3367.

[13] Hinshelwood, C. N. Kinetics of Chemical Change. Oxford Univ. Press, New York, 1940, p. 187.

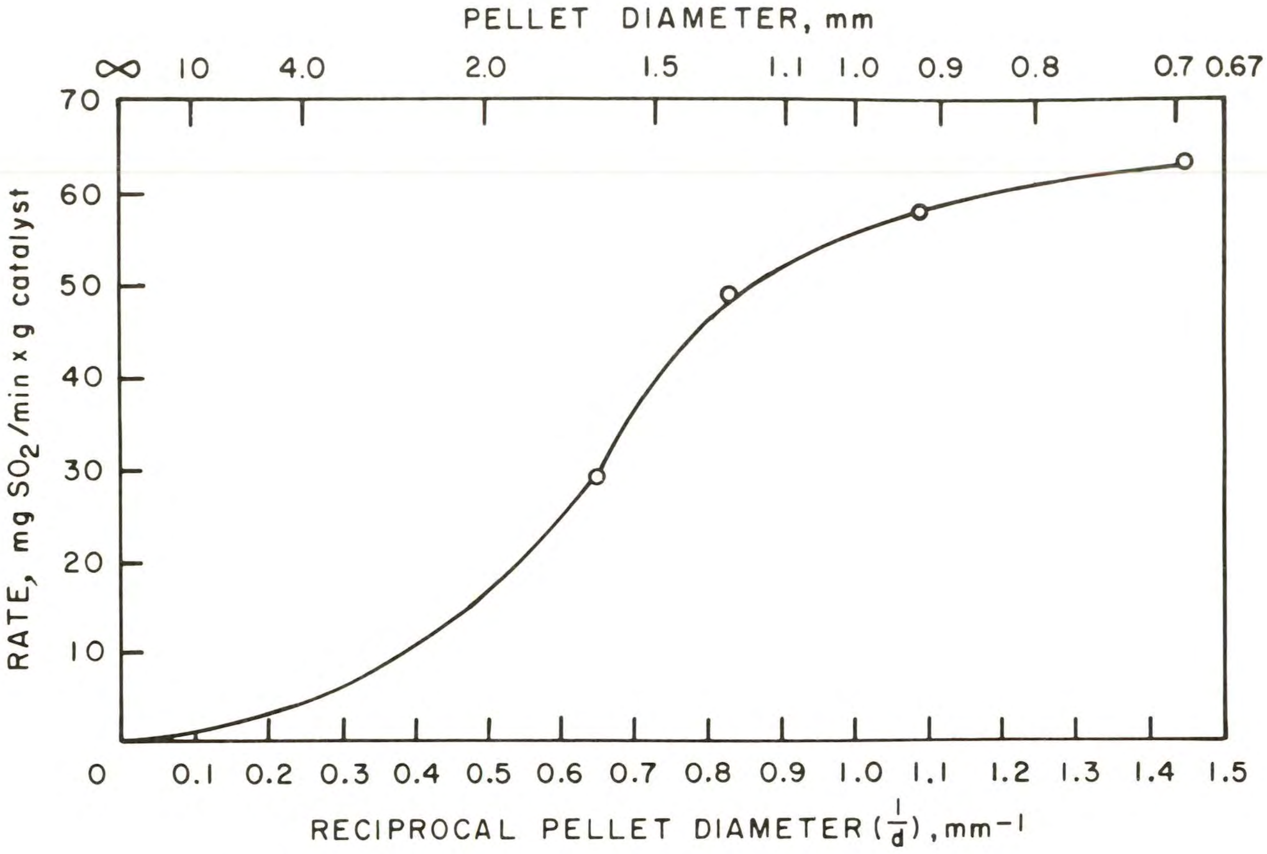

FIGURE 4. - Effect of Catalyst Pellet Size on Reaction Rate.

TABLE 3. - Effect of catalyst pellet size on reaction rate

Pellet size		$\frac{1}{d}$, mm^{-1}	Reaction rate, mg SO_2 removed / min X g catalyst
Mesh	Diameter (d), mm		
Minus 20 plus 30	0.69	1.44	63
Minus 16 plus 20	.92	1.09	58
Minus 12 plus 16	1.20	.83	49
Minus 10 plus 12	1.54	.65	29

Previous studies[14] on iron catalysts with CO and H_2 showed that the optimum pellet diameter varies with reduction temperature. When the reduction temperature was 600° C, particles with diameter of 0.5 mm or less were completely effective. This is in fair agreement with our results.

Temperature

The influence of temperature was studied at SO_2 conversions of less than 25 percent on a catalyst containing 41.2 percent iron and alumina. One would

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[14] Anderson, R. B., F. S. Karn, and J. F. Shultz. Kinetics of the Fischer-Tropsch Synthesis on Iron Catalysts. BuMines Bull. 614, 1964, 45 pp.

expect the catalyst activity to decrease with time owing to sintering and sulfur poisoning of the catalyst. An initial decrease in SO_2 removal was observed, but steady-state values were reached in less than one-half hour. After several days of catalyst usage, a decrease in activity was observed, as shown by the two points at 400° C in figure 5 (the upper point was obtained with a catalyst after a few hours of usage, and the lower value was obtained after several days). This decrease was explained by plugging of pores and sintering, as the apparent porosity had decreased about 5 percent. The apparent activation energy obtained from this Arrhenius plot was 18.3 kcal per mole, which is in fair agreement with Doumani's[15] values of 14 and 18 kcal per mole with iron sulfide-alumina catalysts.

The reaction products also changed as the temperature was changed. Figure 6 shows that the ratio of COS formed to SO_2 removed increased to a maximum at about 400° C and then decreased as the temperature was further increased. The maximum COS formation is perhaps the net result of two opposing reactions: (1) The COS formation from CO and S (reaction 2), which was found to occur above 300° C, and (2) the reverse reaction (COS decomposition), which was found to occur above 400° C. The rate at which these reactions occur depends on the partial pressure of gases present. This is further discussed in the next section.

Partial Pressure of Gases

The effect of sulfur dioxide partial pressure on the reaction rate was investigated at 10 and 20 percent CO (fig. 7). Curves a, b, c, d, e, and f refer to 0.19, 1.00, 1.35, 4.65, 8.55, and 16.70 percent sulfur dioxide, respectively, reacted with 10.0 percent carbon monoxide and the balance nitrogen in each case. Curves g, h, i, and j refer to 0.22, 3.05, 4.73, and 13.10 percent sulfur dioxide, respectively, reacted with 20.0 percent carbon monoxide. The catalyst consisted of 0.960 gram of an equal-weight mixture of iron and alumina with a bulk volume of 1.07 cu cm. The reaction temperature was reduced to 400° C in order to lower the conversion rate and better evaluate the initial slopes of the x-τ plots. It was, however, still impossible to obtain low values of x at this temperature with low SO_2 feed rates; therefore, the curves had to be extrapolated back to low values of x and τ. Inspection of the data in figure 7 shows that, for a given carbon monoxide concentration, the (x versus τ) curves are bunched together at their initial segments regardless of the sulfur dioxide concentration. The flattened-out portions of the curves at high SO_2 concentration resulted from carbon monoxide starvation in the catalyst bed. Despite their early departure from linearity, their small initial segments are still coincidental with the rest of their family of curves. This behavior suggests that the CO-SO_2 reaction is zero order in sulfure dioxide under these experimental conditions.

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[15] Doumani, T. F., R. F. Deery, and W. E. Bradley. Recovery of Sulfur From Sulfur Dioxide in Waste Gases. Ind. and Eng. Chem., v. 36, No. 4, April 1944, pp. 329-332.

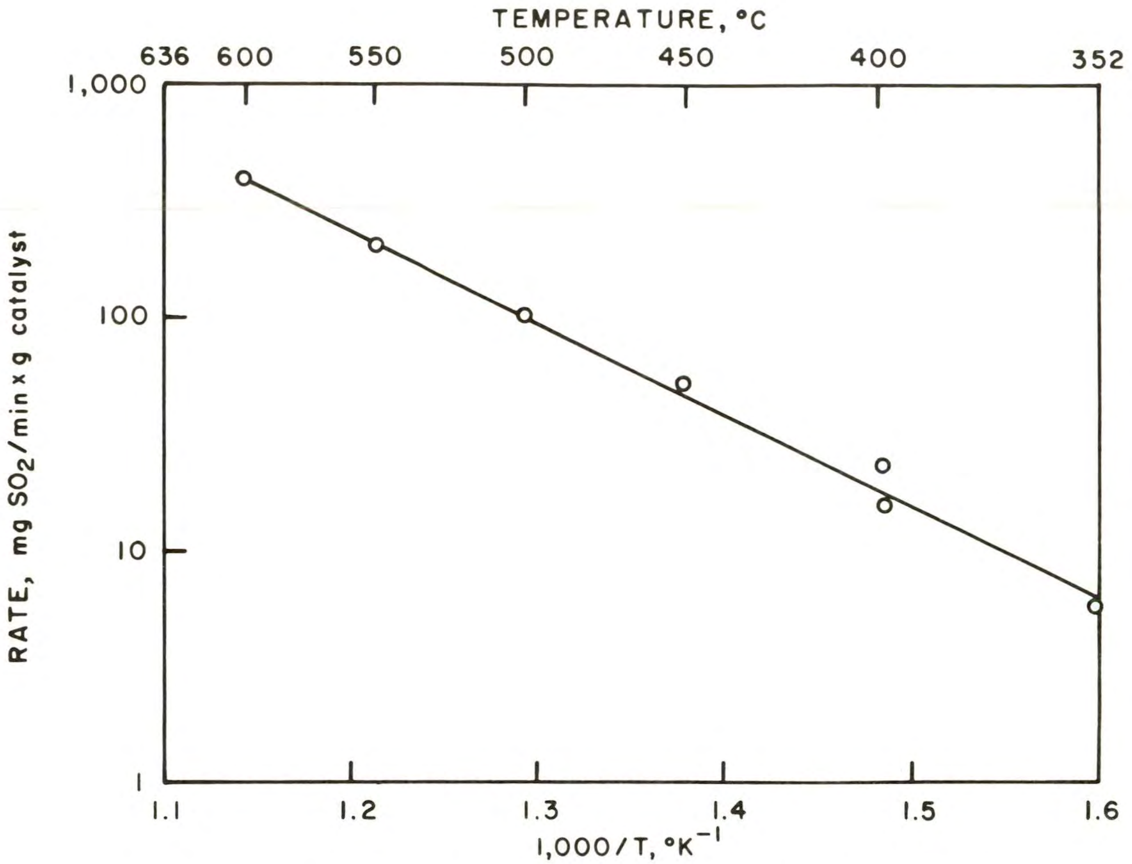

FIGURE 5. - Arrhenius Plot Depicting Effect of Temperature on Reaction Rate.

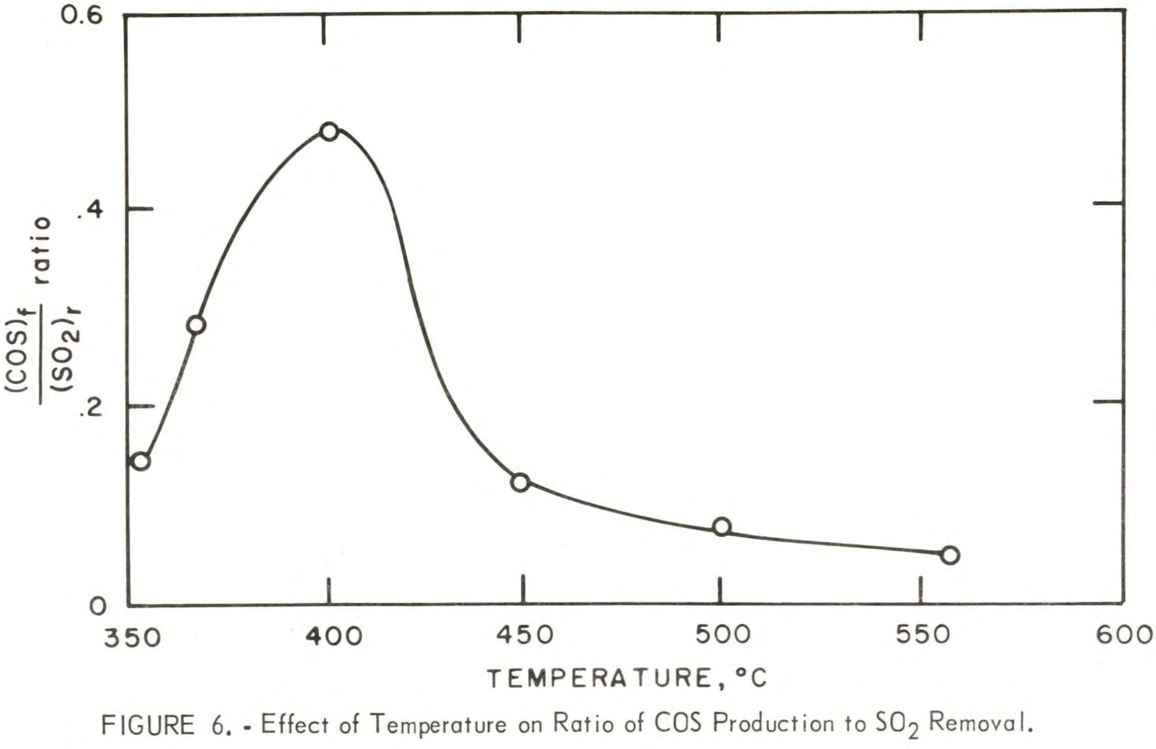

FIGURE 6. - Effect of Temperature on Ratio of COS Production to SO_2 Removal.

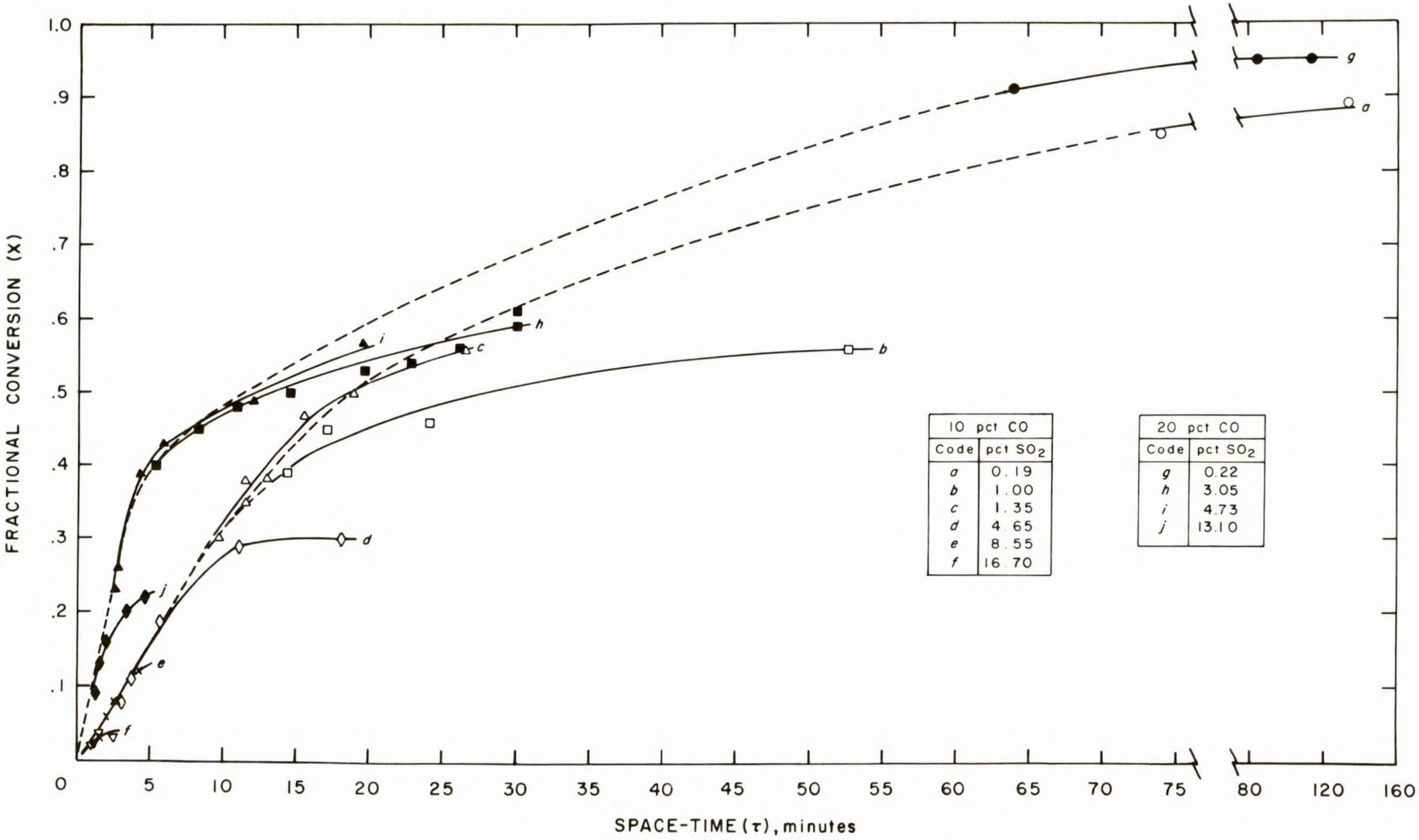

FIGURE 7. - Dependence of SO_2 Conversion on Inlet Gas Compositions.

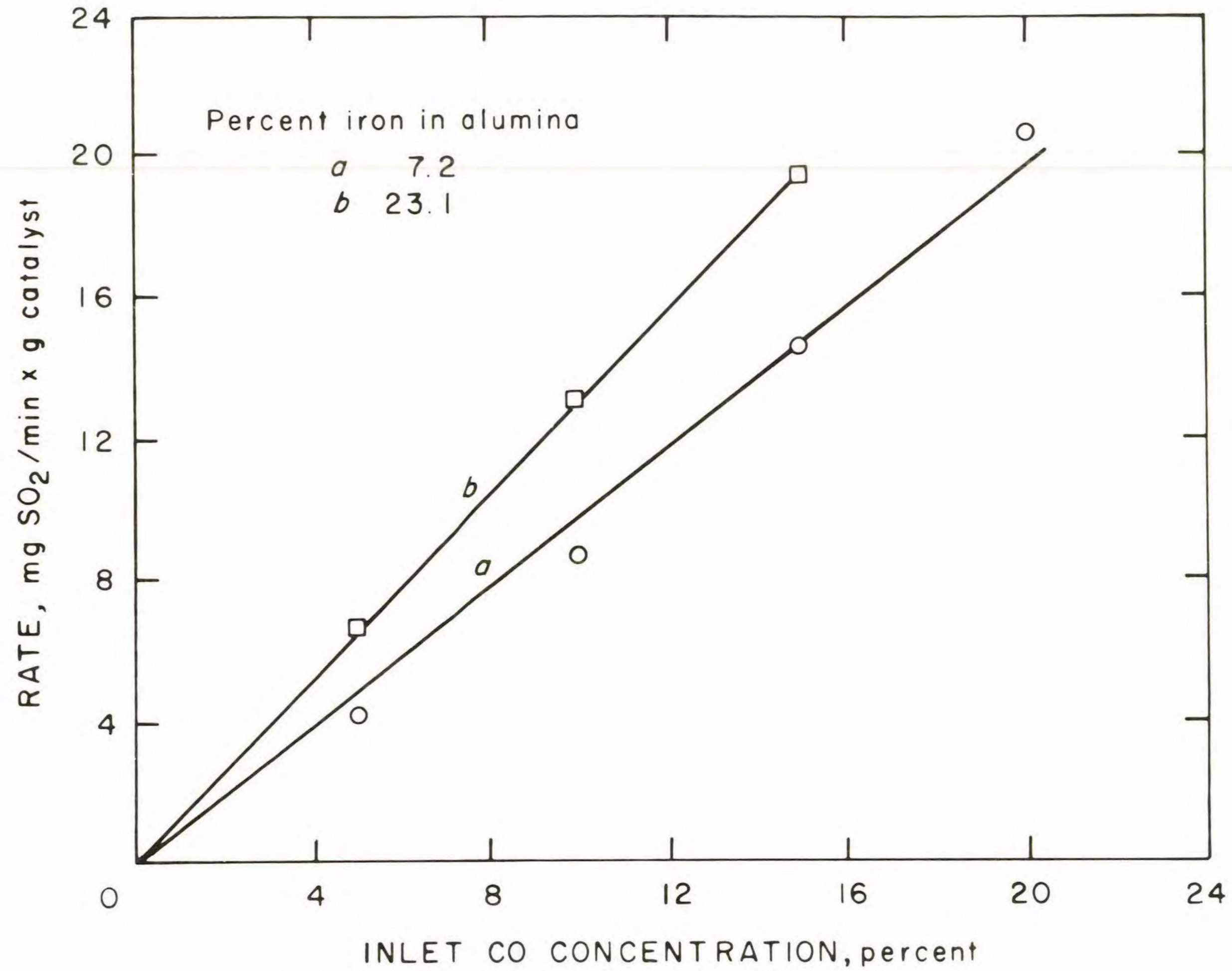

FIGURE 8. - Effect of CO Concentration on Reaction Rate.

The CO dependence of the reaction rate was determined with catalysts of lower activity (less iron in alumina) since the reaction rates could be more accurately determined at lower conversions. The reaction rate was determined at 500° C with various CO concentrations using 4.7 percent SO_2 and the balance nitrogen. The results are shown in figure 8 for 7.2 and 23.1 percent iron in alumina. This curve shows that the rate increases with the reductant concentration. Similar results were obtained with hydrogen as a reductant. The main diluent was usually nitrogen; however, one test was performed with helium and essentially the same reaction rate was obtained.

Experiments in which the concentration of CO far exceeded the stoichiometric amount needed to react with SO_2 indicated no elemental sulfur formation; all the SO_2 was converted to COS. It was hypothesized that the proportion of COS might be decreased by starving the reaction mixture in carbon monoxide. Experiments at 400° C using 1.936 grams of equal quantities of iron-alumina and small concentrations of CO in a 0.5-SLM total gas flow consisting of 4.15 percent SO_2 and the balance N_2 confirmed this hypothesis (fig. 9). As long as carbon monoxide is present, it will react with sulfur to form COS. Therefore,

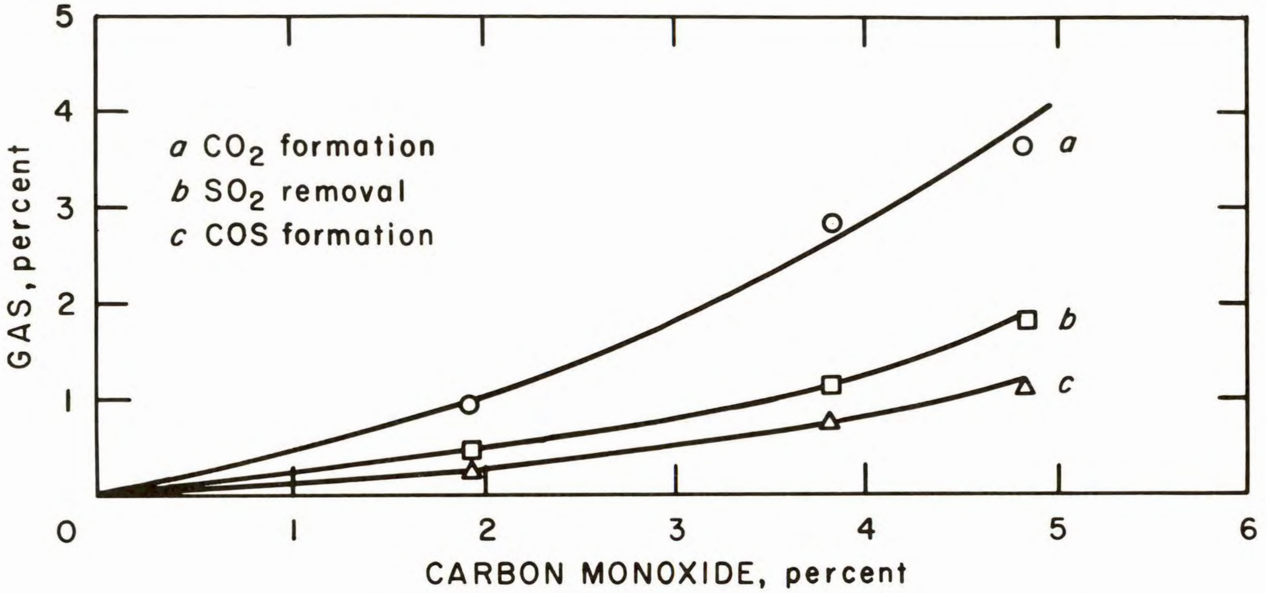

FIGURE 9. - Effect of CO Concentration in Inlet Gas on (*a*) CO_2 Formation, (*b*) SO_2 Removal, and (*c*) COS Formation.

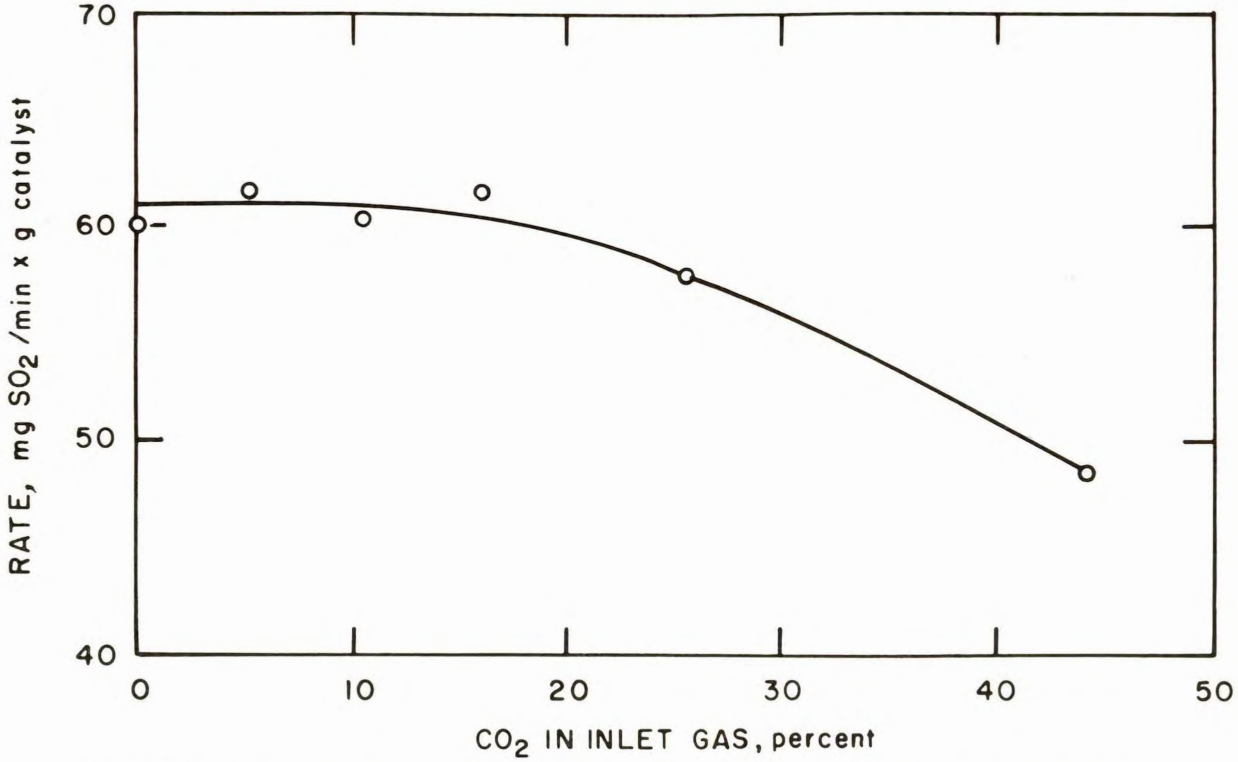

FIGURE 10. - Dependence of Rate of Reaction on Carbon Dioxide Inlet Concentration.

to eliminate COS formation, either reaction 1 or reaction 3 must be forced to completion or else the sulfur must be rapidly quenched before the CO reacts with the sulfur.

The tolerance capacity of the reaction-driving force for additional amounts of carbon dioxide in the inlet gas was also studied. This phase of the investigation is important, not only because carbon dioxide is a product of this reaction, but also because this component is invariably present in combustion and smelter waste gases. The variation of the CO_2 conversion with the percent carbon dioxide in the inlet gas is shown in figure 10. Under our experimental conditions, the reaction rate was practically insensitive to concentrations of carbon dioxide up to about 15 percent, beyond which further carbon dioxide increase resulted in a slight decrease in reaction rate. Because the reacting mixture in this case was 5 percent SO_2, 10 percent CO, and the balance N_2, one would expect that relatively large concentrations of carbon dioxide can be tolerated before the reaction-driving force is nullified or even reversed. The equilibrium constant for this reaction at 400° C is 10^{10}.

The tolerance capacity of SO_2 reduction to small amounts of oxygen was also investigated. Only small quantities (<0.5 percent) of oxygen can be tolerated, as is shown in figure 11. With 2 percent oxygen, no SO_2 reduction was obtained.

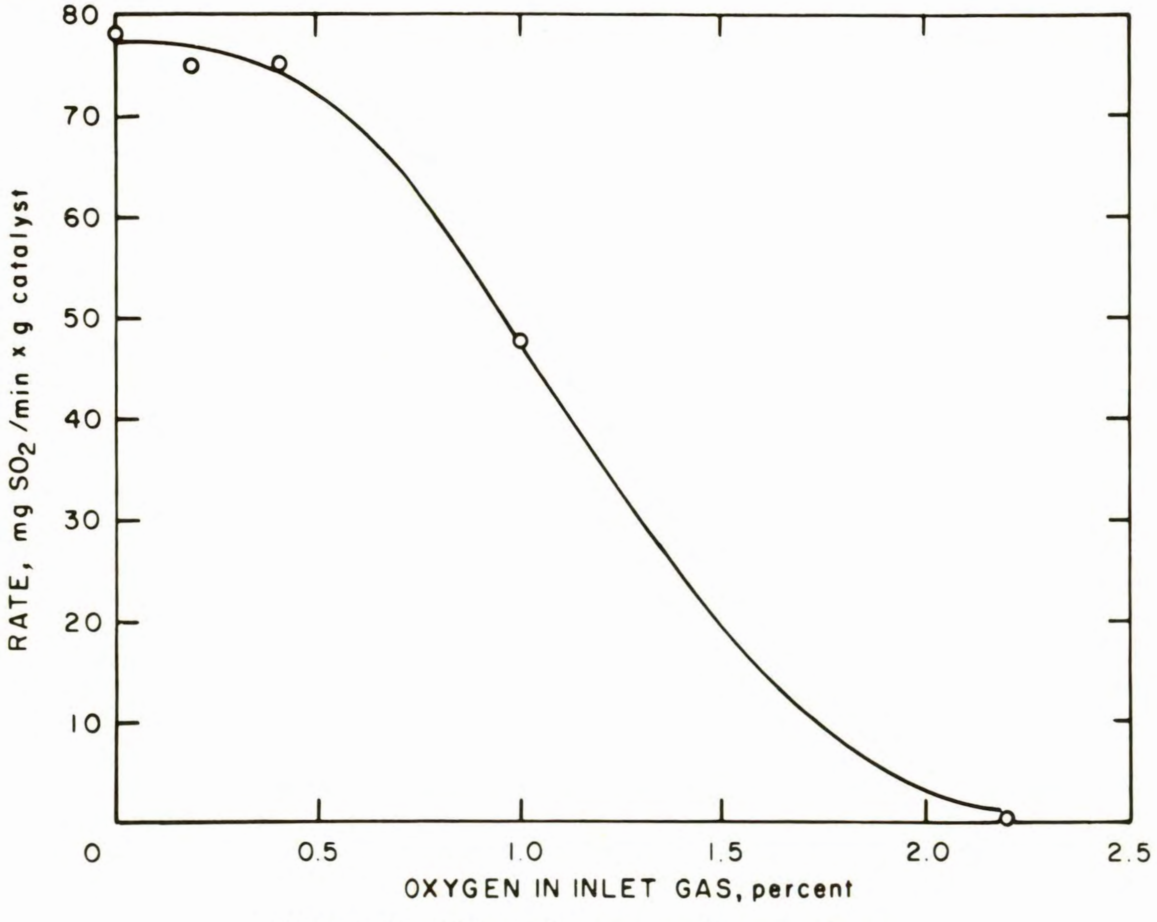

FIGURE 11. - Effect of Oxygen on Reaction Rate.

SUMMARY AND CONCLUSIONS

A bifunctional catalyst of pelletized iron-alumina mixtures can bring about the interaction of low concentrations of SO_2 and CO at low temperatures, whereas the separate components cannot. The marked synergistic effect of iron-alumina mixtures cannot be explained on the basis of catalytic support of iron by alumina to prevent sintering. In the absence of a simpler explanation, it is concluded that the low-temperature reaction of low concentrations of SO_2 and CO occurs on the bifunctional catalyst by a dual-site mechanism.

The reaction rate increased with decreasing pellet diameter up to about 1 mm, where it leveled off. A measurable reaction rate with 41.2 percent iron in alumina was observed at 350° C, and the rate doubled about every 50° C in the range investigated. The apparent activation energy for the reaction was 18.3 kcal per mole.

The initial reaction rate was not influenced by the partial pressure of the sulfur dioxide but increased directly with the CO partial pressure. As the CO concentration increased, the amount of COS also increased. The maximum quantity of COS was observed at 400° C. Up to 15 percent CO_2 could be tolerated without an appreciable decrease in reaction rate. However, oxygen concentrations greater than 0.5 percent drastically decreased the reaction rate.

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