

Catalytic Reduction of Sulfur Dioxide on Iron-Alumina Bifunctional Catalysts

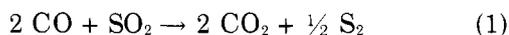
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Mixtures of alumina and iron powder provide efficient catalysts for the interaction of low concentrations of SO₂ with CO. The catalytic reaction rate at 500° C depended significantly on the iron content of the binary catalyst mixture. Mixtures containing 43% freshly reduced iron exhibited a sharp peak in the catalytic activity at 500° C when compared with other catalyst compositions. The normalized reaction rate per gram of iron, instead of per gram of total catalyst, still portrayed a sharp maximum when plotted against the weight fraction of iron in the catalyst. This fact, in addition to nonsynergistic effects observed with iron-silica mixtures, disqualifies interpretations based solely on the antisintering or supportive action of alumina on iron. The results are best explained on the basis of a dual reaction site mechanism with both iron and alumina augmenting their specific sites activity at their interparticle contacts.

The conversion of sulfur dioxide to elemental sulfur is a problem of increasing national and industrial importance. This investigation deals with the interaction of small concentrations of SO₂ (0.7 to 5%) and CO (2 to 10%) on a suitable catalyst.

The reduction of SO₂ by CO has considerable historical background but only limited practical applications. More emphasis in numerous patents had been placed on describing some new details of procedure than on the chemistry and kinetics of reduction. Hanish and Schröder (1885) were the first to establish the stoichiometry of the reaction



Ferguson (1918) and Winternitz (1914) studied the thermodynamic and equilibrium relationships of Reaction 1, using broken porcelain or platinized porcelain as a contact catalyst. The equilibrium constant of Reaction 1 calculated from the recent JANAF thermodynamic compilations is 410 at 1350° K and becomes as high as 2×10^5 and 10^8 at 1000° and 800° K, respectively. Visconti (1945) found that bauxite impregnated with vanadium salts is an efficient catalyst to obtain sulfur from the SO₂-CO reaction.

In the absence of a catalyst, Reaction 1 proceeds very slowly, even at 950° C. Lepsoe (1940) found that pyrrhotite (FeS) is an efficient catalyst at 700° C. At lower temperatures, alumina in various slightly hydrated and acid-soluble forms (boehmite) was an efficient catalyst.

However, Lepsoe's experiments involved large concentrations of the reactants at 500° C;—viz., 63% CO and 35% SO₂. The pronounced adsorption of SO₂ by alumina was manifested by the way the catalyst tenaciously retained SO₂ once it had been exposed to concentrated sulfur dioxide gas mixtures. The efficiency of the alumina catalysts is partly lost if they are exposed to high temperatures for long periods.

The present investigation showed that alumina alone does not catalyze Reaction 1 in the low concentration range. Mixtures of iron and alumina, on the other hand, constitute a remarkably efficient catalyst. The bifunctional catalyst discovery became apparent when preliminary experiments showed that the dimensions of the steel basket used to hold the alumina catalyst had a decisive effect on the sulfur dioxide reaction with CO. This paper will, therefore, be mainly concerned with the mechanism by which catalysis of Reaction 1 occurs by iron-alumina mixtures.

Experimental

A single-pass, vertical, fixed-bed flow reactor was used in this study. The gas feed entered at a measured constant flow and passed through a bottom preheater section and then through the catalyst bed to a section for recovering and measuring the products. A porcelain perforated disk and a mat of quartz wool held the catalyst sample in the middle of a 1.7-in. diam furnace. The catalyst temperature was measured by a Pt vs. Pt-10% Rh thermocouple and controlled to within $\pm 2^\circ \text{C}$. The thermocouple

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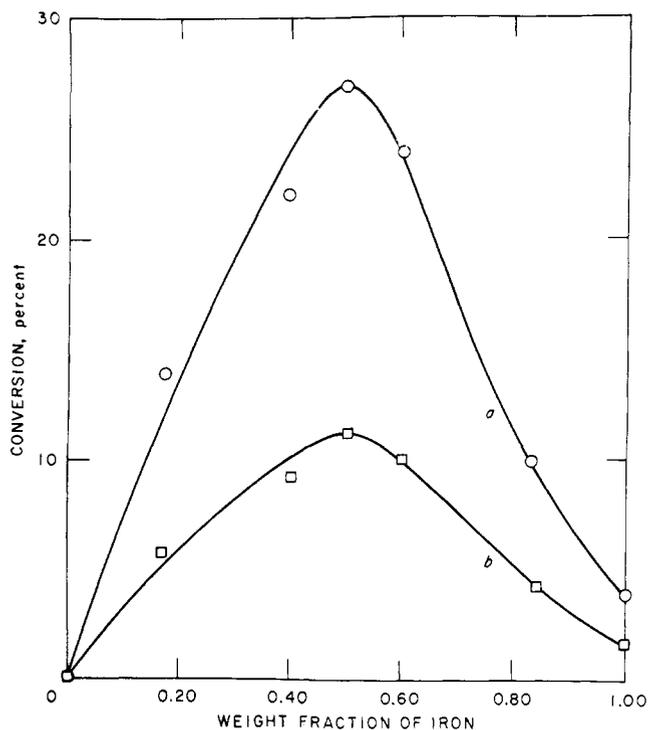


Figure 1. Effect of composition of the iron-alumina catalyst A on the removal of SO₂ at 600°C. Inlet gas flow, 0.5 liter per min

- a. Conversion of CO
b. Conversion of SO₂

well was 0.25 in. in diameter and was located directly below the catalyst bed.

Sulfur dioxide concentration in the inlet and exit gases was determined with a Beckman infrared analyzer (0 to 5%). An MSA infrared gas analyzer was used to determine CO and CO₂ concentrations. A Fisher partitioner gas chromatograph capable of analyzing for CO₂, SO₂, and COS served as a double check on the preceding continuous gas analyzers. The analyzers were calibrated with commercial gas mixtures before and after each test. The analysis was accurate to ±0.05%.

The Brunauer, Emmett, and Teller (BET) surface area of the used catalyst pellets was determined with a Micromeritics instrument, Model 2100, using nitrogen as the adsorbate. The instrument has an accuracy of ±5%, checked by determining the surface areas of standard commercial samples.

Three modes of preparing the iron-alumina catalyst were adopted in this work. Catalyst A consisted of -100-mesh iron powder from Plastic Metals Division of National U. S. Radiator Corp., and -325-mesh alumina from Allied Chemical Corp. (Solvay), mixed in various proportions. Catalyst B was prepared by pelletization of mixtures of 0.05 micron "Gamma Micropolish" alumina from Buehler Ltd., and -10-micron iron powder. Pelletization was accomplished by slurring the mixed powder with a little water prior to heating in Teflon molds at 110°C for about 20 hr. The slightly tarnished pellets were reduced with hydrogen at 600°C for 15 min to remove the surface oxide layers on iron. Catalyst C was prepared by pelletizing mixtures of -10-micron hematite and -0.05-micron γ-alumina. The -16 to +20-mesh oxide pellets were indurated at 1200°C for 2 hr. A portion of the oxide pellets required to give the desired weight of catalyst

was inserted into the reactor, heated in nitrogen, and reduced at 600°C for one hr with hydrogen at a flow of 0.5 liter (STP) per min. After complete reduction of the hematite constituent of the catalyst to iron, the reactor was flushed with nitrogen for about 10 min while simultaneously adjusting the furnace to the desired operating temperature.

Chemically pure-grade gases were supplied to the reactor through calibrated capillary flow meters. Gas flow rates were accurate to ±2% of maximum flow. Moisture was removed from the gases with magnesium perchlorate. 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.

For an integral reactor, the differential reaction rate is defined by the equations of Hougen and Watson (1943) for plug-type flow. If the SO₂ component of the feed is used to indicate the forward progress of Reaction 1, then the fractional removal, x , of SO₂ increases from zero along the bed. For a feed, q_{SO_2} , in mg per min, the amount of SO₂ reacted in an increment of the bed, dw , equals $q_{SO_2} dx$ and

$$Rdw = q_{SO_2} dx \quad (2)$$

where R is the differential reaction rate expressed in mg SO₂ removed per min per gram of catalyst and w is the weight of the catalyst in grams. Hence,

$$\begin{aligned} R &= dx/d(w/q_{SO_2}) \\ &= dx/d\tau \end{aligned} \quad (3)$$

where τ is space-time of SO₂ defined by the ratio w/q_{SO_2} . In this research, kinetic data were generated by changing the feed rate, q , for a given amount of catalyst. The conversion of SO₂ was determined at a number of feed rates with constant feed composition, temperature, and pressure.

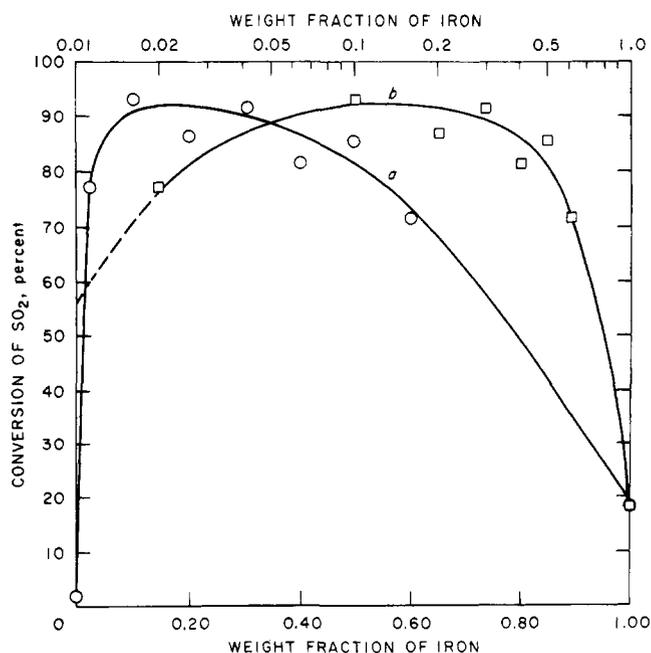


Figure 2. Effect of iron content in catalyst B on the reduction of SO₂ with carbon monoxide at 630°C

- a. Weight fraction of iron on linear scale
b. Weight fraction of iron on logarithmic scale

Table I. Sulfur Dioxide Conversion at Various Feed Rates and Various Compositions of Catalyst C at 500° C

| Iron in catalyst C, % | Bulk density, g/cc | Total inlet flow, cc/min | SO ₂ inlet flow, cc/min | Space-time, τ , min | SO ₂ analysis, % | | | Fractional conversion, % | |
|-----------------------|--------------------|--------------------------|------------------------------------|--------------------------|-----------------------------|---------|---------|--------------------------|-------|
| | | | | | Inlet | Exhaust | Removed | | |
| 7.2 | 0.606 | { | 515 | 24.4 | 0.131 | 4.73 | 3.60 | 1.13 | 0.239 |
| | | | 726 | 34.3 | 0.093 | | 3.90 | 0.83 | 0.175 |
| | | | 945 | 44.7 | 0.071 | | 4.07 | 0.66 | 0.140 |
| | | | 1363 | 64.5 | 0.049 | | 4.29 | 0.44 | 0.093 |
| | | | 1717 | 81.2 | 0.039 | | 4.33 | 0.40 | 0.085 |
| 23.1 | 0.661 | { | 2381 | 112.6 | 0.028 | 4.80 | 4.55 | 0.18 | 0.038 |
| | | | 432 | 20.7 | 0.141 | | 2.86 | 1.94 | 0.404 |
| | | | 599 | 28.8 | 0.102 | | 3.23 | 1.57 | 0.327 |
| | | | 779 | 37.4 | 0.078 | | 3.60 | 1.20 | 0.250 |
| | | | 983 | 47.2 | 0.062 | | 3.70 | 1.10 | 0.229 |
| 41.2 | 0.785 | { | 1503 | 72.1 | 0.041 | 4.74 | 4.15 | 0.65 | 0.135 |
| | | | 1967 | 94.4 | 0.031 | | 4.25 | 0.55 | 0.114 |
| | | | 552 | 26.2 | 0.090 | | 1.03 | 3.71 | 0.783 |
| | | | 994 | 47.1 | 0.052 | | 1.45 | 3.29 | 0.694 |
| | | | 1977 | 93.7 | 0.026 | | 1.90 | 2.84 | 0.599 |
| 62.0 | 1.120 | { | 455 | 21.57 | 0.080 | 4.74 | 2.15 | 2.59 | 0.546 |
| | | | 581 | 27.54 | 0.063 | | 2.44 | 2.30 | 0.485 |
| | | | 788 | 37.35 | 0.046 | | 2.87 | 1.87 | 0.394 |
| | | | 988 | 46.83 | 0.037 | | 3.13 | 1.61 | 0.340 |
| | | | 1497 | 70.96 | 0.024 | | 3.64 | 1.10 | 0.232 |
| 86.3 | 1.899 | { | 1993 | 94.47 | 0.018 | 4.76 | 3.84 | 0.90 | 0.190 |
| | | | 447 | 21.3 | 0.048 | | 4.10 | 0.66 | 0.139 |
| | | | 591 | 28.1 | 0.036 | | 4.11 | 0.65 | 0.136 |
| | | | 799 | 38.0 | 0.027 | | 4.28 | 0.48 | 0.101 |
| | | | 1018 | 48.4 | 0.021 | | 4.42 | 0.34 | 0.071 |
| | | | 1508 | 71.8 | 0.014 | | 4.59 | 0.17 | 0.036 |

To determine the slope of the (x vs. τ) curve, the following method of graphical differentiation proved more accurate. The procedure involved the plot of (x/τ) vs. τ and using the mathematical identity

$$\begin{aligned} [d(x/\tau)/d\tau] &= [(1/\tau)(dx/d\tau) - (x/\tau^2)] \\ &= (1/\tau) [(x/\tau) - I] \end{aligned} \quad (4)$$

where I is the ordinate intercept of the tangent to the (x/τ vs. τ) curve at space-time τ . The slope of the (x vs. τ) curve at τ is thus given by

$$dx/d\tau = (2 x/\tau) - I \quad (5)$$

Hence the differential reaction rate is equal to twice the ordinate of the (x/τ) curve less the intercept that the slope to this curve makes with the (x/τ) axis. The initial reaction rate will be given accordingly by the intercept of the x/τ plot with the ordinate such that, at that point, x/τ will be equal to I .

Results

Sulfur dioxide and carbon monoxide, at concentration levels of 5 to 10% or less, did not react with each other in absence of a catalyst even at temperatures as high as 950°C. No measurable reaction was detected in the 400° to 600°C temperature range with alumina alone or iron alone, but in the presence of mixtures of the two, substantial amounts of sulfur dioxide were removed. Typical experimental results with three grams of catalyst A at 600°C and with 6% SO₂, 5% CO, and the balance nitrogen are shown in Figure 1 which describes the variation of percent removal of SO₂ with the fraction of iron in the alumina catalyst mixture.

When the inlet gas composition was lowered to 0.7% in SO₂ and 2% in CO, then catalyst A was no longer effective, while the pelletized catalyst B was quite efficient.

The results obtained with 0.5 gram of catalyst B at 630°C and with a total inlet flow to the reactor of a half-liter (STP) per min are given in Figure 2. The variation of percent removal of SO₂ with the fraction of iron in the catalyst pellets is shown in curve *a* of this figure. When a logarithmic scale was used for the iron fraction, curve *b* of the same figure resulted and served to indicate that maximum catalytic activity occurred in this case at about 15% iron in catalyst B.

Differential reaction rates at 500°C were determined with various compositions of catalyst C using 4.7% SO₂, 10% CO, and the balance N₂. The results of some typical experiments with 1.936 grams of catalyst C are given in Table I. Also included are the bulk densities of the various catalysts in the second column. The variation of the fractional conversion of SO₂ with the space-time is shown in the curves of Figure 3 for the various proportions of iron used in catalyst C. The initial differential reaction rate, R , was calculated from the curves of Figure 3, and similar other curves according to Equations 3 and 5 of the experimental section. The third column of Table II contains the reaction rate values expressed in mg SO₂ per min per gram catalyst obtained with various catalyst C compositions. The second column of Table II gives the surface area of the used catalysts. The BET surface area of the used catalysts ranged from 1.2 meter² per gram for pure iron to 7 and 11.5 meter² per gram for some iron-alumina mixtures and to 7.8 meter² per gram for pure alumina. No definite trend to correlate catalyst area with its iron content was noted.

Further experiments were performed with iron-silica mixtures. With an equal-weight mixture of iron and cabosil (99.9% pure silica) prepared in a manner similar to catalyst C, the conversion of SO₂ was 3.6 and 15.2% at 500° and 670°C, respectively. The inlet gas nominal flow was 500 ml (STP) per min and contained 4.7% SO₂ and 10%

CO. Under similar conditions, iron alone was not active at 500° and gave a conversion of 9.1% at 650° C.

Discussion

It is evident from the foregoing data that the catalyst effectiveness for Reaction 1 was primarily dependent on the concentration levels of the reactants. Thus, while alumina mixed with iron powder (catalyst A), or even steel scrap filings, could catalyze the reaction at the 4 to 6% reactant level, higher surface activities of the catalyst, particularly its iron component, would be required to deal with concentration levels of SO₂ below the 1% level. One way of increasing the catalyst bed effectiveness was by pelletization and using iron powder in the micron range (catalyst B). This catalyst was quite efficient for reactions of 0.7% SO₂ and 2% CO as indicated by the data in Figure 2.

Maximum catalytic activity was always portrayed at some intermediate composition of the iron-alumina mixtures. Figure 1 shows that with 6% SO₂ and 5% CO, and at 600° C, maximization of catalytic activity was obtained with about 50% iron in catalyst A. Figure 2, on the other hand, shows that for the reaction of 0.7% SO₂ and 2% CO at 630° C, maximum catalytic activity was reached with catalyst B pellets containing about 15% iron. Although the behavioral pattern for the variation of catalyst effectiveness with its fractional iron content is essentially the same in both cases, the degree of skewness of the curve toward the pure alumina side appears to increase with increasing surface activity of the iron used. Also, the concentration levels of both SO₂ and CO appear

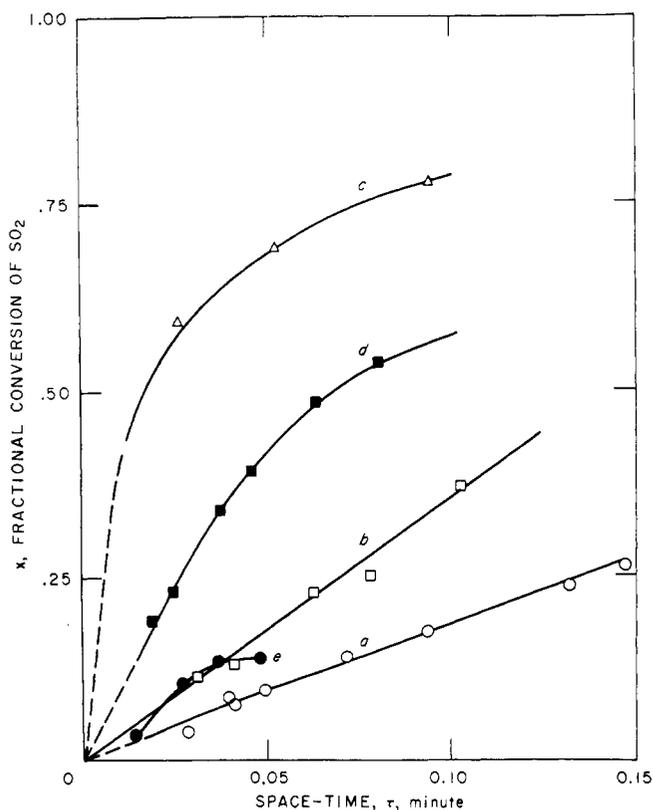
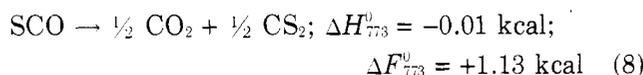
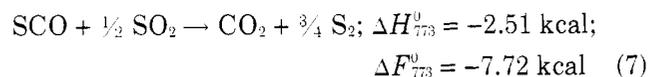
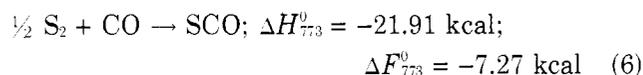
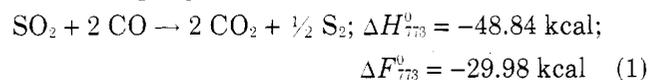


Figure 3. Effect of space-time on the SO₂ conversion at 500° C with various percentages of iron in catalyst C

| Percent iron in catalyst C | |
|----------------------------|---------|
| a. 7.2 | d. 62.0 |
| b. 23.1 | e. 86.3 |
| c. 41.2 | |

to play a role in determining the location of iron required for maximum catalytic activity. These observations suggest that the total activity of the catalyst mixture is more likely determined by a "site-per-site" rather than a gram-per-gram criterion.

Despite their value in indicating catalyst efficiency, conversion data alone cannot be normalized because they are a function of the catalyst weight and the total feed rate, in addition to temperature and pressure. Hence, the need for acquisition of some catalytic reaction rates that could be normalized was apparent. Unlike conversion data, reaction rate data require an exact knowledge of the reaction(s) taking place. Careful examination of the chromatographic peaks revealed the existence of a small but persistent peak immediately following that of sulfur dioxide. Mass spectrographic examination of a sample of reaction products at 500° C revealed the presence of the species SCO⁻, SO⁻, and very small amounts of the fragment CS₂⁻. The percent carbonyl sulfide in the exit gas decreased with increase in temperature and increased substantially when the proportions of carbon monoxide were higher than the stoichiometric requirements of Reaction 1 (Khalafalla et al., 1971). From these facts, and other evidence (Khalafalla et al., 1971), it is concluded that the following sequence of reaction occurs:



Because one mole of SO₂ consumes two moles of SCO in Reaction 7; and two moles of SCO are brought about from two moles of CO by Reaction 6, the net effect is that one mole of SO₂ is consumed by two moles of CO, which is identical with Reaction 1. Hence, the change in concentration of SO₂ can give an indication of the kinetics of Reaction 1 regardless of the postcatalytic Reac-

Table II. Effect of Catalyst C Composition on the SO₂ Conversion Rate at 500° C with an Inlet Gas of 10% CO and 4.7% SO₂

| Iron in catalyst C, % | BET surface area, meter ² /g | Rate, R _{SO₂} , mg SO ₂ /min × g catalyst | Normalized rate, R _{SO₂} , mg SO ₂ /min × g iron |
|-----------------------|---|--|---|
| 0.0 | 7.8 | 0.0 | 0.0 |
| 7.2 | 2.6 | { 8.7 | { 121.0 |
| | | { 9.2 | { 128.3 |
| 23.1 | 4.3 | { 15.4 ^a | { 66.5 ^a |
| | | { 13.6 ^a | { 59.0 ^a |
| 31.9 | 7.0 | { 36.4 ^a | { 114.2 ^a |
| | | { 35.0 ^a | { 109.6 ^a |
| 36.4 | 4.8 | 66.4 | 182.4 |
| 41.2 | 11.5 | 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 | 0.0 |

^a Duplicate runs to indicate reproducibility.

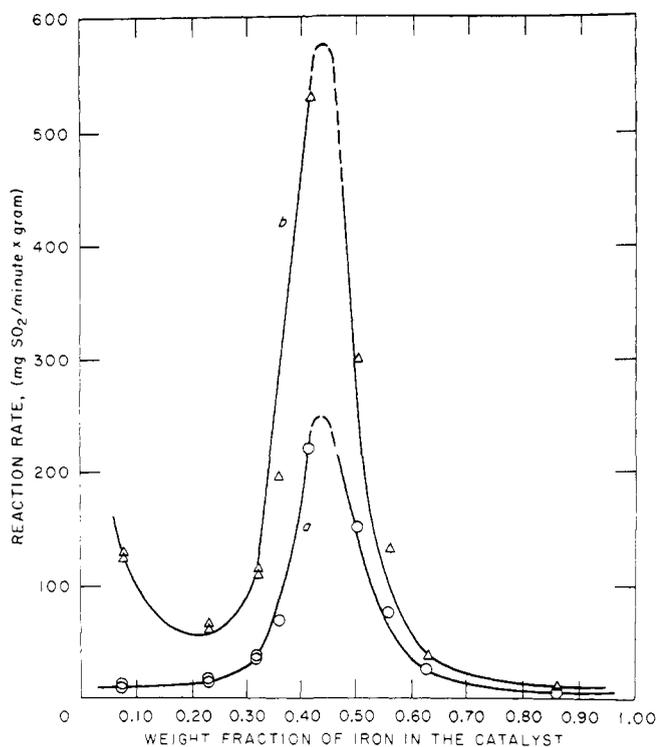


Figure 4. Effect of iron-alumina catalyst composition on the removal rate of sulfur dioxide at 500°C

- a. Rate per gram catalyst
b. Normalized rate, per gram iron

tions 6, 7, and 8. In this investigation, the fraction of SO_2 in the inlet and exit gas was accurately determined at various feed rates and the differential reaction rate was usually based on these quantities. For similar reasons, the fraction of CO_2 in the exit gas could be used to calculate the reaction rate were it not for the possible occurrence of Reaction 8 in the exit hot parts of the reactor. The fraction of CO_2 in the exit gas was slightly more than twice (Khalafalla et al., 1971) but less than 2.5 times the fraction of SO_2 removed, which is consistent with the sequence of Reactions 6 to 8.

The initial differential rate of Reaction 1 was determined at 500°C and with various compositions of catalyst C. These rates are a function of temperature and reactant pressure only. They increase proportionally with the catalyst weight and are independent of the flow rate. The variation of the differential reaction rate with the weight fraction of iron in catalyst C at 500°C is shown as curve *a* of Figure 4. The mixture containing 43% iron exhibited 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 alumina to iron up to about 40% alumina, after which the activity rose very sharply, and then dropped to very low activities when the alumina content exceeded 70%. This behavior excludes interpretations based primarily on the anti-sintering 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 further qualify this statement, the reaction rate data were normalized per gram of iron instead of per gram of total catalyst—i.e., assuming that iron is the only catalyst and that alumina provides a continuum, the only effect of which 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 II. When the normalized reaction rate was plotted against the weight fraction of iron, curve *b* of Figure 4 resulted. This curve still portrayed a sharp maximum at 43% iron, thus disqualifying any interpretation based solely on the anti-sintering effects of alumina.

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, indicates the bifunctional nature of the iron alumina catalyst. Sinfelt and Lucchesi (1963) 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. The small particle sizes of catalysts B and C, together with their pelletization, provide a good interparticle intimacy allowing for very rapid diffusion between particles of any formed gas-phase intermediate.

Summary

A bifunctional catalyst of pelletized iron-alumina mixtures can bring about the interaction of low concentration of SO_2 and CO at 500°C, 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 with the interface between alumina and iron being more active than either of the components.

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