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Active Sites for Catalytic Reduction of SO_2 with CO on Alumina

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The hydroxyl groups associated with the Brönsted acid sites in alumina are more influential in adsorbing sulfur dioxide than the more common Lewis acid sites. Hence alumina in various slightly hydrated, acid-soluble forms, such as boehmite or γ-alumina, are far more efficient than the high-temperature corundum or α-alumina. Catalyst pretreatment with HF diminished its activity because the incorporation of halogens in the alumina lattice enhanced its Lewis acidity and blocked the OH^- groups in the Brönsted sites. In the temperature range 450–600°C, the catalytic activity of alumina was practically unaffected by pretreatment with an organic base, such as quinoline, which normally blocks the Lewis acid sites. Elemental sulfur activates the alumina surface during the catalyst break-in period.

INTRODUCTION

The catalytic reduction of sulfur dioxide by a flue-gas constituent, such as carbon monoxide, offers a unique means of abating air pollution from both pollutants and of profitably recovering sulfur from its effluent gases. More than 68 billion lbs of SO_2 pour annually into the U.S. atmosphere; 75% of it results from combustion of sulfur-bearing fossil fuels. Aside from the limestone or dolomite injection (*1*), which increases the dust loading of the effluent gas and necessitates improved methods of particulate matter collection, dry absorbers such as manganese dioxide (*2*) and alkalized alumina (*3*), as well as wet absorbers, have been suggested as stopgap measures. Methods based on the Claus reaction,

$$2H_2S + SO_2 \rightarrow 2H_2O + \tfrac{3}{2}S_2, \qquad (1)$$

involve the conversion of two-thirds of the SO_2 to H_2S, which then reacts with the remaining SO_2 either in molten carbonate (*4*) or in molten sulfur (*5*) containing minute amounts of an organic nitrogen compound as a catalyst. When the flue gas is relatively rich in SO_2, as is the case with most metallurgical roasters and smelters, then catalytic oxidation to sulfuric acid becomes the method of choice.

Despite its great promise, the removal of SO_2 by catalytic reduction with CO according to

$$SO_2 + 2CO \rightarrow 2CO_2 + \tfrac{1}{2}S_2 \qquad (2)$$

has not received its deserved attention. The potential of this technique depends on the availability of CO as a reductant. In combustion of coal, some CO is formed whose quantity can be adjusted by the coal to air ratio. In practice, this method requires the furnace employing it to be operated near stoichiometric fuel to air, or perhaps slightly on the rich side. Low excess air operation of furnaces is becoming increasingly favored (*6*). The technical problems of producing a flue gas containing a small amount of CO are solvable. The needed CO can also be formed from the abundant CO_2 by regulated reduction in a bed of scrap steel in a previous step. An alternative procedure, which can also be used with metallurgical smelters, is to use a bed of coke to generate the needed CO from the unreacted oxygen. On-site conversion to elemental sulfur would facilitate transportation and storage, because sulfur weighs only half as much as an equivalent quantity of SO_2, and nearly one-third as much as the corresponding quantity of oleum. Elemental sulfur can be readily converted to sulfuric acid or other sulfur products when needed.

Events that take place on a catalyst surface are mostly movements inside a black box to us. Chemisorption and ir (7) absorption studies are commonly used to probe the species that exist on the surface, their adherence and geometric configuration. In dynamic systems, the perturbation method is adopted to learn and speculate about the catalytically reactive species. For this purpose, the alumina catalyst was subjected to planned chemical treatment which would poison some of the sites or otherwise enhance their activity.

EXPERIMENTAL PROCEDURE

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 top 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 the furnace. The catalyst temperature was measured by a platinum, platinum–10%-rhodium thermocouple and controlled to within ±2°C.

Sulfur dioxide concentration in the inlet and exit gases was determined with a Beckman* ir analyzer. An MSA infrared gas analyzer was used to determine carbon monoxide and carbon dioxide concentrations. A Fisher-partitioner gas chromatograph capable of analyzing for CO_2, SO_2, and SCO served as a double check on the preceding continuous gas analyzers. The analyzers were calibrated with commercial gas mixtures and showed an accuracy of ±0.05%.

Chemically pure grade gases were supplied to the reactor through calibrated capillary flowmeters. 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 (abs). Unless otherwise specified, the reactants consisted of 0.5 liter/min mixture of 3% SO_2, 6% CO, and the balance nitrogen.

The Brunauer, Emmett, and Teller (BET) surface area of the used catalyst 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.

A commercial alumina catalyst prepared by Harshaw Chemical Co., Cleveland, Ohio, was used in the chemical pretreatment studies. This catalyst consisted of 99% γ-Al_2O_3 cylindrical pellets one-eighth in. in both diam and length. The BET surface area of the Harshaw alumina catalyst (henceforth referred to as H-alumina) was 90 m^2/g. By contrast, the catalyst prepared from the Buehler alumina (referred to as B-alumina) had a surface area of 7.8 m^2/g. These alumina catalysts were all pretreated at 450°C for 1 hr in flowing nitrogen before adjusting the furnace temperature to the desired operating temperature and putting on the stream of reactant gases. Materials used in the catalyst pretreatment were all chemically pure reagent grade and were used without further purification.

RESULTS AND DISCUSSION

Catalyst perturbation was achieved by subjecting batches of the same alumina to various chemical pretreatments, as well as by flushing the catalyst *in situ* with various gaseous constituents. The effect of these perturbations on the catalyst performance assisted in making scientific speculations on the chemisorbed species and on their site harbingers.

Pretreatment with Chemical Reagents

Two-gram batches of the B-alumina catalyst were immersed in beakers containing 10 ml of either 48% hydrofluoric acid or 99% quinoline for 10 min, and dried at 230°C for about 65 min. The activity of

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

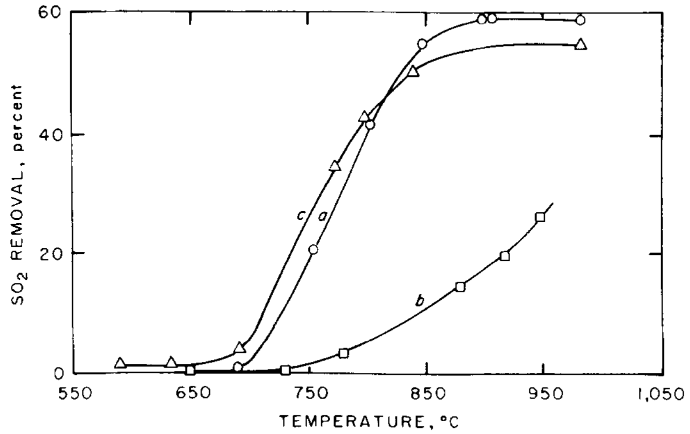

Fig. 1. Effect of pretreatment on the catalytic activity of Buehler alumina for the SO_2–CO reaction. a—Untreated (blank); b—Treatment in 48% HF; c—Treatment in 99% quinoline.

the alumina catalyst subjected to these chemical treatments is shown in Fig. 1. Percent removal of SO_2 was determined as a function of temperature on each catalyst. The results show that pretreatment with HF retarded the reaction while quinoline, if still retained, had virtually no effect.

In another series of tests, the H-alumina catalyst was treated similarly to the B-alumina catalyst, and the results are shown in Fig. 2. Additional treatments with 27% NH_4OH, H_2O, and 2.4% HF were performed on the H-alumina catalyst. The data in Fig. 2 show that HF, either diluted or concentrated, completely inhibited reaction (2) on the relatively active H-alumina catalyst up to 700°C. The other reagents, including quinoline, in the temperature range 450–650°C, gave results that are scattered around the base line of the untreated catalyst.

Isothermal experiments with H-alumina catalysts were conducted at 525°C. In these experiments, the catalyst was treated *in situ* with HF vapor and the effluent-gas analysis was followed with time. While the reactants were temporarily shut off, the HF vapor was injected through the catalyst by heating ammonium bifluoride, $NH_4F \cdot HF$, in an iron crucible to 500°C and transporting the vapor to the reactor with helium flowing at a rate of 0.5 liter/min. The variation with time of the percentage of CO and SO_2 reacted, as well as of the CO_2 and SCO

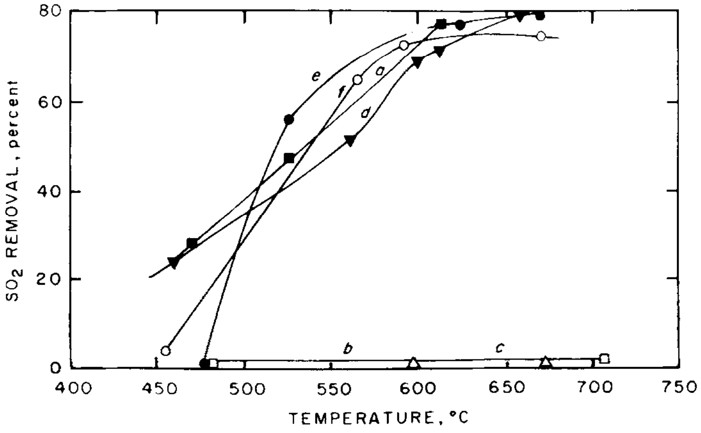

Fig. 2. Effect of pretreatment on the catalytic activity of Harshaw alumina. a—Untreated (blank); b—48% HF; c—2.4% HF; d—Quinoline; e—Water; f—27% NH_4OH.

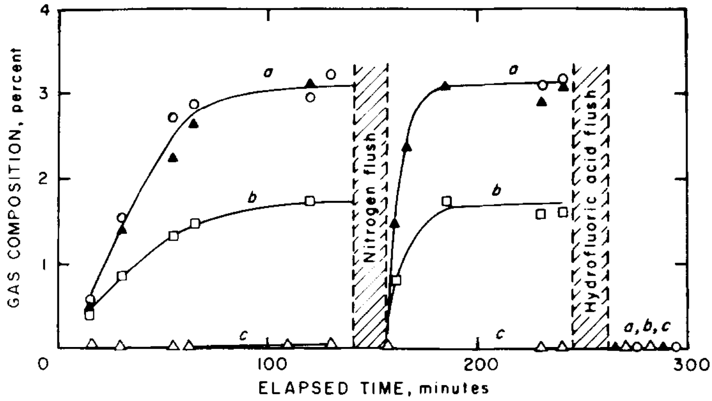

FIG. 3. Effect of HF vapor on the catalytic activity of Harshaw alumina at 525°C. a—CO reacted (○), and CO_2 formed (▲); b—SO_2 reacted; c—SCO formed.

formed, is illustrated in Fig. 3. It should be noted that with this alumina catalyst the activity increases with reaction time to reach a steady, limiting value after about 100 min. Subjecting the catalyst to a 15-min nitrogen flush before restoring the flow of the reactants gave catalyst activities of the same level as before the nitrogen flush. The steady catalyst activity is reached after about 20 min from the introduction of the reactants. The data in Fig. 3 indicate that the HF treatment of alumina completely inhibits its activity to catalyze reaction (2) at 525°C.

Temporal Variation of Catalyst Activity

Except for pelletized iron–alumina catalysts, the other catalysts including alumina alone or iron–alumina powders show a gradual improvement in their activity with time. To examine whether this "breaking-in" of the catalyst is thermal, or due to chemical action by either of the reactants or resultants, experiments were conducted with H-alumina at 540°C and with a pelletized form of α-Al_2O_3 whose BET surface area was 4.2 m^2/g. The former alumina was subjected to a 15-min SO_2 flush (in absence

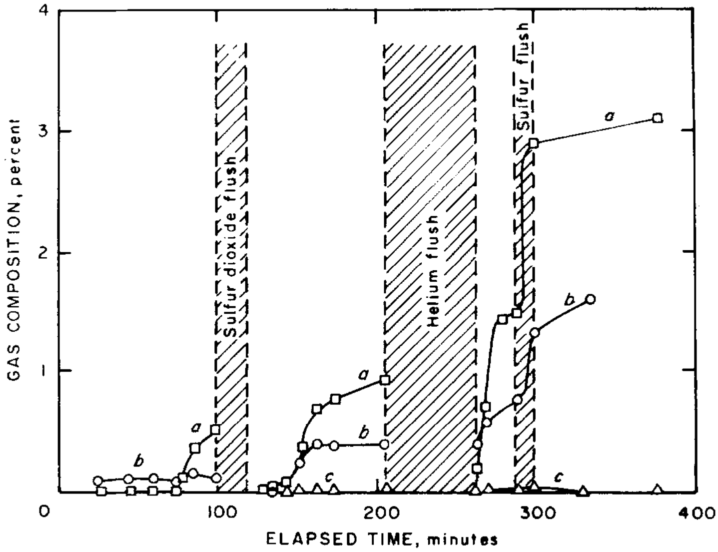

FIG. 4. Effect of sulfur vapor on the catalytic activity of Harshaw alumina at 540°C. a—CO_2 formed; b—SO_2 reacted; c—SCO formed.

of CO) when it reached nearly the midway point in its limiting catalytic activity. Upon restoring the reactants' flow, the catalyst activity increased at the same rate, when it was not treated with 3% SO_2. When the same catalyst was subjected to a 15-min sulfur-vapor flush, the activity of the catalyst was sharply exalted at a much faster rate than would have been obtained without a sulfur flush. The temporal variation of the percent SO_2 reacted and the CO_2 and SCO formed during these events are shown in Fig. 4. When the same pretreatments were repeated on the α-alumina catalyst, no sulfur activation was detected up to 670°C.

Adsorption Sites on Alumina

The foregoing results are best explained in the light of the structural and chemical properties of the alumina surface. Although the surface structure of γ-alumina is not known with certainty, the following analysis by Rideal (*8*) will be adopted. During the dehydration of hydrated alumina, pairs of surface hydroxyl groups combine to form water, leaving surface oxide and isolated hydroxyl groups. For every molecule of water formed, one oxide group is left in the top layer and one aluminum ion is left in an incomplete octahedral site on the next lower layer. The oxide groups develop on dehydration into domains of regular lattice structure, and the hydroxide groups tend to concentrate at the boundaries of these domains. Further dehydration results in the production of two or more oxide ions with electron-donating properties occupying adjoining surface sites and two or more vacancies in adjoining sites, thus producing an abnormally exposed aluminum ion with its concentrated, localized, positive charge behaving as a Lewis site. Although these sites may be beneficial in other catalytic aspects of alumina, for our purpose of ad-

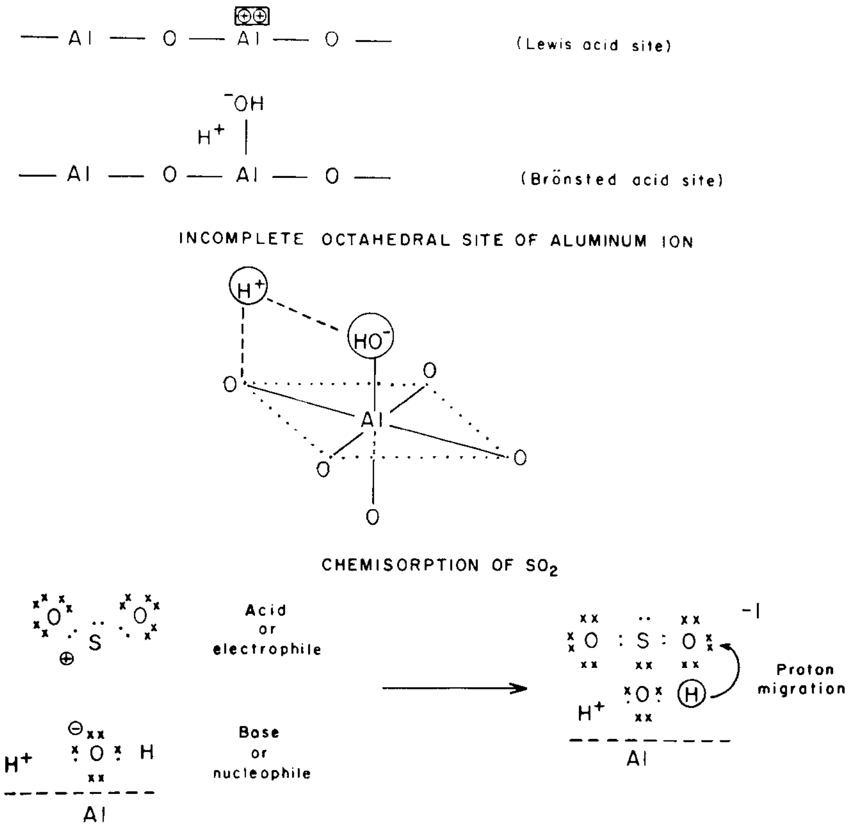

FIG. 5. Sites on alumina catalyst.

sorbing SO_2, the Brönsted are more influential.

An illustration of a typical Lewis acid site, a Brönsted site, and the incomplete octahedral configuration of the aluminum ion in alumina are given in Fig. 5.

Chemisorption is generally regarded as a precursor to catalysis. From its electronic configuration, SO_2 can be regarded as a strong Lewis acid or electrophile. It cannot, therefore, possibly attach to a Lewis acid site, but would probably prefer the basic part of a Brönsted site on the alumina catalyst. A reasonable mechanism for the chemisorption of SO_2 on an OH^- nucleophillic site is shown in Fig. 5.

Admittedly, other adsorption mechanisms are possible. The suggested view is nevertheless supported by the poisoning effect of HF towards the adsorption of SO_2 on alumina. HF replaces the OH^- surface ions with which SO_2 normally tends to hydroxylate and to form a bisulfite intermediate, HSO_3^-. Blocking of the OH^- sites by the strongly coordinated fluorine will prevent the hydroxylation of SO_2. Experience in catalysis shows that the incorporation of halogens into the alumina lattice increases the acidity of its Lewis sites, and hence promotes their catalytic action for petroleum hydrocarbons cracking (*9*), reforming (*10*), or polymerization (*11*). This is because the replacement of surface hydroxyl groups by a halogen, which possesses a much higher electron affinity, enhances the electrophillic character of a nearby Lewis site.

Electron-donating reagents, such as quinoline, will adsorb on the Lewis acid sites. At temperatures between 450–500°C, quinoline has virtually no effect on the catalytic removal of SO_2 by alumina. Hence SO_2 cannot be chemisorbed on the Lewis sites. Quinoline, on the other hand, retards (*12*) and sometimes inhibits the hydrocarbon cracking reactions on alumina or catalysts containing alumina such as zeolites.

The enhancing effect of elemental sulfur will be analyzed after the role of iron in the bifunctional catalyst is investigated in the following paper, and in the light of the electronic behavior of CO and SCO.

REFERENCES

1. Potter, A. E., *Ceram. Bull.* **48** (9), 855–858 (1969).
2. Ludwig, S., *Chem. Eng.* **75** (3), 70–72 (1968).
3. Bienstock, D., Field, J. H., and Myers, J. G., *Bur. Mines (U. S.) Rep. Invest.* 7021, 52 pp. (1967).
4. Aldenkamp, R. D., and Margolin, E. D., *Chem. Eng. Progr.* **66** (11), 73–76 (1969).
5. Wiewiorowski, T. K., U. S. Pat. 3,447,903 (June 3, 1969).
6. Reman, G. H., and Verkoren, H., *in* "The Future of Fuel Technology," (G. N. Critchley, ed.), pp. 133–149. Pergamon Press, New York, (1964).
7. Peri, J. B., *J. Phys. Chem.* **70**, 1482 (1966).
8. Rideal, E. K., *in* "Concepts in Catalysis," p. 150. Academic Press, New York, (1968).
9. Plank, C. J., U. S. Pat. 2,428,741 (October 1947).
10. Hansford, R. C., U. S. Pat. 2,678,923 (May 1954).
11. Oblad, A. G., and Messenger, J. U., U. S. Pat. 2,471,647 (May 1949).
12. Boreskova, E. G., Topchieva, K. V., and Pigusova, L. I., *Kinet. Katal.* **5** (5), 903–909 (1964).