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The Role of Metallic Component in the Iron–Alumina Bifunctional Catalyst for Reduction of SO_2 with CO

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The interaction of low concentrations of sulfur dioxide with carbon monoxide proceeds efficiently on a bifunctional iron–alumina catalyst. The iron component in the pelletized, mixed catalyst was rapidly transformed to pyrrhotite, FeS, with an apparent decrease in activity. The catalyst effectiveness then remained steady for a prolonged period of time. The catalyst decay can be temporarily delayed by carbidizing its iron component. Carbonyl sulfide by-product begins to form when all the iron surface is sulfidized; hence it was absent in the effluent gas during the catalyst break-in period. Red bauxite and Surinam red mud showed promise as commercial catalysts for recovery of sulfur from sulfurous waste gases.

INTRODUCTION

In an earlier communication (*1*) we have shown that mixtures of iron and alumina exhibit a sharp peak in their catalytic activity when compared to the individual components. The normalized reaction rate per gram of iron, instead of per gram of total catalyst, still displayed a sharp maximum when plotted against the weight fraction of iron in the catalyst. This fact, together with the absence of similar synergistic effects with iron–silica mixtures, disqualified interpretations based solely on the antisintering or supportive action of alumina on iron, and proved the bifunctional character of the catalyst.

The method of catalyst perturbation (*2*) was adopted to elucidate the nature of the active sites for reduction of SO_2 on alumina. The results can be explained on the assumption that the hydroxyl groups associated with the Brönsted acid sites of alumina are utilized for the chemisorption of SO_2 to form negatively charged bisulfite ion.

The present investigation deals with the mechanism by which catalysis of the SO_2–CO reaction takes place. Research is also portrayed to identify the active sites on each component of the bifunctional catalyst. Based on these findings, a search was conducted for potentially economic catalysts to reduce SO_2 with CO.

EXPERIMENTAL PROCEDURE

The apparatus and experimental part were described in the previous paper (*2*). The bifunctional catalyst was prepared by pelletizing a mixture of minus 100-mesh powders of Buehler (γ) alumina and hematite and indurating at 1200°C for 2 hr. The portion of the minus 16- plus 20-mesh oxide pellets required to give 2 g of reduced catalyst was inserted into the reactor, heated in nitrogen, and reduced at 600°C for 1 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 one more hour at 450°C before adjusting the furnace to the desired operating temperature. The BET surface area of the bifunctional catalyst ranged from 2.6 to 11.5 M^2/g depending on the percent iron in the catalyst.

Iron nitride, Fe_2N, was supplied by the

Electronic Space Products, Inc., Los Angeles, CA. Red bauxite was supplied by Wards Natural Science Establishment, Inc., Rochester, NY. Surinam and Jamaican red mud were kindly supplied by W. A. Stickney of the Albany Metallurgy Research Center, Albany, OR.

RESULTS AND DISCUSSION

The beneficial effect of iron on alumina catalysts for reduction of SO_2 was attributed (*1*) to a dual site mechanism in which SO_2 is preferentially chemisorbed on alumina while CO is chemisorbed on iron. To further substantiate this hypothesis, we examined the nature of the catalytically active sites in the components of the bifunctional catalyst.

Incorporation of Sulfur in the Iron

Experiments with pelletized iron–alumina catalysts show a sudden drop in the SO_2–CO reaction rate after a quasisteady state of higher activities in the first 15–20 min. Henceforth, the catalyst activity remained constant for a prolonged period. Measurements in this investigation were always taken on the steady-state catalyst, which is believed to be an "alumina–pyrrhotite" mixture. The catalyst is still preferably called "alumina–iron" because one has to start with these constituents. Attempts to use a pelletized mixture of natural powdered pyrite or pyrrhotite with alumina failed to give a measurable rate for the CO–SO_2 reaction. Apparently freshly prepared pyrrhotite, which can be conveniently and rapidly synthesized *in situ* with no additional reagents, is catalytically far superior to the natural occurring material.

Chemical and X-ray analysis of the used catalyst indicated the presence of pyrrhotite, FeS. Some pyrite, FeS_2, was also detected when an active catalyst was used for a long time at relatively lower temperatures and slower flow rates.

Material Balance of the Reaction Products

The production of sulfur from SO_2 by reduction with CO is further complicated by the formation of carbonyl sulfide, SCO, in a post-catalytic reaction step, particularly at low temperatures and with active iron–alumina catalysts. To understand the mechanism by which this by-product is formed, the exit gas from the reactor containing 9.4 g of 41% iron in alumina at 350°C was continuously analyzed for all its constituents. The variations with time of the SO_2 and CO removal as well as the SCO and CO_2 formation are shown in Fig. 1. Virtually all the SO_2 was removed in the first 20 min, while the CO removed and CO_2 formed increased in the initial break-in period. Very little SCO was formed during this period. Material balances of the reactants and products were performed by integrating the different curves in Fig. 1 over the time, i.e., by determining the area under each curve for the first 132 min. This area can be converted to liters (STP) and hence to moles of each gas consumed or produced. The results obtained for each

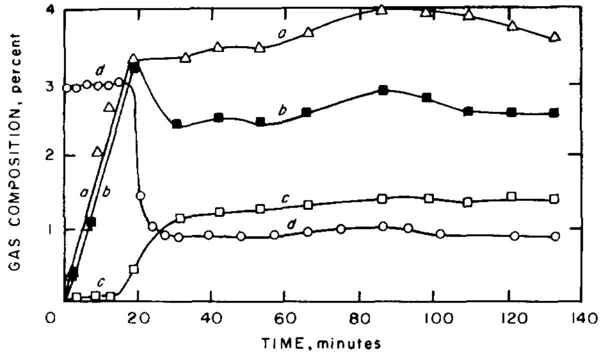


FIG. 1. Variation with time of the percent reactants removed and products formed on an iron–alumina catalyst at 350°C. *a*—CO reacted; *b*—CO_2 formed; *c*—SCO formed; *d*—SO_2 reacted.

TABLE 1
MATERIAL BALANCE FOR THE CO-SO_2 REACTION AT 350°C

Gas component	Moles removed, 0-132 min	Moles removed, 32-132 min
SO_2	0.039	0.021
CO	0.106	0.088
CO_2	−0.077[a]	−0.047
COS	−0.034	−0.032

[a] Negative removal connotes formation of the designated component.

constituent are given in the second column of Table 1.

Apparently the iron component of the catalyst is being transformed to pyrrhotite in the first 20 min by reactions such as

$$3Fe + SO_2 = FeS + 2FeO. \quad (1)$$

The gradual increase in the consumption of CO and the corresponding increase in production of CO_2 vary almost linearly with time in this initial period and are apparently due to reduction of the FeO formed. During this period no carbonyl sulfide is formed. When the iron surface is converted to pyrrhotite, the catalytic reaction begins. SCO begins to form, apparently by the interaction of excess CO with freshly formed sulfur. That this is restricted to the catalyst bed itself and does not happen in other parts of the reactor where some elemental sulfur is condensed can be surmised from the virtual absence of SCO with relatively active alumina catalyst (*2*). This accounts for the abnormally large consumption of CO (about twice the stoichiometric requirements of the CO–SO_2 reaction). Table 1 indicates that the ratio of CO_2 formed to SO_2 consumed in the time between 32 and 132 min amounts to 2.26. From the stoichiometry of the CO–SO_2 reaction, one expects a ratio of 2. This is explained by the thermal instability of SCO with respect to CO_2 and CS_2 which can occur at relatively low temperatures in the presence of a catalyst. Thermodynamic data (*4*) for the reaction.

$$2SCO \rightleftarrows CO_2 + CS_2, \quad \Delta F°_{400} = 304 \text{ cal} \quad (2)$$

reveal that the equilibrium constant for the formation of CO_2 from SCO at 123°C is 0.68. Hence, substantial quantities of CO_2 can be formed from SCO at the slightly heated exit ports of the reactor, especially under flow conditions where CS_2 may interdissolve in sulfur or condense out.

Nitrided Iron Catalyst

With the concept that metallic iron may be catalytically more efficient than pyrrhotite, it was desired to seek methods that can prevent formation of the latter compound and thus maintain the catalytic activity at its initial levels. Experience in the Fischer–Tropsch synthesis of hydrocarbons from H_2 and CO indicated (*5*) that iron nitride, Fe_2N, was a more stable catalyst than iron. Apparently Fe_2N prevents the side reactions of carbon deposition from CO disproportionation, which can be appreciable on an iron catalyst at 500°C, and also Fe_2N is not as easily carburized as iron. Likewise, if Fe_2N were not to sulfidize as easily as iron, then its catalytic activity for the SO_2–CO reaction might not undergo the initial decay. For this purpose a sample of Fe_2N was mixed with alumina powder but not pelletized. The activity of the nitrided catalysts at 760°C was about 25% higher than that of a catalyst containing elemental iron under otherwise identical conditions. The initial surface area of iron nitride and iron powder in alumina were 30.7 and 30.0 M^2/g, respectively. It was surprising that with these unpelletized catalysts the activity increased with time to reach steady, limiting values. X-Ray examination of the used catalysts indicated that both iron nitride and iron powder were converted to FeS. It appears, therefore, that under these conditions, i.e., with powdered and dispersed catalysts, the progress of sulfidization is associated with increased catalytic efficiency. This result, contrary as it may be to the previous finding with pelletized catalysts, suggests that pyrrhotite, when freshly prepared from iron, forms a better catalyst than the parent iron. Doumani *et al.* (*5*) reported that their bauxite catalyst (which contained 9% Fe_2O_3) for SO_2 reduction with hydrogen improved considerably after several hours of use. They observed that the portion at the exit end of the catalyst darkened considerably owing to sulfide formation, which was also proved by chemical analysis. This fact is of practical value because the regeneration of the sulfide catalyst is no longer necessary. If the metal or one of its oxides were the catalyst, regeneration would be necessary because of the metal sulfidization.

The apparent temporal decrease in activity with pelletized catalysts cannot be attributed to sulfidization of the catalyst but must be related to other causes. A possible explanation might be found in the partial loss of pellet internal surface area and porosity by sulfide formation and iron swelling, the molar volume of FeS being greater than that of iron. Despite the loss in pellet porosity, the limiting activity of pelletized iron–alumina catalysts is still persistently higher than the exalted activity of iron powder dispersed in alumina. Thus, while pelletized catalysts can bring about substantial reactions at 400–500°C, powdered catalysts required temperatures as high as 700–750° to bring about the same levels of activity under the same conditions of reactant concentration.

Carbided Iron Catalyst

Experiments were also conducted in which the iron component of the catalyst was carburized through carbon monoxide disproportionation by the Bell reaction:

$$2CO \rightleftarrows CO_2 + C. \qquad (3)$$

Ten grams of an equal-weight mixture of iron–alumina catalyst were treated with pure CO at 570°C for 1 hr. The quantity of carbon and/or carbide formed in the catalyst was calculated from the amount of CO_2 formed and amounted to 3.1%. The pretreated catalyst was then exposed to 3% SO_2 and 6% CO at 470°C, and the SO_2 conversion was measured. The results obtained are shown in curve *b*, Fig. 2. All of the sulfur dioxide was removed in the first 40 min with this carbided catalyst. Without CO pretreatment, complete SO_2 conversion was obtained for only 15 min with a similar, but noncarbided, catalyst, as shown in curve *a* of Fig. 2. The total sulfur formed with the carbided catalyst before the catalyst activity dropped was 1 g (20% S in Fe), while without carbidization, it was only 0.5 g (10% S in Fe). When the untreated catalyst weight was reduced from 10 to 2 g, only 0.1 g (10% S in Fe) of total sulfur was formed before the SO_2 conversion dropped, as shown in curve *c* of Fig. 2. It appears, therefore, that the carbided catalyst can withstand twice the amount of sulfur before dropping in its activity. Neither catalyst was completely sulfidized because pyrrhotite, FeS, contains 36% sulfur.

Chemisorption of Carbon Monoxide on Iron

Carbon monoxide is an exceedingly weak Lewis base, so weak that it does not form complexes with Lewis acids such as aluminum or boron compounds. With transition metals, the lone pair of electrons on carbon can form a very weak dative bond, some-

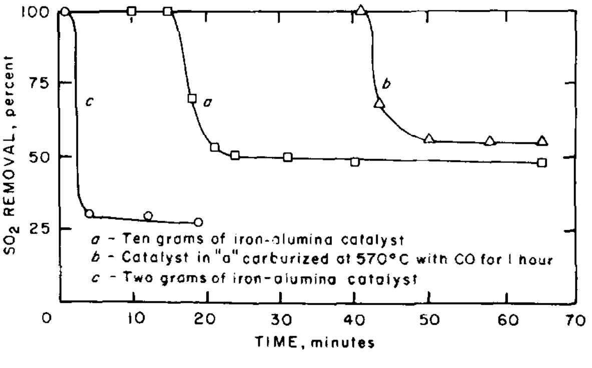
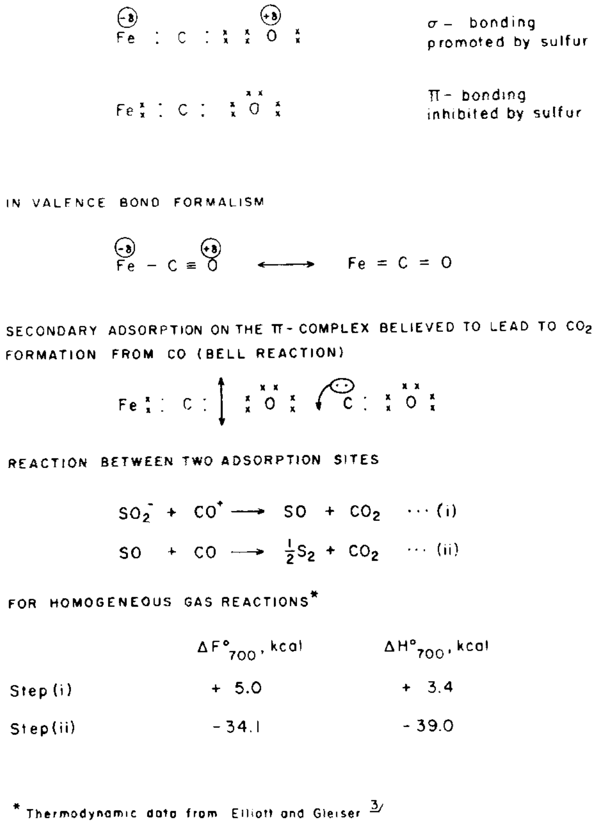


FIG. 2. Effect of iron carburization and catalyst weight on the break-in period of the catalyst.

times referred to as the σ-bond, probably with the electron density remaining close to the C atom. This bond arises from the dative overlap of the filled carbon σ-orbital with an empty metal *d*-orbital. A second dative overlap of a filled *dπ* or hybrid *dpπ* metal orbital with an empty antibonding *pπ* orbital of the carbon monoxide can also take place and gives rise to the π-bond. These two bonding mechanisms are illustrated in Fig. 3.

In the light of these bonding mechanisms, one would expect sulfur to promote the σ-bond and to inhibit the π-bond. This is because sulfur promotes the vacant *d*-orbitals in the former case by strongly occupying the two *sp* electrons donated by the metal in the latter case. Only with the π-bonding mechanism can the secondary adsorption of CO on top of the Fe=C=O complex be permitted. It is believed that when this secondary adsorption is followed by electron shift from the second carbon to the middle oxygen atom in the FeC$\updownarrow$OCO complex, and then bond splitting along the double-headed arrow (see Fig. 3 for the electronic configuration), then the final products would be CO_2 and a carbide. This mechanism is responsible for the carbon monoxide disproportionation or Bell reaction (*6*) and is also believed to be a step in the chemical mechanism of reduction of wüstite (FeO) with carbon monoxide (*7*).

The σ-bonding mechanism can lead to iron carbonyl formation under high pressures of CO where five ligands can be coordinated about a central iron atom. In agreement with experimental observation and the preceding structural considerations, sulfur promotes carbonyl formation (*8*) and inhibits iron oxide reduction (*7*). Chufarov and Antonova (*9*) reported extensive retardation of the Bell reaction on iron catalysts by sulfur and its compounds,



$$SO_2^- + CO^+ \longrightarrow SO + CO_2 \quad \cdots (i)$$

$$SO + CO \longrightarrow \tfrac{1}{2}S_2 + CO_2 \quad \cdots (ii)$$

	$\Delta F°_{700}$, kcal	$\Delta H°_{700}$, kcal
Step (i)	+ 5.0	+ 3.4
Step (ii)	- 34.1	- 39.0

* Thermodynamic data from Elliott and Gleiser 3/

FIG. 3. Iron component of the catalyst.

e.g., $CuSO_4$. Indeed, all inhibitors of the Bell reaction and reduction of iron oxide such as ammonia, mercury, sulfur, selenium, and tellurium were shown to be good promoters (*8*) for metal carbonyl formation where the σ-bonding mechanism is involved.

The foregoing analysis of the CO chemisorption mechanism readily explains why, contrary to original expectation, a surface sulfide on iron can be a better catalyst than the parent iron for the CO–SO_2 reaction. It also discriminates against any mechanism involving an initial CO disproportionation step with carbon being the real reductant in favor of a cationically chemisorbed σ-bonded CO on an iron site detaching an oxygen atom from an anionically chemisorbed SO_2 on an alumina Brönsted site; the resulting sulfur monoxide, SO, acts as an intermediate in the reaction; thus

$$CO + SO_2 \rightarrow CO_2 + SO \qquad (4)$$

followed by further reduction by CO according to

$$CO + SO \rightarrow \tfrac{1}{2}S_2 + CO_2 \qquad (5)$$

or disproportionation of sulfur monoxide according to

$$SO \rightarrow \tfrac{1}{4}S_2 + \tfrac{1}{2}SO_2. \qquad (6)$$

The present results cannot discriminate against either step (5) or (6) in favor of the other. It should be noted, however, that the summation of steps (4) and (5), or of steps (4) and (6), will lead to the same overall reaction

$$2CO + SO_2 \rightarrow \tfrac{1}{2}S_2 + 2CO_2. \qquad (7)$$

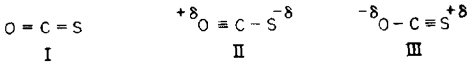
Also, thermodynamic data indicate that only step (4) is endoergic in both its free energy and enthalpy changes, and hence would be the slowest step to require catalysis. On the other hand, steps (5) and (6) are both exoergic and are expected to be relatively fast.

Accelerating Effect of Sulfur on Alumina Catalysts

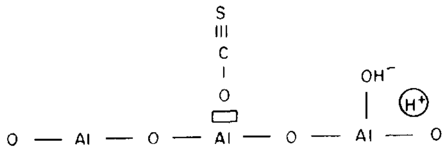
Experimental results in the preceding paper (*2*) indicate that the gradual increase in catalytic activity of alumina alone

$$2SCO + SO_2 \rightarrow 2CO_2 + \tfrac{3}{2}S_2 \qquad (8)$$

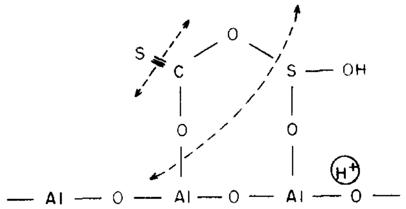
is due to the slow formation of elemental sulfur. This was substantiated by the accelerating effect of suddenly injected sulfur vapor. It appears that carbonyl sulfide, SCO, is a stronger Lewis base than CO, and hence will be able to chemisorb on the alumina Lewis acid sites. In the valence bond formalism, SCO is a hybrid of three resonance structures (*10*) as shown in Fig. 4. Structure III, in which oxygen has a residual negative charge, is probably more favored than the other structures because the oxygen atom is more electronegative than the sulfur atom. The cationically chemisorbed SCO on a Lewis site will readily react with an anionically chemisorbed SO_2 on a nearby Brönsted site by a Langmuir–Hinshelwood mechanism.



ADSORPTION OF SCO ON ALUMINA LEWIS SITE



REACTION MODEL BETWEEN TWO NEIGHBORING SITES



ROLE OF IRON IN BIFUNCTIONAL CATALYST

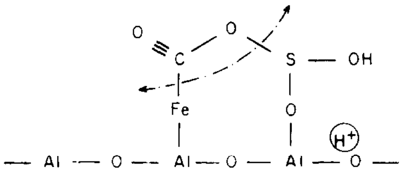


FIG. 4. Resonance structure and chemisorption of SCO.

Although the entire reaction

has not been studied in this investigation, the reaction model suggested here (Fig. 4) between two neighboring alumina sites will lead to the probable formation of CO_2, SO, and S from the primary reaction of one molecule of SCO with SO_2. From there on, the reaction path could follow steps (5) and (6), or a combination thereof.

The role of iron in the bifunctional catalyst can also be explained by the donation of its *sp* electrons to an electrophillic Lewis site on alumina. This results in strengthening the electron vacancy in the iron *d*-orbital and hence promoting the σ-bonding of carbon monoxide. The splitting of the hetero-octacyclic compound along the double-headed arrows in Fig. 4 leads to the formation of CO_2 and SO. The absence of any activity with α-alumina, even after flushing the catalyst with sulfur vapor, proves that the chemisorption of SCO on a Lewis site is a necessary, but not sufficient, condition for catalysis by alumina alone. A neighboring Brönsted site is still needed for anionic adsorption of SO_2, the reaction following a dual site mechanism. Experience with alumina and zeolite catalysts indicates that blocking of the Lewis sites usually strengthens the Brönsted sites and vice versa. Thus, treatment of alumina with hydrogen fluoride enhances the strength of the Lewis sites for ammonia adsorption, but does not create fresh acidic sites.

Potential Catalysts for the SO_2–CO Reaction

Catalysts other than pure alumina or iron–alumina mixtures were tested for their ability to remove SO_2 by interaction with CO. The choice of these catalysts was guided by the preceding basic information. They were mostly naturally occurring minerals or solid waste by-products containing mainly alumina and sometimes iron. Chemical analyses of these materials are given in Table 2. Their catalytic activity was determined at various temperatures using 2 g of the initial mineral form. The percent of SCO formed was also measured, and its ratio to the SO_2 removed was calculated in each case for purposes of normalization. Experimental data with these catalysts are combined in Table 3. The ratio of SCO formed to SO_2 removed always decreased with increase in temperature and became very small at temperatures above 600°C for catalysts made from Surinam and Jamaican red mud wastes. The decrease in SCO proportion with temperature is due not only to its thermal instability, but also to its possible interaction with SO_2 on the catalyst material, according to reaction (9). Electronic consideration and present experimental results indicate that reaction (9) is favored on pure alumina catalysts, with iron exerting a deleterious effect. The milligrams of SO_2 removed per minute per gram of each of these catalysts is shown as a function of temperature in Fig. 5.

The results in Table 2 indicate that aside from the iron–alumina catalysts, red bauxite and Surinam red mud exhibit the highest catalytic activity for the CO–SO_2 reaction. This was followed by Jamaican red mud. On the other hand, zeolite and Buehler alumina, which contained virtually no iron, showed the least activity. The high activity of Jamaican and Surinam red mud

TABLE 2

CHEMICAL CONSTITUTION OF THE CATALYSTS

Catalyst	Al_2O_3	Total Fe	SiO_2	CaO	Na_2O	TiO_2	MgO	LOI
Surinam red mud	20.7	15.7	15.0	6.3	10.4	10.3	0.05	11.3
Jamaican red mud	23.0	27.4	3.9	3.8	3.8	6.4	0.21	16.2
Zeolite(5A)[a]	39.1	0.4	43.4	10.2	4.1	—	—	—
Zeolite(4A)[a]	41.1	<0.1	44.1	—	14.7	—	0.10	—
Red bauxite	53.1	6.6	2.5	0.5	—	—	0.03	26.4
Buehler alumina	99.+	—	—	—	—	—	—	—

[a] Manufacturer's mineral identifying number.

TABLE 3
SULFUR DIOXIDE REMOVAL AND CARBONYL SULFIDE FORMATION WITH DIFFERENT CATALYSTS AT VARIOUS TEMPERATURES

Catalyst	Surface area (m^2/g)	Temp (°C)	Inlet flow (cm^3/min)	SO_2 analysis, %: Inlet	Exhaust	Removed	mg SO_2/g per min	SCO, %	SCO/SO_2 removed
Surinam red mud	7.91	463	518	4.10	2.47	1.63	12.8	0.31	0.19
		508	518	4.10	1.26	2.84	22.0	0.18	0.06
		574	518	4.10	0.04	4.06	31.0	0.05	0.01
		606	518	4.10	0.05	4.05	31.0	0.03	0.01
		644	518	4.10	0.05	4.05	31.0	0.06	0.01
Jamaican red mud	12.23	402	474	4.10	3.61	0.49	3.6	—[a]	—[a]
		419	471	4.10	1.16	2.94	20.6	0.12	0.04
		461	471	4.10	1.03	3.07	21.6	0.06	0.02
		512	474	4.10	0.35	3.75	26.3	0.05	0.01
Zeolite (4A)	5.9	493	481	4.34	3.90	0.44	3.3	0.26	0.59
		614	481	4.57	3.15	1.42	10.4	0.28	0.67
		695	481	4.57	3.43	1.14	8.4	0.33	0.29
		787	481	4.57	3.65	0.92	6.8	0.36	0.39
		828	455	4.85	3.90	0.95	6.4	0.29	0.30
Zeolite (5A)	92.6	472	504	6.34	4.65	1.69	13.2	0.53	0.31
		536	504	6.10	4.00	2.10	16.3	0.20	0.10
		603	504	5.92	3.45	2.47	19.0	0.10	0.04
Red bauxite	100.4	400	500	6.05	4.50	1.55	11.8	0.85	0.55
		449	500	6.05	3.05	3.00	22.9	0.45	0.15
		499	500	6.05	2.50	3.55	26.6	0.25	0.07
		600	500	5.80	1.80	4.00	30.3	0.10	0.02
Buehler alumina	7.4	690	629	3.00	3.00	0.00	0.0	0.00	0.00
		756	629	2.97	2.37	0.60	5.6	0.00	0.00
		804	635	3.00	1.76	1.24	11.8	0.08	0.06
		848	635	3.00	1.38	1.62	15.4	0.07	0.04
		904	635	3.00	1.26	1.74	16.5	0.09	0.05
41 percent iron in Buehler alumina	11.5	353	574	3.11	2.82	0.29	2.5	—[a]	—[a]
		368	564	3.08	2.45	0.63	5.4	—[a]	—[a]
		404	564	3.12	1.45	1.67	14.1	1.50	0.90
		449	563	3.10	0.84	2.26	18.9	0.38	0.17
		501	564	3.10	0.27	2.83	23.6	0.24	0.08
		557	566	3.10	0.07	3.03	25.3	0.14	0.05

[a] Not available.

wastes is very encouraging because over 5 million tons of these wastes are discarded each year in the United States. The utilization of this solid waste for the recovery of sulfur from waste gases has obvious advantages, as two pollution problems may be solved simultaneously.

CONCLUSIONS

The catalytically active sites for the reduction of SO_2 with CO are believed to be the hydroxyl group associated with a Brönsted acid site on alumina and a *d*-orbital electron pair vacancy in iron. In the absence of iron, the reaction with activated γ-alumina alone is slowly promoted by the product sulfur. Carbonyl sulfide is a better reductant than CO for SO_2 on γ-alumina catalysts with no iron present.

The iron–alumina bifunctional catalyst is still superior for SO_2 removal despite the formation of the by-product SCO at lower temperatures. A two-stage catalyst comprised of iron and alumina in one reactor, followed by pure γ-alumina in a second reactor, could remove the last rem-

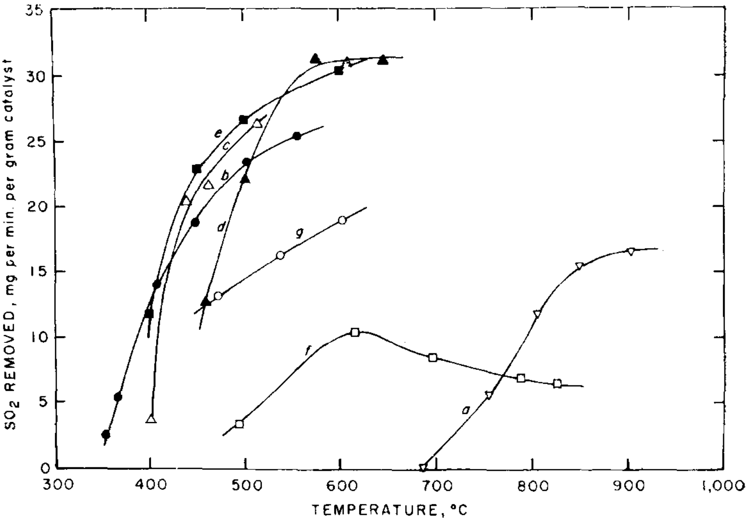


FIG. 5. Catalytic efficiency of various alumina-containing products for the removal of SO_2. *a*—Buehler alumina; *b*—41% iron in alumina; *c*—Jamaican red mud; *d*—Surinam red mud; *e*—Red bauxite; *f*—Zeolite (5A); *g*—Zeolite (4A).

nants of SO_2 and the by-product SCO. X-Ray and chemical analyses, as well as electronic considerations, indicated that freshly formed pyrrhotite on the iron surface together with alumina comprise the true catalyst. The reaction mechanism on both pure alumina and iron–alumina catalysts is believed to involve the formation of sulfur monoxide intermediate, which is either further reduced to elemental sulfur and/or undergoes disproportionation to sulfur dioxide and elemental sulfur. Surinam and Jamaican red mud wastes can be utilized for efficient removal of SO_2 from stack gases and recovery of sulfur.

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