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Kinetic Evidence of a Reactive Intermediate in Reduction of SO_2 with CO

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Rates of SO_2 reduction with CO on single beds of Fe/SiO_2, Fe/Al_2O_3 and $Fe/SiO_2/Al_2O_3$ catalysts were measured. Under comparable conditions, the SO_2 reduction was much greater when both Fe and Al_2O_3 were present. The results could not be explained on the basis of additivity of the separate catalytic contributions of the individual components of the mixtures. Experimental data indicate that a cooperative effect between the Fe and Al_2O_3 component is involved. The exhaust SCO concentration from a single catalyst layer containing Fe was still quite large at 400°C. However, when a second layer of pure Al_2O_3 was present, the SCO exhaust concentration decreased by a factor of ten. These results suggest that a SCO intermediate is first formed on the Fe site. This intermediate then is removed by the alumina component which acts as a catalyst for the SCO–SO_2 reaction. The stepwise reactions at separate active centers explain why both Fe and Al_2O_3 are needed to catalyze the reduction of SO_2 with CO to yield elemental sulfur and CO_2.

INTRODUCTION

Al_2O_3 and SiO_2 have long been used as supports for metal catalysts. The function of a true support is to separate the metal atoms and thereby prevent crystal growth, which decreases the active metal effective surface area. However, in some cases the support is also active, as in the case of hydrogenation–dehydrogenation reactions where the acid oxide performs one function and the metal another (*6*). Bifunctional catalysts have received considerable attention in organic reactions, but very little fundamental research has been reported on the optimum catalyst composition for sulfur production from SO_2. Lepsoe (*4*) reported that bauxites containing iron oxides are good catalysts but gave no explanation why they were effective. Previous research performed at the Twin Cities Metallurgy Research Center reported that the optimum amount of Fe in Al_2O_3 depends on the method of preparation (*2*). In a later publication (*3*), it was reported that the sulfur produced combined first with the Fe and later with CO, forming carbonyl sulfide (SCO). The objective of this report was to determine the functions of the two-component catalyst and to evaluate the role of SCO gas. Evidence is presented in this paper for a proposed mechanism for the catalytic reduction of SO_2 with CO.

EXPERIMENTAL WORK

Apparatus and Procedure

A detailed description of the experimental apparatus has been previously published (*1*). The catalyst was held in a ½-in. diameter Vycor* tube on a perforated porcelain disk. In the experiments with dual

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* Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.

catalysts bed, one catalyst was poured directly above the other. The reaction gases were mixed from commercial tanks, and the inlet and outlet gases were analyzed with a chromatograph and infrared analyzers. The furnace gases were at 1.1 atm and were metered at a nominal flow rate of 0.5 liter (STP) per min. In a typical experiment, the procedure consisted of placing the catalyst (amount needed to obtain 2 g of catalyst after reduction) in the reactor and heating to 600°C in N_2, reducing in H_2 for one hour, and then cooling to operating temperature in He. In the dual bed studies, 1-g layers of each catalyst were used. The reactants (3% SO_2, 6% CO, and the balance He) were passed through the catalyst bed for one hour to obtain steady state conditions. The catalyst effectiveness was then determined from the SO_2 conversion and SCO formation.

Materials

Chemically pure (>99.5%) gases from commercial cylinders were used. The Al_2O_3 and Fe_2O_3 were reagent-grade materials. Two kinds of silica were investigated. "Cabosil" (99% SiO_2) had a low bulk density, while the opposite was true with 98% SiO_2 obtained from Wausau, Wis. The two silicas will be referred to in the text as c-SiO_2 and w-SiO_2, respectively. The materials were agglomerated by blending the minus 100-mesh oxides in the desired ratios, and then extruded as a wet paste mixture through 16-mesh screen. The extruded material was then dried to constant weight at 400°C and screened to minus 16, plus 20 mesh. The pellets were then indurated in air at 1200°C for two hours. X-ray diffraction measurements of the pellets after 1200°C heat treatment indicated the absence of iron silicates. Alumina was converted from the gamma to the alpha form.

The ternary catalyst mixtures ($Fe/SiO_2/Al_2O_3$) were prepared by two methods: (1) mixing the above-mentioned Fe/SiO_2 binary pellets with the Al_2O_3 pellets; and (b) grinding the Fe/SiO_2 and Al_2O_3 (or SiO_2) together to minus 100 mesh, and repelletizing. All the oxide pellets were reduced at 600°C for one hour with 0.5 liter per minute H_2 flow before each test.

RESULTS AND DISCUSSION

Single Catalyst Bed Studies

The SO_2 conversion was measured with the various catalyst mixtures. It is evident from the results shown in Table 1 that no measurable SO_2 conversion occurred with 100% w-SiO_2, c-SiO_2, and Al_2O_3 at 600°C. With pure Fe, some SO_2 removal was obtained. When Fe powder was mixed or supported with SiO_2 powder and pelletized, more than twice as much SO_2 was converted. However, when alumina was pelletized with 41% Fe, almost 9 times more SO_2 conversion was obtained.

To prove that Al_2O_3 was not acting solely as a support, Fe/c-SiO_2 pellets (minus 16, plus 20 mesh) were simply blended with an equal amount of the same size c-SiO_2. The additional SiO_2 decreased the conversion by about two. However, when Fe/c-SiO_2 pellets were simply mixed with Al_2O_3, the SO_2 conversion was five times greater than when they were mixed with c-SiO_2. The simply mixed samples were also ground together and repelletized. This procedure increased the activity of all the catalysts, but the SO_2 conversion was still twofold larger with Al_2O_3 than with SiO_2.

These results indicate that Al_2O_3 does not act merely as a support, but also functions as a catalyst component when pelletized or simply mixed with Fe. Also, the exceptionally high activity of Fe with Al_2O_3 mixture cannot be explained by the additivity of the individual catalytic contributions. The results clearly indicate that a mutual cooperative effect is involved.

From Table 1, another observation can be made. With catalysts that contain alumina, less SCO is formed per percent of SO_2 conversion. The last column indicates that when Al_2O_3 was absent, the (SCO)/$(SO_2)c$ ratio was more than 10 times greater. One would therefore suspect that Al_2O_3 is involved in removing SCO. The Reactions 1 through 6 were, therefore, postulated as the overall reaction scheme.

TABLE 1
EFFECT OF CATALYST COMPOSITION ON THE SO_2 CONVERSION AND SCO PRODUCTION
600°C

Catalysts	Surface area, m^2/g	Conversion, $(SO_2)c$, percent	(SCO), percent	$\frac{(SCO)}{(SO_2)c}$
Single Components				
100% w-SiO_2	46.7	0.0	0.00	0.00
100% c-SiO_2	335.2	.0	.00	.00
100% Al_2O_3	7.8	.0	.00	.00
100% Fe	1.2	4.0	—	—
Supported Fe (pelletized together)				
41% Fe in c-SiO_2	1.7	8.2	0.39	0.048
41% Fe in w-SiO_2	3.8	8.6	.88	.102
41% Fe in Al_2O_3	5.7	72.3	.05	.001
Supported Fe + Oxide (simple mixture)				
50% (41% Fe in c-SiO_2) + 50% c-SiO_2	168.3	3.0	0.15	0.049
50% (41% Fe in c-SiO_2) + 50% Al_2O_3	3.7	15.0	.03	.002
Supported Fe + Oxide (pelletized together)				
50% (41% Fe in c-SiO_2) + 50% c-SiO_2	103.0	19.0	0.60	0.032
50% (41% Fe in c-SiO_2) + 50% Al_2O_3	4.1	44.0	.09	.002

This proposed scheme suggests that the sulfur formed by reaction 1 first reacts with iron to form pyrite (Reaction 2). Pyrite then reacts with CO to form pyrrhotite by Reaction 3. The free energies of these reactions are all negative so these reactions are all possible. Experimental evidence for Reactions 1, 2, and 3 can be seen from Fig. 1, where very little SCO is formed initially but more is formed as the

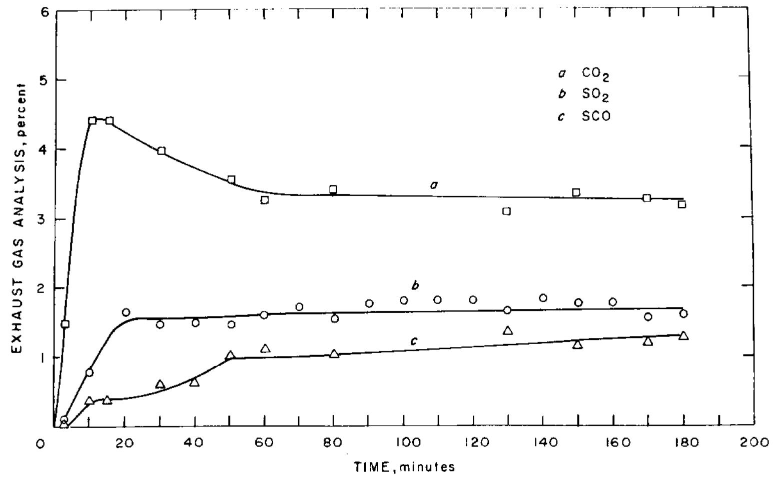
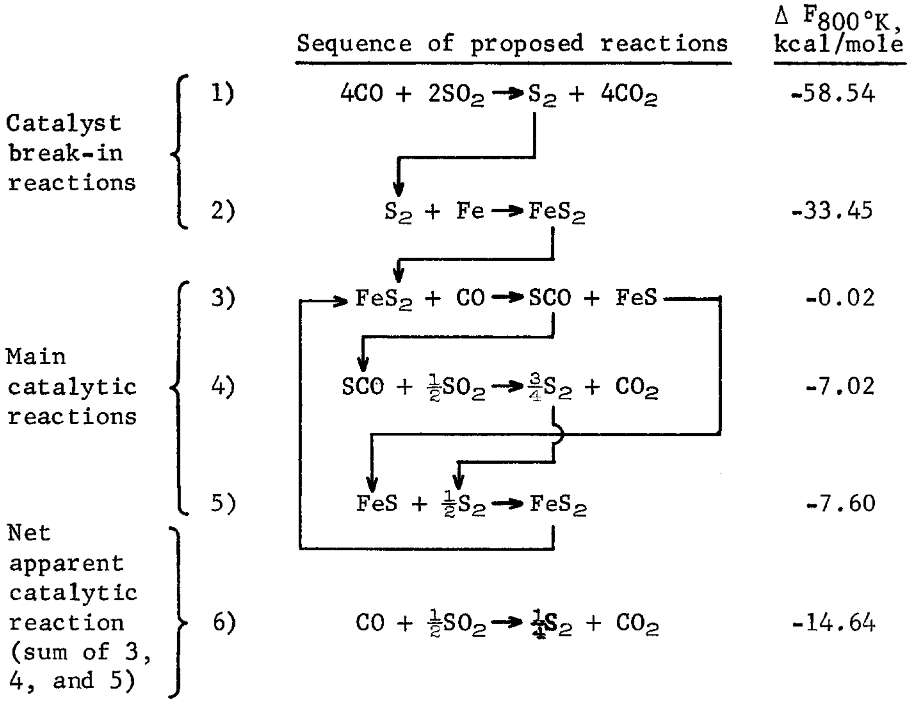


FIG. 1. Exhaust gas-time variation with iron-alumina catalyst at 400°C.



		Sequence of proposed reactions	$\Delta F_{800°K}$, kcal/mole
Catalyst break-in reactions	1)	$4CO + 2SO_2 \rightarrow S_2 + 4CO_2$	-58.54
	2)	$S_2 + Fe \rightarrow FeS_2$	-33.45
Main catalytic reactions	3)	$FeS_2 + CO \rightarrow SCO + FeS$	-0.02
	4)	$SCO + \frac{1}{2}SO_2 \rightarrow \frac{3}{4}S_2 + CO_2$	-7.02
	5)	$FeS + \frac{1}{2}S_2 \rightarrow FeS_2$	-7.60
Net apparent catalytic reaction (sum of 3, 4, and 5)	6)	$CO + \frac{1}{2}SO_2 \rightarrow \frac{1}{4}S_2 + CO_2$	-14.64

iron is converted to iron sulfide. X-ray diffraction and chemical analysis of used catalysts verified the presence of FeS and FeS_2.

Previously it was shown in Table 1 that the percent SCO formed per percent SO_2 conversion is small in the presence of Al_2O_3. Therefore, it appears that Al_2O_3 is a good catalyst for Reaction 4. This hypothesis was verified by the results shown in Fig. 2. Curves a″ and b″ indicate that Reaction 4 is fast either with pure Al_2O_3 or with Fe added, while curves a′ and c′ show that both Al_2O_3 and Fe are poor catalysts for Reaction 1. However, with a mixture of Fe and Al_2O_3 (curve b′), Reaction 1 is fast. Therefore, it appears the function of the Fe component (a precursor to the real catalyst iron sulfide) is to promote the formation of SCO. The more sulfur formed,

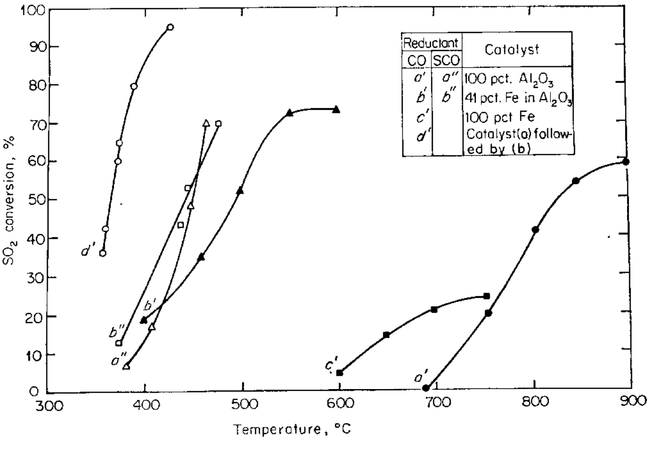
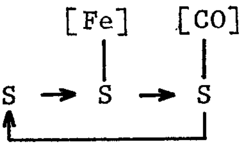


Fig. 2. Effect of reductant on the temperature dependence of the SO_2 conversion on various catalysts.

the farther Reaction 2 will go to the right and the more SCO is formed (Reaction 3). The function of the Al_2O_3 is to interact SCO with SO_2 to form more sulfur, which perpetuates the cycle. Fe and CO are merely sulfur carriers, as shown in the following model:



Mixing the powdered Al_2O_3 directly with the Fe made the sulfur cycling easier by permitting the SCO to contact Al_2O_3 immediately after it was formed. Weisz (*8*) also reported a stepwise reaction involving an intermediate where the two catalyst components were more effective when in intimate physical contact.

To prove that SCO could be formed according to Reaction 3, a used Fe/Al_2O_3 catalyst was heated up in nitrogen to 426°C and then reacted with 6% CO in He. The SCO exhaust analysis is shown in Fig. 3. It is evident from these results that Reaction 3 is a possible step in the overall SO_2 reduction with CO. Other investigators (*7*) have also reported that SCO is formed from iron sulfide and CO. Parish and Urmy (*5*) have reported the formation of SCO by the interaction of sulfur and carbon monoxide on Co–Mo catalyst.

Dual Catalyst Bed Studies

Not all of the SCO was removed even when an Fe/Al_2O_3 catalyst was used. Therefore, attempts were made to decrease this toxic gas to still lower levels. Previously, results had shown that Al_2O_3 decreases the SCO in a single catalyst bed. Therefore, if Al_2O_3 is placed after Fe/Al_2O_3 catalyst, the net reaction should be increased. This indeed was the case, as the results in Fig. 2 indicate. The SO_2 conversion with Al_2O_3 alone (curve a′) was poor; with Fe/Al_2O_3 (curve b′) the conversion was better; with both catalysts on separate layers, over 90% SO_2 conversion was obtained at 410°C (curve d′). The results in Fig. 4 indicate the SCO exhaust was also considerably lower with the dual catalyst (curve b) than with the single Fe/Al_2O_3 catalyst (curve a).

CONCLUSIONS

Experimental results showed that the $CO–SO_2$ reaction is slow with Fe, Fe/SiO_2, or Al_2O_3 but fast with a mixture of Fe or Fe/SiO_2 with Al_2O_3. The synergistic ef-

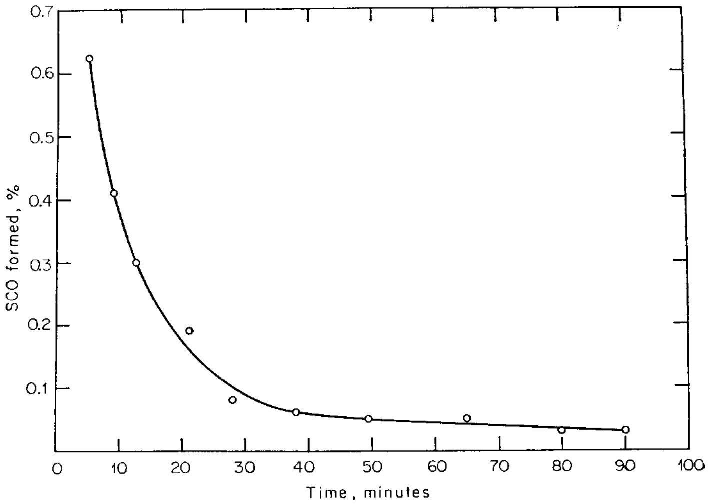


FIG. 3. Carbonyl sulfide formation from used $Fe–Al_2O_3$ catalyst.

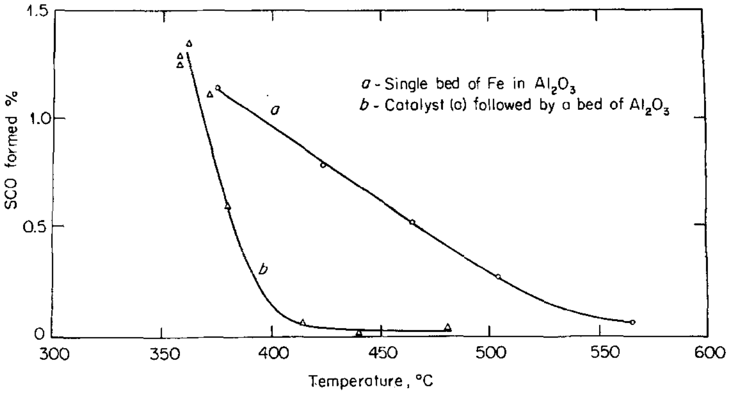


FIG. 4. Temperature dependence of SCO formation with single and dual catalyst bed.

fect of a catalyst containing both Fe and Al_2O_3 is explained by the formation of SCO intermediate and its later reaction with SO_2. Al_2O_3 does not sulfidize readily by itself so a metal must be present that forms a metal sulfide that can react with CO to form SCO. Experimental evidence of the formation of a stable SCO gas was obtained by reacting CO with a used Fe/Al_2O_3 catalyst. The function of Al_2O_3 is to interact the SCO formed with SO_2. Al_2O_3 is more effective in removing the SCO formed if placed in a second layer after the Fe/Al_2O_3 catalyst. With a dual catalyst bed, over 90% SO_2 conversion was obtained at 410°C with an SCO exhaust concentration of 0.05%.

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