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Catalytic Thermal Decomposition of Carbonyl Sulfide and Its Reaction with Sulfur Dioxide

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The thermal decomposition of carbonyl sulfide (SCO) was studied in an integral reactor with various catalysts. An apparent activation energy of 28.7 kcal/mole was measured for SCO decomposition without a catalyst. In presence of a contact catalyst such as alumina or silica, the apparent activation energy was lowered to 5.6 kcal/mole. At temperatures below 635°C, the main decomposition products of SCO were CO_2 and CS_2. At higher temperatures, the main products were CO and S. With pure chi-alumina, the decomposition of SCO at 550°C was 35%, but when a stoichiometric quantity of SO_2 was added to SCO, about 90% of the SCO and SO_2 were converted at a much lower temperature (about 400°C). The degree of interaction of SCO and SO_2 was greater with pure chi-alumina than when transition metals were present.

INTRODUCTION

The thermal decomposition of carbonyl sulfide (SCO) was studied at the U. S. Bureau of Mines as a means of recovering sulfur from sulfurous waste gases. SCO is a common pollutant in petroleum refineries (*1–3*), in iron and steelmaking (*4*), and in the carbonaceous reduction of SO_2 or metal sulfides (*5, 6*). Earlier research (*7*) in this laboratory has shown that less SCO is formed when SO_2 is reduced with CO at high temperatures. The quantity of SCO formed was also found to be related to the type of catalyst used (*8*). Transition metal catalysts that formed unstable sulfides appeared to produce the largest quantity of SCO (*9*). When an alumina catalyst was placed after the transition metal on an alumina catalyst bed at 450°C, less than 0.1% SCO was measured in the exhaust gas (*10*). To examine the variation of the quantity of SCO formed with different catalysts and at various temperatures, an investigation was undertaken to determine the thermal stability of this gas in the presence and the absence of SO_2.

EXPERIMENTAL WORK

Apparatus and Procedure

A detailed explanation of the experimental apparatus has been previously published (*7*). The catalyst pellets (⅛-in. diam) were held in a ½-in. diam Vycor* tube on a perforated porcelain disk. The inlet and outlet reactant gas mixtures were analyzed with a chromatograph and infrared analyzers. The gas mixture (1.1 atm) was metered through the catalyst bed at a nominal flow rate of 0.4 liter (STP)/min. In a typical experiment, the procedure consisted of placing 2 g (about 50 pellets) of dried catalyst in the reactor, heating to 600°C in N_2, reducing in H_2 for 1 hr, and then cooling to operating temperature in He. In the tests involving the addition of CO_2 and CO to SCO, 20 g of catalyst were used. The gaseous reactants were passed through the catalyst, and the SCO and/or SO_2 steady-state conversion was deter-

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

mined. Steady-state conversions were reached in less than 1 hr.

Materials

The gases were chemically pure (>99.5%) as obtained from commercial suppliers. The catalysts were used as received from the manufacturer except the chi-alumina catalysts that were impregnated with transition metals. In the latter case, the evacuated chi-alumina (about 50% porosity) was immersed in nitrate solution containing 5% metal ions and then dried at 400°C. The final metal concentration in alumina varied between 2 and 3%. The alumina crystal structure was identified by X-ray diffraction, and the surface areas were determined by the volumetric BET (Brunauer–Emmett–Teller) nitrogen adsorption method in Table 1.

RESULTS AND DISCUSSION

Decomposition of SCO

The thermal decomposition of SCO (nominal 3.5%) in He was first studied in

TABLE 1
THERMAL DECOMPOSITION DATA OF SCO ON VARIOUS COMMERCIAL CATALYSTS

Catalyst	Surface area (m²/g)	Temp (°C)	SCO inlet (%)	Fraction of SCO decomposed	CO formation (%)	CO₂ formation (%)	Selectivity ratio (CO₂/CO)
None	—	680	6.51	0.19	1.06	0.08	0.075
		720	6.51	0.37	3.29	0.09	0.027
		760	6.51	0.65	4.20	0.05	0.012
α-Al_2O_3(A)	4	592	6.03	0.44	0.94	0.79	0.840
		672	6.12	0.58	2.00	0.77	0.385
		746	6.12	0.69	3.26	0.52	0.159
		762	6.12	0.70	3.40	0.53	0.155
α-Al_2O_3(B)	8	480	3.63	0.34	0.19	0.54	2.842
		592	3.64	0.45	0.66	0.53	0.803
		678	3.69	0.57	1.36	0.43	0.316
		724	3.72	0.63	1.73	0.35	0.202
		762	3.73	0.67	2.09	0.34	0.163
χ-Al_2O_3	100	474	6.33	0.32	0.34	1.03	3.029
		536	6.33	0.38	0.69	1.08	1.565
		648	6.33	0.53	1.96	0.89	0.454
χ-Al_2O_3 + 58% Ti	70	534	6.33	0.37	0.61	1.00	1.639
		618	6.33	0.48	1.45	0.92	0.634
		668	6.33	0.56	2.23	0.80	0.359
		714	6.33	0.61	2.26	0.72	0.319
χ-Al_2O_3 + 2.5% Fe	90	520	5.82	0.32	0.44	0.80	1.818
		549	5.82	0.35	0.62	0.80	1.290
		565	5.82	0.37	0.78	0.81	1.038
		604	5.82	0.43	1.09	0.76	0.697
		640	5.82	0.48	1.48	0.71	0.480
		680	5.82	0.54	2.02	0.65	0.322
		718	5.82	0.62	2.68	0.55	0.205
Silica gel	500	566	6.51	0.35	0.72	0.80	1.111
		590	6.51	0.38	1.00	0.75	0.750
		638	6.51	0.49	1.77	0.79	0.446
		673	6.51	0.57	2.19	0.73	0.33
		710	6.51	0.64	2.80	0.65	0.232

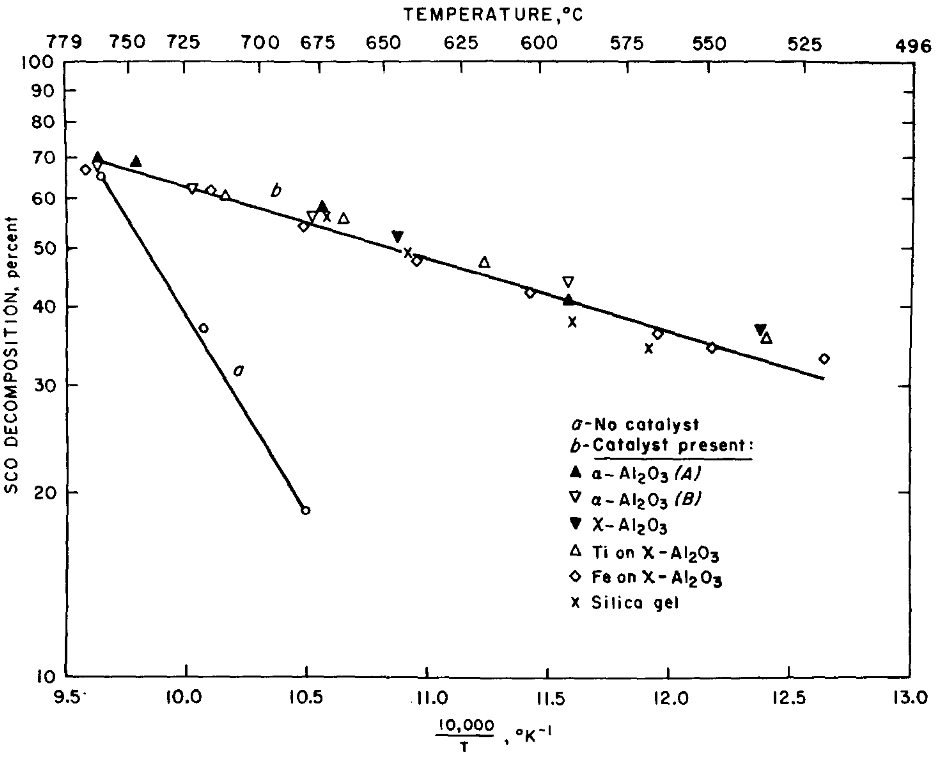

FIG. 1. Arrhenius plots of SCO decomposition.

an empty Vycor reactor. No measurable decomposition of the gas was observed at low temperatures, but at 680°C SCO was 19% decomposed (Fig. 1, Curve a). There were much higher percentages of decomposition when 2 g of either silica gel or alumina catalyst were present (Curve b). The results in Table 1 indicate that at a given temperature the degree of decomposition was approximately the same for the various catalysts regardless of their BET surface areas or chemical composition. The type of adsorption site apparently is not too critical. Neglecting the change in actual gas space time with operating temperature, the percentage conversion at constant feed rate can be taken as a measure of the reaction rate.

The apparent activation energies ($\Delta H\ddagger$) (calculated from the slopes of Curves a and b in Fig. 1) were 28.7 and 5.6 kcal/mole decomposed in absence and presence of a catalyst, respectively. The higher degree of decomposition and the lower $\Delta H^{\ddagger}$ values with catalysts are usually explained by the exothermic heat of chemisorption of the reactant on the catalyst which weakens the interatomic bonds and permits them to rupture more readily.

Carbonyl sulfide can decompose by two reaction paths as shown below:

$$SCO \rightarrow \tfrac{1}{2}CO_2 + \tfrac{1}{2}CS_2 \qquad (1)$$

and

$$SCO \rightarrow CO + \frac{1}{x}S_x, \qquad (2)$$

where x can be 1, 2, 4, 6, and 8. It would seem from the equilibrium constant[†] (K) versus temperature data in Fig. 2 (Curves e to h) that at temperatures below 600°C SCO would decompose more readily via reaction (*1*). However, since thermodynamic

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[†] Equilibrium constants were calculated from thermodynamic data published by Elliott and Gleiser (*11*).

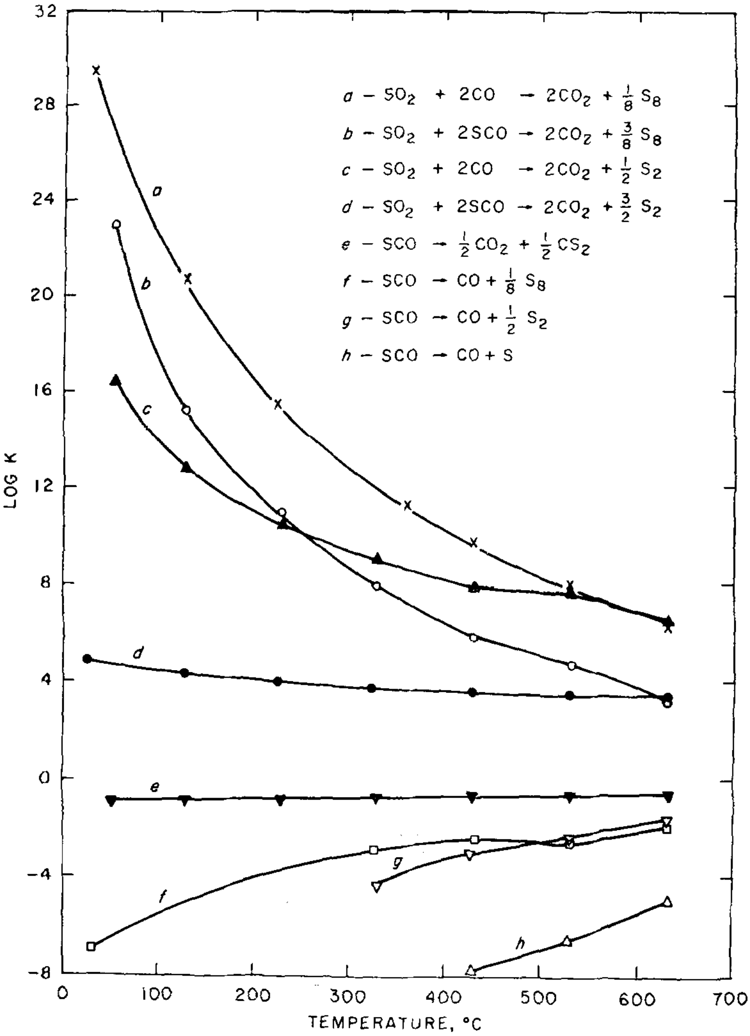

FIG. 2. Effect of temperature on the equilibrium constant of various reactions involving the C–O–S system.

data only give the equilibrium concentrations without regard to how the equilibrium state is reached, the actual decomposition reaction path can be determined only by kinetic means. To determine the relative degrees of decomposition of the two alternate paths, the products produced from SCO decomposition were investigated. It is evident from Fig. 3 and Table 1 that selectivity for reaction (1) (as determined by the molar ratio of CO_2 to CO formed) was much higher at lower temperatures. The percentage of SCO decomposition of reaction (1) would equal that of reaction (2) at a molecular selectivity ratio of one-half. Therefore, reaction (1) is faster than reaction (2) at temperatures below 635°C, while the reverse is true above this temperature. Garlet and Grandet (*12*) and Caddick (*13*) observed that reaction (1) predominates at lower temperatures. By contrast, reaction (2) was found to occur much faster in an electrical discharge at a gas temperature of 25°C (*14*), but here the electron temperature was much higher ($\sim$10,000°C).

Increasing the inlet CO_2 or CO concentration should suppress reactions (1) or

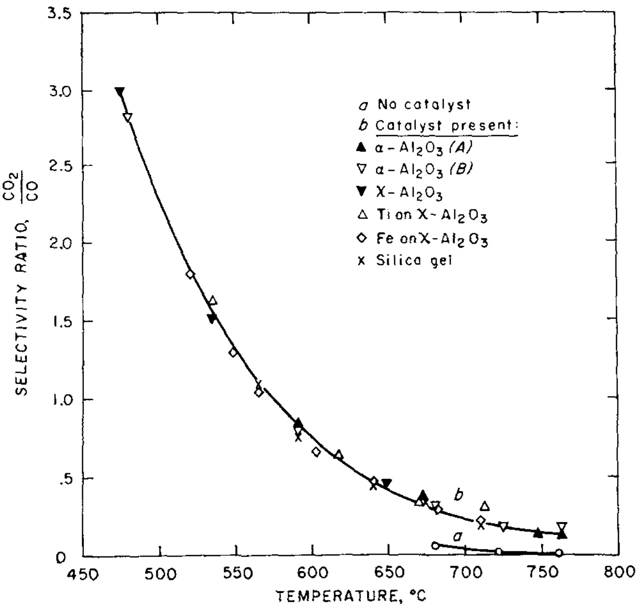

FIG. 3. The dependence of the selectivity ratio for the formation of CO_2 and CO in the decomposition of SCO.

(2), respectively. The quantity of CO_2 and CO formed was therefore studied at different inlet gas concentrations. Different quantities of CO or CO_2 were mixed with 3.5% SCO in He. With no CO added, the quantity of CO formed was almost twice that of the CO_2 (Fig. 4). However, when CO was introduced with SCO, the quantity of CO formed dropped rapidly to zero at a CO inlet concentration of less than 7% (Curve a), while the quantity of CO_2 formed increased only slightly (Curve b).

Upon introducing CO_2 with the SCO in the inlet gas, the quantity of CO_2 formed rapidly decreased to zero at less than 6% CO_2 (Fig. 5, Curve b), while the percentage of CO formed slightly increased (Curve a). These experiments indicate that the decomposition path of SCO can be controlled, and the formation of elemental sulfur can be maximized by adding CO_2. These results are consistent with thermodynamic data and also with those reported by Partington and Neville (*15*).

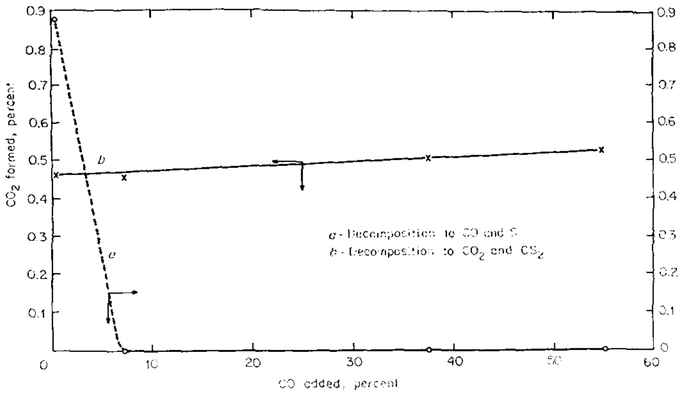

FIG. 4. Effect of CO additions on the thermal decomposition of SCO with a silica gel catalyst.

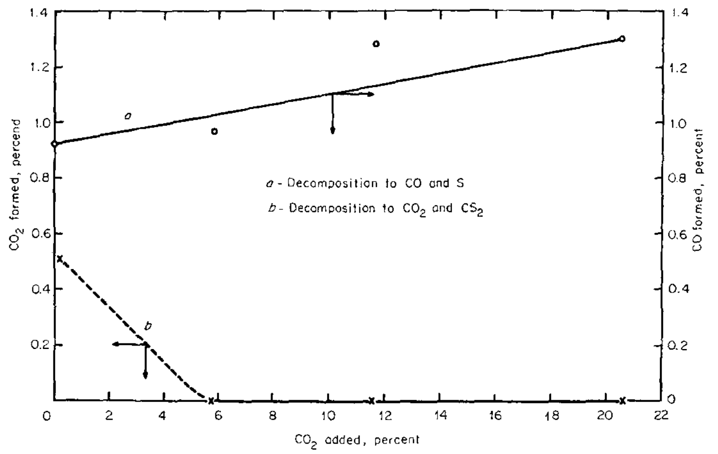

FIG. 5. Effect of CO_2 additions on the thermal decomposition of SCO with a silica gel catalyst.

Oxidation of SCO in Presence of SO_2

The thermal stability of SCO in presence of SO_2 was also studied as these two gases are usually present in processes involving the carbonaceous reduction of sulfurous waste gases (*6*, *16*, *17*). Chufarov and Udinceva (*18*) and Krause (*19*) studied the reaction of SCO and SO_2 using catalyst containing oxides of aluminum and titanium. Walden and Walden (*20*) found that alkali compounds were effective in accelerating the SCO–SO_2 reaction. To determine the optimum catalyst for the SCO–SO_2 reaction, various commercial catalysts were investigated. The gas reactants consisted of 6% SCO and 3% SO_2 in He. According to the stoichiometry of reaction (3),

$$2SCO + SO_2 \rightarrow 2CO_2 + \frac{3}{x} S_x. \quad (3)$$

fair agreement between the SCO and SO_2 conversion was obtained as shown in the last column in Table 2. Since fair agreement was obtained, only the latter is considered in the remaining discussion.

The highest SO_2 conversion was obtained with pure chi-alumina. Alpha-alumina had a lower surface area and was not an effective catalyst. The SO_2 conversion dependence on the temperature is shown in Fig. 6. It is evident from these data that increasing the chromium content of the catalyst decreases the catalyst activity for reaction 3.

The deleterious effect of transition metal

TABLE 2
THE SO_2–SCO INTERACTION DATA ON COMMERCIAL CATALYSTS: MOLAR RATIO OF SO_2:SCO IS 0.5

Catalyst type	Surface area (m^2/g)	SO_2 conversion at 380°C (%)	Range of SO_2 to SCO conversion ratios between 290 and 575°C
100% χ-Al_2O_3	90	88	1.14–1.19
5.8% Cr on γ-Al_2O_3	230	85	1.03–1.11
16% Cr on γ-Al_2O_3	170	70	1.01–1.06
20% Cr on γ-Al_2O_3	190	60	0.96–1.09
40% Ni on γ-Al_2O_3	160	25	1.02–1.03
100% α-Al_2O_3	8	6	0.94–0.96

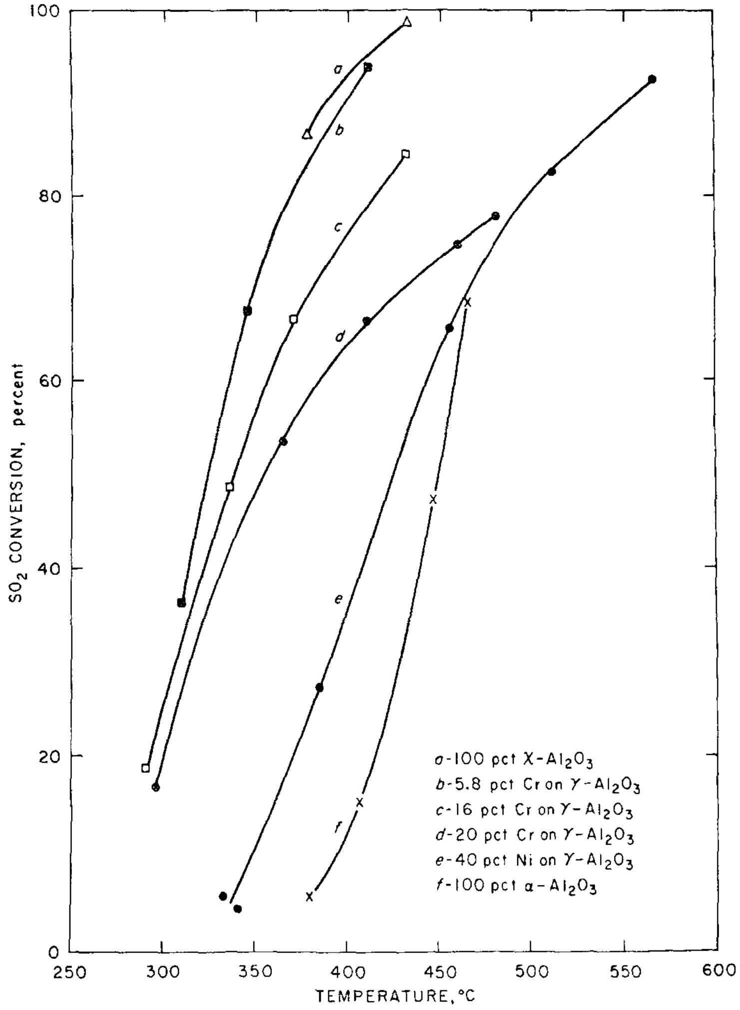

FIG. 6. Effect of temperature on the SO_2 conversion with various commercial catalysts.

on the catalytic activity of alumina for the reduction of SO_2 with SCO was further investigated at a constant metal concentration of about 2.5%. The results of metals in alumina on the CO–SO_2 reaction are also given for comparison purposes (Fig. 7). The SO_2 conversion at 410°C was determined first with CO and then with SCO as reductants. These results indicate that no SO_2 conversion was obtained on pure chi-alumina (Curve 1) with CO, but over 90% SO_2 conversion was obtained with this catalyst when SCO was used as the reductant. Considering only the equilibrium data presented in Fig. 2, opposite results would be expected.

The addition of a transition metal to alumina accelerated the CO–SO_2 reaction, but inhibited the SCO–SO_2 reaction. In a previous investigation (*9*), it was shown that the CO–SO_2 reaction is slow in absence of transition metal. The presence of transition metal was believed necessary to form SCO from an unstable metal sulfide. The SCO formed from the metal sulfide then increased the overall reaction because the SCO was a better reductant than CO. Transition metals in alumina, however, did not appear to enhance the SO_2–SCO interaction. Pure chi-alumina appeared to be the best catalyst for that reaction. These findings are in agreement with other inves-

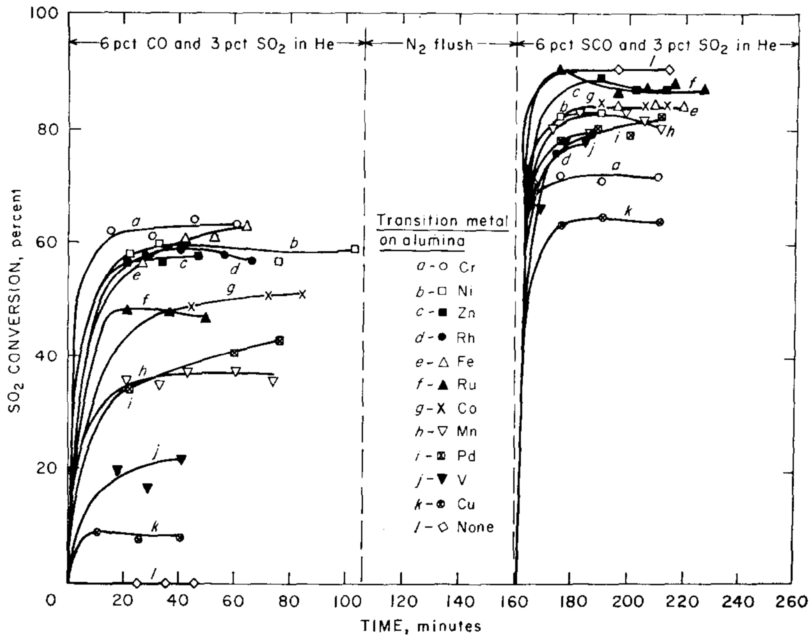

FIG. 7. Effect of transition metals in impregnated alumina catalysts on the SO_2 conversion.

tigators who found that alumina alone (*21*) was effective for SO_2–SCO reaction and that Fe (*22*) added to alumina was an inhibitor.

SUMMARY AND CONCLUSIONS

The experimental results indicated that less than 30% SCO decomposition occurred in a Vycor reactor at temperatures below 700°C. However, in the presence of 2 g of silica or alumina catalyst, more than 55% SCO decomposition was obtained at 700°C. The main products of SCO decomposition below 635°C were CO_2 and CS_2, while above this temperature the products were CO and sulfur. Either decomposition reaction can be favored by adding the products of the other reaction. The apparent activation energy with and without a catalyst was 5.6 and 28.7 kcal/mole, respectively.

The quantity of SCO reacting increased when a stoichiometric amount of SO_2 was added. Over 90% SCO conversion was obtained with 2 g of chi-alumina at about 400°C, while without added SO_2, only 30% SCO decomposition occurred at 520°C. Therefore the interaction between SCO and SO_2 was greater than the SCO decomposition. The percentage of SCO decomposition was not dependent on the composition of the alumina catalyst as compared to the reaction of SCO with SO_2. Transition metals present in alumina decreased the activity of the alumina for the SCO + SO_2 reaction, but the opposite was true for the CO + SO_2 reaction.

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