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Effect of Preadsorbed Sulfur Compounds on Chemisorption of CO and CO_2 on Iron Catalysts

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The effects of the chemisorption of H_2S, SO_2, CS_2, COS, C_2H_5SH, and thiophene on the nitrogen isotherm at −195°C, the carbon monoxide chemisorption at −195°C, and the carbon dioxide chemisorption at −78°C were determined on synthetic ammonia catalysts promoted with MgO, MgO–K_2O, Al_2O_3, and Al_2O_3–K_2O. The nitrogen isotherm gives a measure of the surface area; the CO chemisorption, a measure of the free metallic iron surface; and the CO_2 chemisorption, a measure of the alkali surface. Two types of poisoning are considered: I, poisoning at room temperature by the entire sulfur molecule, and II, poisoning by the residual sulfur left after hydrocracking of the organic part of the sulfur-bearing molecule. Poisoning of type II is comparable to the type experienced in ammonia synthesis and Fischer-Tropsch synthesis. In general, the poisoning did not affect the surface area, but it did decrease both the metallic iron and alkali surfaces. In all cases of Type I poisoning, initial chemisorption of 1 mole of sulfur compound initially decreased the chemisorbed CO + CO_2 by about 1 mole. Type II poisoning was less effective by a factor of 3 or 4 in decreasing chemisorbed CO than Type I poisoning.

The nature and degree of Type II poisoning depends only on the amount of sulfur deposited and is relatively independent of the compound from which it was formed. Hydrogen sulfide cracked partially to hydrogen and some adsorbed complex even at room temperature, and, therefore, only Type II poisoning was studied. For catalysts containing alkali, the iron surface decreases to a minimum as sulfur is added in Type II poisoning, rises to a maximum (somewhat lower than the initial free iron surface), and then gradually decreases. This phenomenon may be the result either of the onset of the formation of polysulfide or surface pyrite or of the nucleation of sulfide crystals. The alkali surface, as measured by carbon dioxide chemisorption, was also decreased by poisoning with sulfur compounds, both at room temperature (Type I) and after the Type I chemisorbed compounds on the surface have been treated with hydrogen at 450°C (Type II). With CS_2 and COS, Type I chemisorption produces a greater effect on the alkali surface than Type II. With C_2H_5SH and SO_2, the decrease in alkali surface is the same whether the C_2H_5SH and SO_2 are held in Type I or in Type II chemisorption.

INTRODUCTION

As a part of the Bureau of Mines' investigation of the sulfur poisoning of catalysts used for converting coal to oil and gas (*1*, *2*), the effect of sulfur compounds on the chemisorption of carbon monoxide and carbon dioxide on iron catalysts was investigated.

Emmett and Brunauer (*3*) have shown the iron catalyst used for ammonia synthesis consists of surfaces of iron, alkali, and relatively inert structural promoter (alumina, silica, etc.) surfaces. They showed that the iron surface could be measured by the chemisorption of CO at −195°C, that the alkali surface could be measured by the chemisorption of CO_2 at −78°C, and that the total surface could be measured by the nitrogen isotherm at —195°C. The Fischer-Tropsch process is known to proceed on iron sites (*1, 4*), and sulfur compounds probably poison by reducing the number of available sites. The alkali, potassium oxide, is known to be an important promoter which increases both the rate of the reaction and the molecular weight of the product formed by the Fischer-Tropsch synthesis over iron catalysts. Conceivably sulfur poisoning may proceed by reaction with the alkali surface, making it less available or effective in its promoter action. The change in alkali surface as a function of sulfur addition may therefore be a factor in the poisoning of this type of catalyst.

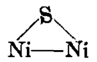
The aim of the present paper is to determine and interpret the effect of adsorbed sulfur compounds on the iron, alkali, and total surface. The use of carbon monoxide chemisorption and carbon dioxide chemisorption to measure iron and alkali surface in the presence of sulfur compounds may be questioned; however, these methods have been used under a wide variety of conditions (*5*) with satisfactory results. Kokes and Emmett (*7*) in particular have examined the problem in detail and have concluded that the analysis is at least semiquantitative. The internal consistency of the present paper supports this conclusion.

In the present research, the chemisorption of CO and CO_2 on singly and doubly promoted fused iron catalysts and on activated steel turnings was determined as a function of H_2S chemisorbed. Similar experiments were made on a doubly promoted catalyst poisoned with COS, CS_2, SO_2, C_2H_5SH, and thiophene.

A number of data may be considered to have relevance to the amount of sulfur necessary for poisoning. A recent paper from this laboratory reported prepoisoning studies of doubly promoted iron catalyst (D3001) with sulfur compounds in the Fischer-Tropsch synthesis. About 0.7 to 0.8 mg S/m^2 was required to decrease the activity to 1% of its initial value (*2*). Theoretical calculations show that the coverage of the 111 face of body-centered cubic iron by covalently bonded sulfur (half of the available iron sites lie immediately below the geometric surface) requires 0.74 mg S/m^2 (*2*). Carbon monoxide chemisorption (Table 1) at —195°C indicates that about 45% of the surface of catalyst D3001 is metallic iron. Since its total surface is 14.8 m^2/g Fe, the total amount of sulfur adsorbed on the metal should be 4.9 mg S/g Fe. Since the catalyst also contains 8.45 mg K_2O/g Fe that can react with H_2S to form KHS, the amount of sulfur so combined is 5.8 mg S/g Fe. The total amount of sulfur combined in both ways with the surface is therefore 10.7 mg S/g Fe or 0.73 mg S/m^2.

The adsorption of sulfur compounds on metallic iron surfaces has not been previously reported in any detail. The most closely related papers deal with the adsorption of hydrogen sulfide on nickel.

Selwood and Den Besten studied magnetic changes in supported nickel catalysts during poisoning with hydrogen sulfide and methyl sulfide (*7*). Their results indicated that at 25°C hydrogen sulfide dissociates into adsorbed hydrogen and sulfur. At high sulfur contents, hydrogen was desorbed. Magnetic data suggested that one molecule of H_2S interacts with 4 Ni atoms, to form 2 Ni–H bonds and one



configuration.

Similar results were obtained by Saleh, Kemball, and Roberts (*8*) in the interaction of hydrogen sulfide with nickel films. By means of the quantitative relationships between the hydrogen formed and the H_2S adsorbed at low coverages of the surface, they showed that the adsorbed complex has the formula H_nS, where n lies between 1 and 2, depending on coverage. The results suggest that one molecule of H_2S covers about 19.5 Å^2 of nickel surface, or a value for surface coverage of about 0.27 mg S/m^2. This value is the coverage of an H_2S complex, whereas both the calculated value described above for the adsorption of sulfur on iron and the experimental values must correspond to either the sulfide ion or the covalently bonded sulfur atom on the metal surface; hence, a direct comparison of coverage by a sulfur-bearing molecule with coverage by sulfur atoms is not valid.

EXPERIMENTAL

The composition of catalysts used in these studies, reduction conditions, surface areas from nitrogen adsorption, and the ratios of the volumes of chemisorbed CO and CO_2 to V_m (the volume of nitrogen corresponding to a monolayer for nitrogen adsorption) are given in Table 1.

Catalyst reduction and adsorption studies were made in Pyrex vessels equipped with special four-way stopcocks (*9*) modified to include a ground joint for introducing and removing samples easily (*1*). The tubes could be closed and removed from the system for weighing on an analytical balance. The catalysts, with one exception, were reduced *in situ* in the adsorption vessel, as described above, at conditions given in Table 1. Catalyst D3001 was reduced in a reaction tube maintained at constant temperature in a metal block heater. From the reactor, D3001 was transferred in CO_2 to a glass storage vessel (*1*). The catalyst was stored in CO_2 and, as required, was transferred to the adsorption vessel as described above through glass connections in a stream of CO_2 by methods that precluded exposure of the catalyst to air. These samples were treated with H_2 at 450°C for 2 hr in the adsorption vessel to remove adsorbed CO_2.

The procedure for determining chemisorbed CO and CO_2 was as follows:

(a) The amount of nitrogen adsorbed at —195°C was determined as a function of relative pressure, i.e., the ratio of the nitrogen pressure to the vapor pressure of nitrogen. From these data V_m was determined by the BET equation. The nitrogen was then removed at room temperature.

(b) The amount of carbon monoxide adsorbed at —195°C was determined as a function of relative pressure. At any given relative pressure the CO isotherm exceeds the nitrogen isotherm determined in step (a) by a constant amount that is taken as the chemisorption of CO.

(c) Earlier work (*1, 10*) had shown that chemisorbed CO decreases the chemisorption of CO_2. To remove the CO, the catalyst was treated with H_2 at 450°C for 1 hr and subsequently was evacuated at 450°C. This treatment has been shown to remove chemisorbed carbon monoxide from reduced fused iron oxide catalysts (*3*). Although this short treatment with H_2 at 450°C is not sufficient to change the surface area, it does permit an unambiguous determination of alkaline surface by CO_2 chemisorption, as will be described later.

(d) The CO_2 isotherm was determined at —78°C; the sample was evacuated at 0°C; and adsorption was again measured at —78°C. The first isotherm represents physical adsorption plus chemisorption, the second physical adsorption only. The difference between corresponding measurements of any given relative pressure is taken as the chemisorbed CO_2.

(e) After this sequence of experiments had been completed, the catalyst was again reduced at 450°C for 1 hr and subsequently evacuated at 450°C to remove the chemisorbed CO_2. At this point, the catalyst is in the same condition as the freshly reduced catalyst.

The next step is poisoning. Two different steps were used; (f) for poisoning by H_2S, and (f′) for poisoning by SO_2, C_2H_5SH, CS_2, COS, and thiophene:

(f) During exploratory poisoning experiments with H_2S by ordinary volumetric techniques at room temperature, H_2 was found in the residual gas. Similar evolution of hydrogen has been reported (*7, 8*) during the poisoning of nickel catalysts with H_2S. Volumetric changes are therefore not adequate to measure the amount of H_2S adsorbed, and instead the sulfur content was measured by the increase in weight of the sample after admission of the H_2S, treatment with H_2 at 450°C for 1 hr, and subsequent evacuation. The next step after (f) is described in (i).

(f′) For poisons other than H_2S, the sample, after poisoning, was evacuated at room temperature and weighed. The increase in weight was assumed to have been

TABLE 1

COMPOSITION, REDUCTION CONDITIONS, AND CHEMISORPTION DATA FOR IRON CATALYSTS

No.	Type[a]	Composition (parts by weight per 100 Fe)					Reduction in hydrogen[b]		Surface area (m^2/g Fe)	Chemisorption on reduced catalyst		
		MgO	Al_2O_3	K_2O	SiO_2	Cr_2O_3	Temp (°C)	Duration (hr)		V_{CO}/V_m[c,f]	V_{CO_2}/V_m[d,f]	$(V_{CO} + V_{CO_2})/V_m$[f]
L1022.1	F	—	0.18	—	0.59	—	450	48	8.40	0.58	0	0.58
P2007.6	F	—	3.30	—	0.28	—	450 500	20	19.8	0.41	0.02	0.43
L3119	F	—	3.22	0.37	0.28	—	450	64	13.4	0.30	0.18	0.48
L2021	F	2.77	—	—	—	—	450	40	15.2	0.50	0.08	0.58
D3001	F	6.84	—	0.85	1.05	0.96	450	40	15.3	0.35	0.25	0.60
									15.3	0.29	0.24	0.53
									13.4	0.48	0.29	0.73
									14.7	0.41	0.26	0.67
									14.6	0.41	0.26	0.67
P1039.2	T[e]	—	—	0.001	—	—	400	16	0.88	0.65	0	0.65

[a] F = fused magnetite catalysts, T = steam-oxidized steel lathe turnings.

[b] Hourly space velocity of hydrogen was about 2,500 in all experiments. Reductions were performed at atmospheric pressure.

[c] V_{CO} is the volume [cc (STP)] of CO chemisorbed at −195°C per gram of iron. V_m is the volume [cc (STP)] of N_2 corresponding to a BET monolayer per gram of iron.

[d] V_{CO_2} is the volume [cc (STP)] of CO_2 chemisorbed at −78°C per gram of iron.

[e] Also contains components normal to carbon steel 1018, typical analysis given as: Fe = 98.72%, C = 0.22%, S = 0.24%, Mn = 0.71%, Si = 0.44%, and P = 0.02%.

[f] V_m is unaffected by poisoning procedures. The surface area is equal to 4.38 times the volume of nitrogen [cc (STP)] required to establish the monolayer V_m on a gram of catalyst.

caused by the total chemisorbed compound (Type I poisoning).

(g) CO and CO_2 isotherms were then determined as in steps (b) and (d) with only evacuation at room temperature performed between steps (b) and (d). For these experiments, the chemisorption of CO_2 may be decreased by the presence of chemisorbed CO.

(h) The catalyst was then treated with H_2 at 450°C for 1 hr to remove organic portions of the sulfur compound, and the oxygen and carbon from the carbon dioxide and was subsequently evacuated. Only chemisorbed sulfur was left on the catalyst. The increase in weight from step (e) to the present step represents the total amount of sulfur chemisorbed (Type II poisoning).

(i) Chemisorption of CO at -195°C and chemisorption of CO_2 at -78°C were determined by the same sequence of operations described in (b), (c), (d), and (e).

The poisoning cycle (f′), (g), (h), and (i) was repeated with organic sulfur compounds until the desired amount of poison had been accumulated. For H_2S the cycle was simplified to steps (f) and (i). The nitrogen adsorption isotherm was determined at the end of the entire sequence of steps, and no change in surface area was detectable.

EXPERIMENTAL RESULTS

Table 1 presents the ratios of the volumes (STP) of CO (V_{CO}) and CO_2 (V_{C_2O}) chemisorbed at -195°C and -78°C, respectively, to the volume (STP) of nitrogen corresponding to a physically adsorbed monolayer, V_m. The highest values of V_{CO}/V_m, 0.58 and 0.65, were found for catalysts L1022.1 and P1039.2, respectively, which had the lowest concentration of materials other than iron. Values of V_{CO}/V_m as high as 1.25 have been observed on reduced magnetite of very high purity (*5, 11*). Chemisorption of CO_2 was appreciable only on catalysts containing K_2O, except for L2021 which contained magnesia as a structural promoter. For all catalysts of the group, $(V_{CO} + V_{CO_2})/V_m$ ranged from 0.43 to 0.73; values of less than 0.50 were found only for catalysts containing alumina as a structural promoter. Data for 5 samples of D3001 show the reproducibility of the experiments.

The changes of V_{CO}/V_m and V_{CO_2}/V_m as increasing amounts of H_2S were chemisorbed on the catalysts of Table 1 are presented in Figs. 1 to 4. In all the tests with H_2S, the catalysts were treated with hydrogen at 450°C before the chemisorption measurements. The quantity V_S/V_m is fundamental because it relates directly to V_{CO}/V_m (a measure of metal surface) and V_{CO_2}/V_m (a measure of alkaline surface). The quantity V_S is the volume (STP) of sulfur atoms. The sulfur content as mg S/m^2 can be converted directly to V_S/V_m by multiplying by 3.07. Both data are referred to the total surface. The important result of these data is that $V_{CO}/V_m + V_{CO_2}/V_m$ is decreased only by 0.2 to 0.55 by a monolayer of sulfur. Except for activated steel turnings P1039.2, V_{CO}/V_m was decreased by less than a factor of 3 by chemisorbing a monolayer of sulfur.

Carbon dioxide was chemisorbed both on catalysts containing alkali and, to a lesser extent, on preparations containing magnesia. On catalysts containing only iron and alumina, almost no carbon dioxide was chemisorbed. For the catalyst containing alumina and alkali (Fig. 2), the decrease of V_{CO_2}/V_m on poisoning by H_2S was less than the decrease of V_{CO}/V_m, but, for catalysts promoted with MgO–K_2O (D3001) (Fig. 3a), the decrease in V_{CO_2}/V_m on chemisorption of H_2S was greater than the decrease of V_{CO}/V_m. For catalyst D3001, the quantity V_{CO}/V_m was decreased only from 0.35 to 0.20 when V_S/V_m increased from 0 to 1.5, and V_{CO}/V_m passed through a minimum and a maximum as sulfur content was further increased. Similar results were obtained during chemisorption of SO_2, CS_2, and COS on this catalyst after it had been treated with hydrogen at 450°C as was done in the H_2S tests.

The effect of H_2S on the chemisorption of carbon monoxide on partly oxidized and reduced carbon steel turnings has been determined, and the results are shown in

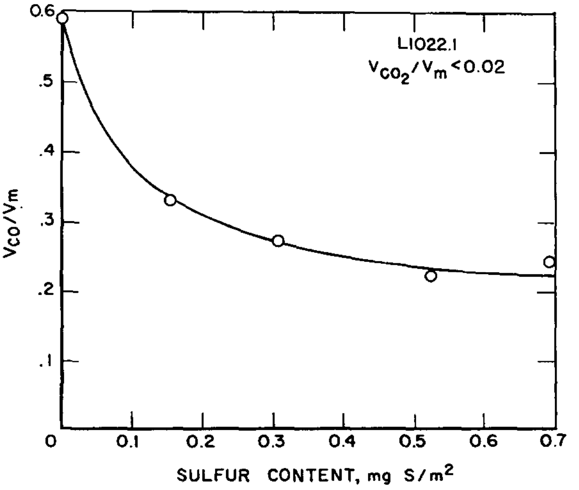


FIG. 1. Effect of H_2S on the chemisorption of carbon monoxide on a reduced fused iron oxide catalyst L 1022.1 with a low concentration of promoters.

Fig. 4. The graph is quite similar to those obtained for more conventional catalysts (Figs. 1 to 3).

Table 2 presents the data for the effect of SO_2, C_2H_5SH, CS_2, COS, and thiophene on the chemisorption of CO and CO_2 on reduced catalyst D3001. In this table, the measurements are presented in the order as obtained, going from left to right and from top to bottom. In general the procedure previously outlined was followed. The first chemisorption experiments were made after

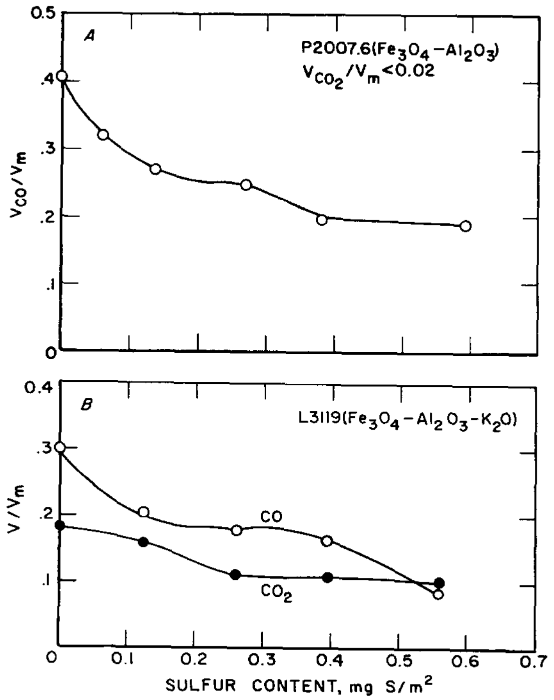


FIG. 2. Effect of H_2S on the chemisorption of CO and CO_2 on reduced, fused iron oxide catalysts containing alumina.

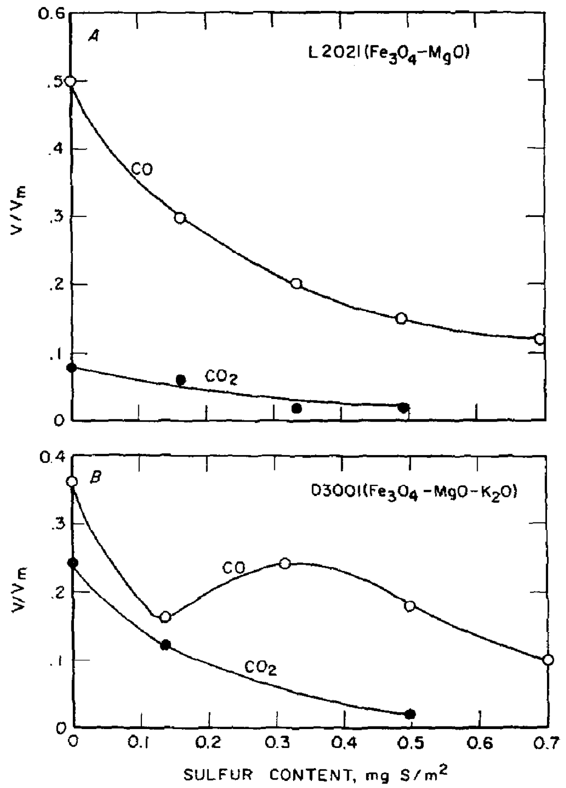


FIG. 3. Effect of H_2S on the chemisorption of CO and CO_2 on reduced, fused iron catalysts promoted with magnesia.

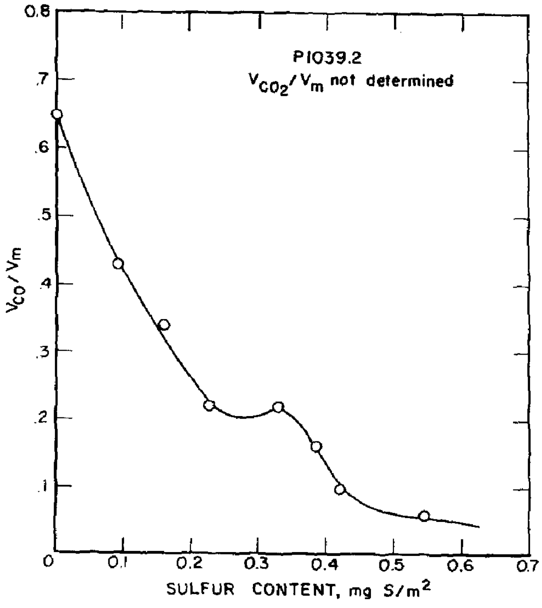


FIG. 4. Effect of H_2S on the chemisorption of carbon monoxide on partly oxidized and reduced steel turnings.

TABLE 2

EFFECT OF ADSORBED SULFUR COMPOUNDS ON D3001 ON THE CHEMISORPTION OF CO AND CO_2[a]

Sequence no.	Sulfur content (mg S/m^2)		Sulfur (V_S/V_m)	Carbon monoxide (V_{CO}/V_m)	Carbon dioxide (V_{CO_2}/V_m)
	Before H_2 treatment	After H_2 treatment			
Sulfur dioxide					
0	—	—	—	0.29	0.23
1	0.092	—	0.28	0.09	0.09
2	—	0.039	0.12	0.24	0.17
3	0.203	—	0.62	0.02	Not det.
4	—	0.190	0.58	0.26	0.13
5	0.353	—	1.08	0.01	0.06
6	—	0.314	0.96	0.20	0.07
7	0.503	—	1.55	0.00	0.00
8	—	0.386	1.18	0.11	0.05
9	—	0.569	1.75	0.05	0.04
10	—	0.732	2.25	0.00	0.03
Carbon disulfide					
0	—	—	—	0.41	0.26
1	0.149	—	0.46	0.22	0.11
2	—	0.088	0.27	0.32	0.17
3	0.237	—	0.73	0.19	0.06
4	—	0.163	0.50	0.33	0.10
5	0.312	—	0.96	0.17	0.03
6	—	0.271	0.83	0.26	0.05
7	0.441	—	1.35	0.10	0.00
8	—	0.427	1.31	0.20	0.03
9	0.617	—	1.89	0.04	0.00
10	—	0.630	1.93	0.16	0.02
Thiophene					
0	—	—	—	0.46	0.26
1	0.044	—	0.13	0.27	0.20
2	—	0.020	0.06	0.40	0.26
3	0.066	—	0.20	0.25	0.18
4	—	0.025	0.08	0.43	0.23
5	0.063	—	0.19	0.23	0.17
6	—	0.035	0.11	0.35	0.21
7	0.069	—	0.21	0.22	0.17
8	—	0.043	0.13	0.32	0.21
9	0.064	—	0.20	0.22	0.17
10	—	0.055	0.17	0.29	0.19
11	0.079	—	0.24	0.22	0.15
12	—	0.074	0.23	0.27	0.18
13	0.098	—	0.30	0.18	0.14
14	—	0.105	0.32	0.23	0.16

exposure of the sample to the sulfur compound at room temperature and evacuation at this temperature. Then the sample was treated with hydrogen at 450°C for 1 hr, and the nitrogen and carbon monoxide sorptions were measured. Following these measurements, the sample was again treated with hydrogen at 450°C for 1 hr, and isotherms for CO_2 were determined.

Values of sulfur chemisorbed were based

TABLE 2 (*Continued*)

Sequence no.	Sulfur content (mg S/m²)		Sulfur (V_S/V_m)	Carbon monoxide (V_{CO}/V_m)	Carbon dioxide (V_{CO_2}/V_m)
	Before H_2 treatment	After H_2 treatment			
			Ethylmercaptan		
0	—	—	—	0.48	0.29
1	0.077	—	0.24	0.16	0.19
2	—	0.030	0.09	0.38	0.23
3	0.121	—	0.37	0.02	0.18
4	—	0.101	0.31	0.35	0.18
5	0.197	—	0.60	0.00	0.14
6	—	0.155	0.48	0.31	0.16
7	0.258	—	0.79	0.00	0.12
8	—	0.196	0.60	0.24	0.12
9	0.297	—	0.91	0.00	0.09
10	—	0.240	0.74	0.19	0.07
11	0.340	—	1.04	0.00	0.07
12	—	0.302	0.93	0.20	0.05
13	0.418	—	1.28	0.00	0.04
14	—	0.362	1.11	0.16	0.04
15	0.460	—	1.41	0.00	0.05
16	—	0.422	1.30	0.12	0.04
17	0.592	—	1.83	0.00	0.03
18	—	0.504	1.59	0.10	0.04
19	—	0.556	1.71	0.09	0.04
20	—	0.536	1.65	0.08	0.00
21	—	0.713	2.19	0.06	0.00
			Carbonyl sulfide		
0	—	—	—	0.41	0.26
1	0.130	—	0.40	0.14	0.00
2	—	0.164	0.50	0.33	0.20
3	0.246	—	0.75	0.19	0.00
4	—	0.294	0.90	0.31	0.13
5	0.390	—	1.20	0.12	0.00
6	—	0.404	1.24	0.27	0.05
7	0.493	—	1.51	0.10	0.00
8	—	0.479	1.47	0.20	0.04
9	0.623	—	1.91	0.02	0.00
10	—	0.610	1.87	0.16	0.03
11	0.733	—	2.25	0.00	0.00
12	—	0.747	2.29	0.10	0.03
13	—	0.884	2.71	0.06	0.04

[a] Table shows sequence of gathering data.

on the weight change of the sample, on the assumption that the sulfur molecule was adsorbed unchanged and remained in this form during evacuation at room temperature and that the chemisorbed molecule was converted to chemisorbed sulfur in the hydrogen treatment. In some cases, part of the sulfur was removed in the hydrogen treatment. Thiophene was not strongly chemisorbed on the catalyst, and most of the adsorbed thiophene was removed by evacuating at room temperature. In the case of carbonyl sulfide, the reduction or hydrogen treatment was not complete, which leads to the incorrect conclusion that the sulfur content after reduction is greater than before. Allowance must be made for this in interpreting the results.

Following hydrogen treatment at 450°C, the sulfur remaining from SO_2, C_2H_5SH, CS_2, COS, and thiophene had qualitatively the same effect on V_{CO}/V_m and V_{CO_2}/V_m that H_2S had (Fig. 3a). Larger changes in these quantities were observed on samples before hydrogen treatment. Poisoning with SO_2 and C_2H_5SH strongly decreased V_{CO}/V_m, but V_{CO_2}/V_m was not greatly different before and after hydrogenation. For CS_2 without hydrogenation, V_{CO}/V_m and V_{CO_2}/V_m decreased somewhat more rapidly with sulfur concentration than after hydrogenation. Small quantities of COS, without hydrogenation, decreased V_{CO_2}/V_m drastically and also decreased V_{CO}/V_m moderately.

Thiophene was not strongly chemisorbed at room temperature, and the largest amount chemisorbed was only 0.11 mg S/g Fe. The chemisorption of thiophene decreased V_{CO}/V_m in the same way that other sulfur compounds did; the decrease was somewhat greater for samples that were not hydrogenated. Both before and after hydrogenation, the chemisorption of thiophene decreased V_{CO_2}/V_m by about the same amount as H_2S did.

DISCUSSION

The experimental results can be divided into two groups: (a) The effect of the chemisorbed sulfur compound before the hydrogen treatment; and (b) the effect of chemisorption of sulfur compounds followed by hydrogen treatment at 450°C, which should reduce the chemisorbed molecules to chemisorbed sulfur. Studies of group (b) should be pertinent to poisoning in the ammonia synthesis, which usually is done at 400° to 450°C, and possibly to the Fischer-Tropsch synthesis for which temperatures of 250° to 350°C are used for the present types of catalysts. Studies of group (b) provide an insight into the atomistics of poisoning.

An unexpected result of the studies of group (b) is that V_{CO}/V_m and V_{CO_2}/V_m decrease less rapidly than V_S/V_m. For example, for reduced Fe_3O_4–Al_2O_3 (P2007.6) chemisorbing H_2S to $V_S/V_m = 1.53$ (0.5 mg S/m^2) decreased V_{CO}/V_m from 0.4 to 0.2. Catalysts containing K_2O and/or MgO chemisorbed appreciable amounts of CO_2. On these catalysts chemisorption of H_2S decreased V_{CO_2}/V_m also. For catalysts promoted with MgO and MgO–K_2O, V_{CO_2}/V_m decreased more rapidly than V_{CO}/V_m as H_2S was chemisorbed, but for catalysts promoted with Al_2O_3–K_2O, V_{CO_2}/V_m decreased less rapidly than V_{CO}/V_m. For this catalyst, the promoter is probably present as potassium aluminate that may be less reactive in adsorbing sulfur compounds.

The chemisorption of CO on catalyst D3001 (Fe_3O_4–MgO–K_2O) decreased slightly with increasing H_2S, then increased, passed through a maximum, and decreased. This general behavior was also found for chemisorption of other sulfur molecules on this catalyst, after hydrogen treatment at 450°C. Possible explanations for the maximum include: (a) The penetration of sulfur atoms into the iron crystallites after a certain concentration of S on the surface is achieved; (b) polysulfide nucleation of iron sulfide crystals with migration of sulfur atoms to the nuclei occurs after a critical concentration of sulfur has been reached; however, FeS_2 pyrite would probably not survive the hydrogen treatment at 450°C; and (c) the alkali promoter or mixtures with alkali sulfides migrates at this temperature uncovering fresh iron surface. On catalysts containing Al_2O_3 and K_2O, the alkali is probably present as an aluminate that may not migrate at 450°C.

In studies of group (a) with the catalyst only evacuated at room temperature after chemisorption of sulfur molecules, V_{CO}/V_m and V_{CO_2}/V_m were decreased by greater amounts per mole of chemisorbed sulfur molecule. Because all sulfur compounds, after hydrogenation at 450°C, had a similar effect on V_{CO}/V_m and V_{CO_2}/V_m, the chemisorptions before and after hydrogenation can be compared to demonstrate the effect of the sulfur-containing molecule or species into which it may dissociate. Sulfur dioxide and ethylmercaptan strongly decrease chemisorption of CO, but chemisorbed CO_2 is not greatly changed. Chemisorption of these molecules seems to be associated with the metallic portion of the catalyst, possibly with dissociation into S and O or C_2H_5 and SH. Carbon disulfide appears to change the extent of both the metallic and K_2O surfaces by small amounts. Carbonyl sulfide decreases CO_2 chemisorption severely and CO chemisorption moderately. This molecule could react with K_2O to form K_2CO_2S or could dissociate to CO and S on the metallic surface. The initial decrease in $V_{CO}/V_m + V_{CO_2}/V_m$ was generally equal to or larger than the increase in V_S/V_m. With increasing loads of sulfur the reduction in $V_{CO}/V_m + V_{CO_2}/V_m$ becomes less.

Possibly, at temperatures of the Fischer-Tropsch (>240°C) and ammonia synthesis (>400°C), the sulfur is chemisorbed in a different form than at room temperature. The large amount of sulfur required to decrease V_{CO}/V_m or V_{CO_2}/V_m appreciably after hydrogenation at 450°C and to poison the catalyst could be the result of more effective packing of the sulfur or to the penetration of sulfur into the layers of iron atoms beneath the surface layer. Bulstuikova, Apel'baum, and Temkin (*11*) found that on exposing the catalyst to moderately large concentrations of H_2S the production of ammonia was decreased substantially. Pure gas was then passed over the catalyst, and the yield of ammonia increased appreciably to a constant value although no sulfur was desorbed. Poisoning curves were based on the constant value obtained after several hours of synthesis. Similar results were obtained by Frear, Shultz, and Elmore (*12*). These data suggest that two types of sulfur poisoning are involved: The first type, which is more effective, is converted to the second over a period of an hour or more.

The relation between the adsorbed sulfur compound and the number of carbon monoxide-adsorbing sites is given by the ratio of ΔV_S to ΔV_{CO}. Initially this ratio is between 1 and 2.5, indicating the number of sulfur-bearing molecules necessary to deactivate one carbon monoxide-adsorbing site. Thus SO_2 addition, 3 (Type I poisoning), 0.20 mg S/m^2 ($\Delta V_S/V_m = 0.55$) decreased V_{CO}/V_m from 0.24 to 0.02. Ethylmercaptan addition, 3, 0.9 mg S/m^2 ($\Delta V_S/V_m = 0.28$) decreased V_{CO}/V_m by 0.36. Carbonyl sulfide inlet 1, 0.13 mg S/m$_2$ ($\Delta V_S/V_m = 0.40$) decreased V_{CO}/V_m by 0.27. Carbon disulfide inlet 1, decreased V_{CO}/V_m by 0.19 with an addition of sulfur of 0.15 mg S/g Fe or ($\Delta V_S/V_m = 0.46$).

Poisoning studies in the Fischer-Tropsch synthesis (*2*) show that about 0.7 or 0.8 mg S/$_m{}^2$ ($V_S/V_m = 2.1$ or 2.5) was required to deactivate the catalyst. Calculated values for surface coverage as large as this can be obtained by assuming the chemisorption of one S per Fe and two S per total K_2O, assumptions that may not be reasonable. In any case, these higher values obtained from catalytic data seem more consistent with chemisorption data for Type II poisoning than Type I poisoning. This conclusion is consistent with the normal conditions of temperature and pressure for the synthesis.

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