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Methanation over Transition Metal Catalysts

III. Co/Al_2O_3 in Sulfur-Poisoning Studies

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Poisoning of Co/Al_2O_3 by H_2S in CO hydrogenation was studied in an all-quartz recycle reactor; the studies were carried out at atmospheric pressure and at 390°C with feed gas containing 1 to 4% CO in H_2 and 13 to 100 ppb H_2S. Sulfur-poisoned catalysts were analyzed using Auger electron spectroscopy (AES). Addition of 13 ppb H_2S reduced the steady-state methanation activity of Co/Al_2O_3 by more than 10^3-fold at 390°C; 90 ppb H_2S reduced the activity 10^4-fold. AES studies showed that the loss in methanation activity resulted from two-dimensional surface sulfide formation; no sulfur was present in the subsurface regions. In the sulfur poisoning of Co/Al_2O_3, carbon plays only a secondary role. Poisoning by sulfur appears to be due primarily to geometric blockage of sites, with one sulfur atom adsorbed per two surface Co atoms. Electronic effects due to sulfur adsorption are also important as evidenced by a 12 kcal/mole reduction in the activation energy for methanation upon poisoning.

INTRODUCTION

The catalytic hydrogenation of CO to CH_4 and higher hydrocarbons has received increasing attention recently. Very extensive purification is required to reduce the H_2S concentration in synthesis gas derived from coal to below 1 ppm H_2S. Even this small concentration of H_2S severely poisons transition metal catalysts (*1–3*). Attempts to regenerate sulfur-poisoned nickel catalysts have been unsuccessful (*4, 5*). The effect of promoters, of alloying, and of support interactions on the sulfur sensitivity of CO hydrogenation catalysts has been only partly examined, but the results have generally been unsatisfactory. Quantitative data on sulfur poisoning of transition metal catalysts are virtually nonexistent.

Several investigations (*6–15*) have been directed at understanding the adsorption of sulfur on transition metals, particularly on Pt and Ni, using recently developed surface-sensitive spectroscopic techniques. Surface studies using LEED on Ni and Pt (*9, 10, 15*) show that for less than one-third of a monolayer the sulfur atoms reside in high-coordination sites and that the nearest neighbor metal–sulfur bond distances are less than those for the stable bulk metal sulfides. This indicates that the sulfur adsorbed on the surface is probably bonded more strongly than in the bulk metal sulfide, indicating that the surface sulfide may be more stable than the bulk sulfide. The adsorption of sulfur on the high-coordination sites is consistent with the observation that sulfur adsorption markedly reduces the CO absorption sites which have low CO stretch frequencies as observed by ir spectroscopy (*12*). A saturated surface sulfide corresponds to one sulfur atom per two surface metal atoms for Ni (*16*), Pt (*15*), Fe (*14, 17*), and Mo (*18*). These surface studies do not quantify the mechanism of sulfur deactivation.

Even though Ni has been investigated extensively in both reaction and surface studies, no satisfactory efforts have been

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made to integrate these two approaches. It has been suggested that sulfur adsorption inhibits dissociation of chemisorbed CO (*6–8*). Whether this inhibition is due to geometric blockage of the active sites or to electronic effects arising from strong metal–sulfur interactions has not been defined. In a recent study (*2*) of the sulfur poisoning of Ni/Al_2O_3 in methanation, it was shown that poisoning by sulfur is due to geometric blockage and that electronic effects are not important. Furthermore, the presence of 13 ppb H_2S in H_2 at 400°C forms a saturated two-dimensional surface sulfide and reduces the steady-state methanation activity of Ni 200-fold. The stability of the surface is at least 12 kcal/mole greater than that of bulk sulfide.

The objectives of this study were to measure the rates of sulfur-induced deactivation of Co/Al_2O_3 and to determine the steady-state CO hydrogenation activity of Co/Al_2O_3 as a function of H_2S concentration in the gas phase. To achieve a better understanding of catalyst deactivation by carbon and sulfur, Auger electron spectroscopy (AES) was used to analyze the surface and subsurface composition of aged catalysts.

EXPERIMENTAL

Apparatus

An all-quartz internal-recycle reactor was used; details are given elsewhere (*2, 19, 20*). The reactor was gradientless, eliminating the problems of concentration profiles in packed beds, particularly those of sulfur. All gas lines exposed to the H_2S-containing stream were either Teflon or quartz, to minimize the adsorption of H_2S. The Teflon tubing was jacketed by polyethylene tubing, and He was flown through the annular space to prevent diffusion of O_2 into the feed gas. Previous studies have shown that most, if not all, of the problems associated with sulfur-poisoning studies can be eliminated by the application of this reactor and associated experimental procedures. (*2*).

Aged catalysts were examined by AES. Argon ion etching was used to obtain depth–composition profiles of the aged catalysts. An antechamber, with ultrahigh vacuum integrity, attached to the Auger electron spectrometer permitted pretreatment and reaction studies of the catalysts under atmospheric-pressure controlled-gas conditions, followed by subsequent surface analysis without exposure to the atmosphere. A detailed design of the antechamber has been presented earlier (*4*).

Materials

Fused α-Al_2O_3 plates (>99.9% purity) were used as the catalyst support, and the Co/Al_2O_3 catalysts were prepared by either metal evaporation or impregnation (*21, 22*). Evaporated catalysts were passivated with 10 ppm O_2, and impregnated catalysts were calcined to oxide before contact with the atmosphere to prevent sulfur contamination from the air during transfer. The advantage of using a fused alumina support for Co is that all the surface Co atoms were exposed to a uniform concentration of reactants and H_2S which permitted direct measurement of rates of poisoning without the need of an a priori poisoning model. The α-Al_2O_3 did not absorb a measurable amount of sulfur (*19, 22*).

The gases were ultrahigh purity and were further purified (*21*). The CO/H_2 mixture was certified "Primary Standard" (Matheson). One part per million H_2S in H_2 was prepared and certified by Matheson; our analysis confirmed that of Matheson.

Analytical

Effluents from the reactor were directly injected into an on-line gas chromatographic analysis system utilizing flame ionization, flame photometry, and thermal conductivity detection. A flame photometric detector with a 2-m silica gel in Teflon column was used to obtain accurate, precise measurement of the H_2S concentration to a detectability limit of ~4 ppb (*2*). The flame ionization detector was used to accurately measure CH_4 and higher hydrocarbons to less than 1 ppm concentration (*21*). A thermal conductivity detector was used to analyze CO and CO_2 (*21, 22*).

Procedure

Each catalyst was prepared just before starting the experiment to avoid possible contamination during a long storage period. After the passivated catalyst was loaded into the reactor, the reactor was purged with UHP H_2 for 8 to 12 hr. One of the following three modes was used to study the poisoning:

(i) *in situ* poisoning,

(ii) presulfiding,

(iii) carbon deactivation prior to sulfur poisoning.

For *in situ* poisoning, the reactor was heated to 390°C in flowing H_2 over a 20- to 25-min period, and then the flow of reactant mixture containing CO, H_2, and the desired concentration of H_2S (13–100 ppb) was started. The transient concentration profiles for CH_4, higher hydrocarbons, CO, CO_2, and H_2S were measured.

For presulfiding, the reactor was heated to 390°C in flowing H_2 over a 20- to 25-min period, and then the desired concentration of H_2S in H_2 (13–10 ppb) was fed to the reactor. Transient H_2S concentration profiles in the effluent were determined as a function of time. When the catalyst was equilibrated with sulfur, as indicated by the observation that the catalyst did not adsorb any more sulfur, the desired feed gas mixture of CO, H_2, and H_2S was fed to the reactor. The transient profiles for the various products and reactants were then determined.

For the sulfur-poisoning experiments in which the catalyst was first deactivated by carbon in a sulfur-free environment, the reactor was heated to 250°C in flowing H_2, and then 1% CO in H_2 was fed to the reactor. The temperature, 250°C, was chosen to avoid any possible sulfur contamination from the system. After operation at 250°C for more than 12 hr, the temperature was increased stepwise to 390°C, and the desired concentration of H_2S was added to the feed gas. The transient curves for products, reactants, and H_2S were determined.

The shut-down procedure was the same in all three modes of poisoning and involved stopping the flow of CO, reducing the temperature to 175°C, purging with H_2 for 1 hr, and cooling to room temperature. The same procedure was used for the sulfur-free studies over Co/Al_2O_3 (*21*). The cooled catalyst was removed from the reactor and stored in a glass bottle under He for AES analysis. Surface and subsurface composition of the poisoned catalysts was determined using AES and Ar^+ etching (*21*).

RESULTS

Reactor Studies

Typical results for the transient methanation activity of Co/Al_2O_3, during sulfur poisoning by each of the three modes used, are presented below.

In situ poisoning. Figure 1 shows the transient methanation activity of Co/Al_2O_3 at 390°C in the presence of an effective H_2S

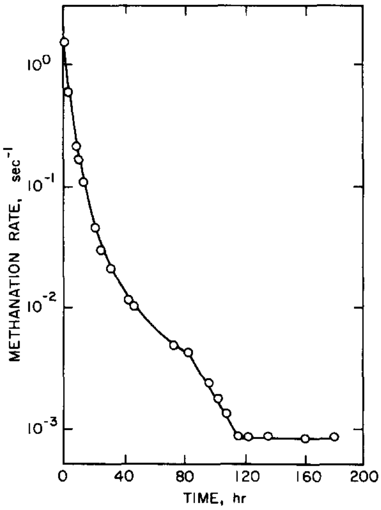

FIG. 1. Deactivation of Co/Al_2O_3 during *in situ* sulfur poisoning. Reaction conditions: 1% CO in H_2 at 390°C; during the first 80 hr, the H_2S concn in feed gas was 6–7 ppb; after 80 hr it was increased to 13 ppb.

concentration of 6–7 ppb up to 80 hr followed by 13 ppb H_2S with 1% CO in H_2. The initial methanation activity is the same as that observed during sulfur-free runs (*21*). The methanation activity of Co/Al_2O_3 dropped by a factor of 3000 before steady-state activity was reached. This steady-state activity is 50-fold lower than that for a carbon-deactivated Co/Al_2O_3 in the sulfur-free runs (*21*). The sulfur concentration, as H_2S, was monitored in the exit stream, which also represents the gas composition in the reactor because it is a CFSTR. No H_2S was detected (detectability limit ≃4 ppb) in the reactor exit stream up to 100 hr, suggesting that all of the H_2S was being adsorbed on the catalyst surface. Neither the reactor nor the alumina adsorbed H_2S (*19, 22*); thus the lost H_2S was being adsorbed on the Co surface. After 100 hr of reactor operation, H_2S began to appear in the reactor exit stream. As the concentration of H_2S in the reactor exit stream approached a constant value of 13 ppb, the methanation activity achieved a steady value indicative of no further sulfur adsorption.

In a different experiment, 83 ppb H_2S was introduced into the reactor at 390°C with a feed containing 1% CO in H_2. The transient methanation activity is shown in Fig. 2. The initial activity was the same as that for a sulfur-free experiment. A steady-state methanation activity was achieved after about 100 hr of reactor operation and was 12,000-fold lower than that in the upper pseudo- steady state in sulfur-free runs. After steady-state activity had been fully established (about 100 hr of reactor operation), the concentration of H_2S was reduced from 83 to 20 ppb, and the methanation activity increased about 2.5-fold. This shows that a dynamic equilibrium exists between H_2S in the gas phase and sulfur adsorbed on the catalyst surface. Therefore, our activity measurements represent true dynamic steady-state methanation activity as a function of gas-phase H_2S concentration. Similar behavior was observed at several intermediate H_2S concentrations.

Presulfided Co/Al_2O_3. To determine what role carbon deactivation played in the sulfur poisoning of Co/Al_2O_3, the Co/Al_2O_3 was presulfided with 87 ppb in H_2S in H_2 at 390°C. The equilibration of the Co surface at 390°C with 87 ppb H_2S in H_2 was demonstrated by the observation that the H_2S concentration in the exit gas equalled that in the feed gas. The amount of H_2S adsorbed per unit Co surface area was similar to that in the *in situ* poisoning run with 83 ppb H_2S. One percent CO and 87 ppb H_2S in H_2 were then fed to the reactor at 390°C. The transient methanation activity profile is shown in Fig. 3. The initial activity of the Co/Al_2O_3 having a sulfur-saturated surface is approximately four orders of magnitude lower than that for a fresh catalyst. The methanation rate decreased only a little over the next 24 hr, and more importantly, the observed methanation activity at 390°C in the presence of 87 ppb H_2S is in agreement with the value observed for the *in situ* poisoning runs. This clearly shows that carbon does not play a significant role in Co/Al_2O_3 poisoning by sulfur; sulfur is the major cause of loss in methanation activity.

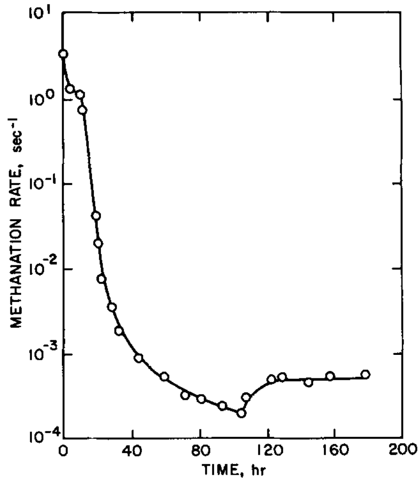

FIG. 2. Transient methanation activity of Co/Al_2O_3 during *in situ* sulfur poisoning and activity recovery upon reduction in the H_2S concentration. Conditions: 1% CO and 83 ppb H_2S in H_2 at 390°C up to 105 hr; H_2S concentration was reduced from 83 to 20 ppb after 105 hr (other conditions were held constant).

Sulfur poisoning of precarbon-deactivated Co/Al_2O_3. To investigate the role of

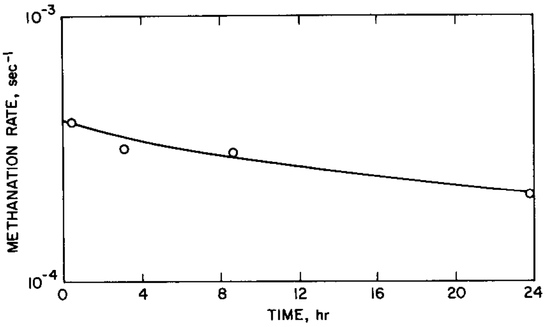

FIG. 3. Methanation activity of presulfided Co/Al_2O_3. Presulfiding conditions: 87 ppb H_2S in H_2 at 390°C for 74 hr. Reaction conditions: 1% CO and 87 ppb H_2S in H_2 at 390°C.

carbon in more detail, and to determine the adsorption of H_2S on carbon-deactivated Co/Al_2O_3, the catalyst was allowed to undergo carbon deactivation under sulfur-free reaction conditions until its methanation activity was reduced by about 100-fold. Under these conditions we have shown (*21*) that a well-carbided surface is formed. At this point, 40 ppb H_2S was introduced into the feed gas containing 1% CO in H_2 with the reactor at 390°C. Figure 4 shows the transient activity behavior; the steady-state methanation activity was similar to that observed for the other two modes of poisoning. No H_2S was detected in the reactor exit stream initially, clearly indicating that all the H_2S fed was adsorbed onto the catalyst surface even though it was already well carbided. The rate of H_2S adsorption over a carbon-deactivated Co/Al_2O_3 was large enough so that all the H_2S present in the gas phase was adsorbed. This sulfur adsorption behavior is similar to that observed for both presulfiding, and *in situ* poisoning experiments.

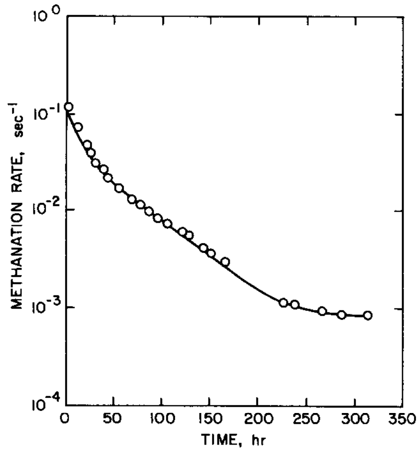

FIG. 4. Transient methanation activity of Co/Al_2O_3 which underwent carbon deactivation prior to contact with H_2S; figure shows poisoning behavior only after addition of H_2S. Carbon deactivation conditions: 1% CO in H_2 at 250°C for 12 hr; 1% CO in H_2 at 295°C for 30 hr; 1% CO in H_2 at 390°C for 2 hr. Reaction conditions (shown here): 1% CO and 40 ppb H_2S in H_2 at 390°C.

Steady-state methanation activity of Co/Al_2O_3 as a function of H_2S concentration. Figure 5 shows the steady-state methanation activity of Co/Al_2O_3 at 390°C as a function of gas-phase H_2S concentration with 1% CO in H_2. Each point represents the results obtained from a single experiment showing the high degree of reproducibility of the data. Figure 5 includes results for evaporated films and for impregnated catalysts and further confirms our earlier observation (*21*) that Co/Al_2O_3 catalysts prepared by different techniques give similar results for methanation activity. Figure 5 also includes steady-state methanation activity results obtained from all three modes of poisoning by sulfur. This clearly demonstrates that the steady-state methanation activity does not depend upon the method of Co/Al_2O_3 poisoning.

It is seen in Fig. 5 that only 13 ppb H_2S reduces the methanation activity of Co/Al_2O_3 at 390°C by about four orders of magnitude; subsequent increase in the H_2S

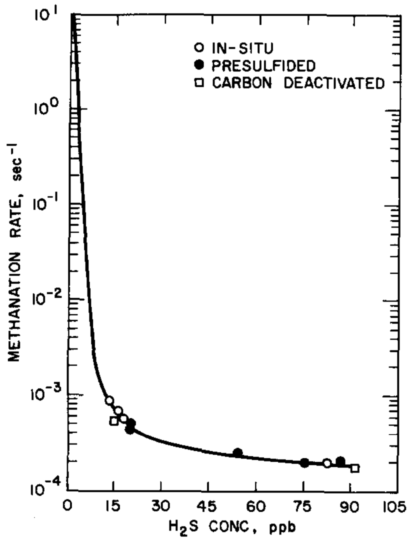

FIG. 5. Steady-state methanation activity of Co/Al_2O_3 as a function of gas-phase H_2S concentration. Reaction conditions: 1% CO in H_2 at 390°C. Each symbol represents the particular mode of sulfur poisoning used, and each data point represents data obtained from a separate run using catalysts prepared by different techniques.

concentration from 13 to 87 ppb decreases the methanation activity only by an additional factor of 4.

Activation energy. The activation energy for methanation determined from steady-state activity after poisoning with 15 ppb H_2S was 16 ± 2 kcal/mole as shown in Fig. 6. This same value was observed for the carbon-deactivated catalyst in the sulfur-free studies (*21*). Identical values for the activation energy were obtained from measurements made over Co/Al_2O_3 poisoned by both: (1) *in situ* poisoning, and (2) presulfiding.

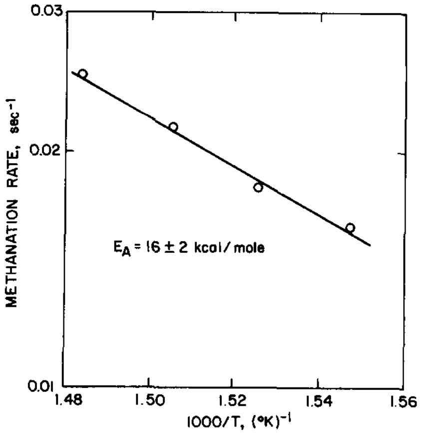

FIG. 6. Dependence of methanation rate on reaction temperature for methanation over sulfur-poisoned Co/Al_2O_3. Reaction conditions: 1% CO and 15 ppb H_2S in H_2; the conditions correspond to reaction over an essentially full two-dimensional surface sulfide.

Rate of poisoning by sulfur. The concentration of H_2S in the reactor exit stream was monitored as a function of time during all sulfur-poisoning experiments. Figure 7 shows data obtained in the experiment with 83 ppb H_2S in the feed gas and for which the transient methanation activity profile is shown in Fig. 2. Initially no H_2S was detected in the exit-gas stream, and thus all H_2S (83 ppb, 64 cm total gas/min) fed to the reactor was being adsorbed on the Co surface. As the catalyst surface became saturated with sulfur, the concentration of H_2S in the exit-gas stream approached that in the feed. After 100 hr, the concentration of H_2S in the exit gas is the same as that in the feed. The hatched area shown in Fig. 7 represents the total number of sulfur atoms adsorbed on the Co surface. Piecewise integration of this area provides the amount of sulfur adsorbed as a function of on-stream time and normalization to the

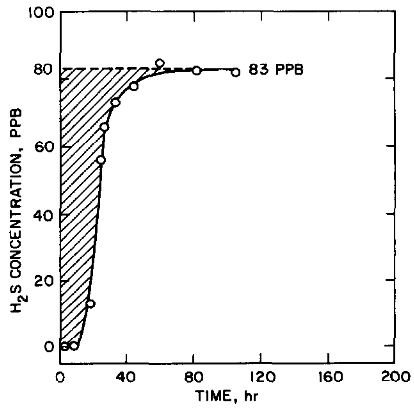

FIG. 7. H_2S concentration in reactor effluent during *in situ* poisoning of Co/Al_2O_3. Reaction conditions: 1% CO and 83 ppb H_2S in H_2 at 390°C. The hatched area represents the total amount of sulfur adsorbed on the catalyst surface.

fraction of total sulfur adsorbed is readily done. It will be shown later by AES analysis of poisoned catalysts that the loss in the methanation activity results from the formation of a saturated two-dimensional surface sulfide on the Co surface. It then follows from these arguments that the fraction of sulfur adsorbed relative to the total sulfur adsorption is equal to the fraction of a saturated sulfur layer, θ_S. Figure 8 shows θ_S as a function of time. The rate of sulfur adsorption ($d\theta_S/dt$) is constant up to about $\theta_S = 0.70$, and then it decreases as the surface approaches saturation with sulfur. Similar observations were made in the experiments using the other two modes of sulfur poisoning.

Total amount of sulfur adsorbed. In all the sulfur-poisoning experiments, the transient H_2S concentration profiles were obtained. It was thus possible to calculate the total amount of sulfur adsorbed in each experiment, by integrating the hatched area (e.g., Fig. 7). By knowing the total metal surface area and the total amount of sulfur adsorbed in each experiment, it was possible to calculate sulfur adsorption density, i.e., the number of sulfur atoms adsorbed per square centimeter of metal surface.

Table 1 gives the sulfur adsorption density for Co/Al_2O_3 obtained from the three different preparation techniques and poisoned by the three different poisoning methods. Values for different runs agree within a factor of 2 due to unaccountable differences in metal surface area. More importantly, the scatter is random in nature. The significance of these results will be discussed under AES Analysis of Sulfur-Poisoned Co/Al_2O_3.

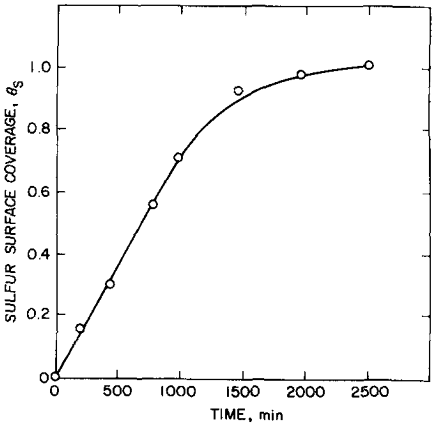

FIG. 8. Sulfur surface coverage (θ_S) as a function of time during *in situ* poisoning of Co/Al_2O_3 by H_2S. Reaction conditions are the same as those in Figs. 2 and 7: 1% CO and 83 ppb H_2S in H_2 at 390°C.

Methanation activity as a function of θ_S[3]. The transient methanation activity profiles (Figs. 1 and 2) obtained during *in situ* poisoning show that the steady-state methanation activity was achieved when the catalyst surface became saturated with sulfur. Changing the feed H_2S concentration by more than a factor of 6 (from 13 to 83 ppb) still resulted in all H_2S being adsorbed on the catalyst surface during the initial stages of *in situ* poisoning. Therefore, the rate of poisoning is equal to the rate of sulfur being fed to the reactor. The transient methanation activity profile for the run with 83 ppb H_2S is shown in Fig. 2; the fractional surface coverage by sulfur (θ_S) as a function of time is shown in Fig. 8. A direct relationship between the rate of methanation and the fractional surface coverage (θ_S) by sulfur is thus obtained. Figure 9 shows the relative methanation activity as a function of $(1 - \theta_S)^2$, the square of the fraction of surface not poisoned by sulfur. The linear relationship between methanation rate and $(1 - \theta_S)^2$ in Fig. 9 shows that the rate-controlling step in methanation requires two surface sites, which are probably adjacent, and that the poisoning by sulfur is primarily a geometric effect.

A similar linear relationship between the methanation activity and $(1 - \theta_S)^2$ was not observed, however, when 13 ppb H_2S were used for *in situ* poisoning. Here the rate of sulfur being fed into the reactor and consequently the rate of sulfur adsorption is so low that carbon deactivation is probably coupled with poisoning by sulfur, and the methanation activity decreases more rapidly than the straight-line relationship shown in Fig. 9.

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[3] θ_S is defined here as the fraction of the final total sulfur uptake observed under reaction conditions.

TABLE 1

Estimated Sulfur Adsorption Density on Co/Al_2O_3 Catalysts

Method of catalyst preparation	Method of poisoning	H_2S conc used (ppb)	$\frac{\text{No. of S atoms}}{\text{cm}^2 \text{ of Co surface}}$
Evaporation	Presulfiding	123	1.2×10^{15}
Single impregnation	*In situ*	83	0.91×10^{15}
Single impregnation	Presulfiding	87	1.75×10^{15}
Single impregnation	*In situ*	34	0.82×10^{15}
Single impregnation	Presulfiding	58	1.25×10^{15}
Multi-impregnation	Precarbon deactivaton	40	1.1×10^{15}
Multi-impregnation	Presulfiding	115	0.60×10^{15}
Multi-impregnation	*In situ*	16	0.87×10^{15}

AES Analysis of Sulfur-Poisoned Co/Al_2O_3

Below, AES analysis of aged Co/Al_2O_3 which was poisoned in the internal-recycle reactor is presented, and then the analysis of Co/Al_2O_3 treated in the antechamber of the Auger electron spectrometer is presented.

In situ poisoned Co/Al_2O_3. Figure 10 shows the AES spectrum of a Co/Al_2O_3 catalyst which had undergone *in situ* poisoning at 390°C for 95 hr with 34 ppb H_2S in the feed gas consisting of 1% CO in UHP H_2. Carbon and sulfur are both present on the surface. A large oxygen peak is due to the presence of alumina since the catalyst used here was prepared by single impregnation. The presence of alumina is confirmed by the aluminum peak at 1400 eV. There is also a small chlorine peak which is believed to be due to adsorption on the surface during/after catalyst placement in the antechamber. Heating the catalyst at 400°C for 1 hr resulted in no changes in the AES spectrum. The observation of alumina by AES shows that the metal film was not continuous. Since alumina is an insulator, surface charging made it impossible to obtain reliable composition–depth profiles by Ar^+ sputtering. In addition, the presence of carbon on the Co surface made it difficult to determine accurately the coverage of the Co surface by sulfur since the attenuation of the Co and sulfur peaks by carbon is not known.

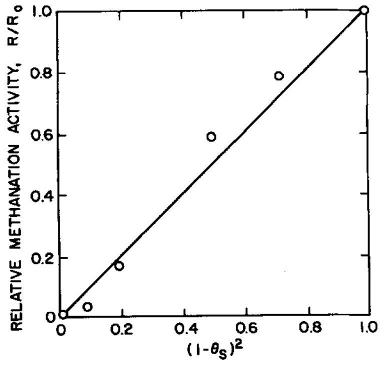

FIG. 9. Relative steady-state methanation activity of Co/Al_2O_3 as a function of the square of sulfur-free surface fraction $(1-\theta_S)^2$. Reaction conditions are the same as those in Figs. 2, 7, and 8.

Figure 11a shows the AES spectrum of another Co/Al_2O_3 catalyst which had been poisoned *in situ* at 390°C with 23 ppb H_2S in a feed gas of 1% CO in H_2. This catalyst was prepared by evaporation and had a continuous metal film covering the alumina surface. A small chlorine peak was again present. The carbon peak is small, but the sulfur peak is large. The oxygen peak in Fig. 11a comes from water adsorbed on the catalyst surface during transfer. The oxygen peak was essentially eliminated by desorption upon heating the sample to 400°C in the Auger chamber and was confirmed to be due to H_2O by residual gas analysis.

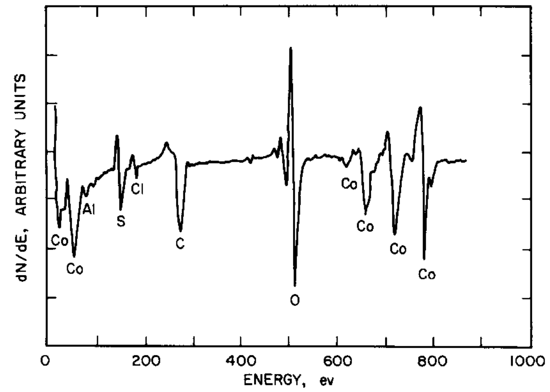

FIG. 10. AES spectrum of *in situ* poisoned Co/Al_2O_3 prepared by single impregnation technique. Reaction conditions: CSTR 1% CO, 34 ppb H_2S in H_2 at 390°C for 95 hr.

Figure 11b shows the AES spectrum of this catalyst after it had been held in the Auger chamber at 400°C for 3 hr; sulfur is now the major contaminant on the surface, although a 10–20% fraction of the surface was covered with graphitic carbon. The S- (151 eV) to-Co (53 eV) peak ratio of unity, by analogy with Ni, represents a sulfur-saturated surface. Windawi and Katzer (*23*) have shown that the ratio of the S (151-eV) peak to the Ni (63-eV) peak is 1.0 for the full two-dimensional surface sulfide. Since Ni and Co have nearly identical ionization cross sections, a S- (151 eV) to-Co (53 eV) peak ratio of 1.0 should also represent a full two-dimensional surface sulfide. This is supported by the fact that S- (151 eV) to-Co (53 eV) ratios greater than 1.0 were never observed in the present study even when an H_2S concentration of 83 ppb was used to poison the catalyst.

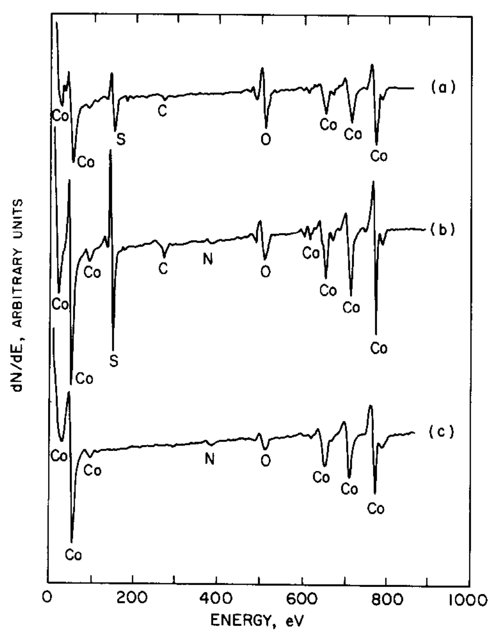

FIG. 11. AES spectra of *in situ* poisoned Co/Al_2O_3 prepared by evaporation technique: (a) directly after removing from the reactor, (b) after heating in the main chamber of the Auger electron spectrometer at 400°C for 3 hr, and (c) sputtered with Ar^+ for 5 min. Sputtering conditions: beam voltage, 2 kV; reaction conditions prior to AES analysis: CSTR 1% CO, 23 ppb H_2S in H_2 at 390°C for 100 hr, filament current, 10 mA.

The surface shown in Fig. 11b was sputtered with an argon ion beam (Ar^+) for total times of 0.5, 1, 2, and 5 min, and an AES scan was taken after each interval. Although there was a small amount of carbon on the surface, no carbon was present in the subsurface region. The sulfur peak decreased with sputtering time and was gone after 2 min. Figure 11c shows the AES spectrum of the catalyst surface after it had been sputtered for a total of 5 min. Under these sputtering conditions, the rate of sputtering would be $\simeq$8–10 Å/min.

Other evidence for the presence of sulfur as a surface sulfide is that in all the reaction studies, the sulfur adsorption density did not change with changes in the H_2S concentrations. If there were sulfur incorporated into the subsurface region, the sulfur adsorption density would be expected to increase with increasing H_2S concentrations in the feed gas. Furthermore, the Gibb's free energy of formation for the bulk cobalt sulfide is -12 kcal/mole (*24*). The relationship for equilibrium between the bulk sulfide phase and gas-phase H_2S concentrations,

$$\Delta G^0 = RT \ln (P_{H_2S}/P_{H_2}),$$

suggests that the concentration of H_2S in the gas phase must be at least 69 ppm to form a stable bulk sulfide. However, a stable surface sulfide on cobalt is formed at 390°C, with only 13 ppb H_2S in gas-phase H_2. The use of the above expression gives a ΔG^0 value for surface sulfide formation of -24 kcal/mole. This shows that the two-dimensional surface sulfide is more stable than bulk cobalt sulfide by at least 12 kcal/mole and explains why the catalyst is severely poisoned even under conditions where the bulk sulfide is not stable. The present study does not define the lowest H_2S concentration in H_2 that would lead to formation of less than a full two-dimensional surface sulfide. The estimated value -24 kcal/mole is only an upper limit on the free energy of formation for two-dimensional surface sulfide formation; the surface sulfide may be significantly more stable.

Presulfided Co/Al$_2$O$_3$. In another set of experiments, a saturated two-dimensional surface sulfide was formed on the catalyst surface using H_2S/H_2 before the CO–H_2 mixture was introduced into the reactor. The surface and subsurface composition of the catalyst was determined by AES after the reaction. Figure 12 shows the AES spectrum for the presulfided catalyst after 95 hr in the reactor at 390°C with 1% CO in H_2. There is no carbon present on the surface; the S- (151 eV) to-Co (53 eV) peak ratio was 1.0 indicating the presence of a two-dimensional surface sulfide. The oxygen peak is due to the support resulting from the discontinuous metal surface as evidenced by an aluminum peak at 1400 eV. The S- (151 eV) to-Co (53 eV) peak ratio would remain 1.0 for a two-dimensional surface sulfide on the metal even for a discontinuous metal surface since sulfur is adsorbed on the metal surface only and not on the Al_2O_3 surface. Upon sputtering the surface of the catalyst shown in Fig. 12 with Ar^+, the sulfur peak rapidly (1.0 min) decreased to zero indicative of a surface sulfide only; there was no carbon present in the subsurface regions. Similar results were observed for Co/Al_2O_3 presulfided with different H_2S concentrations prior to reaction.

Poisoning of carbon-deactivated Co/Al$_2$O$_3$. In another experiment, the Co/Al_2O_3 catalyst was first deactivated by reaction (with carbon) under sulfur-free reaction conditions, and then poisoned by 40 ppb H_2S at 390°C with 1% CO in H_2. The AES spectrum of the catalyst after this run is shown in Fig. 13. Sulfur and graphitic carbon both are present on the surface. The presence of the carbon prevents accurate analysis of the S/Co peak ratio, but the sulfur absorption density measured for this experiment from a sulfur balance (input–output) was the same as that obtained for both the *in situ* poisoning and the presulfiding experiments. The oxygen peak in Fig. 13 is again due to Al_2O_3, as this catalyst was prepared by multiple impregnation. Depth profiles obtained after sputtering (Fig. 14) show that sulfur and carbon were both removed upon sputtering. The sulfur peak intensity quickly went to zero indicating a surface sulfide only. The carbon peak intensity reduced to a steady value of C (273 eV) to Co (53 eV) $\simeq$ 0.5 which was unchanged with further sputtering, and which is indicative of bulk carburization.

These results show that (1) carburization of the Co bulk occurred prior to addition of H_2S to the feed, (2) prior bulk carburization did not affect the ultimate sensitivity of Co/Al_2O_3 to poisoning by sulfur, and (3)

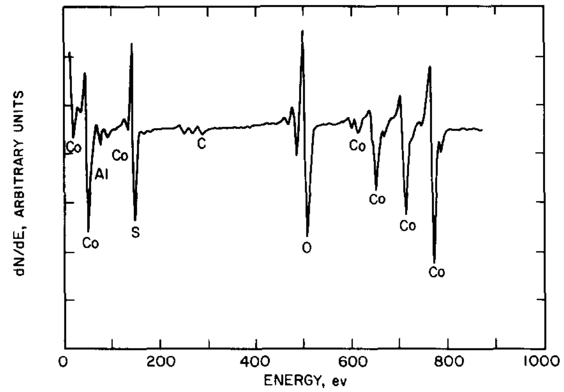

FIG. 12. AES spectrum of Co/Al_2O_3 presulfided in H_2S–H_2 mixture and then used as a catalyst in CO hydrogenation. Co/Al_2O_3 was prepared by single impregnation technique. Presulfiding conditions: 87 ppb H_2S in H_2 at 390°C for 74 hr. Reactions conditions: 1% CO, 87 ppb H_2S in H_2 at 390°C for 95 hr.

prior bulk carburization did not affect the formation of a full surface sulfide. There was more carbon present on the surface and in the bulk of the Co for the catalyst that was reaction (carbon) deactivated in a sulfur-free environment prior to sulfur poisoning than for any other method of poisoning; nevertheless, the steady-state methanation activity was identical to that observed for Co/Al_2O_3 poisoned by other methods.

AES analysis of Co/Al_2O_3 treated in the antechamber. Dissociative chemisorption of CO on sulfur-poisoned Co/Al_2O_3 was studied on evaporated films in the antechamber of the Auger electron spectrometer. The antechamber had been used previously in sulfur-poisoning studies in which H_2S was admitted to the chamber contaminating it with sulfur. Multiple oxidation–reduction cycles cleaned the chamber such that no sulfur contamination of a clean metal surface occurred at 400°C under vacuum or at temperatures below 200°C in a H_2 environment. However, at 400°C in 1 atm of H_2 the catalyst surface was slowly contaminated with sulfur allowing controlled amounts of sulfur to accumulate on the surface. Films were placed in the antechamber and reduced in H_2. An AES spec-

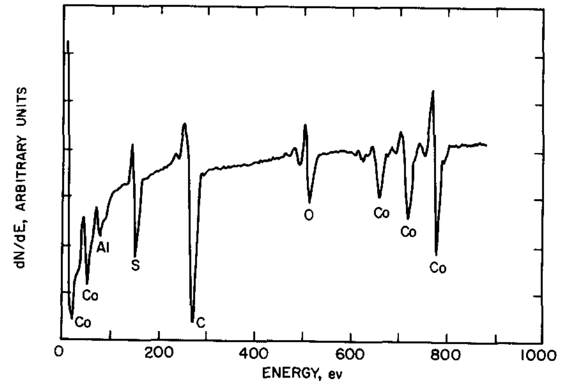

FIG. 13. AES spectrum of carbon-deactivated and then sulfur-poisoned Co/Al_2O_3 prepared by multi-impregnation technique. Carbon deactivation conditions: 1% CO in H_2 at 250°C for 12 hr; 1% CO in H_2 at 295°C for 30 hr; 1% CO in H_2 at 390°C for 2 hr. Sulfur-poisoning conditions after carbon deactivation: 1% CO, 40 ppb H_2S in H_2 at 390°C for 320 hr.

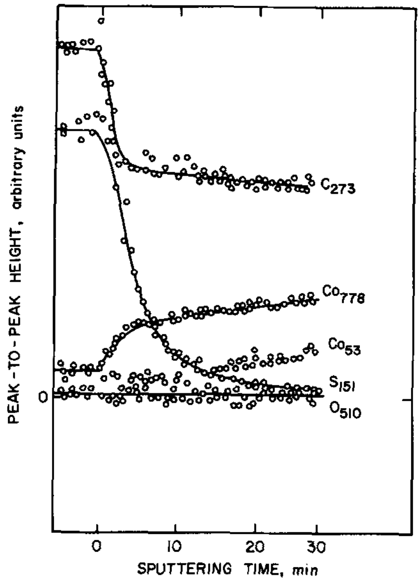

FIG. 14. Depth–concentration profiles of the carbon-deactivated and then sulfur-poisoned Co/Al_2O_3 shown in Fig. 13. Sputtering conditions: Ar^+; beam voltage, 2 kV; filament current, 10 mA; S_{151} and C_{273} peak-to-peak heights were measured at a sensitivity five-fold greater than that used for Co_{53}, Co_{778}, and O_{510}. Carbon deactivation and reaction conditions are as given in Fig. 13.

trum was taken, and the film was heated in H_2 for sufficient time to give the desired surface coverage by sulfur. For one Co/Al_2O_3 evaporated film heating in H_2 was continued until the AES spectrum had a S-(151 eV) to-Co (53 eV) peak ratio of 1.0 indicative of a full surface sulfide layer.

This Co/Al_2O_3 film was exposed to flowing 10% CO in H_2 in the antechamber for 2 hr at 400°C and 1 atm, and the catalyst was then cooled to room temperature in the flowing CO/H_2 mixture. The antechamber was evacuated, the gate valve between the antechamber and the AES chamber was opened, and the surface was examined by AES. The AES spectrum of the resultant surface was identical to that observed before the CO/H_2 treatment; there was no trace of carbon present. Some oxygen was present, but it disappeared quickly on heating indicating that it was due to water adsorbed on the surface. The surface was sputtered with Ar^+ for 1 min. No carbon was observed, and the intensity of the sulfur peak decreased to zero indicating that the sulfur was present only as a surface sulfide.

In another experiment, the same $CO–H_2$ reaction procedure was repeated with a Co/Al_2O_3 film which had approximately 60% of a full surface sulfide layer (S (151 eV) to Co (53 eV) $\simeq$ 0.6). After 4 hr treatment with 10% CO in H_2 at 400°C and 1 atm total pressure, the AES analysis showed that there was no carbon on or below the surface; again the sulfur peak present was sputtered to zero rapidly.

In yet another experiment, a Co/Al_2O_3 film with 30% of a full surface sulfide layer was treated in the antechamber with 10% CO in H_2 for 1.75 hr at 400°C and 1 atm total pressure. Figure 15a shows the AES spectrum of the surface after reaction. There was considerable graphitic carbon present on this surface. The S (151-eV) peak appeared to increase relative to the Co (53-eV) peak, although accurate estimation is difficult due to attentuation of Co and S peaks by carbon. This suggests that the carbon was preferentially covering the Co relative to the sulfur on sulfided cobalt surface. Next, the surface was sputtered with Ar^+ for 25 min (Fig. 15b); the sulfur peak intensity reduced to zero in ~1 min, indicative of surface sulfur only, but the peak for carbon was unchanged. Thus, with 30% of a full surface sulfide, large amounts of carbon are incorporated into the bulk of the Co forming a carbide.

These results help explain the AES observations for the Co/Al_2O_3 catalysts studied in the reactor with H_2S present in the gas phase. Carbon was not present on the surface or incorporated into the bulk of presulfided catalysts in the reactor and in the antechamber. Adsorption and dissociation of CO appear to be inhibited by the presence of sulfur. *In situ* poisoned Co/Al_2O_3 had little carbon on the surface, and there was essentially no carbon in the

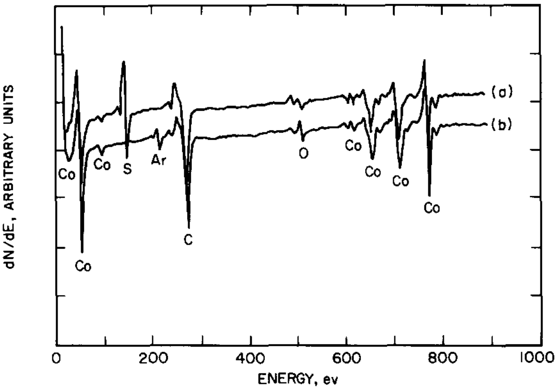

FIG. 15. AES spectra of Co/Al_2O_3 prepared as an evaporated film and treated in the Auger electron spectrometer antechamber; (a) after treatment with 10% CO in H_2 at 400°C for 1.75 hr at 1 atm, (b) after sputtering with Ar^+ for 25 min; sputtering conditions: beam voltage, 2 kV, filament current, 10 mA.

subsurface region even after 95 hr of reaction with 1% CO in H_2 at 390°C. It is inferred that the presence of sulfur on the surface before contact with CO prevented the buildup of carbon on the surface, which in turn inhibited incorporation of carbon into the bulk. Apparently the presence of sulfur on the surface inhibits adsorption and particularly the dissociation of CO, thus preventing growth of surface carbon residues and preventing incorporation of carbon into the bulk of the metal, i.e., bulk carburization.

The Co/Al_2O_3 catalyst which was first deactivated with carbon in a sulfur-free environment had a significant amount of carbon on the surface and had undergone marked bulk carburization prior to sulfur (H_2S) addition. Sickafus (*25*) found that carbon did not diffuse to the surface of Ni (110) when there was sulfur present on the surface, but that it did diffuse to the surface of Ni (110) when the sulfur was sputtered off the surface. By analogy for Co, the carbon incorporated into the bulk during carbon deactivation remained in the bulk during and after the catalyst poisoning by sulfur. The large graphitic carbon peak on the surface for the catalyst deactivated with carbon prior to H_2S contact is suggestive of its inactivity toward hydrogenation.

DISCUSSION

Initial Activity

The initial activity of Co/Al_2O_3 varied depending upon the method of poisoning. For *in situ* poisoning, the initial methanation activity was the same as that for sulfur-free reaction conditions. This is as expected since the *in situ* poisoning runs were started with fresh Co/Al_2O_3. However, the initial methanation activity of presulfided Co/Al_2O_3 was about four orders of magnitude lower than that for fresh catalyst. The activity of presulfided Co/Al_2O_3 changed negligibly with on-stream time thus indicating that the loss in methanation activity was due primarily to sulfur blocking the surface sites active for methanation and suggesting that carbon played no significant role in sulfur poisoning of Co/Al_2O_3. Similar observations have been made for Ni/Al_2O_3 in catalytic methanation (*2*). In the sulfur poisoning of Co/Al_2O_3 which had undergone carbon deactivation prior to sulfur contact the methanation activity just prior to H_2S addition was about two orders of magnitude lower than that in the upper pseudo steady state, and thus the catalyst was in the lower pseudo-steady-state regime or in the carburized state when sulfur poisoning was initiated.

The initial activity behavior shows that there are two types of deactivation present in the Co/Al_2O_3 system; one due solely to carbon, the other due solely to sulfur. The four-orders-of-magnitude reduction in activity caused by sulfur prepoisoning shows how extremely sensitive CO hydrogenation is to sulfur poisoning. Sulfur poisoning under these conditions is due to the presence of a full two-dimensional surface sulfide layer on the metal; it is not due to bulk sulfide formation since bulk cobalt sulfide requires at least a 5000-fold higher H_2S concentration to be thermodynamically stable. The poisoning is due directly to the presence of sulfur and not to sulfur-induced carbon deposition, carbon graphitization, Co carburization, or other sulfur-induced phenomena; AES studies showed that a sulfur-covered ($\theta_S > 0.50$) Co surface will not even form surface carbon even under long-term reaction conditions.

Rate of Poisoning

For *in situ* poisoning, the rate of deactivation was strongly dependent on the rate at which H_2S was fed into the reactor with the feed gas since all H_2S added was adsorbed on the Co surface until an essentially full surface sulfide layer was formed. When the measured methanation rate is related to the amount of sulfur on the surface of the metal, a linear relationship is obtained (Fig. 9) between the methanation rate and $(1-\theta_S)^2$. Only at very low H_2S concentrations, e.g., at 13 ppb H_2S, in the feed gas where the rate of sulfur poisoning is slow enough due to the low rate of sulfur addition so that carbon deactivation is also important, is the relationship between methanation rate and $(1 - \theta_S)^2$ nonlinear. In this case the data fall below the linear relationship because of the contribution to deactivation by carbon. That carbon deactivation is not important at higher H_2S concentrations is indicated by the absence of carbon on the surface of the Co or in the subsurface regions as shown by AES.

These results are very significant in that it is only the second time that a direct measurement of the rate of any reaction as a function of the fraction of unpoisoned surface has been reported. These results serve to illustrate two points: (1) the poisoning by sulfur is a geometric effect in which sulfur blocks the active sites making them inaccessible for the reaction, and (2) the rate-controlling step in methanation requires two surface sites. This supports the mechanism of methanation on Co suggested by the kinetic results (*26*) that the surface reaction is the rate-controlling step.

Sulfur Adsorption Behavior

It can be concluded that the extent of poisoning is the same in all the experiments (Table 1). The atomic density of a Co (0001) surface using the known lattice parameters (*27*), is 1.6×10^{15} Co atom/cm^2. Assuming a S-to-Co atomic ratio of 0.5 to 0.67 for a full surface sulfide layer yields a sulfur adsorption density of 0.8×10^{15} to 1.07×10^{15} Co atoms/cm^2. The measured sulfur adsorption density (Table 1) is in reasonable agreement with the value obtained from low-temperature S adsorption on single-crystal surfaces; the somewhat higher value measured is probably due to a low estimate for the metal surface roughness factor. The average value is 1.06×10^{15} S atoms/cm^2. The variations around this are apparently random with no trends indicated with preparation technique, method of S poisoning, or gas-phase H_2S concentration. These values represent dynamic sulfur adsorption equilibrium values between the gas-phase H_2S concentration and the catalyst surface, since activity recovery upon reducing the gas-phase H_2S concentration was observed as shown in Fig. 2. These results suggest that sulfur is more strongly adsorbed than carbon as indicated by the fact that its adsorption density does not depend on whether or not there is carbon (CO) present and that sulfur even fully replaces the surface carbide carbon for a carbon-deactivated Co sample which was fully carburized prior to H_2S addition. It is very significant that a full surface sulfide layer forms at 390°C independent of whether reaction is occurring and that the sulfur adsorption stoichiometry on the Co surface is essentially that obtained under the ideal conditions of low-temperature UHV single-crystal studies. A similar surface sulfur adsorption stoichiometry of 0.5 to 0.67 (S to surface metal) has been reported from single-crystal studies of Ni (*16*), Fe (*14, 17*), Pt (*15*), and Mo (*18*).

Similarly the steady-state methanation activity is independent of the method of sulfur poisoning, consistent with the observation that the surface density of sulfur is independent of the method of poisoning or the order of its addition relative to the reactants. Clearly, carbon does not play a significant role in the sulfur poisoning of Co/Al_2O_3; sulfur absolutely dominates.

In all the experiments in this work, independent of the method of poisoning, the rate of sulfur adsorption ($d\theta_S/dt$) was constant up to $\theta_S \simeq 0.7$ (Fig. 8), and then it decreased as the surface approached saturation. These results support the observations of Bonzel and Ku (*8*) who reported that the sticking coefficient for H_2S on a clean Pt (111) surface was unity and was constant up to $\theta_S = 0.6$, whereas for θ_S values greater than 0.6 the sticking coefficient rapidly decreased to 0.03. Similar behavior has been observed for the sulfur poisoning of Ni/Al_2O_3 (*2*). The true sticking coefficient cannot be calculated in these experiments because the gas-phase H_2S concentration is not known and thus the molecular collision frequency of H_2S with the surface cannot be estimated. However, the results show that under all conditions, including those for the fully carbided Co surface of the precarbon-deactivated Co/Al_2O_3, the H_2S sticking coefficient is high enough to reduce the H_2S level below our level of detectability (~4 ppb). Since a reduction in the sulfur adsorption rate always occurred at $\theta_S \sim 0.7$, indicating that at this point the H_2S sticking coefficient decreased rapidly, the sticking coefficient for lower coverage must therefore have been large and close to 1.0.

Steady-State Methanation Activity

H_2S (13 ppb) in the feed gas reduces the methanation activity of Co/Al_2O_3 at 390°C by almost four orders of magnitude; subsequent increases in the H_2S concentration cause further reductions in the methanation activity of the sulfur-poisoned Co/Al_2O_3. The AES studies demonstrate that a saturation coverage of Co/Al_2O_3 by sulfur is achieved at 390°C with only 13 ppb H_2S in the feed gas, but these further activity reductions are small compared with the activity reduction caused by 13 ppb H_2S in H_2 (Fig. 5). This indicates that most of the sites that are active for methanation are already poisoned with 13 ppb H_2S in the feed gas at 390°C, resulting in a four-orders-of-magnitude reduction in methanation activity. Some activity sites apparently remain unpoisoned with 13 ppb H_2S; the number of such active sites is further reduced by higher concentrations of H_2S. The results of this work suggest that at 390°C, an essentially full two-dimensional surface sulfide is formed with 13 ppb H_2S in H_2; this two-dimensional surface sulfide is inferred to be inactive for methanation. The remaining low activity of the sulfur-poisoned Co/Al_2O_3 is inferred to be due to pairs of sites which are sulfur atom vacancies on the surface. These sites are speculated to be due to the thermal equilibrium distribution of sulfur vacancies on the surface and gas-phase H_2S according to

$$\begin{aligned}&\mathrm{Co\ Co^SCo^SCoCo^SCo}\\&\qquad + \mathrm{H_2S} \rightleftarrows \mathrm{Co^SCo^SCo^SCoCo^SCo} + \mathrm{H_2}.\end{aligned}$$

Increasing H_2S concentration pushes the above reaction to the right, reducing the number of remaining sulfur vacancies; thus the number of remaining active sites is reduced and so is the catalytic activity. Similar observations and conclusions have been made in the sulfur poisoning of Ni/Al_2O_3 (*2, 19*).

Activation Energy

Identical values of 16 ± 2 kcal/mole for the activation energy were obtained for CO hydrogenation over *in situ* sulfur-poisoned Co/Al_2O_3 and over presulfided Co/Al_2O_3. This value is the same as that for Co/Al_2O_3 in the lower pseudo steady state under sulfur-free conditions (*21, 26*); yet the AES studies showed that there was no carbon present on the surface or incorporated into the bulk for the presulfided catalysts. The AES analyses of Co/Al_2O_3, deactivated to the lower pseudo steady state, showed the presence of multilayer graphitic carbon deposits on the Co surface and carburization of the bulk Co to a significant depth. Although the Co/Al_2O_3 catalysts operating under steady-state conditions in the sulfur-free, lower pseudo steady state and in the sulfur-poisoned state had substantially different surface and subsurface compositions, the catalysts exhibited identical activation energies. This similarity of activation energies indicates that the reaction proceeds, in both cases, on sites which are apparently similar and which would appear to have similar electronic properties. We furthermore infer that the active sites on a carbon-deactivated or carburized Co catalyst and on a sulfur-poisoned Co catalyst are different—at least electronically from the active sites on the fresh Co catalyst in the upper pseudo steady state where the activation energy is 28 ± 2 kcal/mole.

The striking similarity between the activation energy of carbon-deactivated or carburized Co/Al_2O_3 in the lower pseudo steady state and that of sulfur-poisoned Co/Al_2O_3 suggests that methanation proceeds via the same mechanism with probably the same rate-limiting step on both surfaces. Furthermore, we infer that the same types of active sites, having similar electronic properties, are responsible for the methanation activities of carbon-deactivated Co/Al_2O_3 and sulfur-poisoned Co/Al_2O_3. Carburization of the Co bulk appears to change the electronic properties of the active sites for methanation in the same way that sulfur adsorbed only on the Co surface changes the electronic properties of the active sites for methanation. The sulfur layer may be a two-dimensional cobalt sulfide rather than just sulfur adsorbed on the Co surface; formation of two-dimensional surface sulfides has been suggested to occur upon adsorption of approximately a monolayer of sulfur at sufficiently high temperature to allow surface reconstruction (*16*). Sulfur and carbon both have the same electronegativity (*28*) and could change the electronic structure of the surface sites or surface Co atoms in a very similar to identical manner.

The graphite deposits on the Co surface should not be considered to change the electronic properties of the surface sites appreciably since they involve a strong carbon–carbon bonding and exhibit only a weak metal–carbon bonding. The role of graphite deposits can be interpreted as that of geometrically blocking the active sites of methanation.

CO Adsorption on Sulfur-Covered Co Surface

The experiments conducted in the antechamber show that carbon deposition, and hence adsorption and dissociation of CO, is essentially eliminated by the presence of >50% of a monolayer of sulfur on the surface of Co. This observation is consistent with our findings that no carbon was present on the surface or incorporated into the bulk of Co for presulfided Co/Al_2O_3 even after long reaction times, since the bulk carburization must involve dissociation of CO.

These results support the findings of Kishi and Roberts (*6*) that CO dissociation on an Fe film was inhibited by the presence of adsorbed sulfur. Bonzel and Ku (*8*) reported that the binding energy of CO on Pt (110) decreased with increasing sulfur coverage of surface. Rewick and Wise (*7*) suggest that sulfur adspecies fill the CO bridge-bonding sites on the Ni surface; these sites are proposed to be primarily responsible for CO hydrogenation over Ni/Al_2O_3. That sulfur preferentially adsorbs on high-coordination sites, has been reported in the literature (*11, 14*). Therefore, it is expected that sulfur will poison the surface by blocking the sites where CO adsorbs and undergoes dissociation leading to carbon deposition, carburization, graphitization, or hydrogenation to methane.

Summary

Sulfur adsorption on Co is extremely strong; full surface sulfide coverage occurs at 390°C with 13 ppb H_2S in H_2. At this temperature a 5000-fold higher H_2S concentration is required to form the most stable bulk cobalt sulfide (Co_9S_8), indicating that the two-dimensional surface sulfide is at least 12 kcal/mole more stable than the bulk sulfide. The major cause of poisoning by sulfur is geometric blockage of the Co surface. Sulfur adsorption and poisoning are so strong that they dominate entirely over other factors, such as carbon deactivation. A direct measure of the methanation rate as a function of the surface coverage by sulfur has been obtained and shows that the rate-controlling step in methanation involves a pair of surface sites and as suggested by the kinetics (*26*) may involve reaction between a surface-adsorbed carbon and a hydrogen species.

Our results strongly suggest that sulfur adsorption occurs randomly on the Co surface and not via an island-forming mechanism. For an island-forming adsorption mechanism the rate of reaction should be proportional to the fraction of unpoisoned surface; the observed relationship, methanation rate is proportional to $(1-\theta_S)^2$, indicates a statistical uniform coverage of the surface by adsorbed sulfur. Similarly, a Co surface containing 50% of a monolayer of sulfur in islands would leave the remaining Co surface free to decompose CO, depositing carbon; this was not observed. Surface studies show that when 50% of a monolayer of sulfur is present, a completed overlayer structure forms; typically a 2 × 2 structure (*16*) is formed. This would appear to be sufficient to prevent CO adsorption and dissociation at a measurable rate since the sulfur atoms should occupy the high-energy high-coordination sites.

Our results could be interpreted either in terms of one type of active site which is changed electronically by carburization and by sulfur poisoning or in terms of two types of active sites, one associated with a metallic Co surface and the other associated with either a carburized or a sulfur-poisoned Co surface. Our results provide no means of distinguishing between the two possibilities, and the difference may be semantic anyway. In studies of the sulfur poisoning of Ni/Al_2O_3 in CO hydrogenation, we have recently shown that sulfur poisoning is due strictly to geometric blockage of the surface with no electronic effects being observed in the poisoning as evidenced by the fact that the activation energies for methanation over the unpoisoned surface and over the sulfur-poisoned surface (500-fold activity reduction) were identical (*2, 19*). In the case of Ni/Al_2O_3 we inferred that only one type of site was involved. By comparison we would prefer to interpret the results for Co/Al_2O_3 in terms of one type of site which has been changed electronically by carburization and by sulfur poisoning. This is supported by the observation that the selectivity to C_2^+ hydrocarbons relative to CH_4 does not change appreciably upon carbon deactivation or sulfur poisoning although the rate has been reduced more than 100-fold and the activation energy has changed from 28 to 16 kcal/mole (*21, 22*). If the sites had changed radically from fresh to deactivated catalyst, it is unlikely that the selectivity would have remained essentially unchanged even if the selectivity were determined after the rate-determining step. Therefore, our picture of an active site on Co/Al_2O_3 is an ensemble of Co atoms of unknown size, we would speculate three atoms. The undeactivated metallic surface contains many such sites. Deactivation by carbon or sulfur converts the Co metallic surface into a surface and bulk carbide or into a two-dimensional surface sulfide. We speculate that the active sites on these deactivated surfaces are vacancies of S and C atoms leaving an ensemble of Co atoms which catalyze the CO hydrogenation reaction. This ensemble is different than that on a metallic Co surface due to electronic changes in the metal atoms induced by bonding to surrounding Co and/or C or S atoms.

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REFERENCES

1. Dalla Betta, R. A., Piken, A. G., and Shelef, M., *J. Catal.* **40,** 173 (1975).
2. Fitzharris, W. D., Katzer, J. R., and Manogue, W. H., to be submitted to *J. Catal.* (1981).
3. Anderson, R. B., Karn, F. S., and Shultz, J. F., *J. Catal.* **4,** 56 (1956).
4. Colby, S. A., M.Ch.E. thesis, University of Delaware, Newark, 1977.
5. Rostrup-Nielsen, J. R., *J. Catal.* **21,** 171 (1971).
6. Kishi, K., and Roberts, M. W., *J. Chem. Soc. Faraday Trans. I* **71,** 1715 (1975).
7. Rewick, R. T., and Wise, H., *J. Phys. Chem.* **82**(6), 751 (1978).
8. Bonzel, H. P., and Ku, R., *J. Chem. Phys.* **58**(10), 4617 (1973).
9. Edmonds, T., McCarroll, J. J., and Pitkethly, R. C., *Ned. Tijdsch. Vaccuumtech.* **8,** 162 (1970).
10. Edmonds, T., McCarroll, J. J., and Pitkethly, R. C., *J. Vac. Sci. Technol.* **8**(1), 68 (1971).
11. Demuth, J. E., Jepsen, D. W., and Marcus, P. M., *Phys. Rev. Lett.* **32**(21), 1182 (1974).
12. Rewick, R. T., and Wise, H., *Amer. Chem. Soc. Div. Petrol. Chem. Prepr.* 1324 August–September, (1977).
13. Garland, C. W., *J. Phys. Chem.* **63,** 1423 (1959).
14. Legg, K. O., Jona, F., Jepsen, D. W., and Marcus, P. M., *Surface Sci.* **66,** 25 (1977).
15. Fischer, T. E., and Keleman, S. R., *Surface Sci.* **69,** 1 (1977).
16. Perdereau, M., and Oudar, J., *Surface Sci.* **20,** 80 (1970).
17. Grabke, H. J., Peterson, E. M., and Srinivasan, S. R., *Surface Sci.* **67,** 501 (1977).
18. Peralta, L., Berthier, Y., and Oudar, J., *Surface Sci.* **55**(1), 199 (1976).
19. Fitzharris, W. D., Ph.D. thesis, University of Delaware, Newark, 1978.
20. Fitzharris, W. D., and Katzer, J. R., *Ind. Eng. Chem. Fundam.* **17,** 130 (1978).
21. Agrawal, P. K., Katzer, J. R., and Manogue, W. H., *J. Catal.* **69** 312 (1981).
22. Agrawal, P. K., Ph.D. thesis, University of Delaware, Newark, 1979.
23. Windawi, H. M., and Katzer, J. R., *Surface Sci.* **75,** L761 (1978).
24. Rosenqvist, T., *J. Iron Steel Inst.* **176,** 37 (1954).
25. Sickafus, E. N., *Surface Sci.* **19,** 181 (1970).
26. Agrawal, P. K., Katzer, J. R., and Manogue, W. H., submitted to *AIChE J.* (1981).
27. Kittel, C., "Introduction to Solid State Physics," 4th ed. Wiley, New York, 1974.
28. Pauling, L., "The Chemical Bond," 4th ed. Cornell Univ. Press, Ithaca, N.Y. 1966.