

The Oxidizing Properties of γ -Alumina: Infrared Studies of the Adsorption of H_2S and CS_2

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In adsorption or surface reaction studies on γ -aluminas which have been pretreated with oxygen, one may unexpectedly encounter oxidation products. The evidence from H_2S and CS_2 adsorption studies suggests that molecular oxygen, in some adsorbed state, is responsible. To obtain unambiguous reproducible results, the pretreatment of $\gamma-Al_2O_3$ with oxygen should always be followed by a pretreatment with hydrogen.

INTRODUCTION

The catalytic activity of γ -alumina, like those exhibited by most solid catalytic agents, is influenced by the type of pretreatment which has been applied. Several authors (1, 2) have suggested that the degree of surface hydration is the principal factor affecting the catalytic activity of $\gamma-Al_2O_3$. Since "surface hydration" may be interpreted to mean type and number of surface hydroxyl groups, recent work (3) confirms that "surface hydration" may be directly related to catalytic activity of $\gamma-Al_2O_3$ in the dehydration of alcohols. On the other hand, its dehydrogenating activity was influenced by, but not related directly to, "surface hydration." Additional catalytic activity of $\gamma-Al_2O_3$ involving oxidizing properties has been observed. Amorphous aluminas under specified conditions will apparently oxidize adsorbed carbon monoxide to carbon dioxide (4). Upon heating alumina aerogel previously in contact with air, nitric oxide may be given off in substantial amounts (5). In adsorption studies with either H_2S or CS_2 , we have also encountered such oxidizing properties for $\gamma-Al_2O_3$, and it is the purpose of this paper to report these observations. The origin of this oxidizing activity seems to be related to the pretreatment step in which oxygen

is used to eliminate impurities such as carbon compounds from the surface of the $\gamma-Al_2O_3$.

EXPERIMENTS

These studies rely upon infrared spectroscopy to observe the nature of adsorption and surface reactions of H_2S or CS_2 upon $\gamma-Al_2O_3$. The experimental techniques (6) involved preparation of thin infrared-transparent wafers from a powdered $\gamma-Al_2O_3$ (Alon; from Cabot Corp., Boston). After compaction of 10 tons per sq. in. in a 1-in. diameter die, the roughly 0.1 mm thick wafers were pretreated within the *in situ* infrared cell according to one of two basic procedures:

a. by heating in 20 cm Hg of oxygen for 2 hr followed by overnight evacuation at the same temperature, 400°C. This pretreatment produces what will be named "oxidized γ -alumina";

b. by heating the oxidized $\gamma-Al_2O_3$ in 25 cm Hg of hydrogen for 3 hr followed by overnight evacuation at the same temperature, 400°C. This second pretreatment produces what will be named "reduced γ -alumina."

Infrared spectra were recorded using a Perkin-Elmer Model 621 spectrophotom-

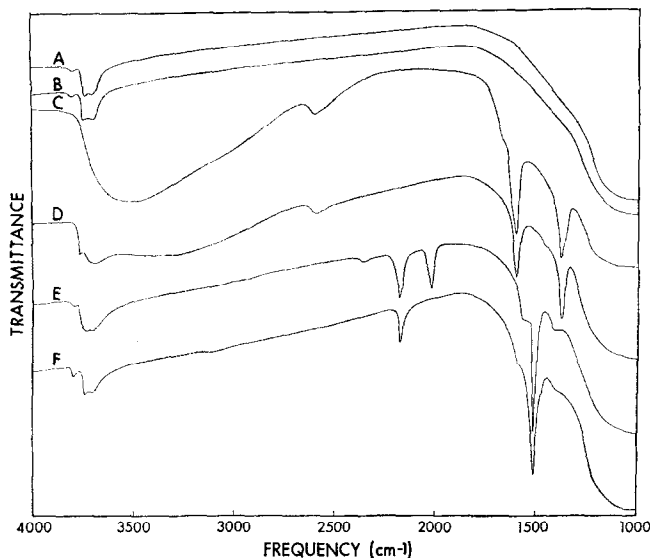


FIG. 1. Infrared spectra for H_2S and CS_2 on γ -aluminas: (A) base line for oxidized alumina; (B) base line for reduced alumina; (C) oxidized alumina exposed to H_2S at room temperature; (D) reduced alumina exposed to H_2S at room temperature; (E) oxidized alumina exposed to CS_2 at room temperature; (F) reduced alumina exposed to CS_2 at room temperature.

eter. Gas-phase interference was eliminated by use of an identical reference cell not containing catalyst. Figure 1 shows the various spectra obtained for adsorption of the gases, H_2S or CS_2 , on both oxidized and reduced aluminas.

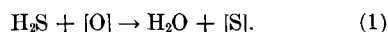
RESULTS

Figure 1A and B present a base line spectral scan characteristic of oxidized and reduced aluminas in an evacuated cell. Only the three absorption bands attributed to hydroxyl stretching frequencies in the 3650 to 3800 cm^{-1} region characterize these scans.

Adsorption of H_2S

Upon contacting H_2S at room temperature, the surface color of oxidized alumina immediately changed from its normal white to violet-green, an observation previously noted (7) with use of oxygen-pretreated $\gamma\text{-Al}_2\text{O}_3$. Figure 1C reveals formation of a broad band at roughly 3550 cm^{-1} and three absorption bands at 2560, 1568 and 1345 cm^{-1} , the latter three attributed as suggested earlier (7) to hydrogen-bonding of H_2S to the surface. The broad band could be attributed to either H_2S or H_2O

hydrogen-bonding, the latter resulting from the possible surface reaction,



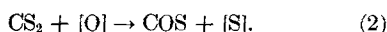
Disappearance of the 3790 cm^{-1} hydroxyl band results from hydrogen-bonding of H_2S .

The occurrence of the suspected reaction (1) was confirmed by mass spectral analysis of gases desorbed from the oxidized alumina after evacuation of gaseous H_2S to 10^{-3} Torr. Both water and elemental sulfur were detected. In addition, the introduction of sulfur vapor into a cell containing newly pretreated oxidized alumina produced the same color change.

Upon repeating the H_2S adsorption experiment using reduced alumina at room temperature, the infrared spectra of Fig. 1D were obtained. Similar evidence for hydrogen-bonding of H_2S is indicated by the 2560, 1568 and 1345 cm^{-1} bands, but the broad band previously noted and now associated with adsorbed water did not appear. Neither product of reaction (1) could be detected by mass spectral identification, thus confirming that the occurrence of reaction (1) follows oxygen pretreatment of the $\gamma\text{-Al}_2\text{O}_3$.

Adsorption of CS₂

Upon contacting CS₂ with either oxidized or reduced aluminas at room temperature, the infrared spectra of Figure 1E and F, respectively, were obtained. The absorption bands at 2156 and 1495 cm⁻¹ are in both cases attributed to physically adsorbed CS₂. The band at 2000 cm⁻¹ observed in Fig. 1E only reveals the formation of COS, a species not previously present. Infrared spectral analysis of the gas-phase surrounding the catalyst wafer confirmed the formation of COS according to the possible surface reaction,



An independent spectral scan for pure COS adsorbed on oxidized alumina confirmed the assignment of the 2000 cm⁻¹ band. The white color of the catalyst changed to green-yellow presumably caused by adsorption of elemental sulfur. These effects related to formation of COS were absent when CS₂ was adsorbed on reduced alumina.

DISCUSSION

Two different mechanisms may be advanced to explain the origin of the oxygen species postulated in reactions (1) and (2), and which may be anticipated to be involved in other oxidations encountered on oxidized alumina. Parkyns (8) proposed that strained oxygen bridges on the surface of alumina formed by progressive dehydration may be responsible for the oxidation of CO to CO₂. Alternatively, adsorbed "molecular" oxygen may be responsible, a source suggested from studies of the oxidation of hydrocarbons on alumina catalysts (3, 9).

In the case of reactions (1) and (2), their instantaneous occurrence solely when contacting oxidized alumina, plus the absence of reaction intermediates, seem to be best explained by the adsorbed oxygen mechanism. Evacuation after pretreatment would result in progressive dehydration of both oxidized and reduced aluminas, and reduced alumina would undoubtedly re-

quire greater dehydration; thus, Parkyns' explanation seemed less likely to be correct. The oxygen adsorbed on the surface corresponds to a low coverage, less than 1% of the surface (10). Repeated dosing with H₂S or CS₂ results in diminishing extent of reactions (1) and (2) on oxidized alumina, confirming that this oxidizing character is associated with the finite amount of oxygen available on the adsorbent. Parkyns also noted (8) that degassing of alumina at temperatures above 450°C removed the active centers for oxidation reactions. This temperature is relatively low for short-term surface recrystallization or annealing effects but degassing at this temperature should effectively desorb most of the adsorbed oxygen.

Because of the sensitivity of the infrared technique in studying surface phenomena on γ -alumina, it is evident that a pretreatment procedure with hydrogen at reducing temperatures, i.e., use of reduced alumina, is necessary to ensure reproducible unambiguous results. This is certainly the case if an oxygen pretreatment of the alumina has been required. In the study of alumina-catalyzed oxidation mechanisms not involving molecular oxygen, the interpretations may be misleading if the "short-term" chemical reactions of adsorbed oxygen are not taken into account.

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