# Role of Reduction Sites in Vapor-Phase Hydrolysis of Carbonyl Sulfide over Alumina Catalysts

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The activity of alumina catalysts at 230°C decreased upon exposure to $O_2$ at elevated temperatures contrary to when pretreated in a stream of either $N_2$ or $N_2$ + $H_2$ mixture. The concentration of reduction sites at the surface of the catalysts, which was estimated from the amount of $SO_2^-$ formed, decreased obviously after exposure to $O_2$ whereas surface basicity or acidity changed slightly. Pentene isomers poisoned the alumina catalyst under reaction conditions; the poisoning effect, despite being scarcely affected by the feed concentration of COS, decreased with increasing feed concentration of $H_2O$ and rather increased with increasing electron-donating nature of pentene isomers. Furthermore, the catalyst was temporarily poisoned by $CO_2$ as well as by $SO_2$; the equilibrium adsorption constants calculated from the kinetics followed the order: $SO_2 \gg COS \gg CO_2$. A mechanistic interpretation suggests that both reduction and Lewis acidic sites are involved in the surface reaction. It is proposed that COS is adsorbed on the former sites to form a negatively charged species, which is then hydrolyzed by water adsorbed on the latter sites.

## INTRODUCTION

Carbonyl sulfide, COS, is a common pollutant in petroleum refineries (*1–3*), in iron and steelmaking (*4*), and in the carbonaceous reduction of $SO_2$ or metal sulfides (*5, 6*). It is also formed in the reaction of $SO_2$ with hydrocarbons (*7–9*), as a result of a side-reaction in the process for sulfur recovery from sour gas. The vapor-phase heterogeneous catalytic hydrolysis appears to be very adequate for the conversion of this sulfur compound in the catalytic reactors of a Claus plant as judged from the large equilibrium constant, log $K_p$ = 3.432 at 500 K for this reaction (*10*). However, only a few kinetics (*11, 12*) or mechanistic (*11, 13*) studies have been published on the hydrolysis of COS. Basic sites on alumina and on NaOH-doped supported cobalt–molybdate catalyst have been considered to be important reaction sites, but their explicit role has not really been demonstrated (*11, 13*). On the other hand, Zdrazil (*14*) noted that $O_2$ tended to poison the catalytic

activity of alumina, alkalized alumina, and cobalt–molybdate. From such conflicting evidence, the catalytic conversion of COS to $CO_2$ and $H_2S$ is evidently not clearly understood. Thus, we have investigated the hydrolysis of COS over two commercial alumina catalysts by using poisoning effect, measurement of surface basicity and acidity, and ESR studies to evaluate the nature of the active sites involved. Our results suggested the participation of sites which have an electron-donating nature rather than so-called basic sites. In this regard, the role of acidic sites is also discussed.

## METHODS

Vapor-phase hydrolysis of COS was carried out using a conventional flow fixed-bed reactor under atmospheric pressure. The reactor consisted of a 15-mm-i.d. Pyrex tube, 300 mm long, with a concentric thermowell and was heated by means of a cylindrical fluidized thermal bath. The catalyst was diluted with glass beads (28–35 mesh), and crushed porcelain (4–5 mesh) was used above the catalyst bed as a preheating medium. Both inert packing materials were previously washed with an aqueous solution of nitric acid and were

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then calcined at 850°C in a furnace for several hours.

Carbonyl sulfide (99.6%, Matheson Co.) was used, but gas chromatographic analysis indicated traces of $CO_2$ in the COS. The distilled water was fed by bubbling $N_2$ through a saturator held at a controlled temperature. As the diluent, $N_2$ (99.99%, Matheson Co.) was used. The total feed rate was always 500 NTPml/min, and the feed composition was COS, 1.5–10 vol%, and $H_2O$, 1.4–10 vol%. The other gases used, $O_2$, $H_2$, $CO_2$, and $SO_2$, were purchased with specified purities of more than 99.98% and were used without further purification. Pentene isomers (reagent grade, Eastman Kodak Co.) were fed by bubbling $N_2$ through another saturator held at 0°C.

The alumina catalysts were supplied by Kaiser Aluminum and Chemical Sales, Inc. (KAS-201, surface area 380 m²/g) and by Cabot Corporation (Alon, 50–100 m²/g). The chemical composition of KAS-201 alumina as specified by the manufacturer is shown elsewhere (15). The KAS-201 alumina supplied in spherical pellets was crushed and sieved with the $-20 + 28$ mesh fraction being retained for this study. The Alon alumina was first compressed at approximately 400 kg/cm² and then crushed ($-28 + 40$ mesh). Silica gel and magnesium hydroxide of reagent grade were supplied by Hewlett–Packard and by Fisher Scientific Co., respectively, but the latter was purified by the same method as described in a previous paper (16).

The gaseous effluent from the reactor was analyzed by gas chromatography. Two columns in series, 1.8 m of Porapak R and 0.6 m of Porapak S, were used at 90°C and at a helium flow rate of 35 NTPml/min. Conversion and yield were calculated on the basis of the material balance of COS. Because negligible side-reaction was observed, the conversion of COS was found to equal the yield of $CO_2$, but the yield of $H_2S$ was always slightly less than that of $CO_2$, presumably due to effects attributed to the separating columns used. Surface acidity or basicity of various pretreated alumina catalysts was determined by means of titration in dry benzene using a benzene solution of 0.01 N butylamine or 0.01 N benzoic acid, respectively. Indicators used were dicinnamalacetone ($pK_a = -3.0$), 4-benzeneazodiphenylamine ($+1.5$), 4-phenylazo-1-naphthylamine ($+4.0$), neutral red ($+6.8$), and phenolphthalein. ESR measurements were carried out at 77 K with a Varian spectrometer operating in the X band, 100 kHz of modulation frequency being adopted. The COS, $CO_2$, and $SO_2$ gases were purified by the freeze-pumping method prior to use for ESR studies. The $g$ values of paramagnetic species were determined by use of the singlet spectrum of char ($g = 2.00276$), and radical concentrations were estimated by comparison with the standard solution of 2,2-diphenyl-1-picrylhydrazyl in benzene.

## RESULTS

### Effect on the Hydrolysis of Pretreatment of Alumina Catalysts with $N_2$, $H_2$, and $O_2$

The reaction was always carried out at temperatures ≥230°C to vaporize trace amounts of elemental sulfur which might have formed on the catalysts. The reactor was heated to the reaction temperature after complete purging of air from the reactor with $N_2$ at room temperature. Constant catalytic activity of the aluminas was observed after a preliminary period of about 2 hr, continuing for more than 8 hr. Preliminary experiments indicated the absence of homogeneous reaction and negligible effects on the catalytic activity from film and pore diffusions.

Table 1 shows the effect of pretreatment at 350°C in a stream of $N_2$ on the catalytic activity of KAS-201 alumina. The conversion of COS over the unpretreated catalyst was 21.8% at 230°C, and it increased gradually with an increase in the pretreatment time and reached 26.6% when alumina was pretreated for 12 hr. However, further pre-

TABLE 1

The Effect of Pretreatment with Flowing $N_2$ on the Catalytic Activity of KAS-201 Alumina[a]

| Pretreatment time (hr) | Conversion of COS (%) |
|:---:|:---:|
| 0 | 21.8 |
| 6 | 25.7 |
| 12 | 26.6 |
| 18 | 24.2 |

[a] Pretreatment, $N_2$ 100 NTPml/min, 350°C. Reaction temperature, 230°C; feed, COS 3.0 vol%, $H_2O$ 9.8 vol%, $N_2$-diluent. Contact time, W/F = 0.0374 g-catalyst · hr/g-mole.

treatment resulted in a slight decrease in the catalytic activity. A similar result was also obtained in the pretreatment with a flowing $N_2$ + $H_2$ mixture (Table 2). In another series of tests, a mixture of $N_2$ and $H_2$ ($H_2$ 23.1 vol%) was first fed over the catalyst for 2 hr at various temperatures and the catalytic activity was then determined at 230°C. The conversion of COS was 20.2% when alumina was pretreated at 230°C, and it increased with an increase in the pretreatment temperature and reached 29.1% when pretreated at 350°C. However, further rises in temperature caused a decrease in the catalytic activity. Alon alumina showed a similar behavior (Table 2).

In contrast, exposure of these alumina catalysts to $O_2$ at elevated temperatures always caused a remarkable decrease in the activity (Table 3). KAS-201 alumina pretreated at 350°C in a stream of $N_2$ for 7 hr or unpretreated Alon alumina gave conversions of 25.6 and 16.1%, respectively, at 230°C, but these decreased to 13.6 and 2.6%, respectively, when they were contacted with a flowing $N_2$ + $O_2$ mixture ($O_2$ 23.1 vol%) at 230°C for 1 hr. The catalytic activity decreased to a negligible value with more severe oxygen pretreatments; the conversion was 1.3% when the KAS-201 alumina catalyst was contacted with pure $O_2$ at 400°C for 10 hr. This decrease in the catalytic activity caused by contact with $O_2$ agrees with the observation reported by Zdrazil ([14]).

The orders of reaction with respect to COS and $H_2O$ in the hydrolysis over KAS-201 alumina catalyst at 230°C which were determined using differential kinetics are shown in Eq. (1),

$$r_0 = k_1 C_{cos}^{1.0} C_{H_2O}^{0.1} \qquad (1)$$

where $r_0$ is initial rate of the hydrolysis of COS, $k_1$ is overall reaction rate constant, and $C_j$ is concentration of $j$ in the feed ($j =$ COS,$H_2O$). Feed compositons ranged from 1.5 to 10 vol% of COS and 1.4 to 10 vol% of $H_2O$. These reaction orders agree well with those obtained over activated alumina and over cobalt–molybdate catalysts ([11, 12]).

## Measurement of Surface Acidity and Basicity on Various Pretreated Alumina Catalysts

The alumina catalysts were crushed and the powder (0.20 g) was pretreated in various atmospheres. Their acidity and basicity were determined and are listed in Table 4. Total acidity ($pK_a \leq +6.8$) of the KAS-201 alumina pretreated with $N_2$ flows at 230°C for 3 hr was as small as 0.047 mequiv/g-catalyst, but it increased to 0.40–0.70 mequiv/g-catalyst upon pretreatment with $N_2$ flows at 350°C, with $N_2$ + $H_2$ at 350°C, and with $N_2$ + $O_2$ at 230 and 350°C. Acid strength also increased upon the

TABLE 2

Variations in the Catalytic Activity of Aluminas with Temperature of Hydrogen Pretreatment[a]

| Pretreatment temperature (°C) | Conversion of COS (%) | |
|:---:|:---:|:---:|
| | KAS-201 alumina | Alon alumina[b] |
| 230 | 20.2 | 10.2 |
| 300 | 27.7 | 15.6 |
| 350 | 29.1 | 15.8 |
| 400 | 24.3 | 15.5 |

[a] Pretreatment, $N_2$ + $H_2$ ($H_2$ 23.1 vol%) 130 NTPml/min, 2 hr. Reaction temperature, 230°C; feed, COS 3.0 vol%, $H_2O$ 9.7 vol%, $N_2$-diluent. Contact time, W/F = 0.0374 (KAS-201) or 0.0523 (Alon) g-catalyst · hr/g-mole.

[b] Determined after an interval of 1 hr.

TABLE 3

Poisoning of Alumina Catalysts with Oxygen[a]

| Pretreatment | Conversion of COS (%) | |
| --- | --- | --- |
| | KAS-201 alumina | Alon alumina |
| $N_2$, 350°C, 7 hr | 25.6 | 16.1[b] |
| Then $N_2 + O_2$, 230°C, 1 hr | 13.6 | 2.6 |
| Then $N_2 +$ 350°C, 1 hr | 4.8 | 1.3 |
| Then $O_2$, 400°C, 10 hr | 1.3 | — |

[a] Pretreatment, $N_2$ 100 NTPml/min, $O_2$ 30 NTPml/min. Reaction temperature, 230°C; feed, COS 3.0 vol%, $H_2O$ 9.8 vol%, $N_2$-diluent. Contact time, W/F = 0.0374 (KAS-201) or 0.0523 (Alon) g-catalyst · hr/g-mole.

[b] Unpretreated.

above pretreatments. On the other hand, the basicity of the alumina pretreated with $N_2$ at 230°C was 0.323 mequiv/g-catalyst, and basicity also increased to 0.43–0.47 mequiv/g-catalyst upon the former two pretreatments whereas it decreased to 0.190 mequiv/g-catalyst or remained almost constant upon exposure to $O_2$. The sites on Alon alumina exhibited stronger acidity than those on KAS-201. Total acidity ranged from 0.56 to 0.79 mequiv/g-catalyst with nature of the pretreatments.

The basicity of the Alon alumina always increased upon pretreatment with $N_2 + H_2$ flows or with $N_2 + O_2$. It is worthwhile to note that the Alon alumina previously exposed to a flowing $N_2 + O_2$ mixture at 230°C had a larger basicity than the alumina pretreated with $N_2$ flows at the same temperature. Thus, no correlation between the catalytic activity and basicity of the aluminas was observed.

## Poisoning of KAS-201 Alumina Catalyst by Pentene during the Hydrolysis

As shown in Table 4, the alumina catalyst has predominantly acidic sites; however, their role in the hydrolysis has not been investigated. Since olefinic hydrocarbons interact with acidic sites, their influence, if any, was investigated by the introduction of pentene into the reactor during the course of the hydrolysis reaction. Introduction of pentene was initiated when a constant catalytic activity was attained at 320°C. The material balance calculations for COS indicated absence of reaction between COS and pentene. An initial decrease in the activity was observed upon the introduction of pentene but this activity was not restored to the previous level even after the feed of pentene was discontinued. Since the

TABLE 4

Surface Acidity and Basicity of Various Pretreated Alumina Catalysts[a]

| Catalyst and pretreatment | Acidity (mequiv/g-catalyst) | | Basicity (mequiv/g-catalyst) |
| --- | --- | --- | --- |
| | Strongest acid ($pK_a$) | Total ($pK_a \leq +6.8$) | |
| KAS-201 alumina[b] | | | |
| $N_2$, 230°C, 3 hr | 0.037 (4.0–6.8) | 0.047 | 0.323 |
| $N_2$, 350°C, 16 hr | 0.166 (1.5–4.0) | 0.399 | 0.465 |
| $N_2 + H_2$, 350°C, 2 hr | 0.214 (1.5–4.0) | 0.435 | 0.427 |
| $N_2 + O_2$, 230°C, 2 hr | 0.219 (1.5–4.0) | 0.455 | 0.190 |
| $N_2 + O_2$, 350°C, 2 hr | 0.520 (−3.0–1.5) | 0.696 | 0.318 |
| Alon alumina | | | |
| $N_2$, 230°C, 3 hr | 0.314 ($\leq$ −3.0) | 0.704 | 0.107 |
| $N_2 + H_2$, 350°C, 2 hr | 0.265 ($\leq$ −3.0) | 0.561 | 0.282 |
| $N_2 + O_2$, 230°C, 2 hr | 0.454 ($\leq$ −3.0) | 0.791 | 0.185 |

[a] Pretreatment, $N_2$ 100 NTPml/min, $H_2$ and $O_2$ 30 NTPml/min.

[b] This alumina had no acid at $pK_a \leq$ −3.0.

KAS-201 alumina used in the experiment developed a nearly black color, this darkening may be attributed to strongly adsorbed pentene forming carbonaceous material on acidic sites, thereby eliminating their participation. Figure 1 shows a decrease in the relative catalytic activity, plotted as $x/x_0$ versus reaction time, where $x_0$ and $x$ are the conversion of COS at 320°C before and during the introduction of pentene, respectively. The decrease in the $x/x_0$ with time, which is a measure of the poisoning effect, was similar even though the feed concentration of COS increased from 3.0 to 6.0 vol%, while that of $H_2O$ and of pentene remained unchanged. However, this decrease became much less with an increase in the feed concentration of $H_2O$ (4.3 → 7.3 → 9.6 vol%) at a fixed feed concentration of COS 3.0 vol%. It is interesting to note that the poisoning effect by 2-methyl-2-butene was stronger than that by 2-methyl-1-butene in exactly the same conditions. The above observations suggest the participa-
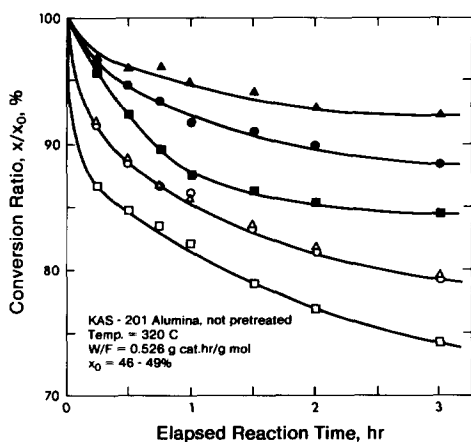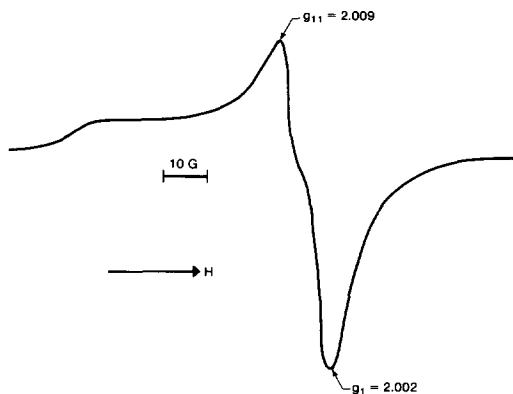


FIG. 2. ESR spectrum of $SO_2^-$ formed on preevacuated Alon alumina at 77 K. Modulation width: 1.0 G.

tion of acidic sites in the hydrolysis reaction.

### ESR Studies on Alumina Catalysts

Reduction sites on solid catalysts are usually destroyed upon exposure to $O_2$. The remarkable decrease in the catalytic activity caused by contact with $O_2$ (Table 3) strongly suggests the participation of reduction sites in the hydrolysis of COS. To examine this notion further, Alon alumina (0.4 g) was evacuated in a quartz tube (2 mm i.d.) at 500°C for 2 hr under $3 \times 10^{-3}$ Torr (1 Torr = 133.3 N/m²). Gaseous $SO_2$ at 10 Torr was introduced at room temperature and followed by thermal treatment at 100°C for 1 hr. Subsequently, the ESR spectrum was measured at 77 K. The preevacuated alumina showed no ESR signal, but a strong ESR signal with axially symmetric $g$ values of $g_{\parallel} = 2.009$ and $g_{\perp} = 2.002$ was observed after exposure to $SO_2$ (Fig. 2). This observation is also in agreement with the results from KAS-201 alumina. These $g$ values agreed with those for $SO_2^-$ formed on alumina and on synthetic zeolites (17–20).

The concentration of $SO_2^-$ formed on various pretreated aluminas was estimated (Table 5). KAS-201 or Alon aluminas preevacuated at 500°C for 2 hr gave $SO_2^-$ concentration of $2.3 \times 10^{16}$ and $7.6 \times 10^{16}$ spins/g-catalyst, respectively, but the con-



FIG. 1. Poisoning of catalyst by pentene during hydrolysis of COS. Feed:

| Symbol | % COS | %H₂O | % Pentene |
|--------|-------|------|-----------|
| ○ | 3.0 | 4.3 | 1.0 (mixture of isomers) |
| △ | 6.0 | 4.6 | 1.0 (mixture of isomers) |
| ▲ | 3.0 | 9.6 | 1.0 (mixture of isomers) |
| ● | 3.0 | 7.3 | 1.0 (mixture of isomers) |
| □ | 3.0 | 4.4 | 1.0 (2-methyl-2-butene) |
| ■ | 3.0 | 4.4 | 1.0 (2-methyl-1-butene) |

TABLE 5

Concentration of Reduction Sites Formed on Various Pretreated Alumina Catalysts by Estimates of $SO_2^-$ Formation[a]

| Catalyst and pretreatment | $SO_2^-$ (spins/g-catalyst) ($\times 10^{16}$) |
|---|---|
| KAS-201 alumina | |
|   Evacuated at 500°C under 3 × 10⁻³ Torr for 2 hr | 2.3 |
|   Similarly evacuated and then oxidized with $O_2$ (20 Torr) at 230°C, or at 350°C for 1 hr | Negligible |
| Alon alumina | |
|   Evacuated at 500°C under 3 × 10⁻³ Torr for 2 hr | 7.6 |
|   Similarly evacuated and then oxidized with $O_2$ (20 Torr) at 230°C for 1 hr | 4.1 |
| Silica gel | |
|   Evacuated at 500°C under 3 × 10⁻³ Torr for 2 hr | None |

[a] ESR was measured at 77 K.

centration decreased to a negligible value or 54% of the initial value when the aluminas were similarly preevacuated and then exposed to $O_2$ at 20 Torr at 230°C for 1 hr. This behavior parallels the observed changes in catalytic activity. No $SO_2^-$ could be detected on preevacuated silica gel. The formation of $CO_2^-$ and $COS^-$ on the aluminas preevacuated at 550°C under 3 × 10⁻³ Torr for 10 hr was not observed although $CO_2$ and COS were adsorbed using the same method as reported for magnesia (16, 21). However, an ESR spectrum which would be due to a product derived from the decomposition of $COS^-$ (21) was seen at 77 K when COS was adsorbed at room temperature.

## Poisoning of Alumina Catalyst by $SO_2$ or $CO_2$

In order to ensure the participation of reduction sites in the reaction, the temporary poisoning of KAS-201 alumina catalyst caused by feeding an acidic gas, $SO_2$ or $CO_2$, with the reactant mixture at 230°C was kinetically studied. The absence of reaction between COS and $SO_2$ during the hydrolysis was supported by the material balance for COS. A reduction in the feed concentration of $H_2O$ from 10.6 to 3.1 vol% at COS 3.0 vol% and $SO_2$ 1.0 vol% caused a negligible change in the poisoning effect; the conversion ratio, $x'/x_0'$, where $x_0'$ and $x'$ are the conversion of COS in the absence or in the presence of $SO_2$, respectively, changed from 16.4 to 16.1%. Hence, the observed effect could not be attributed to the competitive adsorption of $SO_2$ with $H_2O$. The following rate equation (2) was derived on the assumption that COS and $H_2O$ are associatively adsorbed on reduction sites and on acidic sites, respectively, and that the surface reaction of these adsorbed species is rate determining. This assumption is discussed later.

$$r_0 = k_2 \left( \frac{K_{\cos}C_{\cos}}{1 + K_{\cos}C_{\cos}} \right) \left( \frac{K_{H_2O}C_{H_2O}}{1 + K_{H_2O}C_{H_2O}} \right) \quad (2)$$

where $r_0$ is initial rate of hydrolysis of COS in the absence of poison, $k_2$ is surface reaction rate constant, $K_j$ is equilibrium adsorption constant of $j (j = COS, H_2O)$, and $C_j$ is concentration of $j$ in the feed. This rate equation simplifies to the form of Eq. (1) when $K_{\cos}$ is small and $K_{H_2O}$ large. When $SO_2$ or $CO_2$ is added, the initial rate in the presence of a poison becomes

$$r = k_2 \left( \frac{K_{cos}C_{cos}}{1 + K_{cos}C_{cos} + K_iC_i} \right)$$

$$\left( \frac{K_{H_2O}C_{H_2O}}{1 + K_{H_2O}C_{H_2O}} \right) \qquad i = SO_2 \text{ or } CO_2. \quad (3)$$

From Eqs. (2) and (3),

$$r/(r_0 - r) = \frac{1}{K_iC_i} + \left( \frac{K_{cos}}{K_i} \right) \left( \frac{C_{cos}}{C_i} \right). \quad (4)$$

Equation (4) suggests a linear relationship between $r/(r_0 - r)$ and $C_{cos}/C_i$ at a fixed concentration of poison in the feed. Figure 3 illustrates the relationships obtained in the hydrolysis over KAS-201 alumina catalyst at 230°C. Equilibrium adsorption constants of $SO_2$, COS, and $CO_2$ were calculated from the slopes and the intercepts of these lines and are shown in Table 6. It is to be noted that the adsorption constant increased remarkably with increase in the electron affinity of the molecule.

### Hydrolysis of COS over Magnesia and Silica Gel

Pretreatment of magnesia in a stream of $O_2$ was also investigated in terms of its catalytic activity in the hydrolysis reaction (Table 7). The catalytic activity of unpretreated $Mg(OH)_2$ at 230°C decreased from a conversion of 27.7% to one of 4.3% upon exposure to $O_2$ at 230°C for 0.5 hr. On the other hand, it increased remarkably upon preevacuation at 550°C for 6 hr; the conversion was 100% at 230°C. However, this high catalytic activity decreased similarly
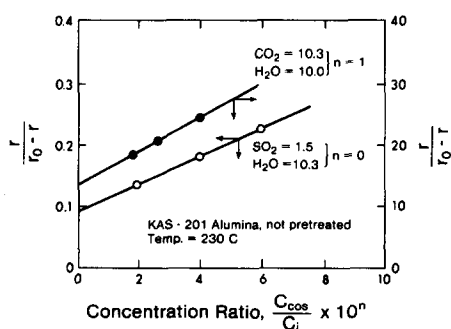
#### TABLE 6

Equilibrium Adsorption Constants for $CO_2$, COS, and $SO_2$ on KAS-201 Alumina Determined by Poisoning Effect[a]

| Molecule | Adsorption constant | Electron affinity of molecule (eV) |
|---|---|---|
| $CO_2$ | 0.6–0.7 | −1.26[b] |
| COS | 16 | 0.0[b] |
| $SO_2$ | 719 | 1.097[c] |

[a] Temperature, 230C, unpretreated KAS-201 alumina. Concentration unit, mole fraction (−).
[b] Ref. (22).
[c] Ref. (23).

upon exposure to $O_2$ at 350°C for 12 hr. Silica gel exhibited no catalytic activity for the hydrolysis reaction (Table 7).

### DISCUSSION

The increase in basicity of the aluminas upon pretreatment at 350°C with flowing $N_2$ or with a flowing $N_2 + H_2$ mixture compared with the basicity with flowing $N_2$ at 230°C conforms to the changes in the catalytic activities as shown in Tables 1, 2, and 4. In contrast to the above, the either almost constant or increase in basicity upon exposure to $O_2$ at 350 or 230°C does not correlate with the corresponding reductions in the catalytic activity (Tables 3 and 4).



FIG. 3. Linear plots of Eq. (4) in the inhibition experiments.

#### TABLE 7

Hydrolysis of COS over Magnesia and Silica Gel Catalysts[a]

| Catalyst and pretreatment | Conversion of COS (%) |
|---|---|
| $Mg(OH)_2$, unpretreated | 27.7 |
| Then $O_2$, 230°C, 0.5 hr | 4.3 |
| $Mg(OH)_2$, evacuated at 550°C under $3 \times 10^{-3}$ Torr for 6 hr | 100 |
| Then $O_2$, 350°C, 12 hr | 14.8 |
| Silica gel, unpretreated | Negligible |

[a] Pretreatment, $O_2$ 30 NTPml/min. Reaction temperature, 230°C; feed, COS 3.0 vol %, $H_2O$ 8.3 vol %, $N_2$-diluent. Contact time, $W/F$ = 0.0750 g-catalyst · hr/g-mole.

The reason for this increase in basicity upon exposure to $O_2$ was not clarified; however, it is apparent that the so-called basic sites are not important for the hydrolysis of COS. This result does not agree with other views previously reported (11, 13). On the other hand, the observed formation of $SO_2^-$ on the preevacuated aluminas and the agreement between the remarkable decrease in both the concentration of $SO_2^-$ and the catalytic activity upon exposure to $O_2$ strongly suggests the participation of reduction sites in the hydrolysis of COS (Tables 2 and 5). As gaseous oxygen is adsorbed on reduction sites as $O_2^-$ at the surface of alumina at low temperatures (24–26), this oxygen species may be converted to the surface oxygen anion $O^{2-}$ upon heating at 230–400°C, thereby poisoning the reduction sites. The low but visible activity of the $O_2$-pretreated KAS-201 alumina, in spite of negligible formation of $SO_2^-$ (Tables 3 and 5), is presumably attributed to a weak reduction of the surface by COS during the initial stage of the hydrolysis reaction.

The role of acidic sites is considered next. Olefinic hydrocarbons are usually adsorbed on electron-acceptors such as acidic sites. The adsorption on Lewis acidic sites forming positively charged complexes is strong when its ionization potential is low (27–29). On the other hand, 2-methyl-2-butene and 2-methyl-1-butene give identical tertiary carbonium ions upon adsorption on Brønsted acidic sites. Since the former butene is thermodynamically more stable than the latter in gaseous state, the equilibrium adsorption constants can be expected to follow the order: 2-methyl-2-butene < 2-methyl-1-butene. Hence, the observation of catalyst poisoning upon introduction of pentene and the stronger poisoning by 2-methyl-1-butene (9.12 eV) (30) support the notion of participation of Lewis acidic sites in the reaction (Fig. 1). In addition, the negligible effect on the poisoning from changes in the feed concentration of COS indicates noncompetitive adsorption of pentene with COS. In contrast, the somewhat improved activity with increase in the feed concentration of $H_2O$ at COS 3.0 vol% is evidence for competitive adsorption of pentene with $H_2O$ (Fig. 1). Thus, it may be concluded that $H_2O$ is adsorbed on Lewis acidic sites, $Al^{3+}$, whereas COS adsorption does not seem to be involved with these sites. Adsorption of COS on Lewis acidic sites, $Al^{3+}$, in the absence of $H_2O$ was already observed by means of ir (15). In the present case, however, since $H_2O$ is present and is strongly adsorbed on the acidic sites as suggested by the zero reaction order dependency shown in Eq. (1), the amount of COS adsorbed by $Al^{3+}$ seems to be negligible.

The reaction mechanism must also be discussed in relation to the role of the reduction sites. The adsorption of $SO_2$ on the surface via hydroxyl sites, –OH, over both alumina and zeolites has already been reported (15, 31, 32). However, the negligible change in the poisoning effect of $SO_2$ with a large change in the concentration of $H_2O$ in the feed indicates that this $SO_2$ adsorption has no effect on the conversion of COS even if present. As a result, the very strong poisoning by $SO_2$ is attributed to the adsorption of $SO_2$ on reduction sites. The observation of $SO_2^-$ formation (Fig. 2) and the stability of $SO_2^-$ formed on alumina at 200°C (20) support this view. On the analogy of $SO_2$ adsorption, it is very probable that reduction sites work as sites for adsorption of COS. The kinetic study on the poisoning effect of $SO_2$ and of $CO_2$, which was based on a dual-site mechanism, revealed an increase in the adsorption constant for $SO_2$, COS, and $CO_2$ with a rise in the electron affinity (Fig. 3 and Table 6), providing strong evidence for the adsorption of these acidic gases on the reduction sites with formation of negatively charged molecules during the hydrolysis. Here, the poisoning effect of $CO_2$ is not attributed to the equilibrium of the hydrolysis reaction as judged from the equilibrium reaction constant, $2.70 \times 10^3$ at 227°C (10).
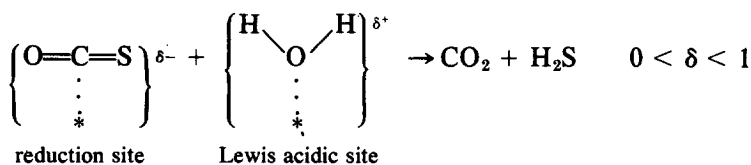
Lunsford and co-workers observed the formation of $CO_2^-$ and of $COS^-$ on S-centers over degassed magnesia, these centers being rapidly destroyed upon exposure to $O_2$ (16, 21). The substantial decrease in the catalytic activity of $Mg(OH)_2$ and of magnesia formed by the evacuation of $Mg(OH)_2$ upon exposure to $O_2$ (Table 7) is thus additional evidence for the important role of reduction sites in the hydrolysis reaction. The negligible activity of silica gel, which had no reducing activity (Tables 5 and 7), is also consistent with this view. In the present work, however, the formation of $CO_2^-$ and $COS^-$ was not observed on the aluminas but there was a suggestion of $COS^-$ formation, as described before. The minimal evidence of $CO_2^-$ and $COS^-$ is presumably due to the low electron affinity of the $CO_2$ molecule and of COS (Table 6), and at the same time to the low electron-donating nature of the reduction sites as compared with those on degassed magnesia.

It has been shown that bare unsolvated hydroxyl ions and the oxide-ion defect, i.e., an exposed and coordinatively unsaturated $O^{2-}$, are electron-donating sites at the surface of alumina (33). Hence, it is believed that the latter type of electron-donating sites plays a role as reduction sites during the hydrolysis of COS. The increase in the catalytic activity of the aluminas upon pretreatment with flowing $N_2$ and with a flowing $N_2 + H_2$ mixture at elevated temperatures (Tables 1 and 2) could be due to formation of these electron-donating sites through elimination of $H_2O$ and/or surface lattice oxygen. However, it seems that the subsequent severe pretreatments rather destroy these electron-donating sites (Tables 1 and 2). As the amount of so-called basic sites was of the order of $0.6 \times 10^{20}$–$2.8 \times 10^{20}$ sites/g-catalyst whereas that of the reduction sites was $10^{16}$–$10^{17}$ spins/g-catalyst (Tables 4 and 5), only a small portion of the electron-donating sites could play a role as reduction sites.

As shown previously, $H_2O$ is first adsorbed on Lewis acidic sites with formation of a positively charged molecule. In the event of dissociation occurring with the aid of so-called basic sites, it would be expected that the formed hydroxyl group carries less positive charge because the accompanying $H^+$ upon abstraction by a basic site would be neutralized. Under such conditions, the dissociation of $H_2O$ may lead to a decrease in the interaction with a negatively charged adsorbed COS molecule. Therefore, it is postulated that the hydrolysis initiates through ionic interaction of these adsorbed molecules. This step may be rate determining.

$$\left\{ \begin{array}{c} O{=}C{=}S \\ \vdots \\ * \end{array} \right\}^{\delta-} + \left\{ \begin{array}{c} H{\diagdown}{}_O{\diagup}H \\ \vdots \\ * \end{array} \right\}^{\delta+} \rightarrow CO_2 + H_2S \qquad 0 < \delta < 1$$

reduction site        Lewis acidic site

In the present work, the participation of the so-called basic sites in the hydrolysis of COS and the mechanism for activating $H_2O$ on the surface of $Mg(OH)_2$ and of magnesia catalysts have not been clarified. In the case of the Alon alumina catalyst, kinetic studies and poisoning by pentene, $CO_2$, and $SO_2$ were not investigated. The reaction mechanism, however, seems to be the same as that over the KAS-201 alumina catalyst.

## REFERENCES

1. O'Hara, F. J., Keely, W. M., and Fleming, H. W., *Anal. Chem.* **28**, 466 (1956).
2. Sample, G. E., U.S. Patent 2,434,868 (1948).
3. Huxley, E. E., U.S. Patent 3,358,421 (1967).
4. Richardson, F. D., and Fenchan, C. J. B., *J. Iron Steel Inst. London* **179**, 4 (1954).
5. Kiaer, T., *Eng. Mining J.* **155**, 88 (1954).
6. Fleming, E. P., and Fitt, T. C., *Ind. Eng. Chem.* **2**, 2249 (1950).
7. Cameron, D. J., and Beavon, D. K., Paper presented at February, 1970 Meeting of Canadian Natural Gas Processors Association, Edmonton, Alberta, Canada.
8. Sawyer, F. G., Hader, R. N., Hardon, L. K., and Morningstar, E., *Ind. Eng. Chem.* **42**, 1938 (1950).
9. Zawadski, J., Ostrouch, S., and Kwiecinski, G., *Premysl Chem.* **22**, 558 (1938).
10. Stull, D. R., Westrum, E. F., and Sinke, G. C., "The Chemical Thermodynamics of Organic Compounds," pp. 219, 220, 229, 230. Wiley, New York, 1969.
11. Namba, S., and Shiba, T., *Kōgyō Kagaku Zasshi* **71**, 93 (1968).
12. George, Z. M., *J. Catal.* **32**, 261 (1974).
13. George, Z. M., *J. Catal.* **35**, 218 (1974).
14. Zdrazil, M., *Chem. Prumysl roc.* 24/29, cis 11 (1974).
15. Chuang, T. T., Dalla Lana, I. G., and Liu, C. L., *J. Chem. Soc., Faraday Trans. I* **69**, 643 (1973).
16. Lunsford, J. H., and Jayne, J. P., *J. Phys. Chem.* **69**, 2182 (1965).
17. Wang, K. W., and Lunsford, J. H., *J. Phys. Chem.* **73**, 2069 (1969).
18. Wang, K. W., and Lunsford, J. H., *J. Phys. Chem.* **75**, 1165 (1971).
19. Ono, Y., Tokunaga, H., and Keii, T., *J. Phys. Chem.* **79**, 752 (1975).
20. Ono, Y., Takagiwa, H., and Fukuzumi, S., *J. Catal.* **50**, 181 (1977).
21. Lin, M. J., Johnson, D. P., and Lunsford, J. H., *Chem. Phys. Lett.* **15**, 412 (1972).
22. Dispert, H., and Lacmann, K., *Hahn-Meister-Inst. Kernforsch. Berlin, HMI-B* **198**, 34 (1974).
23. Celott, R. J., Bennet, R. A., and Hall, J. L., *J. Chem. Phys.* **60**, 1740 (1974).
24. Eley, D. D., and Zammitt, M. A., *J. Catal.* **21**, 366 (1971).
25. Che, M., McAteer, J. C., and Tench, A. J., *Chem. Phys. Lett.* **31**, 145 (1975).
26. Losee, D. B., *J. Catal.* **50**, 545 (1977).
27. Cvetanovic, R. J., Duncan, F. J., and Falconer, W. E., *Canad. J. Chem.* **42**, 2410 (1964).
28. Moro-oka, Y., and Ozaki, A., *J. Amer. Chem. Soc.* **89**, 5124 (1967).
29. Akimoto, M., and Echigoya, E., *Bull. Chem. Soc. Japan* **49**, 3687 (1976).
30. Watanabe, K., Nakayama, T., and Mottl, J., *J. Quant. Spectrosc. Radia. Transfer* **2**, 369 (1962).
31. Deo, A. V., Dalla Lana, I. G., and Habgood, H. W., *J. Catal.* **21**, 270 (1971).
32. Khalafalla, S. E., and Haas, L. A., *J. Catal.* **24**, 115 (1972).
33. Flockhart, B. D., Leith, I. R., and Pink, R. C., *Trans. Faraday Soc.* **65**, 542 (1969).