

A Study of the Kinetics and Mechanism of COS Hydrolysis over Alumina

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The role of surface sites on γ -alumina in the mechanism of hydrolysis of carbonyl sulfide was investigated using a combination infrared cell-recycle flow reactor. Zero-order and first-order behavior were observed for H_2O and COS, respectively. The use of acidic (acetic acid) and basic (NaOH, NH_3 , and pyridine) site-blocking agents reveal basic sites to be essential for the hydrolysis surface reaction. Competitive adsorption of COS and H_2O base centers was evident; however, an Eley-Rideal surface reaction mechanism involving adsorbed H_2O seemed most compatible with the experimental observations. Catalytic deactivation with time and with exposure to oxygen were evaluated and explanations put forward.

In the processing of H_2S -rich streams to form elemental sulfur using the modified Claus technology, some COS frequently is present in the feedstream entering the catalytic converters. The failure to hydrolyze the COS in the converters results in the appearance of COS in the process tailgas, and consequent expensive downstream incineration to SO_2 or an alternative cleanup procedure. In spite of the importance of COS hydrolysis to natural gas processing, the published information on this reaction, its mechanism and its kinetics is rather sparse (1-7).

In earlier studies (1, 6, 7), the importance of reducing sites on the alumina surface was established with the suggestion that the hydrolysis mechanism involves both reducing and Lewis-acid sites. Based on the poisoning effect of pentenes upon the catalytic activity of alumina for the hydrolysis of COS, it was proposed that COS forms negatively charged species on reducing centers and that this species then undergoes hydrolysis with water adsorbed on Lewis-acid centers.

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Further consideration of the evidence for the proposed mechanism suggests an alternative explanation for the decrease in catalytic activity observed in the presence of pentenes (1). The role of reduction centers in the mechanism seems evident but not sufficiently clear. Pentenes, having low basic strength, should react only with strongly acidic centers which at reaction conditions should already be poisoned by adsorbed water. Since Kaiser alumina catalyst developed a nearly black color when pentenes were present (1), presumably from the formation of coke, which may block the access of reactant molecules to active centers on the surface, a decrease in catalytic activity would be expected.

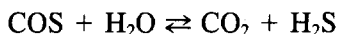
Another argument for reexamination of the mechanism arises from the fact that Alon alumina, in spite of its stronger acidity, was less active than Kaiser alumina. The latter is also distinguished by considerably higher basicity. Therefore, additional experiments were carried out with alumina catalysts of different levels of basicity using a more versatile continuous flow recycle reactor. The earlier studies utilized a small conventional differential fixed-bed reactor.

EXPERIMENTAL DETAILS

The recycle reactor design enabled ir

transmission spectral scans to be measured through a thin catalyst wafer at steady-state reaction conditions, and at the same time, sampling of reaction products for gas chromatographic analysis. A general description of the ir cell-recycle reactor is available (8, 9). The steady-state rate measurements enable effects such as poisoning and deactivation to be readily discerned. Preliminary tests in which the thickness of the catalyst wafer was varied, preceding this work and in studies of several other alumina-catalyzed reactions, have always verified that wafer thicknesses of the order of 0.1 mm eliminate internal diffusion limitations. With proper care, intrinsic reaction rates may be measured over a range of reaction conditions.

The COS feed flow rate was determined using the GC analysis of the N₂-COS feed mixture and carefully metered nitrogen flow rate. In the absence of reactions other than the hydrolysis reaction,



the fractional conversion of COS could be determined by comparison of GC peak areas for COS and CO₂ in the exit stream, assuming reaction stoichiometry to be preserved. The liquid water feed was regulated using a Sage Model 335 syringe pump. Although minute flow fluctuations related to evaporation of water droplets occurred, the rates were evaluated over considerably larger time spans at essentially steady state. (Also, the Results section will demonstrate that the reaction rate is not influenced by the concentration of water.) A small fraction of the product stream could also be sampled alternately with the feed stream for GC analysis. Using a 1.8-m column of Porapak Q followed by a 3.6-m column of Porapak T, maintained at 80°C, N₂, CO₂, H₂S, COS, and H₂O separated quite well in an elution time of 5 min.

In all experiments, oxygen-free nitrogen purchased from Linde provided the diluent for the reaction mixtures of gases. Carbonyl sulfide was obtained from Matheson.

High-purity oxygen, added at 1–2 mol% concentrations, in poisoning experiments, was purchased from Linde. Other chemicals were also used for poisoning tests: acetic acid glacial reagent from Fisher Scientific (up to 1 mol%), pyridine from Raylo Chemicals (up to 1 mol%), and ammonia from Matheson (up to 1.5 mol%). In additional experiments, the use of higher concentrations of ammonia did not result in significant difference from the results obtained by using 1.5 mol%.

The alumina catalysts were either a pure form (Alon obtained from Cabot) or Alon doped by the addition of 1% by weight of sodium hydroxide (alkalized alumina). The alkalinized alumina was prepared by dissolving NaOH in water and mixing the solutions and Alon to form a paste. After the mixture was dried at 120°C in an oven, it was re-ground to powder for the preparation of wafers. All catalysts were activated by heating in air at 600°C for 3 h to oxidize organic impurities such as paper fibers (during pelletizing, the wafer surface is pressed in contact with paper). After cooling, the catalyst wafers were placed within the reactor without further pretreatment. The Alon and NaOH-doped (1%) Alon exhibited surface areas of 91 and 75 m² g⁻¹, respectively.

RESULTS

Determination of Reaction Order

Measurements of steady-state reaction rates at 230°C and near atmospheric pressure, varying the concentration of only one reactant, provided the data plotted in Figs. 1 and 2. Over 5 to 17 mol% of H₂O, Fig. 1 shows zero-order behavior with respect to water for both pure and alkalinized aluminas (curves 1 and 3). At 290°C, pure alumina does not become saturated with water on the surface until the water vapor concentration reaches 10 mol% (curve 2). At low surface coverages, non-zero-order behavior is exhibited. The rapid increase in rate at low water concentrations also suggests that water is strongly adsorbed on the surface of

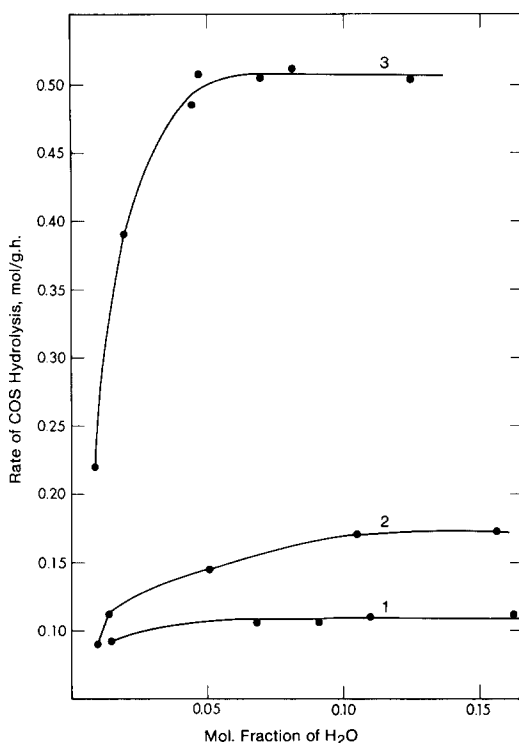


FIG. 1. Determination of reaction order with respect to water. (1) Alon at 230°C, (2) Alon at 290°C, (3) 1% NaOH/Alon at 230°C.

alumina catalysts. This changing reaction order was also observed earlier (14) and fitted to a rate expression involving competitive adsorption of H₂O and COS.

Figure 2 shows first-order behavior for COS over all reaction conditions tested. Both Figs. 1 and 2 clearly reveal that the alkalinized alumina is more active than pure alumina in catalyzing the hydrolysis of carbonyl sulfide.

From rate measurements over the range 196 to 290°C, rate constants were calculated for a zero-order water, first-order carbonyl sulfide rate expression. An Arrhenius plot of the rate constants yielded the following activation energies: 20.1 kJ/gmol for pure alumina, and 17.6 kJ/gmol for alkalinized alumina.

Factors Influencing Catalytic Activity of Alumina

1. Influence of time. During long-term

use, the activity of alumina for hydrolysis of COS appears to decline and accordingly, some experiments of increased duration were performed. The results of these experiments conducted under similar conditions are plotted in Fig. 3. Curves 1 and 3 contrast pure and NaOH-doped aluminas over a 24-h period of continuous operation. Both catalysts exhibit a rapid decline in activity which becomes somewhat stabilized after 24 h. The NaOH-doped alumina remains the better catalyst of the two.

2. *Influence of alkaline agents.* The most active of the catalysts examined has clearly been the catalyst containing 1% of NaOH, even after the trend of the activity to decline with time. To examine the role of alkaline agents further, about 1.5 mol% of ammonia was added to the feed in place of an equal amount of nitrogen. Curve 2 of Fig. 3 shows a promoting effect similar to, but smaller than, that from NaOH-doping. Comparing curves 1 and 2, taken under identical conditions but for the presence of ammonia, the cessation in flow of ammonia results in a drop in activity to the level exhibited by pure alumina without ammonia present. Readmission of ammonia restores the activity to the previous increased level.

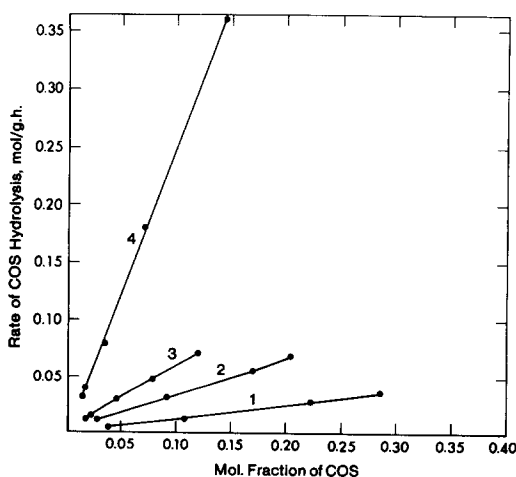


FIG. 2. Determination of reaction order with respect to carbonyl sulfide. (1) Alon at 196°C, (2) and (3) Alon samples of different activity at 230°C. (4) 1% NaOH/Alon at 230°C.

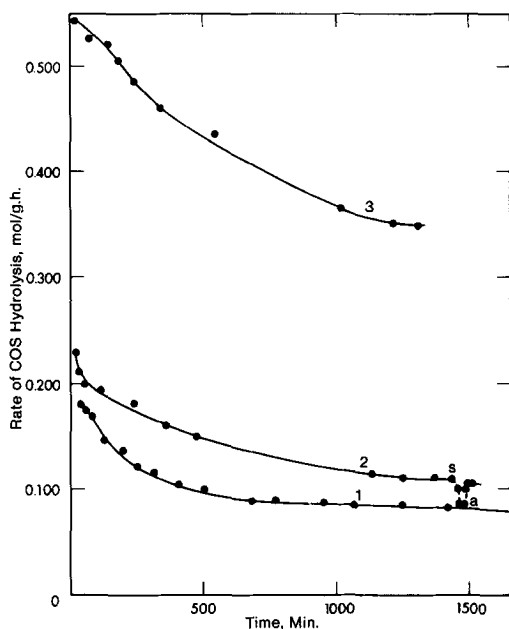


FIG. 3. Dependence of COS hydrolysis reaction rate at 230°C with time. (1) Alon. (2) Alon in the presence of ammonia in the reaction mixture. (s) NH_3 has been stopped, (a) NH_3 has been readmitted. (3) 1% NaOH/Alon.

Numerous such experiments were performed even with catalysts partially deactivated and this enhancement of activity always appeared. In these tests, the activity was only enhanced when ammonia was present.

A corresponding addition of 1% of pyridine resulted in a 1.4-fold increase in activity at 230°C.

3. Influence of acetic acid and oxygen. In contrast to the role of alkaline agents, the addition of an acidic agent such as acetic acid (up to 1% in feed gas, in place of nitrogen) resulted in a rapid decline and ultimate cessation of catalytic activity, as shown in curve 1 of Fig. 4. Although curve 1 relates to pure alumina, the same total deactivation was observed when using the alkalized alumina.

Curve 2 of Fig. 4 shows that the presence of oxygen is also destructive to the hydrolysis activity, but unlike acetic acid, the destruction of catalytic activity is not total.

Only short-term deactivation effects were examined in these studies.

4. Competition between reactant adsorbates. Experiments were carried out to establish whether active centers of the same (or different) type on the alumina surface are involved in the chemisorption of COS and H_2O . In these experiments, the water in the feed was temporarily discontinued and the catalyst was in contact with COS and N_2 alone. The rate of COS hydrolysis was measured as quickly as possible after varying periods of exposure to COS- N_2 alone. As both curves in Fig. 5 show, the catalytic activity clearly declined as a result of such preexposure to COS. Upon resumption of flow of H_2O , the activity is gradually restored to near-normal level. Both catalysts exhibited identical trends, the activity of alkalized alumina always being the higher of the two.

During the tests with pure alumina, which are shown in Fig. 5, its spectral scans were recorded for the catalyst wafers at specified intervals designated B on curve 1.

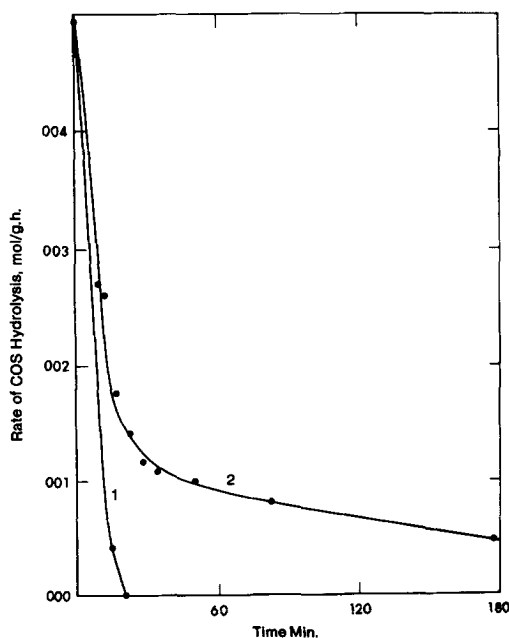


FIG. 4. Effect of acetic acid (curve 1) and oxygen (curve 2) on the reaction rate of COS hydrolysis.

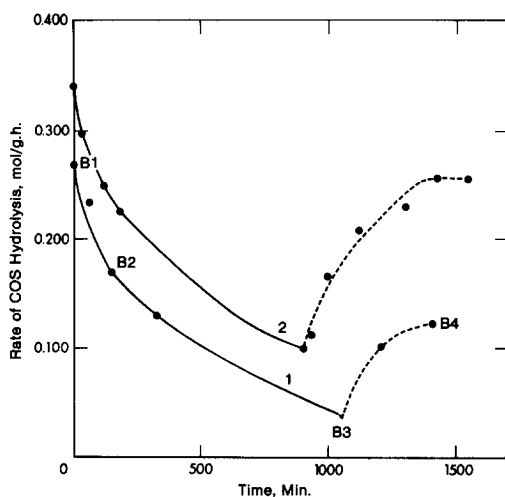


FIG. 5. Competition between carbonyl sulfide and water for active sites on alumina surface. Solid line corresponds to the time of catalyst contact with COS in the absence of H_2O , whereas dashed line corresponds to the time in the presence of both COS and water. At points B2, B3, B4 the corresponding ir spectra shown in Fig. 6 were recorded. (1) Alon, (2) 1% NaOH/Alon.

5. *Infrared scans of catalyst surface.* As mentioned earlier, the recycle reactor was designed to enable ir transmission spectra to be recorded through the catalyst wafer at steady-state reaction conditions. Since compensation for the gas phase absorbance was provided, the recorded spectra provided information concerning the adsorbed species, edited to show only the absorption bands in the spectral regions of interest, are shown in Fig. 6.

In the lower frequency region, the spectra designated by A1, . . . , A5 relate to the explanation of some irreversible deactivation effects observed during this study. Spectrum A1 represents a baseline, i.e., alumina catalyst at $230^\circ C$ in the absence of reactants. The baseline was recorded after the normal pretreatment procedure. Spectrum A2, recorded after 1 h at $230^\circ C$, shows a pair of bands at $1570\text{--}1470\text{ cm}^{-1}$, corresponding to the characteristic vibrations of carboxylate species. This species formed on the surface quite rapidly and the

band intensities stabilized with continued reaction time.

Earlier, the catalyst pretreatment differed in that it was first placed in the reactor and then heated to $400^\circ C$ in a stream oxygen. Recording the spectra at different time intervals during this procedure, a band with maximum intensity at 1370 cm^{-1} slowly emerged over a 20-h period as shown by the spectrum A3. Upon contacting reactants at $230^\circ C$, the band broadened and shifted to a lower frequency as shown by the spectrum A4. The pellets submitted to this pretreatment procedure exhibited a very poor catalytic activity, hence the adoption of the alternative pretreatment procedure. Since the reactor could not be heated to $600^\circ C$, prior heating in a separate furnace was necessary.

When 1–2% of oxygen was added to the feed, a broad band between 1250 and 1400 cm^{-1} was formed as shown in spectrum A5. As may be seen, the two spectra, A4 and A5, are very similar. The appearance of this band was accompanied by an immediate large deactivation of the catalyst as shown by curve 2 of Fig. 4. In the cases illustrated by spectra A3 and A4, the deactivation was progressive and depended upon the extent of time for pretreatment within the reactor.

The spectra designated B1, . . . , B4, which are also shown in Fig. 6, illustrate

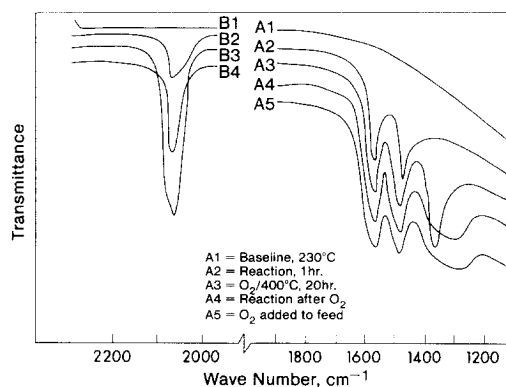


FIG. 6. Infrared spectra of adsorbed species formed during COS hydrolysis (for explanation of symbols, see Results).

another poisoning effect observed during the experiments. These spectra were recorded using an "indirect" approach because in the region of $2100\text{--}2000\text{ cm}^{-1}$ gaseous COS exhibits very strong ir absorption. Despite the fact that the apparatus was designed for reliable elimination of gas phase absorbance by the reaction mixture (8, 9), in the presence of gaseous COS at any practical concentration level all of the available energy between 2100 and 2000 cm^{-1} was absorbed. This prevented the detection of bands possibly originating from adsorbed species with vibrational frequencies in this spectral region. From observations at various temperatures throughout this work, the only band which might have been attributable to adsorbed COS would have had to occur solely in this critical region. As a result, direct ir observations of adsorbed intermediates originating from COS were not detectable. The indirect solution to this problem involved stopping the COS feed. After a few minutes, the COS was eliminated from the gas phase and the residual chemisorbed COS, presumably chemisorbed COS, could be recorded. The presence of such strongly adsorbed COS molecules was confirmed by the sharp band at 2070 cm^{-1} in the B spectra of Fig. 6. The intensity of this band changed during the series of experiments illustrated by curve 1 in Fig. 5. Spectrum B1 was recorded using fresh catalyst at the start of the reaction. After 3 h of operation, the water feed was discontinued for 150 min. The COS feed was also discontinued for a few minutes while the indirect measurements were taken of spectrum B2. Both feeds were then resumed until steady-state catalytic activity was resumed. The same procedure was subsequently repeated for about 1000 min, enabling spectrum B3 and the corresponding steady-state activity to be recorded. Finally, after normal operation for a further 450 min, the spectrum B4 and the somewhat restored catalytic activity were obtained.

In Fig. 7, the measured catalytic activi-

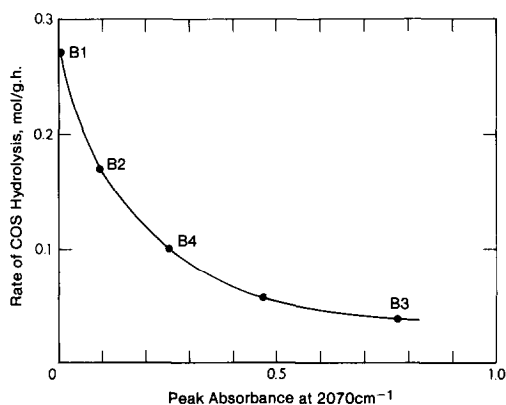


FIG. 7. Reversible autoinhibiting effect of COS.

ties, expressed as reaction rates, were plotted as a function of peak absorbance of the carbonyl sulfide band at 2070 cm^{-1} . The interesting feature of this plot is the autoinhibiting effect of COS upon the rate of hydrolysis. More precisely, during the time between recording the spectra, B1 and B3, the concentration of strongly adsorbed carbonyl species has progressively increased whereas the catalyst became seven times less active. The resumption of normal reaction conditions resulted in partial displacement of adsorbed COS in the time between B3 and B4 but the activity was not entirely restored.

DISCUSSION

Kinetics of Hydrolysis

The study of hydrolysis reaction rates reveals that water clearly adsorbs very strongly as shown in Fig. 1 and it is able to displace adsorbed COS as shown in Fig. 5. The rapid saturation of the surface with water molecules and the autoinhibiting effect of adsorbed COS suggests that the reaction mechanism may involve preferentially adsorbed water species reacting with COS molecules. The results also reveal that the partial poisoning effect of O_2 does not change the reaction order (see curves 2 and 3 in Fig. 2). The addition of NaOH, known for its drastic effect upon the surface properties of alumina (10, 13), also did not change the reaction order. Since the rate

behavior of the alkali alumina generally paralleled that of the pure alumina, but at an increased level, the reaction mechanism likely is the same on both pure and alkali-aluminas.

These experiments extend the range of validity of first-order behavior for COS from the 4% reported previously (2) to beyond 25% COS and confirm the preliminary observation of changing order for water (14), but only at partial pressures of water less than that corresponding to saturation of the surface. At higher partial pressures, the earlier (14) observed negative order for water may have resulted from experimental error (nonideal mixing) associated with the spinning-basket type reactor. The Langmuir-Hinshelwood rate expression suggested (14) would be expected to have limited validity, i.e., when both water and carbonyl sulfide exhibit non-zero order of reaction behavior.

The kinetic behavior of alumina for the hydrolysis of COS is similar to that of cobalt molybdate on alumina, as shown by Zdražil (3). The activation energies calculated for both pure and alkali-aluminas (Alon-based) are significantly lower than those obtained by George (4) for cobalt molybdate on alumina. This suggests that aluminas, and particularly alkali-aluminas, are the better catalysts for hydrolysis of carbonyl sulfide.

Nature of Active Centers Involved in COS Hydrolysis

The addition of NH_3 resulted in a reversible rate-promoting effect which implies that no new active centers were formed. To test whether NH_3 -enhanced reaction rates were attributable to improved product removal, either CO_2 or H_2S were added to feed mixtures. Although NH_3 might be expected to react with CO_2 or H_2S , the observed conversions remained unchanged. Increases in product concentrations did not influence the reaction rates thus the observed conversions were never near equilibrium levels.

The fact that the catalytic activity was generally increased by poisons of acid centers such as ammonia, pyridine, and sodium hydroxide, testifies against the participation of acid centers in the hydrolysis mechanism. On the other hand, the severe poisoning when acetic acid was introduced proves that sites with basic character are involved. Acetic acid chemisorbs on both basic sites and acid-base pairs (15). The addition of alkali metal hydroxides to alumina can poison both Brønsted and Lewis-acid sites (16). Since acetic acid also poisoned the NaOH-doped alumina activity, where the acid sites have already been eliminated by poisoning with sodium hydroxide, then acetic acid must chemisorb only on basic sites. The elimination of basic centers influenced the reaction rate, and thus, basic centers, where water is adsorbed, are likely the exclusive reaction centers.

These basic centers could be identical to the reducing sites whose participation in COS hydrolysis was suggested earlier (1). Such a double role, both basic site and reducing center, was reported by Ghorbel *et al.* (17). They believed that Lewis-base centers on alumina, while catalyzing butene isomerization, can also behave as reducing centers while forming tetracyanoethylene anion radicals. As a Lewis-base, the center is a donor of two electrons; while as a reducing center, it donates only one electron. The lack of correlation between basicity and catalytic activity for COS hydrolysis (1) may result from measurements of surface basicity with one indicator ($\text{p}K_a = 9.3$). Basic sites even weaker than those capable of reacting with phenolphthalein may be involved when water is one of the reactants.

The poisoning of COS hydrolysis by pentene (1) remains to be explained. The evident explanation is that the poisoning is really blocking of the alumina surface by carbonaceous material formed from pentene. Chemical poisoning of acidic sites by pentene seems unlikely for the hydrolysis reaction because pentene is a very weak base, capable of interacting only with very

strongly acidic sites not available in an atmosphere of water vapour. The authors reported the poisoning effects of pentene on a commercial alumina, Kaiser S-201, slightly alkalized with sodium ions. With prior chemical removal of strongly acidic sites, blocking of the surface by coke seems to be the more logical explanation.

Deactivation of Alumina Catalysts

The poisoning action of acetic acid was observed to be nearly immediate and complete, whereas that of oxygen was much slower inclining to level with time, attributed to chemical and physical processes, respectively. The acetic acid reacts chemically with base centers whereas oxygen may react with the H_2S product to form elemental sulfur which physically blocks active centers. The oxidation of H_2S on γ -alumina has been observed (1, 3).

Experience with the operation of staged catalyst beds in modified Claus process sulfur recovery plants indicates that COS hydrolysis occurs in the initial catalyst bed, generally the bed at the highest temperature (about 310 to 350°C). Failure to react in the first bed results in the passage of COS through the remaining downstream beds, largely unconverted, even though their temperatures exceed 230°C. The explanation may lie in the physical blocking effect of elemental sulfur which at reaction conditions is always present on the commercial catalyst in substantial amounts. Only at the higher temperatures in the first-stage bed might the sulfur content of the catalyst be sufficiently minimized through desorption or evaporation to enable the hydrolysis reaction to proceed to some extent.

Oxygen may also contribute a chemical as well as a physical component to its poisoning action. Adsorbed sulfur may further react with oxygen to form sulfur dioxide which, in turn, chemisorbs on reducing sites and poisons the hydrolysis reaction (1). Because reducing sites may act as basic centers, the observation of SO_2 poisoning (1) and the interpretation expressed herein

of the participation of base sites are in agreement. Figure 6 shows an ir absorption band at 1370 cm^{-1} which may be attributed to an interaction between SO_2 and reactive oxygen (18) in the alumina surface.

The band at 1370 cm^{-1} in Fig. 6 resembles another band observed (13) during an ir study of SO_2 adsorption on alumina. The authors provided two interpretations, strongly chemisorbed SO_2 molecules or a sulfate-like stable surface species. The ir evidence presented in Fig. 6 does not permit discriminating between the two possibilities. The samples of catalyst pretreated in oxygen giving spectra A3 displayed poisoning effects. A related band appeared very rapidly in spectra A5 when O_2 was added to the feed mixture. Akimoto and Dalla Lana (1) also reported a decrease in the activity for hydrolysis with 1.5% SO_2 in the feed. The deactivation processes represented by spectra A4 and A5 would be expected to be analogous ones, chemical poisoning originating with oxygen.

Finally, the formation of the carboxylate species attributed to the region $1570\text{--}1470\text{ cm}^{-1}$ may also contribute to the initial deactivation of the alumina catalyst.

The mechanism of Hydrolysis of Carbonyl Sulfide

The evidence presented clearly suggests that both COS and H_2O compete for the same sites active for the hydrolysis reaction. The nonlinear character of the dependence shown in Fig. 7 is attributed to the heterogeneity of the active sites on the surface. The deactivation by COS is more pronounced, the lower the concentration of water vapor present, because of increased COS adsorption. Whether COS remains on the surface as a reactant or as a deactivating influence when the surface is saturated with water has not been demonstrated. The B spectra verify its presence as an adsorbate at reaction conditions. Carbonyl sulfide can be partly displaced from the surface by readmission of water to the reaction system.

The competitive occupancy of the same sites by both water and COS is in contradiction to the earlier interpretations (1-3, 14), where adsorption of COS and water on two adjacent different sites was proposed. Considering the retarding influence on the reaction rate of adsorbed COS, the competitive occupancy of the same sites, the first-order dependency of carbonyl sulfide, and the low activation energy of the reaction, the possibility of an Eley-Rideal mechanism is the preferred interpretation from this study, especially when the surface is saturated with adsorbed water.

The evidence suggests that both pure alumina and alkalized alumina catalyze the hydrolysis reaction through essentially identical active sites and reaction mechanisms. The higher catalytic activity of alkalized alumina may be attributed to a higher concentration of active centers or to improved accessibility to the active centers on alkalized alumina. Using the following premises:

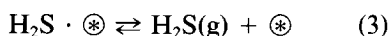
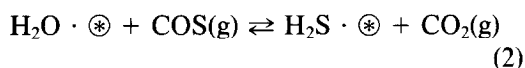
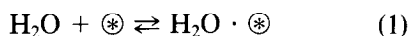
(i) H₂O adsorbs upon basic sites to form an activated intermediate.

(ii) COS either reacts directly with adsorbed H₂O, or else is loosely physically adsorbed enabling contact with adsorbed H₂O.

(iii) Products H₂S and CO₂ are not adsorbed on the surface, or if not, desorb extremely rapidly.

(iv) H₂O adsorbs very strongly such that its adsorption equilibrium constant, *K_w*, is very large.

(v) The reaction equilibrium is very much on the product side; a simplified reaction mechanism may be written,



Following this mechanism, if the rate of reaction step (2) is dominant, such that steps (1) and (3) exist at near equilibrium,

[rate 2]

$$= \frac{k_2 L [P_{\text{H}_2\text{O}} P_{\text{COS}} - P_{\text{CO}_2} P_{\text{H}_2\text{S}} / K_{\text{equil}}]}{[1 + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + P_{\text{H}_2\text{S}} / K_{\text{H}_2\text{S}}]} \quad (4)$$

With simplifying assumptions (iii) and (iv):

$$\begin{aligned} [\text{rate 2}] &\approx k_2 L P_{\text{H}_2\text{O}} P_{\text{COS}} / K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} \quad (5) \\ &\approx K' P_{\text{COS}} \end{aligned}$$

Equation (4) describes the rate when *P_{H2O}* is below the saturation level for chemisorption upon alumina, and non-zero order behavior is encountered. Equation (5) fulfills the zero-order behavior for H₂O and first-order behavior for COS observed experimentally.

CONCLUSIONS

1. The hydrolysis of carbonyl sulfide shows first-order behavior for COS and zero order for H₂O over a wide range of concentrations.

2. Pure and alkalized alumina exhibit very similar catalytic behavior in spite of their difference in catalytic activity.

3. Poisoning of active centers by deliberate addition of acidic or basic agents points to basic centers being the active sites.

4. The poisoning effect of oxygen is realized, most likely, via the formation of a sulfur-containing surface species.

5. Some contribution of surface carboxylates to the catalyst deactivation is suggested.

6. An Eley-Rideal type reaction mechanism is believed to represent the experimental observations most satisfactorily.

ACKNOWLEDGMENTS

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