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The low-temperature hydrolysis of carbonyl sulfide and carbon disulfide: a review

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Abstract

The impetus to reduce the emission of sulfur-containing compounds into the environment has become increasingly important in recent years. This paper reviews the progress made towards reaching this goal and highlights the significant contributions made towards developing effective catalysts for the removal of carbonyl sulfide and carbon disulfide. Novel promoter materials, new catalyst morphologies, new reactor designs and developments for the future are reviewed and discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, there has been renewed interest in carbonyl sulfide hydrolysis and the processes used to remove sulfur from chemical feedstocks. Over the last two decades it has become increasingly apparent that recent emissions of sulfur compounds into the atmosphere have been unacceptably high. Furthermore, the realization that present oil reserves may not last for much more than 30 years, and may have to be replaced with sources containing much higher amounts of sulfur, has provided fresh impetus to modify and improve existing desulfurization technology.

The scale of the problem is large, and the increasingly restrictive pollution control standards are continually being introduced to address this situation. Many industrial processes utilize hydrocarbon feedstocks, and their utilisation leads invariably to the release of harmful by-products. In the northern hemisphere 93% of the global output of SO_2 is produced as a result of the power requirements of heavy industry — a significant problem since SO_2 is the starting material in the cycle which ultimately produces acid rain (Fig. 1). COS is also commonly released into the atmosphere and is found to exist in trace amounts in the troposphere (500 pptv) where its lifetime has been estimated at 2–7 years [1]. Although the chemical reactivity of COS/CS_2 in the atmosphere is low it has been shown to contribute to the formation of SO_2 and to promote photochemical reactions. It has been speculated that by increasing the sulfur content of the stratosphere, through the emission from heavy industry, automobiles, coal-fired power stations etc., there will be measurable climatic changes within the next century [2].

The sulfur content of industrial feedstocks not only affects the environment, but also provides economic problems within the petrochemical industry. The detrimental effect that sulfur has upon many catalysts has been well documented [3]. Levels of sulfur as low as 1 ppm can effectively poison the activity of

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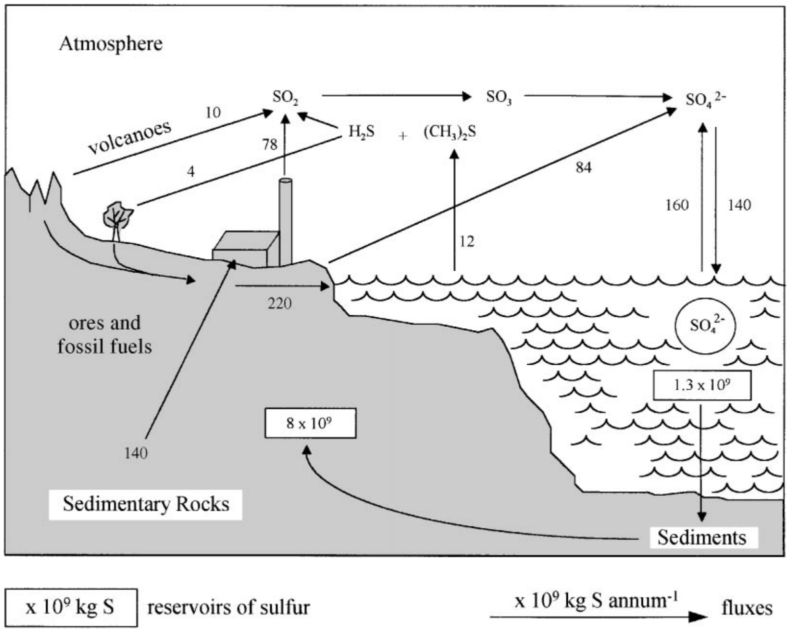


Fig. 1. The sulfur cycle.

modern bi-metallic reforming catalysts, ideally feedstocks containing <0.1 ppm of sulfur are preferred. As little as 4 mg of sulfur per gram of catalyst on the surface of the Fe–Cu–K catalyst used in the Fischer–Tropsch process [4] decreases the activity by ca. 50%. Product selectivities are also adversely affected by sulfur poisoning leading to the production of higher proportions of methane and other low molecular weight fractions, as opposed to the often more desirable C_{5+} compounds. Apart from affecting the catalysts, the presence of feedstock sulfur can also lead to increased corrosion of the reactors used in refining processes [5]. Raw materials that have undergone desulfurization, consequently, are less hazardous, less corrosive and can be used to manufacture odour-free products.

All hydrocarbon feedstocks arising from crude oil contain some sulfur. The amount of sulfur varies with its location of origin [6]. North African crude oil contains very little sulfur (−0.2 wt.%), whereas light Arabian oil (1.5 wt.%), and oil from Kuwait (2.5–4.0 wt.%) are rich in sulfur. In general, natural gases that contain H_2S are termed “sour” gases, whereas those that are H_2S-free are termed “sweet”. A typical composition of natural gas is presented in Table 1. The form that sulfur takes in these reserves varies. Mercaptans, thiophenes, carbonyl sulfide, hydrogen sulfide and sulfates are the compounds commonly encountered irrespective of the origin of the crude oil.

2. Desulfurization technology — current position

Since the range of sulfur compounds found in crude oil is large, a two-stage sulfur removal process is used. Preliminary treatment involves hydrogenation of sulfur contained in organo-sulfur compounds

Table 1
Typical composition of the main compounds contained in natural gas

Component	North Sea	Groningen	Ekofisk	Indonesia
CH_4 (%)	93.8	81.2	85.4	84.9
C_2H_6 (%)	4.5	2.8	8.4	7.5
C_3H_8 (%)	0.4	0.4	2.8	1.6
C_4H_{10} (%)	0.04	0.1	0.9	0.03
C_5H_{12} (%)	0.02	0.09	0.2	0.1
N_2 (%)	0.7	14.2	0.4	1.8
CO_2 (%)	0.5	1	1.8	4
Total sulfur as H_2S (ppm)	5	–	30	2

using cobalt–molybdenum sulfide catalyst supported on γ-Al_2O_3, typically containing 3% Co and 12% Mo by weight as oxides [7]. The catalyst is operated at 280–400°C and 30–50 bar [8]:

$$C_nH_mS_x + 2xH_2 \leftrightarrow C_nH_{(m+2x)} + xH_2S$$

Subsequent removal of the hydrogen sulfide produced is achieved by scrubbing the exit gases and/or the use of absorbents (e.g. ZnO) [9–13]. Both processes are extremely efficient in removing hydrogen sulfide although COS and CS_2 still remain, albeit in lower concentrations.

For gas feeds that contain <2% H_2S, hydrogen sulfide is absorbed by a quinone solution which oxidizes H_2S to give elemental sulfur and hydroquinone. Air/oxygen is subsequently used to oxidize the hydroquinone to quinone and the solution centrifuged to remove the sulfur. Alkanoamines are also commonly used as effective H_2S absorbents, but suffer from an inability to absorb COS in appreciable amounts [10].

The reaction of zinc oxide with hydrogen sulfide is capable of reducing sulfur content to below detection limits of 0.02 ppm, with zinc oxide being converted to zinc sulfide in the process. A number of alternative processes for the high temperature removal (402–802°C) of H_2S using zinc ferrite [11] and zinc titanate [12] have been investigated. Unfortunately, in highly reducing atmospheres, such as those encountered in the Shell gasification process, these materials tend to become reduced resulting in loss of strength and sorbent capacity [13]. Regeneration of zinc ferrite and zinc titanate is possible, but involves the control of highly exothermic oxidation reactions using dilute oxygen/nitrogen streams and SO_2 is formed in low concentrations as a result of this procedure.

One of the simplest methods to remove sulfur from a feed-gas makes use of activated charcoal as an absorbent. Often the absorption capacity of the charcoal is enhanced by the presence of transition metals such as copper. Molecular sieves (e.g. zeolite A) are also commonly used [14]. Molecular sieves, however, present new problems for H_2S removal because H_2S and CO_2 react together within the framework of the zeolite to produce COS and H_2O. The problem is amplified further by the ability of molecular sieves, such as zeolites A and X, to absorb water and force the equilibrium position of the reaction between CO_2 and H_2S far to the right; increasing COS concentration [15]. The incorporation of high loadings of bivalent cations has gone some way to alleviating this problem, but this still requires further development. Consequently, this technology can only be usefully applied for feedstocks with very low carbon dioxide concentrations. In all absorption techniques, low boiling-point compounds, such as carbonyl sulfide do not tend to be absorbed very well, while heavier hydrocarbons tend to saturate the absorbent. This method of removal is, therefore, limited in its applicability.

For a typical 1000 t per day ammonia plant, the removal of H_2S, using either scrubbing or absorption techniques, is avoided when the feedstock contains sulfur levels above 200 ppm [16]. In these instances, where the sulfur content of the crude oil is too high, an alternative high temperature oxidation process (the Claus process) is used. It is anticipated that in the future the importance of Claus technology will increase as the sulfur content rises for the fuels available commercially (Fig. 2).

3. Claus process

The Claus process was developed by Chance and Claus [17] in 1894 and works well for gas streams containing greater than 20% (by volume) H_2S and less than 5% hydrocarbons. Recent research on the Claus process and H_2S selective oxidation has been reviewed by Piépla et al. [18]. The industrial process uses an inexpensive, medium purity (−0.1 wt.% Na) activated alumina with a high specific surface area (300 $m^2\,g^{-1}$) at a temperature close to 300°C. Alumina is an effective catalyst as it has a weak affinity for the products of the hydrolysis reaction. Although some plant performance data [19] suggest that a titania-based catalyst is more active for the Claus conversion and the hydrolysis reactions, alumina-based catalysts still dominate the market-place due to the lower cost and the long-term history of application in sulfur recovery plants.

The first stage of the Claus process is the thermal oxidation of one-third of the initial H_2S concentration in a high temperature burner at 100°C:

$$2H_2S + 3O_2 \leftrightarrow 2SO_2 + 2H_2O$$

The SO_2 produced in this first step reacts with the residual H_2S to produce elemental sulfur and water.

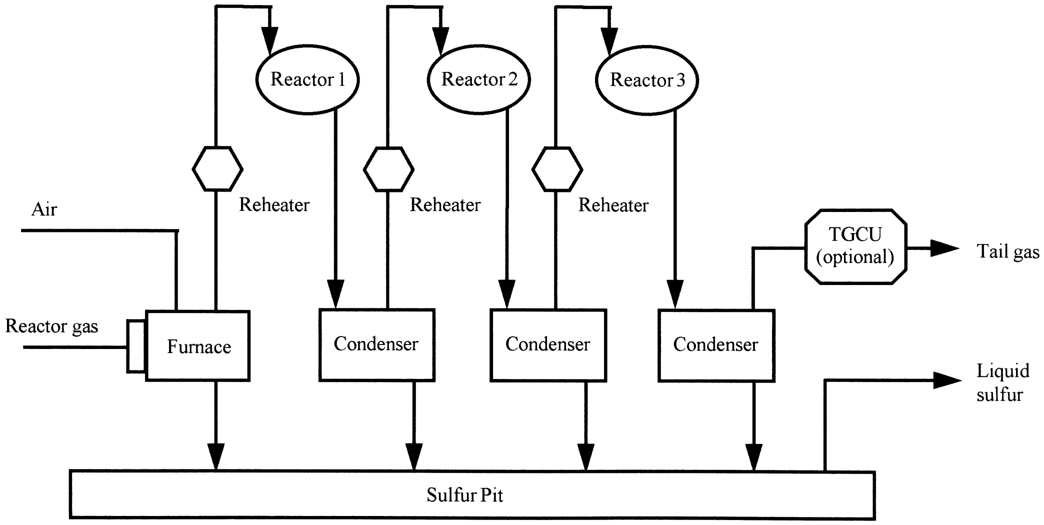


Fig. 2. Schematic design of a typical Claus unit for sulfur recovery.

The reaction between H_2S and SO_2 is called the Claus reaction:

$$2H_2S + SO_2 \leftrightarrow 3S + 2H_2O$$

Although the use of improved tail gas purification technology, in the form of the Claus process, can be highly effective, other problems exist. Installation and maintenance is extremely expensive and the high cost of operation has prompted much work trying to reduce the temperature of the Claus process, which is currently limited by the condensation of sulfur for its minimum operating temperature. Furthermore, disposal of the recovered sulfur in itself presents environmental problems [20].

Presently, the efficiency of the Claus process for the recovery of sulfur is only 90–93% of that contained in flue gases. To meet the requirements of increasingly stringent pollution leglisation that operate in a number of industrialized countries, it is now required that this remaining sulfur also be removed. At this stage of processing, the residual sulfur is mainly in the form of compounds such as carbonyl sulfide (COS) and carbon disulfide (CS_2). These sulfur-containing compounds are found naturally in crude oil and are also formed, in approximately even amounts, during the high temperature stage of the Claus process and may account for up to 50% of the sulfur lost in the tail gas [21]. Formation of COS and CS_2 results from hydrocarbons present in the flue gas, reacting with many of the other sulfur species present in the combustion step. COS and CS_2 are produced according to the reactions shown below:

$$CO_2 + H_2S \leftrightarrow COS + H_2O$$

$$CO_2 + 2H_2S \leftrightarrow CS_2 + 2H_2O$$

$$CH_4 + SO_2 \leftrightarrow COS + H_2O + H_2$$

$$CH_4 + 2S_2 \leftrightarrow CS_2 + 2H_2S$$

A range of methods have been employed to reduce the amount of sulfur exiting the reactor as COS and CS_2, including; combustion, absorption, hydrogenation, oxidation with sulfur dioxide and hydrolysis.

4. COS and CS_2 removal

The methods developed for the removal of COS and CS_2 are largely the result of the chemical and physical properties of each of the compounds (Table 2). Carbonyl sulfide is relatively unique among the sulfur-containing impurities of hydrocarbon feedstocks being odourless, tasteless and colourless [22]. COS is a polar molecule with the following calculated partial charges [13].

Table 2
Selected chemical and physical properties of COS, CS_2, CO_2 and H_2S

Properties	Carbonyl sulfide	Carbon disulfide	Carbon dioxide	Hydrogen sulfide
Molar mass	60.07	76.14	44.01	34.08
Bond length (Å)	1.16 (C–O) 1.56 (C–S)	1.56 (C–S)	1.16 (C–O)	1.33 (S–H)
Bond energy (eV)	3.12 (OC–S) 6.81 (O–CS)	4.463	5.453	–
Ionization potential (eV)	11.2	10.09	13.78	–
Electron affinity (eV)	0.46	1.0	−0.6	–
Dipole moment (esu)	0.72×10^{-18}	0	0	0
IR data (cm^{-1})	2062, 859, 521	1535, 396	2352	2614, 1182, 2627
Melting point (°C)	−138	−108.55	sub −78	−85.55
Boiling point (°C)	−50.2	46.25	–	−59.55
Critical point (°C)	105	273	31	−173
Critical pressure (MPa)	6.6	7.4	7.4	8.94
Critical density ($kg\,m^{-3}$)	–	–	0.46	–

$$\underset{(\delta-=-0.27)}{O} = \underset{(+0.11)}{C} = \underset{(\delta+=+0.16)}{S}$$

Before the days of more restricted sulfur emission norms, the tail gases from Claus plants were usually incinerated and then vented, converting the unrecoverable carbonyl sulfide and carbon disulfide to the less offensive, but still harmful, SO_2. Technology does exist for decreasing SO_2 emissions, e.g., using CaO as an absorbent [23–25]. However, the reaction of SO_2 and O_2 with CaO to produce $CaSO_4$, is very fast and rapidly consumes CaO and is not viable on an economic basis.

An alternative proposal to reduce the levels of COS and CS_2 involves hydrogenation, which can take advantage of the hydrogen present in the Claus process. Using a Co–Mo–Al_2O_3 type catalyst [26], the sulfur-containing compounds are reduced to H_2S and are processed in subsequent steps of the Claus process or by using tail gas cleanup (TGCU) technology [27]:

$$CS_2 + 4H_2 \leftrightarrow 2H_2S + CH_4$$

$$COS + 4H_2 \leftrightarrow H_2S + CH_4 + H_2O$$

The composition of the catalyst used is such that the amount of cobalt is usually 3–4 times less than molybdenum, with Mo giving rise to a “surface-layer” coverage of MoO_3. The cobalt is located in the upper portions of that Mo layer [28]. Unfortunately, the expense of the Co–Mo–Al_2O_3 catalyst combined with the high temperature required for effective reduction, at present restricts commercial exploitation. Furthermore, under the operating conditions of the Claus converters, the SO_2 partial pressure tends to be much higher than that of CS_2 and COS, resulting in the SO_2 being preferentially hydrogenated.

A further treatment for the removal of CS_2 and COS takes advantage of the high levels of SO_2 to oxidize CS_2 and COS to carbon dioxide and elemental sulfur [29]:

$$SO_2 + 2COS \leftrightarrow 2CO_2{+}3S$$

$$SO_2 + CS_2 \leftrightarrow CO_2{+}3S$$

As for the hydrogenation reaction, however, the Co–Mo–Al_2O_3 catalyst used in this process is relatively expensive while the alumina catalysts are prone to severe deactivation due to carbon dioxide poisoning.

5. COS and CS_2 hydrolysis

Attention has been recently focused on the hydrolysis of COS and CS_2 to achieve the very high levels of sulfur depletion now considered necessary. However, despite hydrolysis of the CS_2 and COS compounds being thermodynamically feasible under Claus process conditions, COS and CS_2 hydrolysis do not proceed to 100% conversion on the standard alumina Claus catalyst. Consequently there is an incentive to study the Claus reaction at lower temperatures, which are more economically viable, and which offer potentially higher conversions of COS and CS_2 via the hydrolysis reactions.

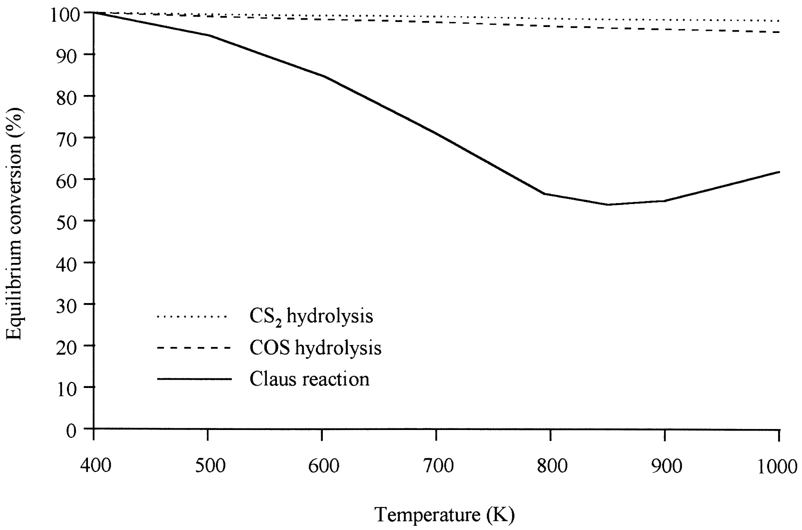


Fig. 3. Equilibrium conversions vs. temperature [26].

In the first reactor, containing an alumina catalyst, the conversion of COS and CS_2 is limited to ~75% for COS and ~50% for CS_2 at an outlet temperature of ~340°C [30]. The remaining COS and CS_2 is not hydrolyzed to any marked extent by the alumina catalysts in the second and third reactors which have undergone a degree of inevitable sulfation, and a decrease in activity, as the levels of H_2S decrease [31]. Despite only partial conversion, the removal of COS/CS_2 from the first bed is still regarded as the most efficient way to deal with the problem of sulfur loss and titania-based catalysts may provide a way in which complete COS/CS_2 conversion can be achieved.

The temperatures at which the removal of COS and CS_2 is achieved varies according to the application. In most cases the reaction has been carried out at high temperatures (200–400°C) and with relatively high concentrations of both water and COS. Under such conditions the thermodynamic equilibrium of both COS and CS_2 hydrolysis indicates that equilibrium conversions exceed 98% irrespective of the conversion limits for the Claus reaction [26] (Figs. 3 and 4).

Both the rate of reaction and the position of equilibrium are strongly affected by reaction temperature. The forward reaction is favoured thermodynamically by lower temperatures and with higher concentrations of steam. The activation energy for COS hydrolysis tested on alumina is surprisingly low, being approximately 25.3 kJ mol^{-1} for Kaiser 201 alumina [33,84] (Table 3).

The kinetics of COS and CS_2 hydrolysis have been the subject of numerous research papers. George [29], Landau et al. [34] and Namba and Shiba [35] showed that the hydrolysis of COS on a Co–Mo alumina-based catalyst, was first-order with respect to COS and zero-order with respect to H_2O. Fiedorow et al. [36] similarly demonstrated a zero-order and first-order behaviour of H_2O and COS, respectively, for a γ-alumina catalyst. Tong et al. [33,37] and Vermeersch [84] indicated that excess water disrupted COS hydrolysis, which was described as being a

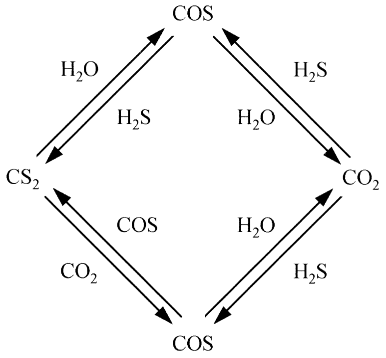


Fig. 4. Interconversion of COS/CS_2 and CO_2.

Table 3
Comparison of activation energies for COS hydrolysis

Catalyst	Temperature (°C)	E_a (kJ mol^{-1})	ΔH (kJ mol^{-1})	References
Co–Mo/Al_2O_3	320–378	50.21	–	[29]
NaOH/γ-Al_2O_3	196–290	17.57	–	[36]
γ-Al_2O_3	196–290	20.08	–	[36]
γ-Al_2O_3	80–120	26.51	1017.1	[89]
Kaiser 201	270–330	25.27	83.22	[33]
CRS 31	270–330	41.77	67.35	[33]

first-order reaction with respect to carbonyl sulfide. A reaction order of 0.4 with respect to water was observed between the partial pressures of 1.0–2.6 bar (230°C) while above that partial pressure water exhibited an order of −0.6. The effect of water on the rate of hydrolysis varied for different catalysts and with the temperature range investigated. A rate expression for the positive order region was derived as

$$r_0 = \frac{kK_{\cos} K_{H_2O} P_{\cos} P_{H_2O}}{(1+K_{COS} P_{COS}+K_{H_2O} P_{H_2O})^2}$$

where, K is the equilibrium constant for component I, k the rate constant for the surface reaction; and P the partial pressure of components in the feed.

Huisman et al. [38] investigated the effect of water on the hydrolysis of CS_2 over titania using in situ infrared techniques. At temperatures less than 252°C, a negative order with respect to water was observed, while at higher temperatures, between 252 and 327°C, a positive order with respect to water was observed. At ≥327°C, the reaction rate displayed a zero-order dependence with respect to water. At all temperatures investigated the order with respect to CS_2 was observed to be unity and was independent of temperature.

Between 127 and 327°C the effect of H_2O on the temperature dependence of the reaction was described by the following equation:

$$\text{Rate} = k\text{'}e^{E_a/RT} P_{CS_2} \theta_{H_2O}(1 - \theta_{H_2O})$$

where, θ_{H_2O} is the water required to form hydrogen thiocarbonate, and $(1-\theta_{H_2O})$ the site blocking of CS_2 adsorption by water.

The effect of water upon the rate of hydrolysis is more readily observed with strongly hydrophilic catalysts, such as alumina, than on less hydrophilic catalysts, such as titania. Tong [39] investigated the possibility of water vapour lowering catalytic activity by blocking micropores via capillary condensation. Using the Kelvin equation, at a typical vapour concentration of 30 mol%, the limiting radii of cylindrical pores expected to be effected by capillary condensation of water was calculated to be 0.34 nm or less. The contribution to the total surface area of the catalysts used for COS hydrolysis, by small pores was, therefore, considered to be negligible in most catalysts.

The kinetics of CS_2 hydrolysis is considered to be more complicated than COS hydrolysis. This is due to the interaction between CO_2 and CS_2, as well as COS being a proposed intermediate in the CS_2 hydrolysis reaction. Furthermore, the low reactivity of CS_2 is also a severe problem as CS_2 is present in similar concentrations to COS in acid gas streams but contains twice the number of sulfur atoms. Since CS_2 is non-polar, a reduced interaction between the polar hydroxyl groups/H_2O on the catalyst surface and CS_2 is considered to occur. CS_2 has been estimated to be 2–3 times more resistant to conversion when compared with COS under comparable conditions [30].

By studying the kinetic studies of CS_2 hydrolysis, Tong et al. [37,40] found that the products of the hydrolysis reaction did not affect the rate of reaction through competitive adsorption. It was shown that 2 mol% of either H_2S or CO_2 had a negligible effect on the conversion of CS_2 in the temperature range 230–340°C with either alumina or titania as catalysts. The intrinsic rate functions of the hydrolysis for CS_2 were found to be best described by an Eley–Rideal model, as had been proposed for the hydrolysis of COS. As with COS hydrolysis the order of reaction with respect to water was affected by the reaction temperature, being negative at lower temperatures, positive in the mid-temperature range and zero-order at higher temperatures.

6. Catalysts for COS and CS_2 hydrolysis

The number of catalysts that have been investigated for the hydrolysis reactions of COS and CS_2 have been numerous and have mainly involved alumina and/or titania. Despite the various improvements to catalyst formulation that have been suggested, however, alumina continues to be the catalyst that is used commercially, particularly high purity forms [41,42]. Initially, non-uniform grains/particles of bauxite were used but were later replaced in favour of spherical pellets which were proposed to offer improved strength and attrition resistance coupled with better gas–catalyst mixing. Subsequently, there has been a return to using the traditional bauxite-based materials as evidence has indicated improved performance when compared to synthetic promoted catalyst formulations.

The activity and deactivation of the Claus catalyst is strongly affected by many reaction parameters. Diffusivity, pore radius distribution, reactant concentration and reaction temperature all play an important role in achieving and maintaining optimum catalyst performance [26]. In order to develop better catalysts, each reaction parameter needs to be examined and controlled so that the next generation of Claus/hydrolysis catalysts can cope with the often varied conditions found in modern commercial plants. Many problems need to be addressed and overcome. For example, catalyst operation at low temperatures frequently results in condensation of sulfur in the capillary pores of the solid thereby inhibiting the rate of hydrolysis by blocking access to reactive sites. For a Kaiser 201 catalyst at 300°C, capillary condensation of sulfur vapour in the pores below 2.2 nm diameter reduced the surface area by as much as 55% [26]. To combat such difficulties, an important modification that is made to modern catalysts involves an increase in the pore sizes from micropores to macropores [42]. Macropores are less easily blocked by sulfur and also improve intra-particle mass transfer and, recently, it has been suggested that the average pore diameters of the alumina catalysts be increased from 600–750 nm to >1 μm [43]. A convention has been proposed whereby porosity of an alumina catalyst is expressed as a ratio; the volume of pore diameters greater than 1 μm divided by the volume of pore diameters >0.1 μm ($V_{1.0}/V_{0.1}$). A ($V_{1.0}/V_{0.1}$) ratio >0.7 has been demonstrated to lead to superior catalyst performance [44].

The presence of sulfur as SO_2 has also required the development of new catalysts. Frequently in Claus reactors, the conversion of COS declines above 200°C as the oxidation of H_2S to SO_2 becomes significant. Under such circumstances the coexistence of SO_2 and O_2 results in sulfation of the alumina catalyst which greatly increases the acidity of the catalyst and decreases catalytic activity for the hydrolysis reaction [32,45]. Reactivation of the catalyst in a flow of H_2S [46] at elevated temperatures is feasible, however this step leads undesirable emission of SO_2 [47]. Similarly, it has also long been established [48] that the presence of SO_2 alone in the reactor inhibits the hydrolysis of COS and CS_2 [49]. Lavalley et al. have investigated this inhibition and found that SO_2 decreased the catalytic activity to 33–50% of the theoretical thermodynamic conversion limit. The effect of SO_2 was attributed to competitive adsorption of SO_2 with COS onto the same Brønsted base sites; the former being more strongly absorbed. Removal SO_2 from the feed restored the initial activity showing that SO_2 poisoning was almost entirely reversible.

Lavalley and co-workers [50] reported deactivation of titania catalysts that were impregnated with $(NH_4)_2SO_4$ [47]. To determine the scale of the effect of sulfation upon the rate of COS hydrolysis, three oxides, Al_2O_3, TiO_2 and ZrO_2 were sulfated by direct impregnation with $(NH_4)_2SO_4$ or by exposure of a sulfided catalyst to oxygen. With sulfate levels of 0.8 $\mu mol\,m^{-2}$, TiO_2 retained higher activity when compared with Al_2O_3, and ZrO_2 retained the highest activity overall [51]. In addition, introduction of O_2 as a pulse during the reaction produced irreversible deactivation in all samples, the effect being greatest in the alumina sample (Fig. 5). IR spectroscopy indicated [50] that SO_2 adsorption occurred at the most basic (type I) OH groups, the same active sites that are considered to be involved in the production of the hydrolysis reaction intermediate. It was concluded that the sulfation of metal oxides poisoned the basic sites and created Brønsted acid sites which reduced the activity of the catalysts. In contrast to the irreversible deactivation observed with alumina, the activity loss for titania for the hydrolysis of COS, caused by the addition of SO_2 and O_2 was largely reversible. They proposed that titania reacts to produce sulfates that are unstable at the temperatures encountered in the Claus converters [32,51]. The mechanism

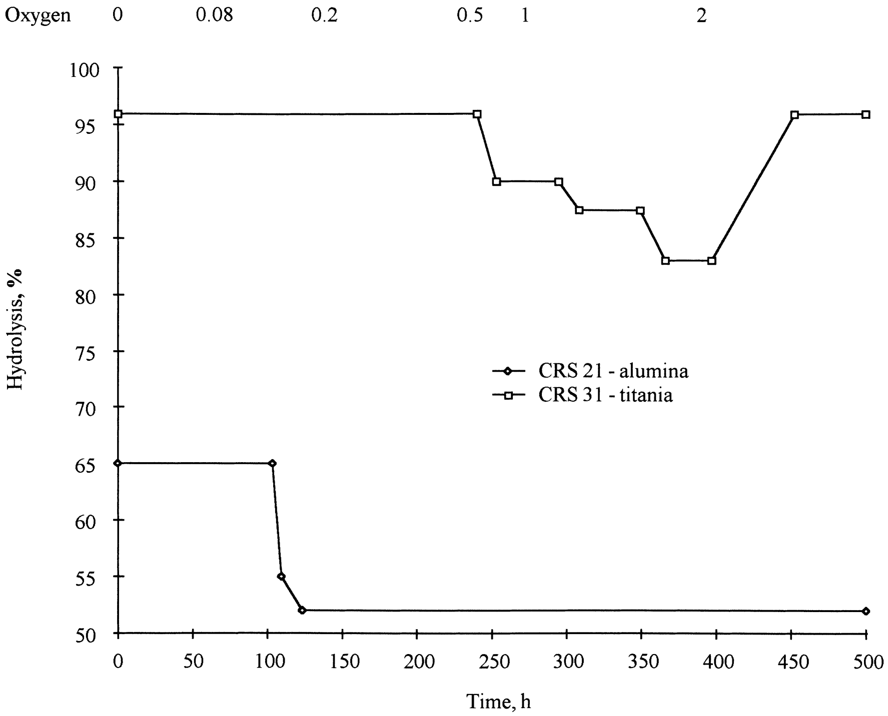


Fig. 5. Comparison of the effect of oxygen on CS_2 hydrolysis on alumina and titania [51].

of irreversible sulfate formation has not yet been completely identified, but it appears to be related to the presence of oxygen in the reactor system. It is generally estimated that 100–200 ppm oxygen comes into contact with the alumina catalyst even in a well regulated Claus burner/reheater unit [52].

Sulfate formation was described by Saussey et al. [53] as proceeding according to the following two processes [54]:

1. *Two step SO_2 oxidation.* SO_2 is initially chemisorbed in the form of a hydrogen sulfite species which subsequently undergoes oxidation to produce SO_4^{2-} and H^+:

   $$SO_2 + OH^- \leftrightarrow HSO_3^-$$

   $$HSO_3^- + \tfrac{1}{2}O_2 \leftrightarrow SO_4^{2-} + H^+$$

2. *H_2S oxidation.* This process was found to occur even at low temperatures, when SO_2 oxidation does not occur. The detailed process of H_2S conversion to sulfate remains unclear, as does the nature of the catalytic sites.

To counteract the problem of sulfation an oxygen elimination catalyst (AM-protection catalyst) has been developed by Rhone–Poulenc [33,84]. The AM-protection catalyst is placed on top of the alumina catalyst in each reactor to prevent oxygen coming into contact with alumina, hence protecting the alumina catalyst against sulfation. In use, the AM catalyst noticeably improves the hydrolysis of COS and CS_2. However, there are disadvantages; in particular, the catalyst bed has to be protected to ensure that oxidation of the AM guard bed does occur during the reactor loading or start-up.

As described previously, the presence of CO_2 in the Claus process can create potential problems by being a source of COS and as a catalyst poison. Whereas CO_2 does not affect the adsorption of H_2S on γ-Al_2O_3 [55], CO_2 does poison the alumina catalysts used in COS and CS_2 hydrolysis. Chuang et al. [56] investigated the poisoning of γ-Al_2O_3 by CO_2 produced from the reaction of COS with SO_2, and found catalyst deactivation to be extremely rapid and negligible activity was observed after 1.5 h at 285°C. However, George [29] found no evidence of deactivation when using a Co–Mo–Al_2O_3 catalyst.

7. Catalyst promotion

The search for catalyst additives to overcome some of the problems and to improve the performance of the high-purity Al_2O_3 catalysts continues to be an actively researched topic. Although the patent literature gives examples of many different promoter/catalyst combinations (Table 4), little emphasis has been directed towards elucidating the mechanism by which promotion occurs. Church et al. [57] and Machida et al. [58] suggest that promotion proceeds by the stabilization of the surface area of γ-Al_2O_3. George [59] proposed that the promotion proceeds via the modification of the surface of the support. In the case of alumina, this would involve modification of the acidity/basicity of the surface. For hydrolysis reactions, surface basicity is one factor suggested as being important and, consequently, increasing the relatively small population of basic sites on γ-Al_2O_3 surfaces may go some way to improving catalyst performance.

George [59] investigated the effect of NaOH adsorbed on Chromsorb-A and alumina. At relatively low (3.9 wt.%) loadings of NaOH on Chromsorb-A and alumina, the rate of COS hydrolysis was found to be increased ~25 times by the presence of a base. The initial rates were increased by a factor of 10^3. However, when excess Na was deposited on the alumina surface, the activity of the hydrolysis of CS_2 was found to be inferior to that of the unpromoted alumina catalyst. A similar effect was observed by Nedez and Ray [44] for CS_2 hydrolysis using Na_2O as dopant (see, Figs. 6–8). A minimum level of 1000 ppm of Na_2O was found to be necessary for improved catalyst activity but, at >2500 ppm Na_2O, was observed.

Auroux et al. [60] modified the surface of a γ-Al_2O_3 with sodium and iron. Less than 1 wt.% Na produced no characteristic differences in the shape and position of the oxygen 1s and aluminium 2p bands as examined by XPS. A similar observation was noted for 0.1–1.0 wt.% Fe. At >1.0 wt.% Na, however, a shift in the oxygen and aluminium bands was observed together with an increase in the surface basicity and the activity of the catalyst. Conversely, catalysts containing high levels of iron became more acidic in nature and were, therefore, less active for the hydrolysis reaction.

A series of catalysts for the hydrolysis reaction were prepared by Tan et al. [61] each impregnated with alkali metal oxides. Of the dopants tested, most produced an increase in activity with the order of activity being:

$$\begin{aligned}&Cs_2O/\gamma\text{-}Al_2O_3 > K_2O/\gamma\text{-}Al_2O_3,\, BaO/\gamma\text{-}Al_2O_3\\&\quad > Na_2O/\gamma\text{-}Al_2O_3,\, CaO/\gamma\text{-}Al_2O_3\\&\quad > MgO/\gamma\text{-}Al_2O_3.\end{aligned}$$

The optimum concentration of the additive was found to be 4 wt.%, the exception being Cs_2O, for which the activity increased linearly with the loading of Cs_2O.

Table 4
Promoters disclosed in the patent literature

Composition	Temperature range (°C)	Patent
Activated Al_2O_3-containing TiO_2	220–280	Fr. 2 236 555
MoO_3 and ThO_2 or UO_2 on γ-Al_2O_3, 18.5 wt.% U and 13.5 wt.% Mo	200–350	UK 1 307 875
Al_2O_3 with activator (−0.1 wt.%) containing Ca, Sr, Ba, Mg, Cd, Zn, Mo	100–400	Fr. 2 126 257
Al_2O_3-supported Co–Mo catalyst	316–342	Ger. 2 165 561
Al_2O_3 containing 1–20 wt.% groups VIA and/or VIII metals	300–500	Ger. 2 203 494
Supported UO_3 and/or U_2O_8	440	UK 1 215 808
1.0–90 wt.% MoO_3 and 10–99 wt.% Al_2O_3	110–500	US 4 810 475
Silica gel	250–300	US 4 968 502
Yttrium oxide in combination with Co, Ni, Fe oxide	150–350	US 4 374 819
Platinum sulfide on alumina		US 4 444 987
Molybdenum on alumina with a second catalyst comprising of a group VIB and an alkali on Al_2O_3	150–200	EP 0 380 184

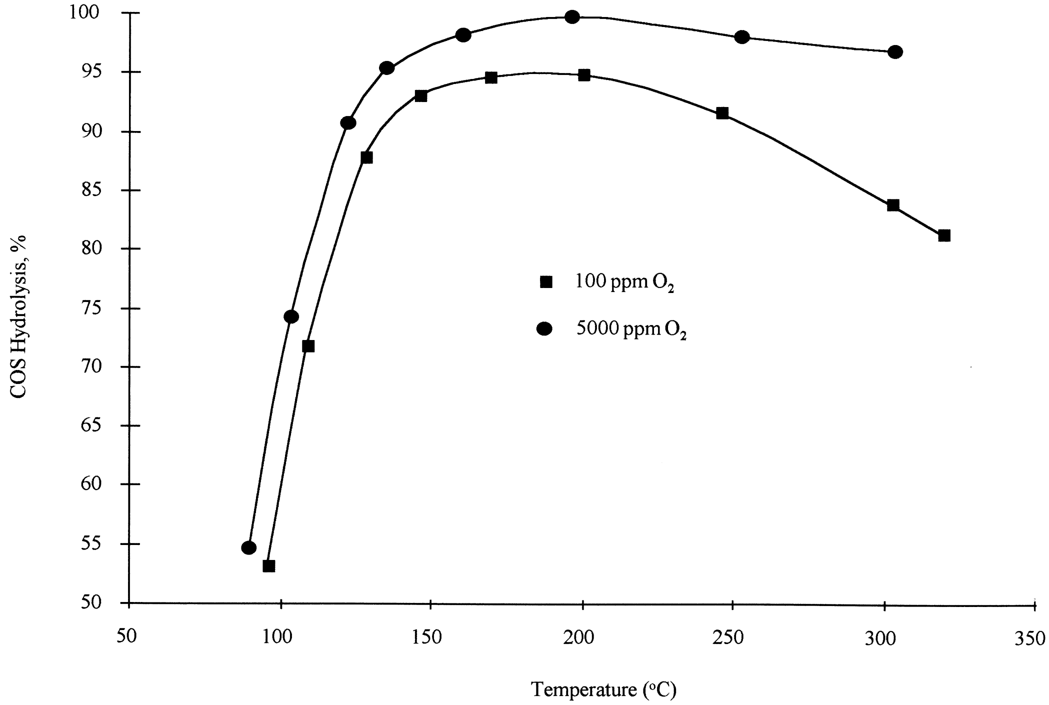


Fig. 6. Effect of temperature on catalyst activity when oxygen is present in the system.

Church et al. [57] investigated the effect of promotion by rare-earth and alkaline earth promoters on γ-Al_2O_3. Additive concentrations between 2–5 mol% were studied and a similar activity series to that described by Tan et al. [63] was observed. DRIFT spectroscopy demonstrated that the hydroxyl groups present on the surface of the promoted samples and pure alumina were identical. Consequently, the role of the promoters in these catalysts was described as being structural, with the larger cations providing the highest stabilization.

Norskov et al. [62] demonstrated that the hydrodesulfurization activity of transition metal sulfides could be understood in terms of the binding energy

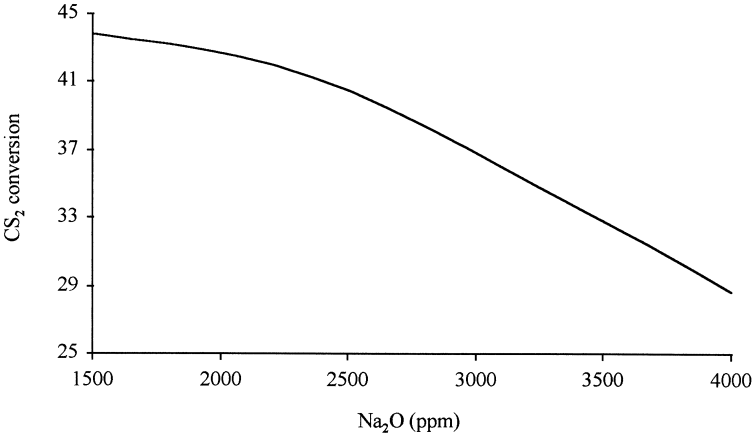


Fig. 7. CS_2 conversion against the concentration of Na_2O on an alumina catalyst.

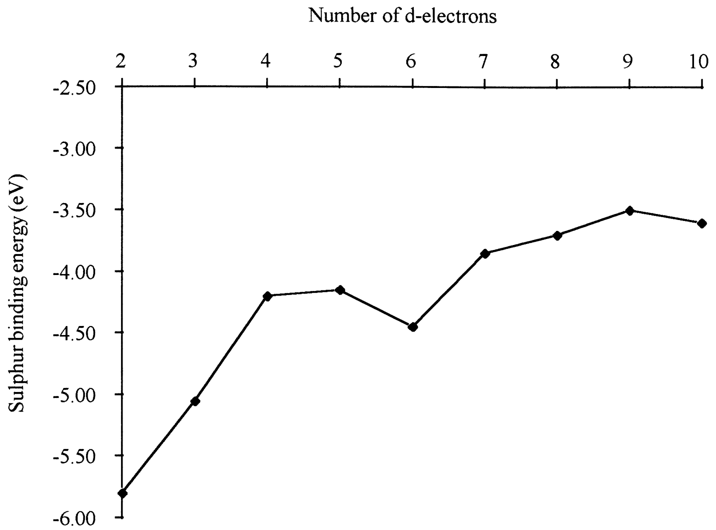


Fig. 8. The calculated variation in the sulfur binding energy in various transition metal sulfides. The trends in the sulfur binding energies follow the trends in the hydrodesulfurisation activity of the sulfide catalysts.

of the sulfur to the transition metal. Tong [63] similarly related the activity of transition metal promoted alumina catalysts to the position of the transition metal promoter in the periodic table. A relationship was proposed that related the activity of the promoted catalyst to the sulfur binding energy of the M–S bond of the promoter material.

Of the transition metals tested, the iron promoted catalyst was found to have highest hydrolysis activity. From these studies it was apparent that a Fe–S binding energy of intermediate strength (−4.5 eV) provided optimum catalyst performance [62]. These data agree with the principle proposed by Sabatier [64] stating that “for a catalyst exhibiting maximum activity in a given reaction, the complexes formed will have intermediate heats of formation”.

In spite of extensive efforts that have been directed towards catalyst development, a satisfactory catalyst which is effective for both Claus conversion and CS_2 and COS removal has yet to be developed.

8. Reaction mechanism studies

Over the years the descriptions of the elementary processes involved in COS/CS_2 hydrolysis have been numerous and often contradictory. Outlined in this paper are some descriptions offered during the study of COS/CS_2 hydrolysis that illustrate the difficulty in assessing reaction pathways accurately.

George [59] proposed that the hydrolysis of COS proceeded via a concerted mechanism (Fig. 9). The surface of the catalyst was suggested to be partially covered with OH^-, as well as by adsorbed H_2O, and carbonyl sulfide adsorbed by an ion–dipole interaction. In an alternative proposal COS may adsorb on alumina-based catalysts, as described by Chuang et al. [56]. In this case, it is proposed that COS adsorbs, forming a Lewis acid/base complex, by the interaction between a surface aluminium ion and the COS sulfur atom. This adsorbed surface complex consequently reacts with adsorbed H_2O.

Fiedorow et al. [36] and Huisman et al. [47] obtained evidence, using IR spectroscopy, that COS was adsorbed on the alumina surface at basic hydroxyl groups. Hydrogen thiocarbonate was formed during this process, and this intermediate can readily decompose to form H_2S and CO_2 [65]. Huisman et al. [47] proposed that there was evidence from IR spectroscopy that the decomposition of the intermediate proceeded via a hydrogen carbonate intermediate, although it was noted that such hydrogen carbonate formation could have occurred as a result of adsorption of CO_2 from the gas phase.

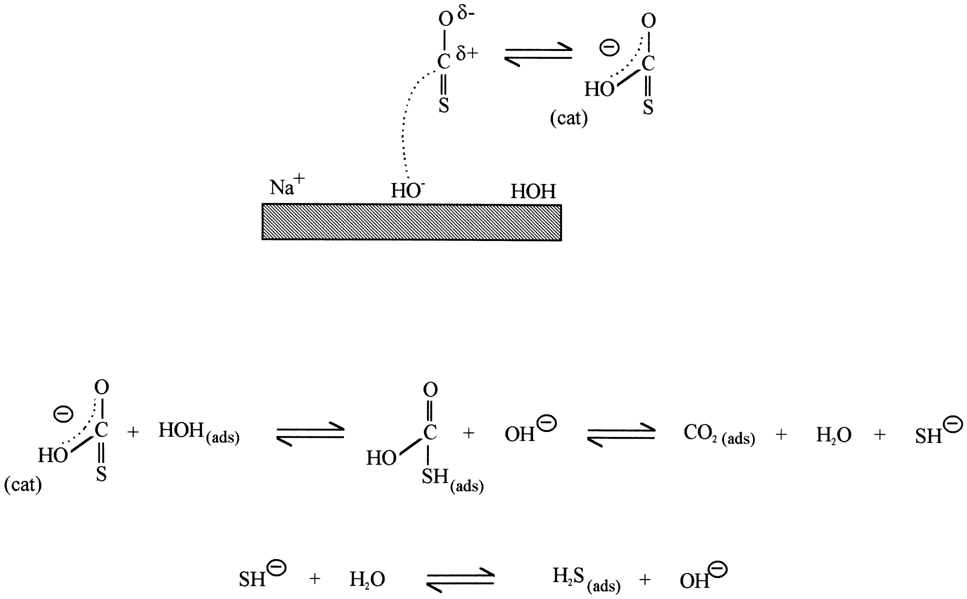


Fig. 9. The concerted mechanism as proposed by George [59].

Akimoto and Dalla Lana [66–68] suggested an alternative mechanism incorporating reduction sites and Lewis-acid sites in the vapour phase hydrolysis of COS. The reduction sites were described as unsolvated hydroxyl ions, or as exposed and co-ordinatively unsaturated O^{2-} present on the alumina surface [69]. Pentenes were shown to poison the alumina catalyst by competing with water for Lewis-acid centres on the catalyst surface. The extent of the poisoning effect was hardly affected by the concentration of COS, but was found to decrease with increasing concentration of H_2O [66–68]. The poisoning effect was related to the degree of electron donation by the pentenes with compounds capable of significant electron donation giving the highest level of deactivation (Fig. 10, Table 5).

Consequently, it was proposed that reduction sites and Lewis-acid sites were involved, with COS being adsorbed to form negatively charged species, which is hydrolyzed by adsorbed water:

$$\begin{array}{ll} O{=}C{=}S^{\delta -}+ & H{-}O{-}H \leftrightarrow CO_2+H_2S \quad 0<\delta<1 \\ * & * \\ \text{(Reduction site)} & \text{(Lewis-acid site)} \end{array}$$

Further consideration of the evidence led Fiedorow et al. [36] to re-investigate the role of the reduction sites using acetic acid and basic site blocking agents, NaOH, NH_3 and pyridine. As can be expected, acetic acid caused severe poisoning of the hydrolysis reaction with the acid adsorbing on the base sites (Fig. 11). Addition of NaOH, NH_3 and pyridine confirmed minimal participation of these acid sites in the hydrolysis mechanism. Huisman et al. [47] also found that exposure of the catalyst to formic acid led to a reduction in the activity of γ-Al_2O_3 catalysts but that exposure of the catalyst to pyridine effected an increase in the surface basicity and improved catalytic performance. These data confirmed that the basic sites were catalytically important. An alternative explanation for the decrease in catalytic activity observed in the presence of pentenes was then suggested by Fiedorow et al. [36]. It was suggested that the effect of pentenes may be attributed to the formation of coke, which may block the access of reactant molecules to the active centres on the surface, in contrast to the weakly basic pentenes competing with water for acidic sites, as was first proposed.

Rossi et al. [70] used the adsorption of hexafluoroisopropanol to measure the surface basic strength of a range of oxides (Fig. 12). In this study the basic sites of the titania surface were found to be stronger than those found for alumina. George [29,59] concurred with the proposal that the extent of surface basicity

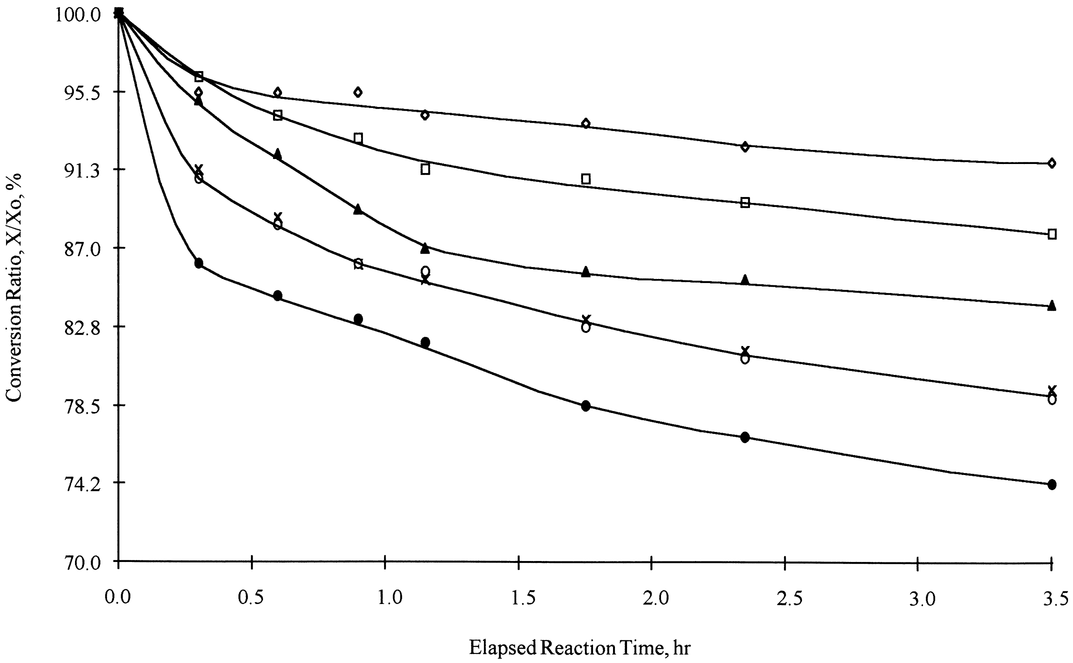


Fig. 10. Poisoning of catalysts by pentenes during hydrolysis of COS feed [68–70].

and catalytic activity were related and observed that doping alumina with sodium hydroxide resulted in an increase in the rate of hydrolysis. The increased rate was explained in terms of increased participation of basic sites on the catalyst surface and the presence of protons in the reactants.

Zotin and Faro [42] similarly found that the basic sites were the catalytically active sites for hydrolysis. Using SO_2 adsorption for a full series of Al_2O_3 catalysts a correlation between the density of basic sites and the increasing intrinsic activity of the catalyst was found. Impregnation of sodium (as sodium nitrate) not only increased the density of sites but also increased their basicity to such a point that the chemisorbed SO_2 species were held irreversibly. Under such circumstances the strongly held SO_2 species were shown to affect observed conversion levels in some cases.

Table 5
Key for experimental in Fig. 10

Symbol	% of COS	% of H_2O	% of 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)

Fiedorow et al. [36] also designed experiments to establish whether the active centres involved in the chemisorption of COS and H_2O on the alumina surface were identical. To achieve this, the water feed to the catalyst was temporarily disrupted and the catalyst reacted with COS and N_2 alone (Fig. 13). Following the disruption to the water feed, the rate of hydrolysis was measured as quickly as possible after varying periods of exposure to the N_2–COS atmosphere. Upon restoration of H_2O flow, the catalytic activity was gradually restored to near the level observed prior to the cessation of the H_2O feed. This suggested that COS reacted with pre-adsorbed water. An Eley–Rideal [37] type mechanism was proposed to explain these observations and involved the following features/steps.

1. H_2O adsorbs on basic sites to form an activated intermediate.
2. COS either reacts directly with adsorbed H_2O or is physically adsorbed enabling reaction with adsorbed H_2O.

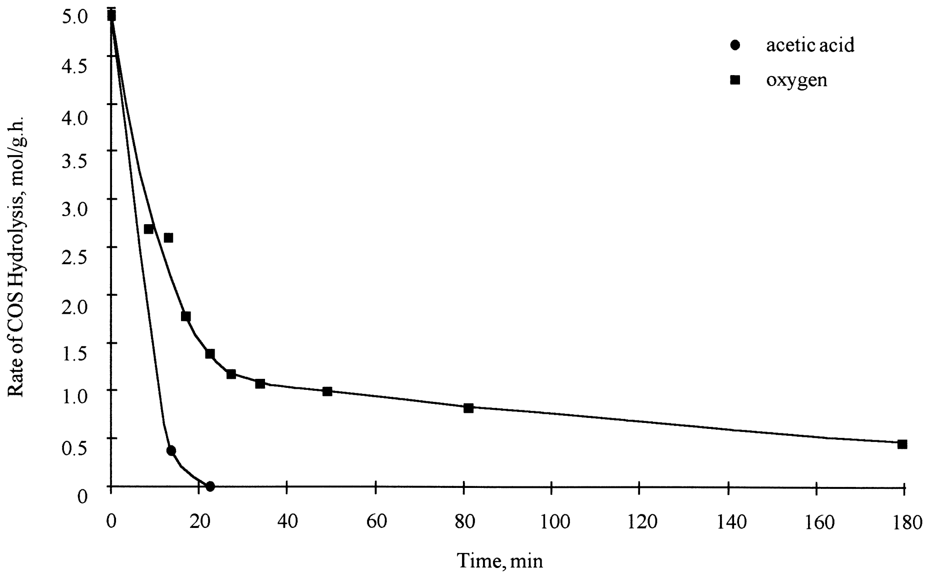


Fig. 11. Effect of acetic acid (●) and oxygen (■) on the reaction rate of COS hydrolysis [36].

3. Products H_2S and COS are not adsorbed on the surface, or they desorb rapidly.
4. H_2O adsorbs very strongly such that its adsorption equilibrium constant is very large.
5. The reaction equilibrium is very much on the product side.

However, a different pathway could be possible where the rate determining step of reaction related to the competition between H_2O and COS for adsorption sites on the alumina (*=adsorbed species):

Adsorption

$$COS + Al_2O_3 \leftrightarrow Al_2O_3 \cdot COS^* \qquad (1)$$

$$H_2O + Al_2O_3 \leftrightarrow Al_2O_3 \cdot H_2O^* \qquad (2)$$

Reaction

$$COS^* + H_2O^* \leftrightarrow CO_2{}^* + H_2S^* \qquad (3)$$

Desorption

$$Al_2O_3 \cdot CO_2{}^* \leftrightarrow Al_2O_3 + CO_2 \qquad (4)$$

This particular mechanism was proposed for the removal of COS from a feed containing hydrocarbons. It was shown that if the concentration of H_2O exceeds 30%, then COS adsorption becomes inhibited on Al_2O_3 and Eq. (2) dominates over Eq. (1) to the detriment of the hydrolysis reaction. Deason et al. [71] described a process in which an alumina catalyst could be operated successfully with levels of water in the feedstream greatly exceeding this 30% maximum value; however, periodic regeneration of the catalyst at elevated temperatures was required using an inert gas.

Tong et al. [33] and Vermeersch [84] investigated the mechanism and the performance of titania

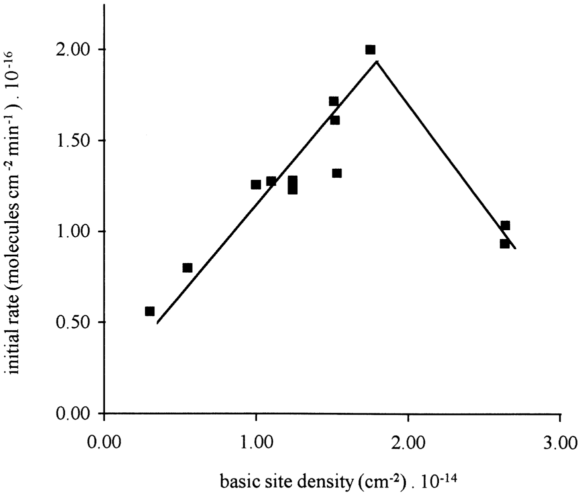


Fig. 12. Correlation of initial rate as a function of basic site density.

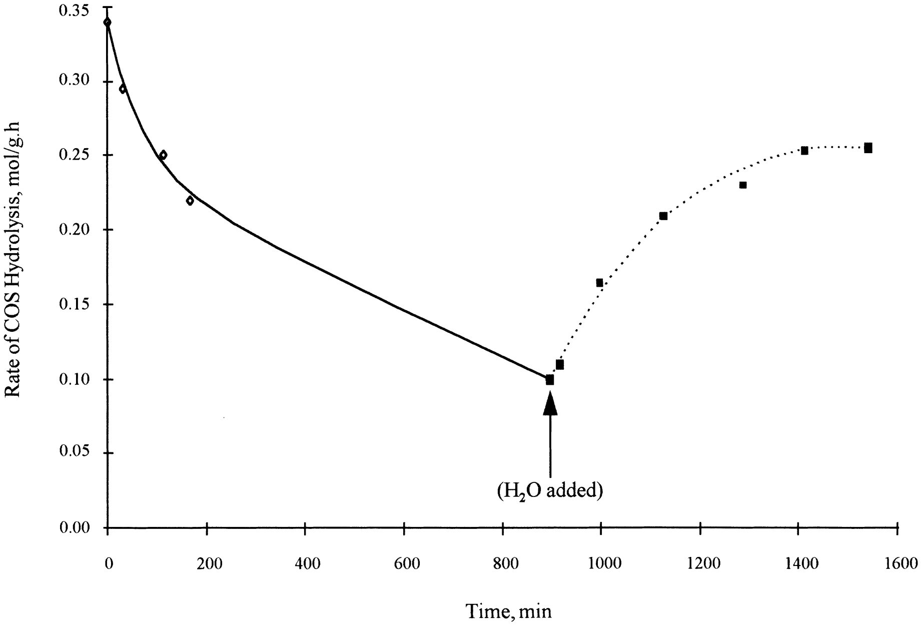


Fig. 13. COS and water competition.

(CRS31) compared with the alumina-based industrial catalysts at temperatures above 270°C. The titania-based catalyst appeared to become an increasingly more active hydrolysis catalyst, compared to alumina, as the temperature of the reaction was increased. Thermogravimetric measurements demonstrated that alumina, because of its inherent hydrophilic character, retained large amounts of adsorbed water even up to 500°C. Under the same conditions, titania retained no water at 300°C. Analysis of the intrinsic rate functions for the hydrolysis of COS, led Tong et al. to describe an Eley–Rideal model for both catalysts over the temperature range, 270–330°C. It was concluded that absorption of water inhibits the hydrolysis reaction on both catalysts, but more so for alumina. The lower activity of alumina compared to titania was explained by the observation that the higher stability of the water on the alumina surface increased the likelihood of adsorbed water inhibiting access of COS molecules to the active basic sites, even at elevated temperatures.

Recently, Hoggan et al. [72] used FTIR spectroscopy to study the adsorption of COS on γ-Al_2O_3. On a highly dehydroxylated alumina (activated at 1173K), two bands were observed at 1990 and 1960 cm^{-1}. The band at 1990 cm^{-1} was considered to be characteristic of the formation of species A, proposed to occur on weakly acidic sites (Fig. 14). The other band was assigned to species B and/or C and involved very weak basic sites. In the presence of very basic O^{2-} sites, COS adsorption was expected to lead to the formation of thiocarbonate $(CO_2S)^{2-}$ intermediate species, however, no such species were detected in this study. For gas phase carbon dioxide the wave number is lower than that observed for adsorbed carbon dioxide species; the Lewis acidity of the surface contributing to the shift. Conversely, for adsorbed COS species a reduction in the wave number is observed compared with COS in the gas phase.

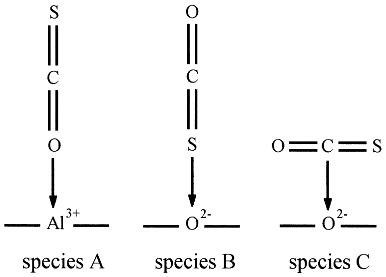
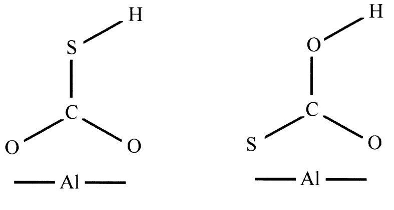


Fig. 14. Slightly perturbed COS species.



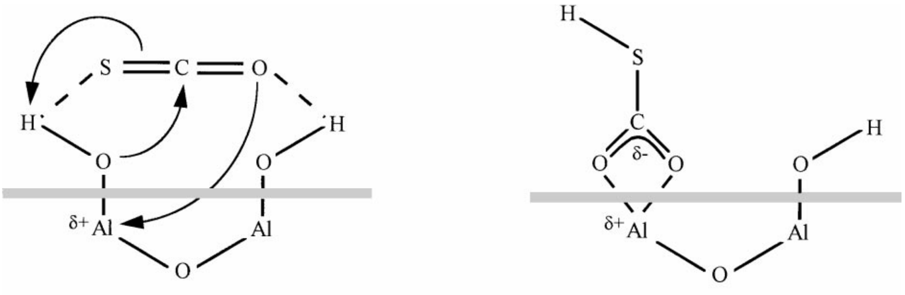
Type 1
HTC species

Type 2
HTC species

Fig. 15. Hydro-thiocarbonate species as suggested by Lavalley et al.

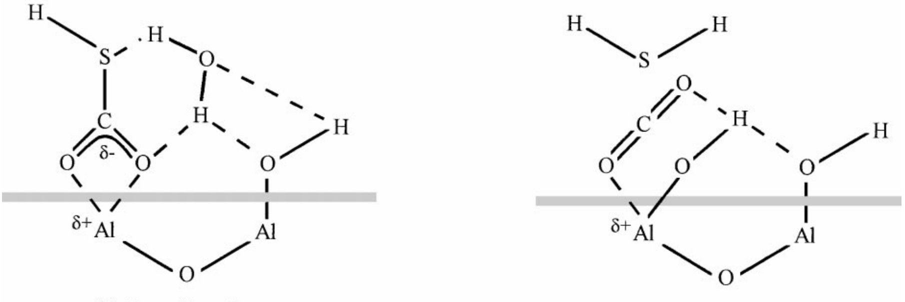
In a related study, Lavalley et al. observed two bands near 1575 and 1325 cm^{-1} and a hydrogen thiocarbonate species was proposed. The formation of this species requires the presence of a surface hydroxyl group, analogous to the hydrogen carbonate species formed CO_2 adsorption on basic alumina. Similar species were recorded previously [55] when an alumina catalyst was exposed to H_2S containing traces of CO_2. A bidentate mode of bonding was assumed, leading to two postulated structures (Fig. 15) and the type 1 hydro-thiocarbonate (HTC) species was favoured by Lavalley et al. Quantum chemistry calculations for the COS hydrolysis mechanism on alumina substrate suggest that the initial chemisorption of COS on the OH base site proceeded via a physisorbed phase through which the orientation proceeds to maximize COS polarization via the HTC species (Fig. 16).

Huisman et al. [47], investigating the complexes formed on γ-Al_2O_3 and TiO_2, demonstrated the presence of hydrogen thiocarbonate species on both surfaces. However, markedly different frequencies of absorption for the hydrogen thiocarbonate species on each of the surfaces were recorded, suggesting that the configuration of the hydrogen thiocarbonate complex differed [37]. This contrasts with the work of Lavalley et al. [55] but the difference is tentatively assigned to the amount of COS used in the two studies. On the alumina catalyst, hydrogen thiocarbonate remained intact up to temperatures of 202°C. On the titania catalyst the bands assignable to hydrogen thiocarbonate disappeared by 102°C, and the formation of SH species has been shown to occur simultaneously with this



a) Initial step

(b) HTC species formation



(c) Transition State

(d) Product Formation

Fig. 16. COS mechanism established by quantum chemical calculations.

process. It is considered that the mechanism for the CS_2 hydrolysis on titania proceeds via a hydrogen thiocarbonate mechanism at temperatures below 250°C. At higher temperatures, the mechanism of hydrolysis changes and involves the sulfidation of the catalyst surface which subsequently undergoes hydrolysis:

$$TiO_2 + CS_2 \leftrightarrow TiS_2 + CO_2, \quad \Delta G_{300} = +21.07\,\text{kJ mol}^{-1}\ TiO_2$$

$$TiS_2 + 2H_2O \leftrightarrow TiO_2 + 2H_2S_2, \quad \Delta G_{300} = -37.29\,\text{kJ mol}^{-1}\ TiO_2$$

Pulse experiments by Huisman et al. [47] showed that about 40% of the surface oxygen atoms of titania are exchanged after reaction of the catalyst with CS_2. In comparing the titania and alumina catalysts for CS_2 hydrolysis, the effect of temperature on the rate of reaction was less pronounced. For an alumina catalyst the relatively large amount of water adsorbed on the surface meant that the sulfidation-hydrolysis mechanism as described for titania does not have a significant role.

9. Theoretical studies of the hydrolysis mechanisms

A thiocarbonate intermediate species similar to that observed on alumina, and on titania when operated at low temperatures, has been proposed by Wilson and Hirst [73] using a high-level method of molecular orbital theory (G-2 theory). Based on calculations of the various reaction channels on the potential surface for COS and OH radicals, a four-centred species was proposed through which the reaction proceeded in a single step (Figs. 17 and 18).

Wilson et al. mapped out the potential energy suface of the OH COS system and found a large number of stationary points. At 298K, the reaction to form the carbon adduct has an activation barrier of $\Delta H^{+}(298\text{K})=+21.1\,\text{kJ mol}^{-1}$ and the overall reaction was exothermic ($\Delta H\,(298\text{K})=-110.2\,\text{kJ mol}^{-1}$). The rotation of the OH adduct (1), to place hydrogen in closer proximity to the sulfur, forms an adduct capable of an intramolecular H-atom transfer to give the products CO_2 and HS. Using this model, the reaction was believed to proceed slowly implying a catalyst is active in the observed reaction.

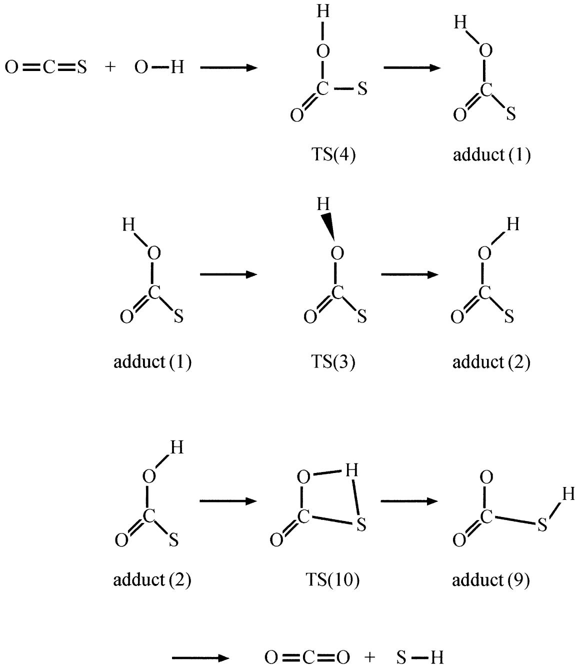


Fig. 17. Reaction scheme for the carbon-bonded adducts.

Computational modelling of the addition of OH radicals to CS_2 has been investigated by McKee [74] (Figs. 19 and 20). Apart from the obvious importance of this study for CS_2 hydrolysis, the reaction of CS_2 with OH is an important reaction in the atmospheric chemistry and is considered to be the major pathway for conversion of CS_2 to COS, and ultimately leads to SO_2 formation. Currently the accepted mechanism for atmospheric SO_2 formation involves the formation of $HOCS_2$ species which subsequently reacts with O_2.

$$OH + CS_2 + M \leftrightarrow HOCS_2 + M$$

$$HOCS_2 + O_2 \leftrightarrow \text{Products}$$

Using the model, the addition of OH radicals to the sulfur atom was predicted to be exothermic ($\Delta H=-24.7\,\text{kJ mol}^{-1}$) and the addition of OH to the carbon atom was also found to be exothermic ($\Delta H=-126.7\,\text{kJ mol}^{-1}$). Although, thermodynamically, it would appear that bonding of OH to carbon is more favourable, better agreement with the experimental data was found when the OH was presumed to bond to the sulfur atom. It was found that the OH

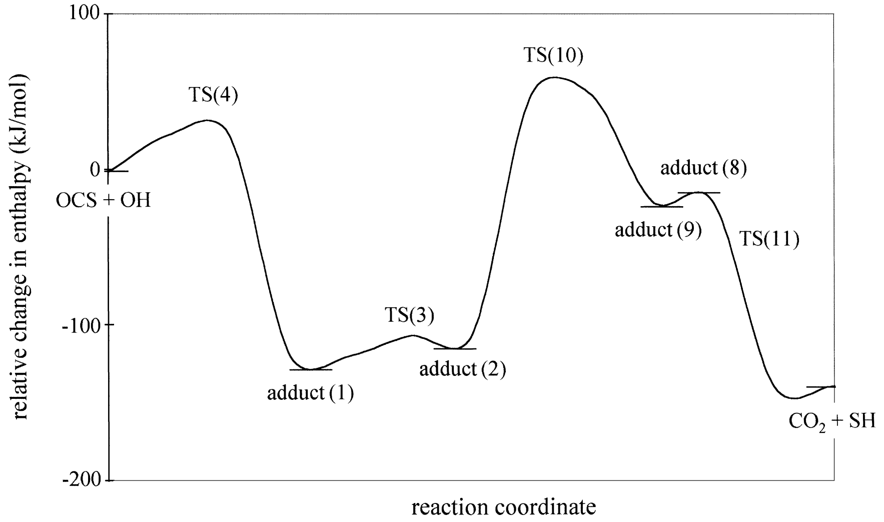


Fig. 18. Reaction scheme for the carbon-bonded adducts.

added to the sulfur without activation, whereas to a carbon atom required an activation of 29.3 kJ mol^{-1}. The product was therefore formed under kinetically controlled conditions rather than under thermodynamically controlled one (Fig. 18).

10. Future prospects

Although γ-Al_2O_3 is used extensively as an industrial catalyst, there is scope for future catalysts to be based on alternative materials. For example, TiO_2 can exhibit enhanced activity and an attempt to combine the high activity of TiO_2 together with the high surface area of γ-Al_2O_3 has been studied by Rigge et al. [75] using a coprecipitation preparation procedure. Highly dispersed alumina–titania catalysts were produced that gave improved performance. Such a study indicates that potential exists to design new catalysts with enhanced activity through control of the surface area of the material.

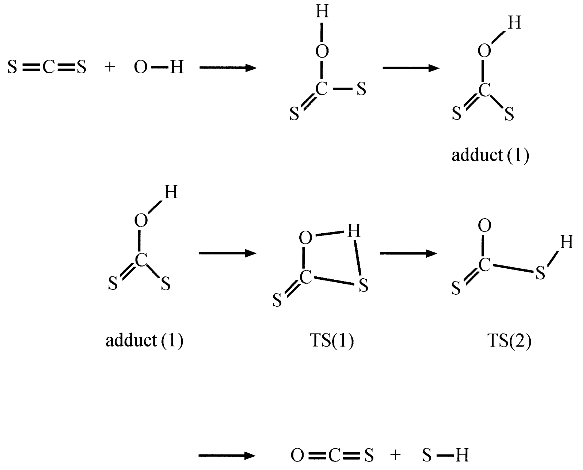


Fig. 19. Reaction scheme for the carbon-bonded adducts.

Another approach that has potential is the introduction of promoters, in particular, with the aim of decreasing the hydrophilicity of the catalyst surface. It is considered that, if the surface hydrophilicity is decreased, it is possible that deactivation during the hydrolysis reactions can be minimised. For example iron [60] has been demonstrated to be a useful promoter and it is suggested that additional studies of this interesting area are now considered.

Other catalytic materials of current research interest are based on ZrO_2. Mixed oxides ZrO_2/Al_2O_3 and ZrO_2/TiO_2 have been prepared by Lahousse et al. [76] and these materials may prove to be useful in producing high surface area catalysts. Recently, a combined FTIR, reactivity and quantum chemistry investigation of COS hydrolysis has been reported by Aboulayt et al. [77] and it has been shown that, when compared with Al_2O_3 and TiO_2, ZrO_2 is an active catalyst and the activity hierarchy of these catalysts per unit surface area is $ZrO_2 \gg Al_2O_3 > TiO_2$.

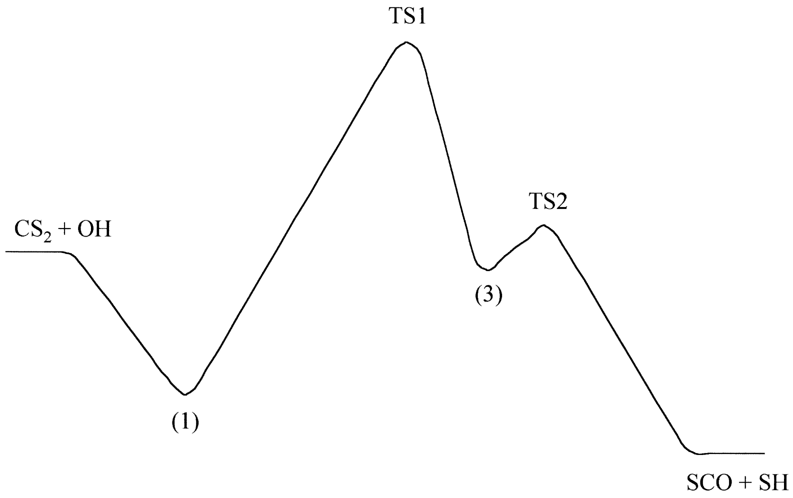


Fig. 20. Reaction scheme for the carbon-bonded adducts.

The possible existence of a thiocarbonate intermediate in the COS hydrolysis reaction suggests that sulfide catalysts may be of interest. Interestingly, COS hydrolysis has been examined [78] and characterised [79] for ZnS as a catalyst.

High area α-Fe_2O_3 produced by partial dehydration of α-FeOOH at 200°C [80] exhibits a uniform porous structure with surface area of ca. $100\,m^2\,g^{-1}$ [81]. This material was extremely active for H_2S and COS removal at 40–60°C, however, the catalyst deactivated rapidly. This study shows that iron catalysts could be a useful basis for future high activity catalysts if the surface area can be stabilised under reaction conditions. As noted previously, iron has been shown to promote catalyst performance [60] and this effect may be linked to the preparation of a dispersed iron oxide species. In addition, a naturally occurring mineral, sepiolite ($Si_2Mg_8O_{30}(OH)_4(H_2O)_{12}$) has been demonstrated to have sustained activity [82,83]. This material has an open, fibrous structure and is not prone to severe fouling by sulfur.

This review has shown that there have been many advances in the design of suitable catalysts for COS and CS_2 hydrolysis. It is considered that future improvements are most likely to result from detailed investigation of the catalyst preparation procedures, to produce stable, high surface area materials, and the study of catalyst promoters. Such catalysts can be expected to play a significant role in the reduction in sulfur emissions.

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