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# Carbonyl sulphide hydrolysis using alumina catalysts

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## Abstract

The hydrolysis of carbonyl sulphide over two alumina catalysts (surface areas 150 and 300 $m^2 g^{-1}$) has been studied. Virtually all previous studies have focussed upon concentration ranges for the reactants ([COS] typically>1000 ppm) and temperatures (typically>100°C) that are much higher than those experienced in real industrial processes. In the study presented here, the concentration of carbonyl sulphide investigated is 150 ppm and temperatures in the range 30–250°C are investigated. At higher temperature (250°C) the data obtained are in agreement with previous studies and the reaction follows Langmuir–Hinshelwood kinetics with the surface hydrolysis of a thiocarbonate being the rate determining step. At lower temperatures (30–60°C) the data indicate that the rate of COS hydrolysis decreases monotonically with increasing [$H_2O$]. These data are consistent with Langmuir–Hinshelwood kinetics where the products are not adsorbed and either (a) the adsorption of COS is rate determining or (b) the surface reaction of adsorbed COS and an intermediate derived from $H_2O$ is rate determining. The current experiments cannot differentiate between these possibilities. Under these conditions it is the surface area of the alumina catalyst that is the important design parameter, a feature not observed in previous high temperature studies. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrolysis; Alumina catalyst; Carbonyl sulphide; Langmuir–Hinshelwood kinetics

## 1. Introduction

Over the last two decades it has become increasingly apparent that emissions of sulphur compounds, including COS, into the atmosphere have been unacceptably high. Furthermore, not only does the sulphur content of industrial feedstocks affect the environment by leading to the formation of acid rain, it also presents problems within industry itself. The detrimental effect that sulphur has on industrial heterogeneous catalysts is well known [1]. Levels of sulphur as low as 1 ppm can effectively poison the activity of a modern bimetallic reforming catalyst. As little as 4 mg of sulphur per gram of catalyst on the surface of the Fe–Cu–K catalyst used in the Fischer–Tropsch synthesis process decreases the observed activity by 50% [2]. In addition, it is found that the presence of feedstock sulphur can lead to increased corrosion of the reactors used in refinery processes [3]. Well-established procedures have been used for many years to remove sulphur compounds by hydrodesulphurisation by conversion of the sulphur containing compounds to hydrogen sulphide [4]. Raw materials that have undergone desulphurisation are, consequently, less hazardous, less corrosive and can be used for the manufacture of odour free products.

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With the introduction of stringent legislation to reduce sulphur emissions, fresh impetus is being given to modifying and improving existing desulphurisation technology. However, dehydrosulphurisation does not remove or significantly affect one sulphur containing compound, namely carbonyl sulphide. An alternative technology has to be used for the removal of carbonyl sulphide and this is based on the formation of hydrogen sulphide by hydrolysis:

$$COS + H_2O \leftrightarrow H_2S + CO_2 \quad (1)$$

A large number of studies have investigated this reaction [5–16] and to date alumina and/or titania have been identified as potential catalysts. Developments include the investigation and optimisation of the catalyst morphology and new formulations are increasingly being introduced to maximise the active site density or to reduce the likelihood of site blockage. Recent developments have included increasing the average pore diameters of the alumina catalysts from 600 to 750 nm to diameters in excess of 1 μm to enable reduction in the possibility of site blockage by sulphur adsorption [17].

While a large number of studies have been made of the hydrolysis reaction it is observed that virtually all utilise reaction conditions that are significantly removed from the conditions typically found in industrial process streams. In particular, the requirement is to treat low concentrations of carbonyl sulphide (typically ≤150 ppm) at near ambient temperature (30–60°C). The conditions used in previous studies are shown in Fig. 1 (150 ppm=0.0225 kPa partial pressure at 1.5 bar) and it is apparent that few of the previous studies investigate these conditions and usually much higher carbonyl sulphide concentrations (typically ca. 5000 ppm) and higher temperature (typically >100°C) are studied.

In this paper we present a study of alumina catalysts for the hydrolysis of carbonyl sulphide for which the concentration of carbonyl sulphide investigated is 150 ppm together with temperatures in the range 30–250°C. The aim is to investigate the reaction mechanism under industrially relevant conditions.

## 2. Experimental

Two γ-alumina samples were selected for study. The first was supplied by Brockmann and had a surface area of 150 $m^2\,g^{-1}$ and the second was an ICI alumina with a surface area of 300 $m^2\,g^{-1}$; both were used without further treatment. The catalysts were tested in a fixed bed microreactor at gas hourly space velocities of 100 000–500 000 $h^{-1}$. Carbonyl sulphide (BOC,

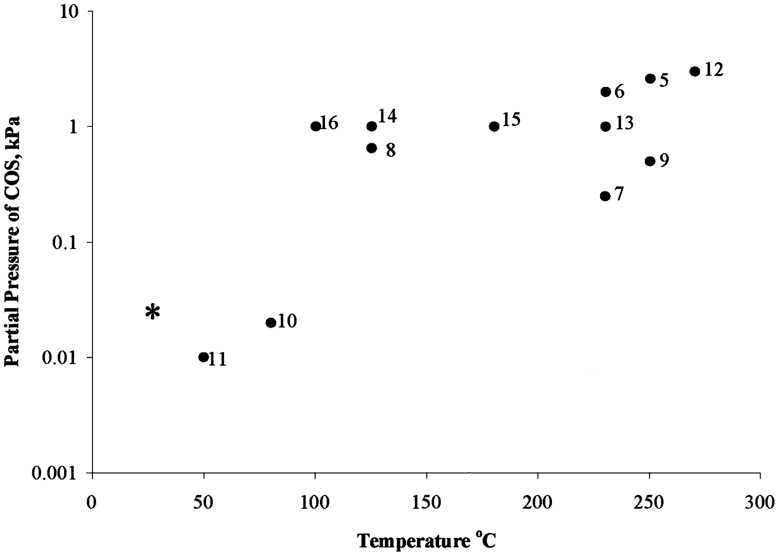

Fig. 1. Reaction conditions for previous studies concerning COS hydrolysis and atmospheric pressure, the numeric labels correspond to quoted reference, with * indicating the partial pressure of COS being used in this study.

1% in $N_2$) and nitrogen were fed to a saturator via calibrated mass flow controllers. The water saturator comprised two bubblers, one being maintained at 20°C and the second at a controlled temperature and in this way the concentration of water in the diluted carbonyl sulphide gas stream was maintained at the saturated vapour pressure of water at the temperature set in the second saturator. This was found to be the most effective method for delivering low, controlled concentrations of water to the reactor. The exit gases from the reactor were analysed using gas chromatography using a pulsed flame photometric detector.

## 3. Results and discussion

The initial experiments were carried out to determine the lifetime of the alumina catalysts and the stabilisation period required prior to the acquisition of kinetic data. It was found that the catalysts were particularly stable following a period of ca. 5 h stabilisation, during which time deactivation was observed. Hence, the catalysts were allowed to stabilise for 5 h prior to data collection. Representative data for the effect of time on stream on COS conversion are shown in Fig. 2.

Experiments were then carried out with the lower surface area alumina (150 $m^2 g^{-1}$, Brockmann). The hydrolysis of COS was investigated with a fixed concentration of COS (150 ppm) but with varying water concentration at a fixed total gas hourly space velocity. The results for two temperatures are shown in Fig. 3. At higher temperature the results are consistent with the results of the previous studies [1–3,5,8,9]. Clearly alumina is very active under these conditions and the data are consistent with a mechanism proposed by Hoggan et al. [18] in which the reaction proceeds via the formation of a surface thiocarbonate upon adsorption of COS and the rate determining step is the reaction of this surface species with a surface hydroxyl group. The data are consistent with Langmuir–Hinshelwood kinetics where the products of reaction are not strongly adsorbed, given by

$$\text{rate} = \frac{k_1[\text{COS}][\text{H}_2\text{O}]}{(1 + K_2[\text{COS}] + K_3[\text{H}_2\text{O}])^2}, \tag{2}$$

where $k_1$ is the rate constant ($k_1 = k \cdot K_{\text{COS}} \cdot K_{\text{H}_2\text{O}} \cdot XS^2$ where $XS$ is the total concentration of available active sites) and $K_2$ and $K_3$ are equilibrium constants

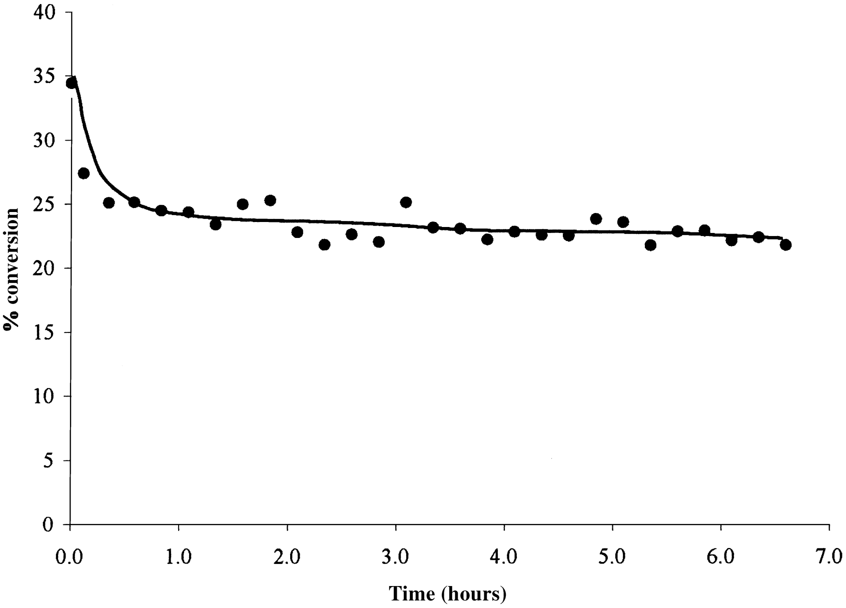

Fig. 2. COS conversion as a function of time on stream. Reaction conditions: alumina (0.5 g, 300 $m^2 g^{-1}$), 30°C, 100 000 $h^{-1}$, 300 ppm COS, 1200 ppm $H_2O$.

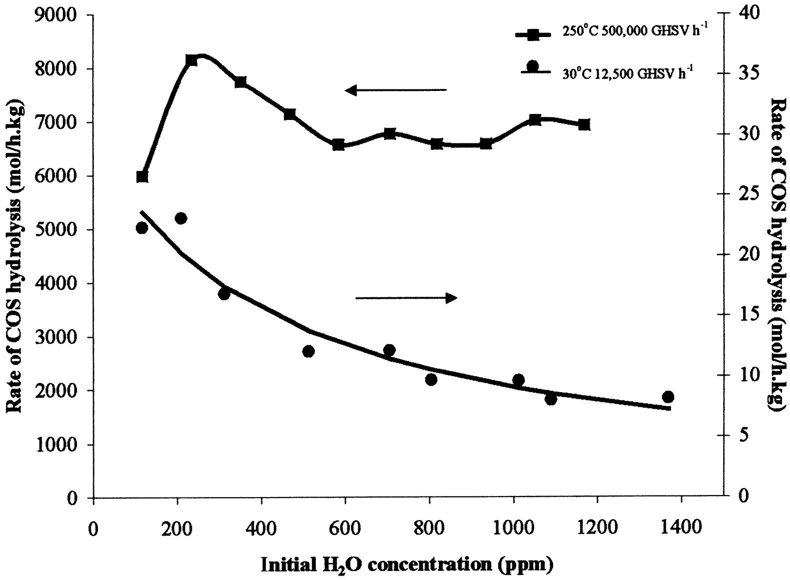

Fig. 3. Rate of COS hydrolysis as a function of [$H_2O$] at constant [COS]=150 ppm, alumina 150 $m^2 g^{-1}$. Key: (■)=250°C, 500 000 $h^{-1}$; (●)=30°C, 12 500 $h^{-1}$.

for the adsorption of COS and $H_2O$, respectively. At 250°C the alumina is a very active catalyst with rates of COS hydrolysis in the range $6\times10^3$–$8\times10^3$ mol $kg^{-1}$ $h^{-1}$ being observed. As expected, at the lower temperature of 30°C the rate is significantly lower. However, the rate of COS hydrolysis is observed to decrease significantly as the concentration of water is increased. This indicates that the rate determining step at the lower temperature is different than that determined for the high temperature study. It is apparent that water is acting as an inhibitor and the data can be described using Langmuir–Hinshelwood kinetics with the adsorption of COS being the rate determining step or the surface reaction of adsorbed COS and an intermediate derived from $H_2O$ being rate determining, Eq. (3), where $k_1$ is the rate constant ($k_1{=}k{\cdot}XS$ where $XS$ is the total concentration of available active sites). The data in Figs. 4–6 show good agreement between experimental and calculated results for both of the models presented (Eqs. (2) and (3)).

$$\text{rate} = k_1 \frac{[\text{COS}]}{(1 + K_3[\text{H}_2\text{O}])}. \qquad (3)$$

The higher surface area alumina was also investigated at 60°C and the same relationship between the rate of COS hydrolysis and increasing water concentration at constant space velocity was observed (Fig. 5) although the rate was significantly higher. At 30°C, the rate of COS hydrolysis was examined at constant [$H_2O$] with increasing [COS] at constant space velocity and temperature and the results are shown in Fig. 6.

It is therefore clear that the rate determining step of COS hydrolysis on alumina catalysts is dependent on the reaction temperature. At high temperatures, which are of limited industrial interest, the rate determining step is the surface reaction and the results we have obtained are in agreement with previous studies [18]. However, at lower temperatures the competitive adsorption between the two reactants dominates with either the rate of COS adsorption being rate limiting or the surface reaction of adsorbed COS and an intermediate derived from $H_2O$ being involved in the rate determining step. Under these circumstances, it is clear that an alumina with a high surface area will give the highest activity. The design of active catalysts for low temperature COS hydrolysis will therefore depend mainly on methodology that can yield high surface aluminas that maintain high surface area when exposed to relatively high but variable concentrations of water vapour. In addition, this study shows that the previous investigations have concentrated on

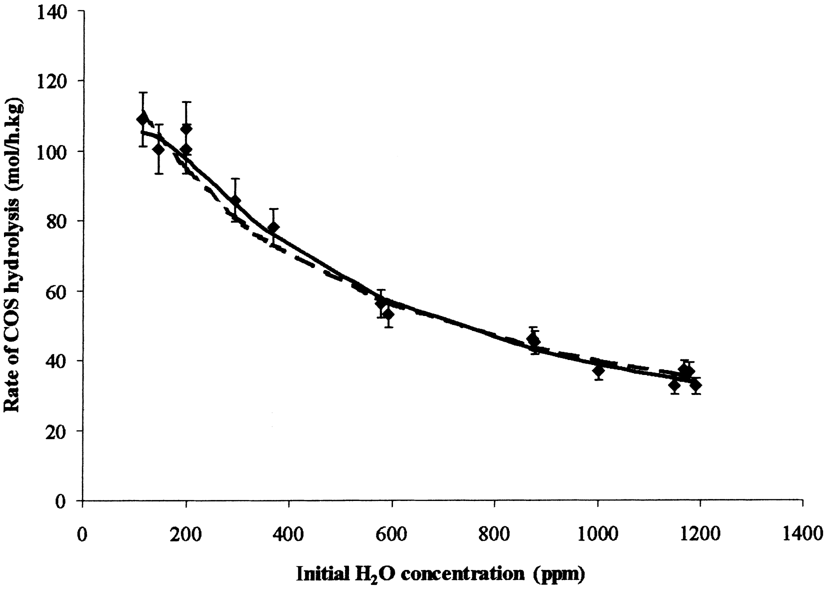

Fig. 4. Rate of COS hydrolysis as a function of [$H_2O$] at constant [COS]=150 ppm, 30°C, gas hourly space velocity 100 000 $h^{-1}$. Key: experimental data (●), calculated data for COS adsorption limited model (Eq. (2)) (- - -), calculated data for surface reaction type model (Eq. (3)) (———).

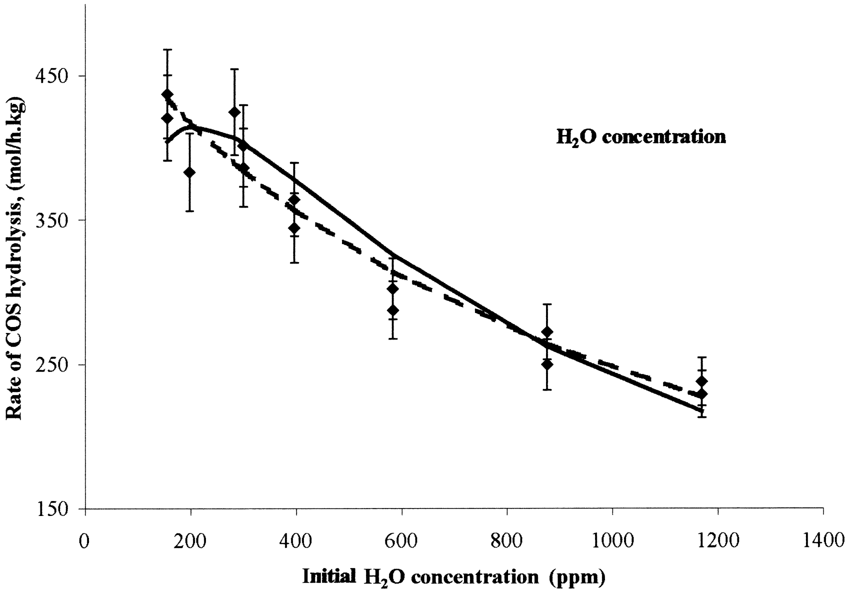

Fig. 5. Rate of COS hydrolysis as a function of [$H_2O$] at constant [COS]=150 ppm, alumina 300 $m^2 g^{-1}$, 60°C, 500 000 $h^{-1}$. Key: experimental data (●), calculated data for COS adsorption limited model (Eq. (2)) (- - -), calculated data for surface reaction type model (Eq. (3)) (——).

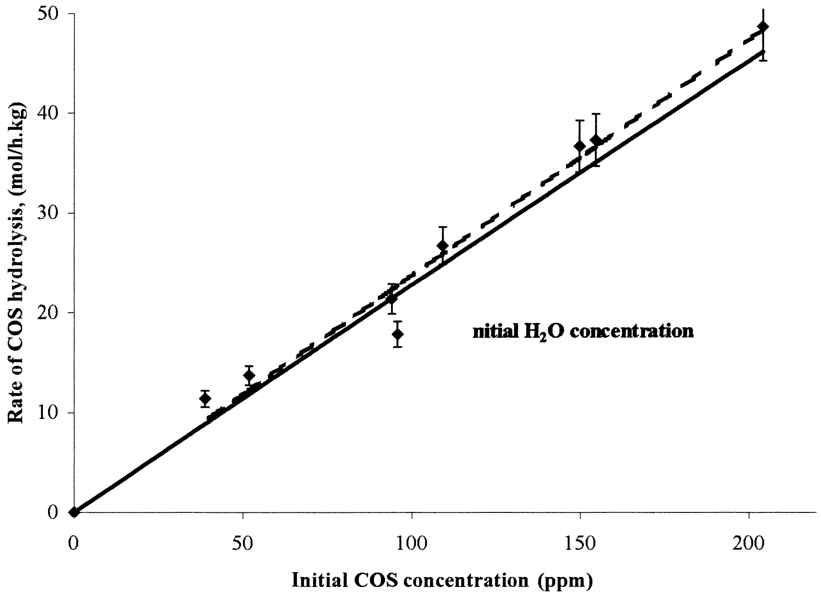

Fig. 6. Rate of COS hydrolysis as a function of [COS] at constant $[H_2O]=1200$ ppm, alumina 300 $m^2\,g^{-1}$, 100 000 $h^{-1}$. Key: experimental data (●), calculated data for COS adsorption limited model (Eq. (2)) (- - -), calculated data for surface reaction type model (Eq. (3)) (——).

inappropriate reaction conditions and that future studies should concentrate on the study of lower COS concentrations and temperature <100°C.

## 4. Conclusions

The hydrolysis of carbonyl sulphide over two alumina catalysts (surface areas 150 and 300 $m^2\,g^{-1}$) has been studied. At higher temperature (250°C) the data obtained are in agreement with previous studies and the reaction follows Langmuir–Hinshelwood kinetics with the surface hydrolysis of a thiocarbonate being the rate determining step [18]. However, at lower temperature (30°C) this mechanism is not operative and the reaction is observed to follow Langmuir–Hinshelwood kinetics with the adsorption of carbonyl sulphide and/or the surface reaction of adsorbed COS and an intermediate derived from $H_2O$ being the rate determining step. The current experiments cannot differentiate between these possibilities at present and future work examining the nature of the species upon the catalyst surface at low temperature is currently underway. Under these conditions it is the surface area of the alumina catalyst that is the important design parameter, a feature not observed in previous high temperature studies.

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