Low temperature hydrolysis of carbonyl sulfide using γ-alumina catalysts

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The hydrolysis of COS using alumina as catalyst in the temperature range 10–80 °C is described in detail. The rate of COS hydrolysis is found to be approximately first order in [COS] but is significantly inhibited with increasing [H_2O]. Addition of CO_2 is also found to have an inhibiting effect on the rate of hydrolysis, but no marked effect is observed when additional H_2S is present in the feedstock. The reaction in this temperature range is contrasted with the previous studies at higher temperatures and it is suggested that the reaction proceeds *via* reaction of adsorbed COS with surface hydroxyl groups on the alumina. Supporting evidence for this is provided from experiments in which water was not co-fed with COS, or the flow of water vapour was interrupted. In both cases, an initial increase in the rate of COS hydrolysis is observed. The rate of COS hydrolysis can be significantly enhanced by the addition of Fe, Co, Ni, Cu and Zn to the alumina.

KEY WORDS: carbonyl sulfide hydrolysis; γ-alumina

1. Introduction

Recently, there has been increased interest in the hydrolysis of carbonyl sulfide as a reaction for removing traces of COS from hydrocarbon or synthesis gas feedstocks, and this topic has recently been reviewed [1]. COS is not affected significantly by the standard method of desulfurisation using hydrogenation followed by adsorption of the H_2S produced. However, COS can act as a potent catalyst poison for a number of catalysts and the effects of sulfur on industrial catalysts has been well documented [2]. COS hydrolysis has been found to be catalysed by alumina and alumina-supported transition metal oxides, and most previous studies have concentrated using temperatures in excess of 100 °C [3–10] and only relatively few studies have been at temperatures between 50 and 100 °C [11,12]. In this paper, we present a detailed study for COS hydrolysis in the temperature range 10–80 °C using alumina and doped alumina catalysts.

2. Experimental

2.1. Catalysts

γ-alumina (Synetix) was used without modification. The surface area was determined to be 300 m^2/g, by nitrogen adsorption using the BET method, with a mean pore size of 2.6 nm. Doped catalysts were prepared using an incipient wetness method in which a solution of the metal nitrate was adsorbed onto the γ-alumina, dried (120 °C, air, 4 h) and calcined (500 °C, 5 h).

2.2. Catalyst testing

A standard laboratory microreactor, using a stainless-steel U-tube reactor, was used to study the COS hydrolysis reaction. COS (BOC, 5000 ppm in N_2) was further diluted with nitrogen to the required feed level and the overall flow rate was controlled using calibrated mass flow controllers. Water was introduced using a saturator system and the overall gas hourly space velocity (GHSV) of the reaction mixture was standardised at 122000 h^{-1} for most experiments. The reactor, containing 0.5 g (0.65 ml) catalyst, was immersed in a water bath under thermostatic control to achieve the required temperature in the range 10–80 °C. Reactant and products were analysed using gas chromatography with a pulsed flame photometric detector permitting the detection of COS as low as 1 ppm. The reactor and reaction conditions were evaluated to ensure that mass transfer limitations were not observed.

Catalysts were stabilised in the reactor for 5 h prior to testing, during which time the catalyst performance stabilised. For all data presented in this paper, a fresh stabilised catalyst was used for each data point. All experiments were conducted at 1.6 bar reactor pressure.

3. Results and discussion

The hydrolysis of carbonyl sulfide was investigated at 30 and 60 °C for a range of concentrations, [COS] $=$ 40–205 ppm and [H_2O] $=$ 100–1200 ppm. The results for the variation in the rate of COS hydrolysis at constant [H_2O] with variation in [COS] is shown in figure 1. The hydrolysis rate increases linearly with increasing [COS] and the order

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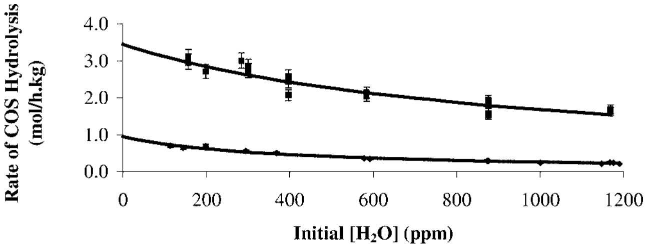


Figure 1. Rate of COS hydrolysis as a function of [H_2O] with 150 ppm COS. (♦) 30 °C, GHSV 122000 h^{-1} and (■) 60 °C, GHSV 610000 h^{-1}.

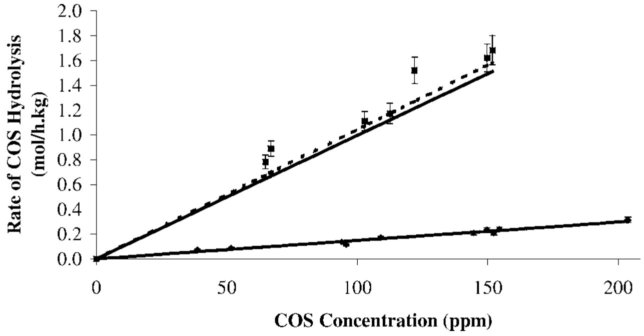


Figure 2. Rate of COS hydrolysis as a function of [COS] with 1200 ppm H_2O. (♦) 30 °C, GHSV 122000 h^{-1} and (■) 60 °C, GHSV 610000 h^{-1}.

of reaction with respect to COS is approximately unity. At both 30 and 60 °C, water inhibited the rate of hydrolysis, and the rate decreased with increasing [H_2O] at constant [COS] (figure 2). Calculations, using the Kelvin equation, indicated that for alumina with a mean pore radius of 2.6 nm capillary condensation of water would not occur under the reaction conditions studied, or even at water concentrations considerably in excess of those used (*e.g.*, >3000 ppm [H_2O]). Hence, the inhibition by water is not due to capillary condensation but probably results from competitive adsorption at the active sites for H_2O and COS.

The activation energy for the hydrolysis reaction was determined for a range of conditions ([COS] = 150 ppm, [H_2O] = 200, 400, 800 and 120 ppm; [COS] = 75 ppm, [H_2O] = 200 and 400 ppm) for the temperature range 10–80 °C. The mean activation energy was independent of the initial reaction concentrations used and was determined to be 45 ± 10 kJ/mol. This is much higher than activation energies determined for COS hydrolysis on alumina catalysts at temperatures higher than 100 °C [4]. In addition, at these higher temperatures the previous studies have indicated that the inhibition effect of water is not observed [3–5]. This indicates that the surface processes occurring at temperatures in the region 10–80 °C are possibly different than those occurring at higher temperatures.

The effect of the reaction products on the hydrolysis reaction was also investigated for the alumina catalyst. Addition of H_2S at constant [COS], [H_2O] and GHSV did not affect the rate significantly. However, addition of CO_2 exhibited a marked inhibition on the rate of the hydrolysis reaction (figure 3). Again, the significant inhibition observed at 30 °C is in marked contrast to the minor inhibition observed by Tong *et al.* [6] when 10000 ppm CO_2 was added to the reaction mixture at higher temperatures. Huisman *et al.* [8], using infrared spectroscopy, have shown that hydrogen carbonates and hydrogen thiocarbonates are present on the catalyst surface during the hydrolysis reaction on γ-alumina. Hydrogen thiocarbonates have also been proposed by Hoggan *et al.* [13] for the adsorption of H_2S and CO_2 on γ-Al_2O_3. Addition of CO_2 could lead to the formation of these species leading to inhibition both by site blocking and by reaction of surface hydroxyls. Formation of a surface hydrogen carbonate would involve the reaction of CO_2 with a surface hydroxyl and, hence, this suggests that the hydrolysis reaction at the low temperatures investigated in this study may involve reaction of COS with surface hydroxyl groups on the γ-Al_2O_3, as proposed by Hoggan *et al.* [13].

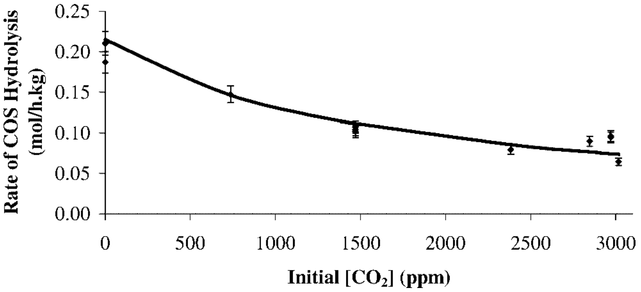
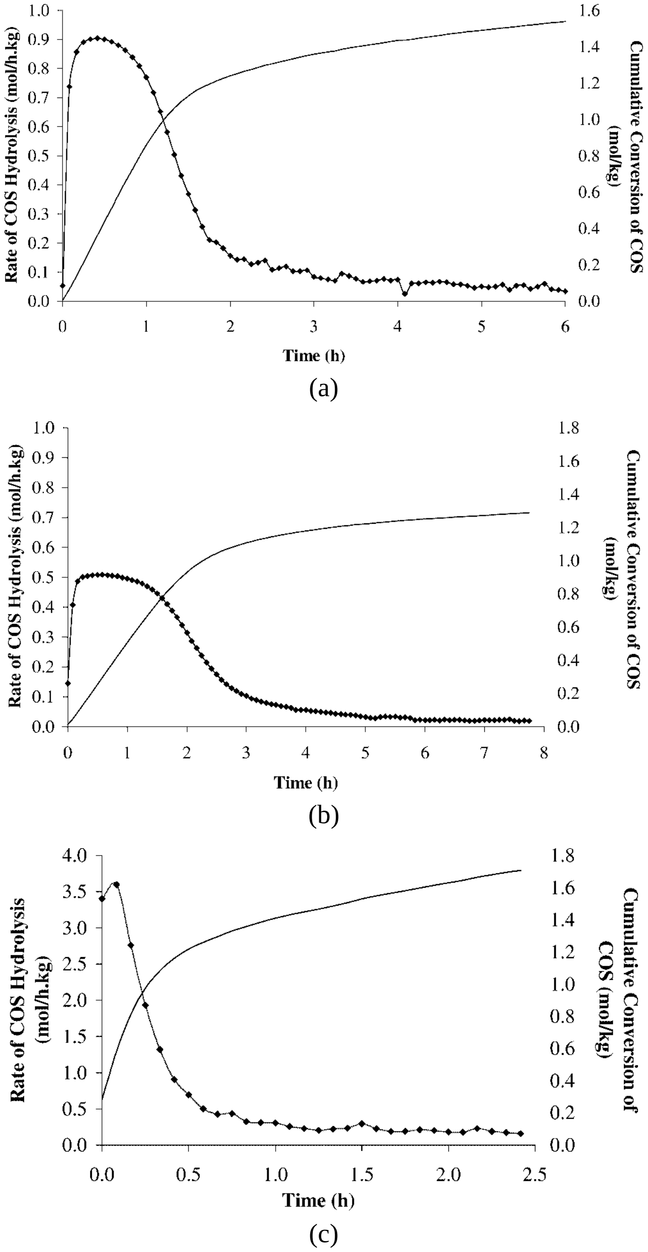


Figure 3. Rate of COS hydrolysis as a function of [CO_2] with 1200 ppm H_2O and 150 ppm COS, GHSV 122000 h^{-1} at 30 °C.

To investigate the reactivity of surface hydroxyl groups, a series of experiments were carried out in which only COS was fed to the reactor (figure 4 (a)–(c)) at 30 and 60 °C. For all conditions tested, COS conversion was initially observed to occur rapidly, but this was followed by a decrease in the reaction rate. The maximum COS conversion rate was dependent upon the initial [COS] and temperature. Further experiments were conducted in which an alumina catalyst was tested under standard reaction conditions but, following stabilisation, the water feed to the reactor was stopped; this procedure was investigated for two concentrations of water (figure 5 (a) and (b)). When the water feed was stopped, a significant increase in the rate of hydrolysis was observed prior to the reaction rate decreasing to a level lower than that observed when COS and H_2O were co-fed to the reactor. During the period of interruption to the water feed, the cumulative COS conversion data are also shown in figure 5. Resumption of the water vapour flow resulted in the hydrolysis rate slowly recovering to the level observed prior to the interruption. This effect could be observed several times on the same catalyst. These results confirm the inhibition of water on the rate of reaction and adds evidence to the proposal that COS reacts with a surface hydroxyl at the low temperature investigated in this study. The observed increase in rate at 30 °C contrasts with the previous study by Fiedorow *et al.* [14] when interruption of the water vapour feed for the reactor at 230 °C led to a decrease in the rate of reaction. This further confirms that the reaction mechanism is different in the low temperature region (*i.e.*, <100 °C) when compared with the previous high temperature studies. The

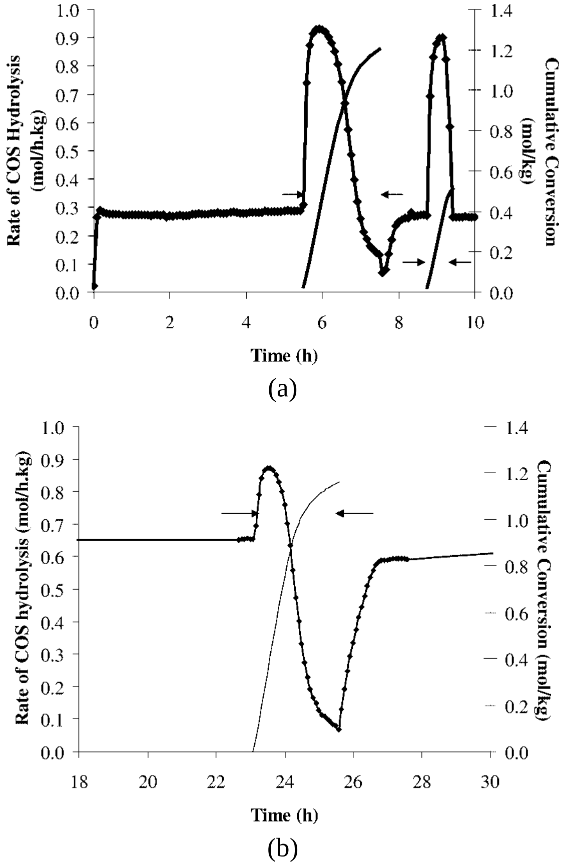


(a)

(b)

(c)

Figure 4. Rate of COS hydrolysis with 0 ppm H_2O at GHSV 122000 h^{-1}: (a) 150 ppm COS, 30 °C, (b) 80 ppm COS, 30 °C and (c) 150 ppm COS, 60 °C.



(a)

(b)

Figure 5. Effect of interruption of water feed on the rate of COS hydrolysis: (a) 150 ppm COS, 1200 ppm H_2O, 30 °C, GHSV 122000 h^{-1}, and (b) 150 ppm COS, 200 ppm H_2O, GHSV 122000 h^{-1}, 30 °C. Arrows indicate the period of interruption of the water feed.

Table 1
Effect of additives on the rate of COS hydrolysis using an alumina catalyst.[a]

Additive[a]	Surface area (m^2/g)	Hydrolysis rate	
		Intrinsic (mol COS/m^2 h)	Specific (mol COS/g_{cat} h)
None	300	0.75×10^{-6}	2.3×10^{-4}
Fe	270	0.8×10^{-6}	2.2×10^{-4}
Co	230	1.0×10^{-6}	2.3×10^{-4}
Ni	230	1.1×10^{-6}	2.5×10^{-4}
Cu	230	0.9×10^{-6}	2.1×10^{-4}
Zn	230	1.2×10^{-6}	2.8×10^{-4}

[a] Reaction conditions: additive 3 wt%, [COS] 150 ppm, [H_2O] 1200 pp, GHSV 122000 h^{-1}.

experiments reported in this study suggest that the reaction proceeds by the reaction of adsorbed COS with a surface hydroxyl species on γ-Al_2O_3 in the temperature range 30–60 °C. The surface hydroxyls are replenished by adsorption of water on the surface; however, water adsorption leads to significant inhibition of the reaction rate for the low temperature reaction.

In an attempt to increase the rate of COS hydrolysis, a series of catalysts were prepared containing Fe, Co, Ni, Cu and Zn (3 wt%). The addition of these additives decreased the surface area of the catalyst (table 1). No significant changes were observed in the powder X-ray diffraction spectrum which was typical of a high area γ-alumina catalyst. The results are shown in table 1. All these additives increase the intrinsic catalyst activity (mol COS hydrolysed/m^2 h). However, due to the general decrease in surface area of the promoted catalysts, on a mass basis only Ni and Zn enhance the specific catalyst activity (mol COS hydrolysed/g_{cat} h). The effect of Ni and Zn promotion is to increase the specific activity by *ca.* 10–20%. The effect is considered to be due to stabilisation of surface sulfide species, and demonstrates that the alumina surface can be modified to give improved catalyst performance under the mild reaction conditions utilised in this study.

Acknowledgement

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