Ambient temperature hydrolysis of carbonyl sulfide using γ-alumina catalysts: effect of calcination temperature and alkali doping

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The hydrolysis of COS using γ-alumina as catalyst at 20 °C is described and discussed. In particular, the effect of calcination on the catalyst activity is investigated. Catalysts calcined at 100 and 500 °C are found to give the highest catalyst activities, in terms of both specific (mol COS converted/g catalyst/h) and intrinsic (mol COS converted/m^2 catalyst/h) activity. Calcination at other temperatures leads to diminished catalyst activity. The effects are discussed in terms of the known surface chemistry of γ-alumina involving physisorbed water, surface dehydroxylation and defect formation. The addition of alkali additives (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Si^{2+}) is also reported. Only K^+ and Cs^+ give a sustained enhancement in catalyst activity, whereas all the other additives act as catalyst poisons for the steady-state performance measured following 5 h time-on-stream. Interestingly, addition of Na^+ and Mg^{2+} leads to a very high initial activity (>95% COS conversion) but the effect is very short-lived and, after 5 h time-on-stream, a much lower steady-state activity (~15–30% COS conversion) is observed.

KEY WORDS: carbonyl sulfide hydrolysis; γ-alumina; catalyst preparation.

1. Introduction

Heterogeneously catalyzed reactions using gas-phase reactants that are capable of being operated at ambient temperature have received considerable attention in recent years. Unfortunately, there are few examples of these reactions as, for most reactants, high temperatures are required to achieve initial activation or dissociative chemisorption. Most attention has focused on the ambient temperature oxidation of carbon monoxide [1,2], mainly owing to the renaissance in the use of supported gold nanocrystals as catalysts. Carbon monoxide oxidation is a reaction of immense commercial importance with respect to respiratory protection, and the current commercial catalyst is hopcalite, a copper–manganese mixed oxide that has been used unchanged for several decades [3–6]. Another reaction, that is less well studied to date, is the hydrolysis of carbonyl sulfide:

$$COS + H_2O \rightleftharpoons CO_2 + H_2S$$

that can also be catalyzed at ambient temperature using alumina catalysts [7]. The reaction is an essential process in the removal of residual low levels of sulfur in a number of industrial processes, *e.g.*, ammonia synthesis. COS is not affected by standard methods of desulfurization and residual COS, if not removed from the reactants, could act as a potent catalyst poison [8]. In many previous studies of COS hydrolysis, reaction temperatures in excess of 100 °C [9–16] have been used. However, we have recently shown that the reaction can be effectively observed at 30 °C [17]. In this paper, we extend this study and show that the catalyst activity of γ-Al_2O_3 can be significantly affected by the calcination temperature and the addition of alkali dopants.

2. Experimental

2.1. *Catalysts*

γ-Alumina (Synetix) was used in these experiments and, prior to use, it was calcined (100–600 °C) using two heating methods. First, a standard time of heat treatment was used, the γ-alumina being placed in a preheated furnace for 2 h and then cooled in a desiccator. Second, a standard heating rate (1 °C/min) was used. Doped catalysts were prepared using an incipient wetness method using a solution of the metal nitrate which was adsorbed on the γ-alumina, dried (120 °C, air, 12 h) and calcined (500 °C, 2 h).

2.2. *Catalyst testing*

A standard laboratory microreactor, using a stainless-steel U-tube reactor, was used. COS (BOC, 5000 ppm in N_2) was further diluted with nitrogen to 150 ppm and the overall flow rate was controlled using calibrated mass flow controllers. Water was introduced using a saturator system and a controlled amount of 1200 ppm was introduced into the reactor. The gas hourly space velocity

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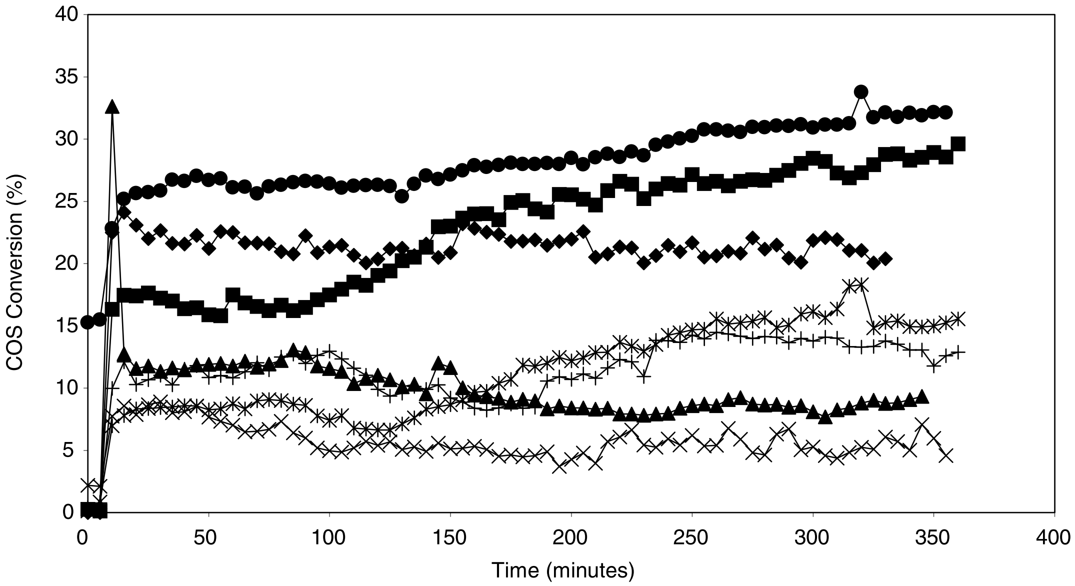

Figure 1. Effect of time-on-stream on COS hydrolysis (20 °C, 150 ppm COS, 1200 ppm H_2O, GHSV = $1.23 \times 10^5\ h^{-1}$). ◆, Unmodifed γ-Al_2O_3 calcined at temperature for 2 h; ■, 100 °C; ▲, 200 °C; ×, 300 °C; ✳, 400 °C; ●, 500 °C; +, 600 °C.

(GHSV) was standardized at $1.23 \times 10^5\ h^{-1}$ in all experiments. The reactor containing 0.5 g (0.65 ml) catalyst was immersed in a water bath at 20 °C. Reactants and products were analyzed using gas chromatography with a pulsed flame photometric detector permitting the detection of COS at levels as low as 1 ppm. Catalysts were stabilized in the reactor for 5 h prior to testing, and during this time the catalytic performance was observed to stabilize. All experiments were conducted at 1.5 bar reactor pressure.

3. Results and discussion

The hydrolysis of carbonyl sulfide was investigated at 20 °C over a series of γ-alumina samples that had been heated in air at a constant temperature for 2 h (100–600 °C) and also the unmodified sample. The unmodified sample had been studied in detail in our previous investigation [17], and the aim of these experiments was to determine the effect of calcination on catalytic performance. The catalysts were investigated under the standard reaction conditions and, during the 5 h initial reaction period, the catalytic activity stabilized (figure 1). It is apparent that the calcination temperature has a marked effect on the catalyst activity and COS conversions in the range 5–30% were observed. Calcination at 100 and 500 °C led to a significant improvement in the COS conversion using γ-Al_2O_3 as catalyst (figure 2). A further set of samples were prepared for which the γ-Al_2O_3 was heated at a constant rate (1 °C/min) until the desired temperature was obtained (200–600 °C). Following this, the sample was cooled in a desiccator. These materials were investigated for COS hydrolysis under identical conditions and the data for COS conversion are also shown in figure 2. Again, the sample treated at 500 °C shows an enhancement in performance compared with the other calcined samples. However,

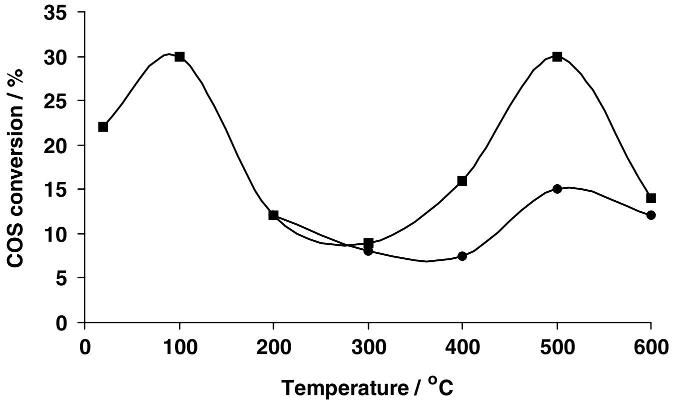

Figure 2. Effect of calcination temperature of γ-Al_2O_3 on catalyst activity for COS hydrolysis at 20 °C. ■, Samples calcined at constant temperature for 2 h; ● samples calcined with constant heating rate (1 °C/min).

Table 1
Effect of calcination temperature on specific and intrinsic activity of γ-Al_2O_3 [a]

Calcination temperature (°C)	Specific activity (mol COS converted/g_{cat}/h)	Intrinsic activity (mol COS converted/m^2/h)
Unmodified	1.7×10^{-4}	5.7×10^{-6}
100 [b]	2.3×10^{-4}	8.2×10^{-6}
200 [b]	0.92×10^{-4}	3.1×10^{-6}
300 [b]	0.69×10^{-4}	2.6×10^{-6}
400 [b]	1.2×10^{-4}	4.9×10^{-6}
500 [b]	2.3×10^{-4}	9.7×10^{-6}
600 [b]	1.1×10^{-4}	5.1×10^{-6}
200 [c]	0.92×10^{-4}	3.3×10^{-6}
300 [c]	0.65×10^{-4}	2.5×10^{-6}
400 [c]	0.58×10^{-4}	2.5×10^{-6}
500 [c]	1.2×10^{-4}	4.5×10^{-6}
600 [c]	0.92×10^{-4}	4.1×10^{-6}

[a] 20 °C, GHSV = 1.23×10^5 h^{-1}, 150 ppm COS, 1200 ppm H_2O.
[b] Calcined at constant temperature for 2 h.
[c] Calcined at constant heating rate, 1 °C/min.

Table 2
Effect of additives on the rate of COS hydrolysis using γ-Al_2O_3 catalyst [a]

Additive	Hydrolysis rate					
	Specific activity [b] (10^{-4} (mol COS/g_{cat}/h))			Intrinsic activity [c] (10^{-6} (mol COS/m^2/h))		
	1%	3%	5%	1%	3%	5%
Li	2.3	1.1	1.3	7.7	3.7	4.3
Na	1.4	2.3	2.3	5.6	9.2	9.2
K	0.62	3.1	3.8	2.2	10.6	13.7
Cs	1.8	2.3	2.7	6.0	7.6	10.8
Mg	1.2	2.3	1.6	4.0	9.7	5.3
Ca	2.0	1.8	1.4	7.9	6.6	5.1
Ba	1.1	1.6	2.3	3.4	4.1	8.0
Sr	1.9	1.8	1.6	5.5	6.9	6.1

[a] 20 °C, GHSV = 1.23×10^5 h^{-1}, 150 ppm COS, 1200 ppm H_2O.
[b] Undoped γ-Al_2O_3 specific activity 2.3×10^{-4} mol COS/g_{cat}/h.
[c] Undoped γ-Al_2O_3 intrinsic activity 9.7×10^{-6} mol COS/m^2/h.

the COS conversion observed is significantly lower than that observed with the previous series and this is considered to be due to the significantly longer calcination time used for these samples.

Investigation by powder X-ray diffraction did not reveal any changes in the amorphous nature of the γ-Al_2O_3 sample due to the heat treatment. The BET surface area of the calcined materials generally decreased with increase in calcination temperature (from 300 m^2/g for the unmodified γ-Al_2O_3 to 220 m^2/g for the sample calcined at 600 °C). The intrinsic (mol COS converted/m^2/h) and specific (mol COS converted/g/h) activities of the samples are given in table 1 as a function of calcination temperature. It is apparent that both the specific and intrinsic activities show distinct maxima for heat treatments at 100 and 500 °C. The surface of γ- and α-Al_2O_3 is known to be terminated in hydroxyl groups, which can function as a Brønsted acid [18,19]. Calcination of γ-Al_2O_3 is known to remove the surface hydroxyl groups generating water and, at high temperature, surface defects are also formed [19]. The observed differences in catalytic performance of the heat-treated γ-Al_2O_3 samples (figure 2, table 1) can, therefore, be rationalized as follows. The increase in catalytic activity observed on heating the unmodified sample to 100 °C is due to the removal of physisorbed water. We have previously shown [17] that adsorbed water can act as an inhibitor for the COS hydrolysis reaction, simply by blocking access to the active sites. Calcination at higher temperatures (200–400 °C) leads to the removal of surface hydroxyl groups, that have been implicated as important in the reaction mechanism of COS hydrolysis [7], hence the catalyst activity decreases. Increasing the temperature to 500 °C leads to the formation of defects, which provide additional active sites for the adsorption of the reactant and, consequently, the catalytic activity is enhanced. These experiments show that it is important to explore fully the preparation conditions of γ-Al_2O_3 when used as a heterogeneous catalyst, even for a relatively simple reaction.

In our previous work [17], we investigated the effect of the addition of metal cations as promoters (Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) and a small enhancement in catalyst activity was noted. Previous studies have suggested that alkali metal cations can also function as activity promoters and enhanced activity was noted from Cs^+ and K^+ [20]. We have now investigated the effect of alkali metal additives for three levels of additive concentrations and using the preferred calcination conditions identified above (500 °C, 2 h). The data for COS conversion are shown in table 2 for the specific and intrinsic activities determined after steady-state performance had been attained after 5 h time-on-stream. It is apparent that, for most concentrations, the alkali additives act as catalyst poisons, which is unexpected. This may be caused by blocking the active sites due to the impregnation method. There is no promotional effect observed with the alkaline earth additives (Mg^{2+}, Ca^{2+}, Ba^{2+}, Si^{2+}) at steady-state performance. However, a significant promotional effect is observed with K^+ and Cs^+, but this is only marked at the 5% concentration level. For Na^+, K^+ and Cs^+, the steady-state catalyst activity increases with increasing additive concentrations, which is in agreement with the study of Tan *et al.* [20]. Interestingly, two additives, Na^+ and Mg^{2+}, at all concentrations, showed a significant enhancement of the rate of COS hydrolysis for the initial 3–4 h testing period [figures 3(a) and (b)]. This effect was not observed with the other additives, *e.g.*, Cs^+ [figure 3(c)]. The origin of this effect is unclear but could be due to retention of sulfur on the catalyst surface, *i.e.*, the catalyst acts as an adsorbent in addition to catalyzing the hydrolysis reaction. However, the H_2S production rate was also

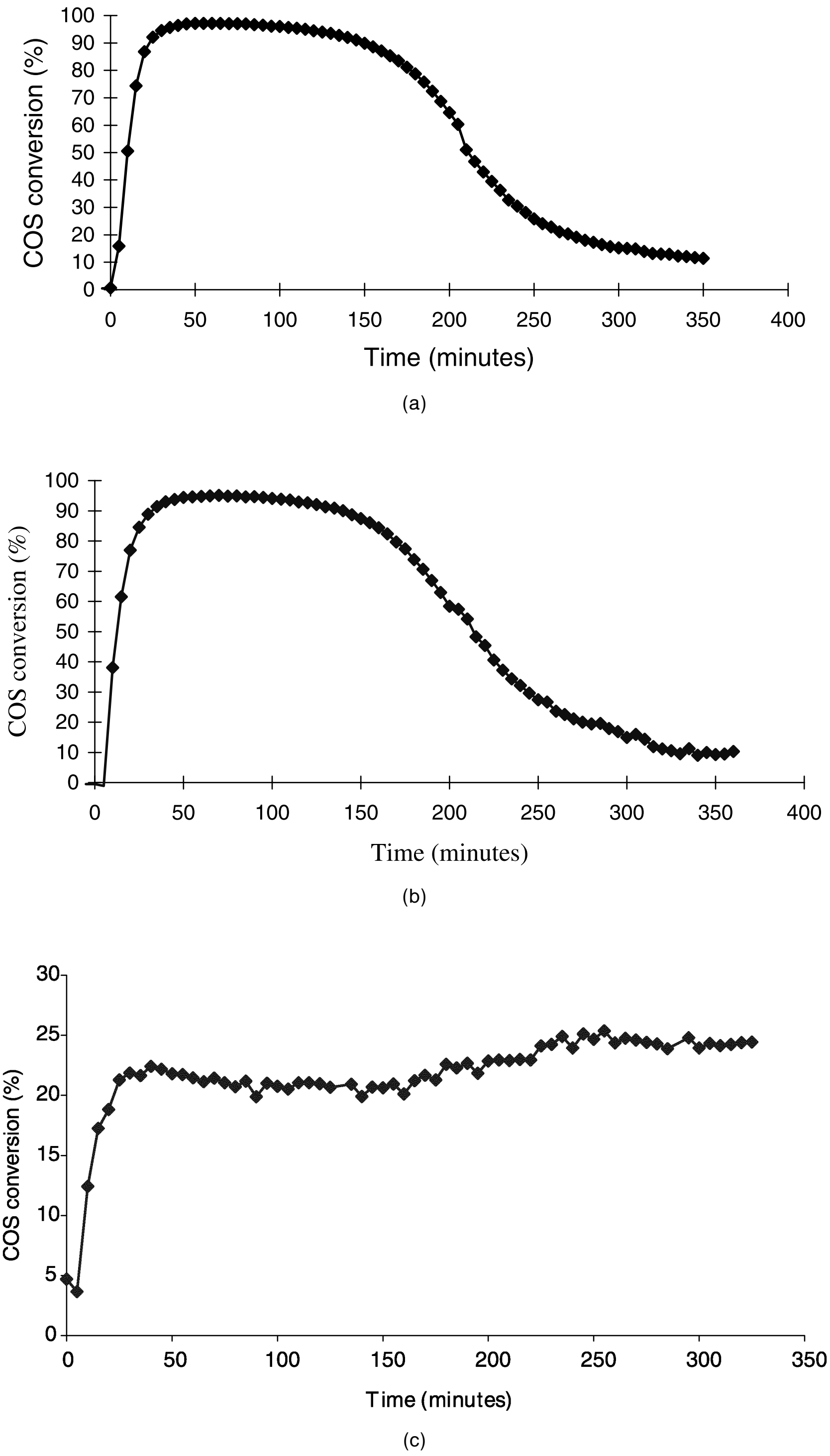

Figure 3. Effect of time-on-stream on COS hydrolysis at 20 °C for modified γ-Al_2O_3 catalysts: (a) 1% Na^+; (b) 1% Mg^{2+}; (c) 1% Cs^+.

monitored and was found to be significantly enhanced during the initial 3–4 h, and correlated exactly with the enhanced conversion. This indicates that Na^+ and Mg^{2+} may be able to act as significant catalyst promoters but the effect is, unfortunately, short-lived. In addition, the promotional effects observed for K^+ are considerably higher than those observed with Zn^{2+} and Fe^{3+} in our previous study [17] and confirm that the catalyst activity for the ambient temperature hydrolysis of carbonyl sulfide can be significantly affected by the preparation conditions since, for example, alkali metal cations could be present as adventitious promoters in commercial alumina samples, thereby complicating the study of such catalysts.

Acknowledgment

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