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Hydrogen sulphide emission control by combined adsorption and catalytic combustion

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Abstract

The removal of low concentrations of hydrogen sulfide by adsorption and catalytic combustion has been studied. Concentration of hydrogen sulfide by adsorption from waste-gas streams is best effected by molecular sieve 13X, if the stream is dry, and by activated carbon, if the gas stream is moist.

Low-temperature catalytic oxidation of hydrogen sulphide in moist gas streams can be effected over activated carbon. The reaction appears to involve ionized hydrogen sulfide, dissolved in water condensed in the pores of the carbon.

At high temperatures, both supported platinum and palladium catalysts are found to be oxidation catalysts. Palladium is the best catalyst for methane oxidation but is partially deactivated in the presence of sulfur-containing gases. In contrast, platinum was more active for the same reaction in the presence of sulfur-containing gases.

Both metals were found to promote the oxidation of hydrogen sulfide above ca. 150°C. The power rate laws describing the kinetics of reaction were determined.

Keywords: Adsorption; Oxidation; Hydrogen sulphide; Odour control; Catalytic oxidation

1. Introduction

Hydrogen sulphide may be present in waste-gas streams at concentrations between 2 and 1000 ppm. At lower concentrations, the gas has an unpleasant odour: at higher concentrations, it can be life-threatening.

The means of removing hydrogen sulphide depend on the concentration. On an industrial scale, removal is effected by the Claus reaction [1] or by modifications of the same process [2]. At lower concentrations, adsorption [3] or oxidation to sulphur oxides [4] is preferred. In the latter case, allowable emission levels are higher and adsorption, particularly of sulphur trioxide, is more effective.

The present studies were focused on the possibility of concentrating small amounts of hydrogen sulphide by adsorption, followed by desorption and catalytic combustion to remove the pollutant. This solution is relevant to smaller amounts of sulphides generated by reactions in sewage systems [5].

Molecular sieves [3], silica gel [6] and activated carbons [3] have been used to adsorb hydrogen sulphide from waste-gas streams Molecular sieves have the highest capacity for adsorption from dry-gas streams [3]. Activated carbons are more efficient from wet-gas streams [7], such as are generated by sewage.

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The efficiency of the overall process depends on the efficiency of concentration of hydrogen sulphide by adsorption, on the temperature of desorption and on the efficiency of catalytic combustion. The present studies were initiated to study their effects separately, and in combination.

2. Experimental

Adsorption and reaction of H_2S on adsorbents was studied using a flow reactor. Mixtures of gases were prepared with the aid of Brooks 5850E mass-flow controllers and, where necessary, humidified by passage through water maintained at a pre-set temperature. Adsorbents (prepared as 255–350 μm sieve fractions) were packed in a 0.6-cm i.d. glass reactor mounted in the constant temperature (±1 K) zone of an electric furnace. Exit gases were separated using a GS Q capillary column and analysed using a Shimadzu GC 14B equipped with flame photometric detector.

Catalytic combustion was also carried out in a tubular reactor. The active catalysts consisted of precious metals (ca. 0.2 wt%) distributed throughout a washcoat which was maintained on a ceramic monolith (210 cells/inch^2). A sample was cut (0.5 cm high and 0.5 cm diameter) and mounted in a flow reactor between two layers of quartz wool. Small diameter thermocouples were located before, in and after the catalyst block. Exit gases were analysed chromatographically, using a Shimadzu GC 8A fitted with a CTR column.

Initial experiments focused on the determination of 'light-off' temperatures. Gas mixtures containing 1.8% methane and 21% oxygen (balance helium) were passed through the catalyst bed at room temperature. After stabilisation, the temperature of the bed was raised at 5°C/min until oxidation was initiated, as shown by a temperature rise across the bed and by the conversion of methane. The 'light off' temperature was recorded as the temperature at which the conversion of methane reached 10%.

Subsequent experiments focused on the measurement of initial rates of oxidation of hydrogen sulphide using catalysts supported on monoliths. The extent of the linear portion of the curve of H_2S loss vs. residence time was first established in order to determine the initial rate period. Subsequent measurements were made for a variety of inlet concentrations (see below), care being taken to ensure isothermal conditions.

Characterisation of the adsorbents and catalysts was carried out by gas adsorption/desorption and by mercury porosimetry. Important characteristics of adsorbents are reported in Table 1. The monoliths were found to have a total surface area of 27 m^2 g^{-1}, the metal surface area being too small to measure.

3. Results and discussion

3.1. Catalytic oxidation

Sewage gases contain significant amounts of methane and, as a result, the oxidation of methane–hydrogen-sulphide mixtures was first explored.

Table 1
Hydrogen sulphide adsorption capacities

Material	Ref. [a]	Apparent surface area (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	Adsorption capacity (mol×10^5 g^{-1})	
				dry [b]	moist [c]
Molecular sieve 13X	3	490	0.25	10.0	0.8
Activated carbon (untreated)	7			5.2	6.2
Activated carbon (heat treated at 200°C)		1005	0.38	0.2	2.1
Graphpac GB		105	0.08	0	0
Silica gel	6	407	0	0	0

[a] Refers to author(s) who have recommended the use of this adsorbent.
[b] Adsorption from 10 ppm H_2S in He (200 ml min^{-1}).
[c] Adsorption from 10 ppm H_2S and 0.9% H_2O in He (200 ml min^{-1}).

Table 2
Light-off temperatures (°C) for methane oxidation over noble metals in the absence or presence of H_2S or SO_2

Metal	No H_2S or SO_2	20 ppm H_2S	20 ppm SO_2
Pd	370	470	450
Rh	450	450	470
Pt	525	480	470

Noble-metal catalysts have been reported to be active for the oxidation of sulphur dioxide [7] and, as a result, were chosen for examination of their activity for methane and hydrogen sulphide oxidation.

In the absence of sulphur-containing gases, supported Pd was found to be the most active catalyst for methane oxidation (lowest light-off temperature). This is in agreement with previous findings [8,9]. In the presence of hydrogen sulphide, however, the activity pattern changed, with oxidation over supported Pd being inhibited and oxidation over supported Pt being promoted (Table 2). Experiments in the presence of sulphur dioxide revealed that at least some of these effects were due to the action of the sulphur dioxide or sulphur trioxide.

The experiments involved a gas flow (50 ml $\min^{-1}$) of 1.8% methane : 21% oxygen : balance N_2 passed through a monolithic catalyst (0.5 cm length).

These findings can be explained in terms of differing mechanisms of oxidation of methane over the noble-metal catalysts. In the case of palladium, adsorbed oxygen on the metal surface is known to be an important intermediate in the oxidation of hydrocarbons [8,9]. If hydrogen sulphide and sulphur dioxide are oxidised to sulphur trioxide, formation of a metal sulphate on the surface and deactivation of the catalyst can be expected.

Similar effects can be expected over rhodium, where the oxide is again an intermediate in the reaction [10]. In the case of platinum, however, the oxide is not formed and hydrocarbon oxidation is promoted by the metal [11]. In this case, interaction of sulphur trioxide with the support is more probable, the resulting aluminium sulphate being expected to promote the oxidation of hydrocarbons as a result of increased acidity on the surface [12].

Although the catalytic activity of platinum is promoted by sulphur-bearing gases, palladium is still at least as efficient as platinum even after partial deactivation (Table 2). As a result, the kinetics of oxidation of hydrogen sulphide over both, supported Pd and Pt, were examined [13]. An initial rate approach was adopted and the kinetics of reaction were examined for the 150–250°C range. The inlet concentrations of hydrogen sulphide was varied between 0.0026 and 0.0055 kPa, while oxygen was varied from 5 to 22 kPa. The rate expressions obtained can be summarised as follows:

$$\mathrm{Pt}\,\frac{-\mathrm{d}(\mathrm{H_2S})}{\mathrm{d}t} = k_{\mathrm{Pt}} P_{\mathrm{H_2S}}^{1.1\pm0.1} P_{\mathrm{O_2}}^{0.5\pm0.1},$$

$$\text{where } k_{\mathrm{Pt}} = 73.5 \exp \frac{(-62.7 \pm 1.4)}{RT}$$

$$\mathrm{Pd}\,\frac{-\mathrm{d}(\mathrm{H_2S})}{\mathrm{d}t} = k_{\mathrm{Pd}} P_{\mathrm{H_2S}}^{1.7\pm0.1} P_{\mathrm{O_2}}^{0.2\pm0.1},$$

$$\text{where } k_{\mathrm{Pd}} = 1187 \exp \frac{(-59.5 \pm 1.4)}{RT}$$

where the units of activation energy are kJ mol^{-1}

The predictions from these kinetic equations agreed with experimental results to a correlation coefficient of 0.96 (Pt) and 0.99 (Pd).

These kinetic expressions are somewhat surprising in that they infer a Langmuir–Hinshelwood model involving a rate determining reaction between more than one adsorbed hydrogen-sulphide molecule and dissociatively adsorbed oxygen. The full implications of the model are explored elsewhere [13], but it is useful to note that significant oxidation occurred at temperatures in excess of ca 150°C, with Pt being a somewhat more efficient catalyst than Pd. The low light-off temperature for hydrogen sulphide contrasts sharply with the high values recorded for methane (Table 2).

3.2. *Adsorption–desorption – removal of hydrogen sulphide*

The performance of various adsorbents for the adsorption and desorption of hydrogen sulphide was then examined. Factors of importance were defined to be the adsorption capacity of the adsorbent, the selectivity of adsorption – bearing in mind the complexity of sewage gases – and the desired match between desorption temperature and catalyst operating temperature (>150°C).

Adsorption capacities were measured from breakthrough curves, typical examples of which are shown

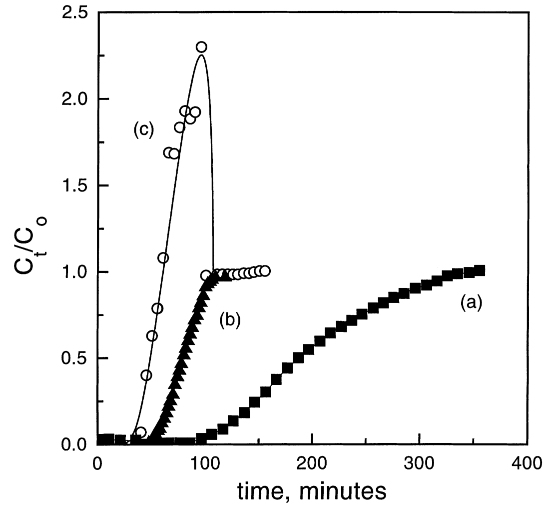

Fig. 1. Comparison of breakthrough curves at total flow rate of 200 ml min^{-1} and 25°C. (A) Breakthrough of H_2S in dry gas over 0.1 g molecular sieve 13X, 10 ppm H_2S in He; (B) breakthrough of water over 0.5 g molecular sieve 13X, 10 ppm H_2S+0.9% H_2O in He; and (C) breakthrough of H_2S over 0.5 molecular sieve 13X, 10 ppm H_2S+0.9% H_2O in He; C_0 is the initial concentration and C_t the outlet concentration.

in Fig. 1. The amount of H_2S adsorbed from dry gas (curve a) could be measured by comparisons with results obtained when the reactor was packed with nonporous α-alumina particles. Adsorption capacities measured over different adsorbents are summarised in Table 1.

With moist gas, the results were totally different. The breakthrough curve for water (curve b) was similar in shape to that for dry hydrogen sulphide (curve a) (Fig. 1), but that for H_2S temporarily exceeded the inlet concentration (curve c), an effect suggested to be caused by the displacement of adsorbed H_2S by water [7,14]. As a result of such displacement, the adsorption capacity of molecular sieve for H_2S present in a moist stream of gas was significantly less than from a dry stream (Table 1).

The results for adsorption of hydrogen sulphide on activated carbon showed a different trend (Fig. 2). In the presence of water, breakthrough of hydrogen sulphide took much longer and the amounts adsorbed were much higher than would be expected on the basis of the previous results.

It seemed possible that the extra takeup of hydrogen sulphide was the result of a chemical reaction, possibly involving oxygen [3,7]. As a result, the removal of hydrogen sulphide was determined in the presence of oxygen (Fig. 3). No large differences were observed unless water vapour was also present. The amount of

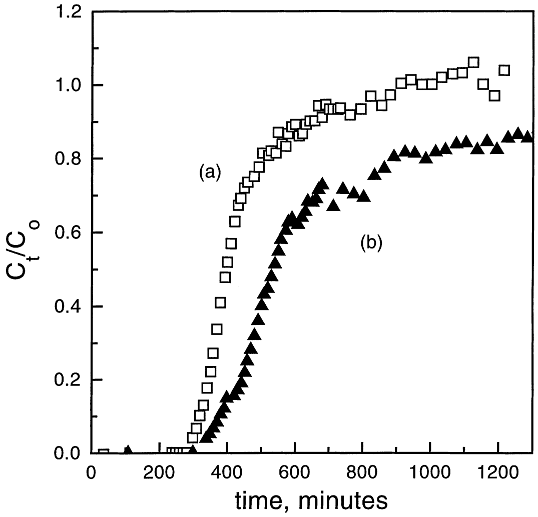

Fig. 2. Breakthrough curves of hydrogen sulphide on activated carbon at 25°C. (a) Untreated carbon: 10 ppm H_2S; (b) Untreated carbon: 10 ppm H_2S and 0.9% H_2O; C_t, outlet concentration of H_2S; and C_0, initial concentration of H_2S.

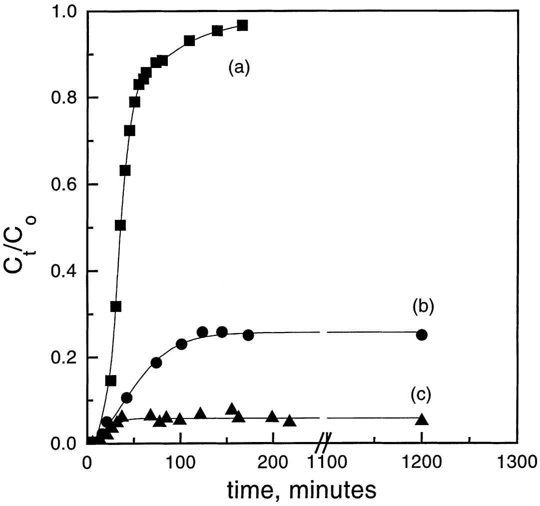

Fig. 3. The effect of water on the removal of H_2S. Untreated carbon (0.1 g loading): 10 ppm H_2S; 21% O_2; total flow= 200 ml min^{-1}. (a) H_2O=0; (b) H_2O=0.9%; and (c) H_2O=2.2%.

hydrogen sulphide removed was also found to increase as the partial pressure of oxygen increased.

The effect of temperature was also studied but, surprisingly, removal of hydrogen sulphide decreased as temperature increased from ca. 65% at 25°C to ca. 8% at 35°C. This was found to be due to the effect of temperature on the water content of the adsorbent. As temperature increased, the amount of water condensed in the pores of the carbon decreased and, as a result, the conversion of hydrogen sulphide decreased.

The oxidation of hydrogen sulphide dissolved in water has been found to be catalysed by transition-metal ions [15]. As a result, the effect of oxygen and of metal ions on the present system was investigated. Oxygen was found to increase the steady-state conversion of hydrogen sulphide from ca. 35% to ca. 80% as the concentration increased from 2.5 to 21% oxygen. Transition-metal ions on carbon, on the other hand, had no effect on the process.

As a result, the dependence of the reaction on the partial pressures of reactants were studied in detail. The partial pressure of water was varied from 0.9 to 2.2% in a series of studies of the initial rates, the hydrogen sulphide partial pressure being varied from 0.5 to 2.1 kPa and the oxygen pressure from 2 to 22 kPa. The apparent power rate law took the form

$$\frac{-\mathrm{d}(\mathrm{H_2S})}{\mathrm{d}t} = k(P_{\mathrm{H_2S}})^a (P_{\mathrm{O_2}})^b$$

with the values of a and b reported in Table 3.

Earlier work had suggested that the reaction could be occurring in water condensed in the pores of carbon [16]. This was found to be the case in the present system. The efficiency of the reaction was found to be proportional to the pore volume of the carbon, the extent of reaction decreasing as the pores were filled with elemental sulphur produced by the reaction. The effect of water actually reflects the relationship between the partial pressure of water and the amount condensed in the carbon, as determined by weight change at various partial pressures and temperatures. However, the role of water was found to be more than a solvent for hydrogen sulphide. The use of methanol and decanol – both dissolving more hydrogen sulphide than water – gave no reaction to remove the gas.

Similarly, the role of carbon was found to be more than the provision of a porous medium. The use of γ-alumina or molecular sieve 13X, both with well-developed pore structures, gave no reaction, even though water and hydrogen sulphide were both adsorbed.

The most satisfactory explanation of the observed results involves the formation and further reaction of sulphide ions. It is known that hydrogen sulphide can ionise as follows [17]:

$$\mathrm{H_2S = H^+ + HS^-}$$

$$\mathrm{HS^- = H^+ + S^{2-}}$$

with $\mathrm{S^{2-}}$ being favoured at pH>ca. 14 and $\mathrm{HS^-}$ favoured between pH 7 and 13.

Reaction between $\mathrm{HS^-}$ and dissociatively adsorbed oxygen ($\mathrm{O^*}$) would then lead to sulphur and water:

$$\mathrm{H_2S = H^+ + HS^-}$$

$$\mathrm{HS^- + O^* = OH^- + S^*}$$

$$\mathrm{H^+ + OH^- = H_2O}$$

Although plausible, this sequence of reactions does not explain the role of carbon. It seems possible that carbon adsorbs $\mathrm{HS^-}$ or $\mathrm{O^*}$ during the course of reaction, but this could not be proved.

4. Conclusion

It is clear that removal of hydrogen sulphide can be affected by catalytic oxidation, but that the system chosen depends on the operating conditions.

Table 3
Parameter estimates for power law modelling of hydrogen sulphide oxidation on activated carbon

Water content, %	H_2S order, a	O_2 order, b	Rate constant [a] ($k\times10^7$)	Correlation coefficient, r
0.9	0.50	0.46	1.46	0.99
1.7	0.45	0.50	1.51	0.99
2.2	0.50	0.45	5.01	0.99

[a] The units of the rate constant are mol g^{-1} s^{-1} $(kPa)^{-(a+b)}$; T=25°C.

Under conditions where waste gas streams are moist and the amounts of hydrogen sulphide are not too large, low-temperature oxidation over activated carbon is highly efficient. Conditions must be adjusted such that significant amounts of water are condensed in the pores of the carbon. These conditions will depend on the moisture content of the gas, the pore size and the temperature.

At high temperatures, or greater concentrations of hydrogen sulphide, catalytic combustion over supported Pt or Pd is effective. The reaction is efficient at temperatures >150°C, care being necessary either to ensure that sulphur trioxide produced is less than the legislative limit for emission or that adsorption of the trioxide is effected. When the waste gas is dry, molecular sieve 13X is an efficient means of concentrating hydrogen sulphide before periodic operation of the catalytic combustor.

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