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The catalytic combustion of methane and hydrogen sulphide

Joo H. Lee[a], D.L. Trimm[a,*], N.W. Cant[b]

[a]*School of Chemical Engineering & Industrial Chemistry, University of New South Wales, Sydney NSW 2052, Australia*
[b]*School of Chemistry, Macquarie University, NSW 2109, Australia*

Abstract

The odorous components of sewage gas consist mainly of ca. 15–40 ppm hydrogen sulphide. The gas may also contain methane. The catalytic combustion of hydrogen sulphide and methane has been studied using palladium- and platinum-based monolithic catalysts. Platinum-based catalysts perform better in the presence of hydrogen sulphide and kinetic equations have been derived. The relationships were used to design an industrial converter, which has operated satisfactorily for two years.

Keywords: Catalytic oxidation; Hydrogen sulphide oxidation; Sewage treatment; Pd monolithic catalysts; Pt monolithic catalysts; Kinetics of H_2S oxidation

1. Introduction

The control of sewage and digester gases is essential on safety and environmental grounds. The gases are malodorous and can build up in enclosed areas to levels that can be life-threatening. The actual composition of the gases depends on local food sources, but methane is known to be a major component. Most of the odour originates from sulphides [1], but unexpected compounds in the sewer (such as gasoline, solvents etc.) can add to the problems.

The odour threshold of the main source of smell (hydrogen sulphide) is 0.02–0.03 ppm, with the smell becoming offensive at about 0.15–0.3 ppm [2]. Various methods of odour control are available, including soil bed biofilters, chemical scrubbing, adsorption or chemical treatment. Catalytic combustion has the advantage that units can be sized to suit particular applications [3,4]. It may also be possible to co-combust methane and other hydrocarbons in the gas to achieve self sustaining operation. The present studies were initiated in order to study the possible application of catalytic combustion to the control of such odours.

Previous studies of the catalytic oxidation of methane have been carried out [5–9]. The catalytic activity of precious metals depends on the methane : oxygen ratio. Metallic palladium is not a good catalyst for methane oxidation but palladium oxide is perhaps the best catalyst [8]. The kinetics of methane oxidation over platinum depend on the surface coverage of oxygen, with the apparent orders of reaction being affected by the oxygen pressure [5,6]. Overall the order of activity for methane oxidation under conditions pertinent to vehicle exhausts was found to be [9]

$$\mathrm{Pd/Al_2O_3} > \mathrm{Rh/Al_2O_3} > \mathrm{Pt/Al_2O_3}.$$

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*Corresponding author. Tel.: +61-2-9385-43430; fax: +61-2-313-7191.

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This order has been found to change when methane is in excess [10].

The oxidation of hydrogen sulphide over precious metals has received less attention [11–13]. Catalytic oxidation leads to the production of sulphur dioxide which, over Pt catalysts, will be oxidised to sulphur trioxide [12]. This, in turn, may react with alumina or ceria in the catalyst washcoat to form the corresponding sulphates [14].

The sequence of events may be critical to the combined and individual oxidation of methane and hydrogen sulphide. The formation of metal sulphides is a common cause of catalyst deactivation [14,15]. The formation of sulphur oxides and sulphates may [16,17] or may not [14,16] deactivate the catalyst. A washcoat sulphate may also inhibit the reaction of sulphur oxides with precious metal [16].

A number of porous materials (bauxite, alumina, carbon and molecular sieves) have also been used as catalysts for the oxidation of hydrogen sulphide [18]. In general, such catalysts oxidised the gas to elemental sulphur. Steijns et al. [19] proposed an oxidation–reduction mechanism based on the autocatalytic effect of product sulphur, but this has been disputed by many workers [20–22].

Sreeramamurthy and Menon [20] together with Ghosh and Tollefson [18] have suggested that the rate-controlling step in the catalytic reaction involves adsorbed hydrogen sulphide and adsorbed oxygen. Cariaso and Walker [23] suggest a reaction between adsorbed oxygen and gas phase H_2S. None of these workers have focused on the precious metal catalysts which are the subject of the present study.

Two approaches to the catalytic combustion of sewage gas are possible, given the comparative lack of reactivity of methane. It may be possible to oxidise hydrogen sulphide without oxidising methane, or it may be possible to oxidise both methane and hydrogen sulphide, thereby generating enough heat to make the reaction self sustaining. Both possibilities have been studied, using supported Pd (reported to be the best catalyst for the oxidation of methane under lean conditions) and supported Pt (a selective catalyst for sulphur trioxide production). The present paper reports the catalytic oxidation of hydrogen sulphide in the absence and presence of methane on both catalysts.

2. Experimental

Experiments were conducted using a conventional flow rig fitted with on-line chromatographic detection of products. Reactant gases (H_2S:N_2 mixtures, methane, oxygen and nitrogen) were fed to the reactor via Brooks 5850E mass flow controllers. The reactor consisted of a quartz tube (2.1 cm i.d., 45 cm length) held in an electrically heated furnace. A sample of monolithic catalyst (cylindrical: 2.1 cm dia, 2.4 cm length) was mounted in the reactor in the constant temperature zone of the furnace. The temperature of gases at the front and the back of the monolith were monitored using K type thermocouples.

Exit gases were analysed using two on-line chromatographs. O_2, N_2, CO, CO_2 and CH_4 were separated on a CTR1 column (343 K, 2 m) (Alltech Associates) fitted to a Shimadzu GC-8A TCD chromatograph. H_2S and SO_2 were separated on packed GSQ megabore column (30 m, 423 K for H_2S; 363 K for SO_2) fitted in a Shimadzu GC-14B FPD (flame photometric detector). Considerable problems were experienced with the latter system, the column/detector system needs about two weeks continuous running in order to stabilise.

Sulphur trioxide could not be determined gas chromatographically. Gases leaving the reactor were bubbled through mild alkali solution for a given time and the alkali back titrated.

Catalysts were kindly supplied by Johnson Matthey CSD Australia. They consisted of ceramic monoliths of cell density 210 cells per inch^2, coated with a washcoat of mixture of δ- and γ-alumina and the precious metal. The metal contents were Pt and Pd (1.4 g l^{-1}). Attempts to measure metal surface area were unsuccessful, the amount of carbon monoxide detectable being insignificant.

A monolith sample was cut from the block and mounted in the reactor. The system was rinsed with air and gases were introduced. Unless otherwise stated, the flow rate of H_2S, O_2 and N_2 was 950–1500 ml min^{-1} to give a space velocity at reactor temperature between 11 000 and 20 000 l h^{-1}. The concentration of H_2S was varied between 17 and 41 ppm.

For light off experiments, the gas mixture was run for 1 h and the temperature increased (5 K min^{-1}) until light off occurred. For kinetic experiments the

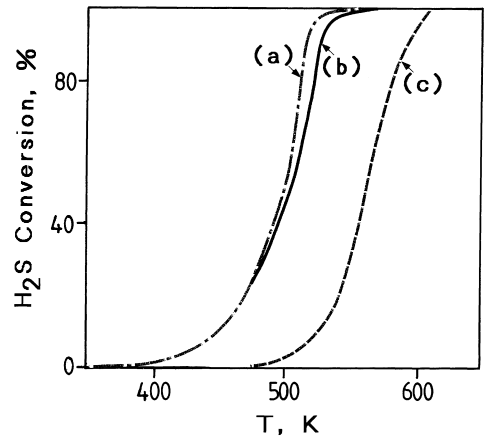

Fig. 1. Light off curves for hydrogen sulphide: (a) Pd monolith; (b) Pt monolith; (c) homogeneous oxidation H_2S=25.9 ppm.

system was operated for 5–7 h to establish steady state.

3. Results and discussion

Preliminary experiments were carried out with hydrogen sulphide alone and light off temperatures over supported Pt and Pd catalysts were compared with the temperature at which homogeneous oxidation was initiated. As shown in Fig. 1, both catalysts were equally active and catalytic oxidation was initiated some 80 K below homogeneous oxidation.

The selectivity of the reaction was found to vary with the catalyst. Oxygen was always in considerable excess (20% O_2:15–40 ppm H_2S) and the formation of elemental sulphur was not observed. At low temperatures (ca. 433 K), the selectivity to sulphur dioxide was almost 100% over both catalysts. At higher temperatures (523 K), 90.3% of inlet H_2S was converted to SO_2 over the Pd catalyst, with 1.3% SO_3 being detected by titration. Over the Pt catalyst the corresponding figures were 25% conversion to SO_2 and 38.2% conversion to SO_3.

The discrepancies in the sulphur balances are thought to result from oxidation of H_2S to sulphur trioxide followed by reaction with components of the washcoat to form sulphates. Sulphur dioxide reacts slowly with both alumina and ceria [14], whereas sulphur trioxide reacts rapidly to form inorganic sulphates. Since Pd is a less efficient catalyst for the oxidation of SO_2 to SO_3 than Pt [12,17], it is suggested that sulphur trioxide and the resulting sulphates are favoured mainly over the latter catalyst. In agreement with this, aluminium sulphate traces were detected by X-ray diffraction in washcoat scraped from the used Pt catalyst. The amounts concerned were too small to close accurately the sulphur balance. Hence the loss of sulphur as sulphate seems probable but is unproven.

Attention was then focused on the oxidation of methane and hydrogen sulphide. For methane alone, palladium-based catalysts were found to be significantly more active, the light off temperature being ca. 200 K less than when H_2S was present (Fig. 2). However, with Pt-based catalysts, the order was reversed (Fig. 3). Over palladium catalysts, the light off temperature was higher while, with platinum, the catalytic activity was, if anything, slightly increased (light off temperature decreased) in the presence of sulphide. Such increases have been observed in other systems [24] and are attributed to the formation of washcoat sulphates and their interaction with precious metals during the hydrocarbon oxidation.

The effect of hydrogen sulphide on the reactivity of Pd-based catalysts was not unexpected. Palladium oxide is known to be a good oxidation catalyst for hydrocarbons [8,17], but competition for surface sites reduces activity. Adsorption of sulphur – either sul-

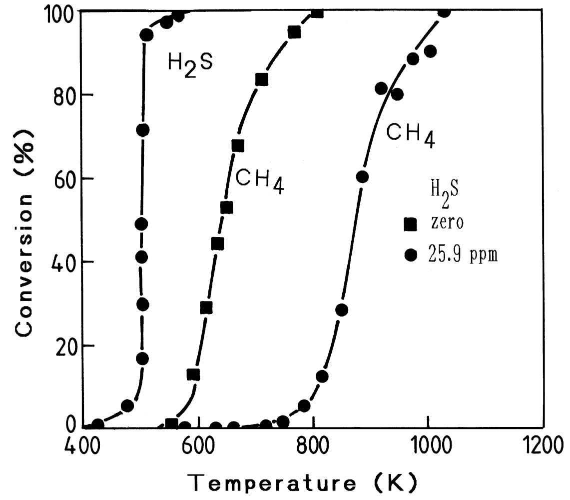

Fig. 2. Light off curves for hydrogen sulphide, methane and hydrogen sulphide–methane mixtures. Pd catalyst.

Table 1
Catalytic combustion of odorous gases from Sydney sewage pumping station (catalyst Pt:monolith; operating temperature 673 K)

Average inlet concentrations	Date	Exit H_2S (ppm)	Conversion (%)
H_2S: <30 ppm	July 1994	0.56	98.6
RSH: <1 ppm	September 1994	0.09	99.5
VOC: <2 ppm	November 1994	0.2	99.9
CH_4: <1 ppm	March 1995	0.1	99.9
Fatty acids: Trace	August 1996	0.1	99.5

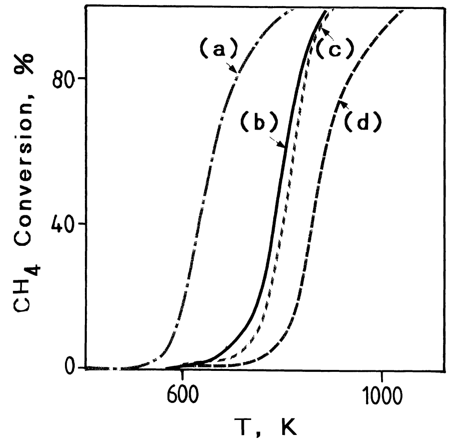

Fig. 3. The conversion of CH_4 in the presence or absence of H_2S in the feed: (a) Pd catalyst in the absence of H_2S in the feed; (b) Pt catalyst in the presence of H_2S in the feed; (c) Pt catalyst in the absence of H_2S in the feed; (d) Pd catalyst in the presence of H_2S in the feed.

phide or sulphate – should reduce available surface sites.

The system appeared to be highly suitable for application under industrial conditions. In preparation for on-line testing, analysis of a sewage pumping station effluent was carried out. In contrast to sewage treatment plants, the gases contained small amounts of methane (Table 1). As a result, attention was focused on hydrogen sulphide oxidation.

Detailed kinetic studies were undertaken over the platinum-based catalyst. Initial rates were found to exist up to 0.31 s residence time, and no evidence of mass transfer control was found. For variations of H_2S between 0.001 and 0.004 kPa and oxygen between 6.7 and 20.9 kPa, the following kinetic equation was established.

$$\frac{-\mathrm{d}(\mathrm{H_2S})}{\mathrm{d}t} = 73.7\exp\left(\frac{-62\,700}{RT}\right)(P_{\mathrm{H_2S}})^{1.12}(P_{\mathrm{O_2}})^{0.51}.$$

The equation described the observed reaction rates, (with the activation energy units of J mol^{-1}) to within 99% confidence limits.

On the basis of these results, a commercial size unit was installed in Sydney in July 1994. Ongoing results are summarised in Table 1. It is pleasing to note that no signs of catalyst deactivation have been observed after two years on line, although the mild steel casing has had to be replaced by stainless steel.

Catalytic combustion is seen to offer a practical solution to the problems of odorous gas control. Low cost operation over a period of two years shows continued efficiency for precious metals based combustors.

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References

[1] P. Crisp, Private communication, 1994.
[2] N.I. Sax, Dangerous Properties of Industrial Materials, Van Nostrand Reinhold, New York, 1968.
[3] D.L. Trimm, Appl. Catal. 7 (1983) 249.
[4] J.H. Lee, D.L. Trimm, Fuel Process. Technol. 42 (1995) 339.
[5] N. Mouaddib, C. Fuemi-Janton, E. Garbowski, M. Primet, Appl. Catal. A 87 (1992) 129.
[6] R.J. Farrauto, M.C. Hobson, T. Kennelly, E.M. Waterman, Appl. Catal. A 81 (1992) 227.
[7] R. Burch, P.K. Loader, Appl. Catal. A 122 (1995) 169.
[8] R. Burch, F.J. Urbano, Appl. Catal. A 124 (1995) 121.

[9] S.H. Oh, P.J. Mitchell, R.M. Siewert, in: R.G. Silver, J.E. Sawyer, J.C. Summers (Eds.), Catalytic Control of Air Pollution, ACS Symposium Series 495, Chapter 2, ACS, Washington, DC, 1992.

[10] E.L. Tollefson, A.I. Chowdhury, in: Proceedings of the Nineth International Congress on Catalysis, vol. 1, 1988, p. 276.

[11] J.L. Hoyos, H. Praliaud, M. Primet, Appl. Catal. A 98 (1993) 125.

[12] K.C. Taylor, Ind. Eng. Chem. Prod. Res. Dev. 15 (1976) 264.

[13] U. Feuerriegel, W. Klose, W. Sloboshanin, S. Goebel, J.A. Schaefer, Langmuir 10 (1994) 3567.

[14] B.I. Whittington, C.J. Jiang, D.L. Trimm, Catal. Today 26 (1995) 41,47.

[15] J. Oudar, Catal. Rev.-Sci. Eng. 22 (1980) 171.

[16] P.M. Torniainen, X. Chu, L.D. Schmidt, J. Catal. 146 (1994) 1.

[17] G.C. Bond, Catalysis by Metals, Academic Press, New York, 1970.

[18] T.K. Ghosh, E.L. Tollefson, J. Chem. Eng. 64 (1986) 969.

[19] M. Steijns, P. Koopman, B. Nieuwenhuys, P. Mars, J. Catal. 42 (1976) 96.

[20] R. Sreeramamarthy, M.G. Menon, J. Catal. 37 (1975) 187.

[21] Y. Iwasawa, S. Ogasawara, J. Catal. 46 (1977) 132.

[22] I. Coskin, E.L. Tollefson, Can. J. Chem. Eng. 58 (1980) 72.

[23] O.C. Cariaso, D.L. Walker Jr., , Carbon 13 (1975) 233.

[24] X.C. Guo, R.J. Madix, Catal. Lett. 39 (1996) 1.