The effect of SO_2 on the activity of Pd-based catalysts in methane combustion

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The effect of SO_2 on Pd-based catalysts for the combustion of methane has been investigated. It is shown that while SO_2 poisons Al_2O_3- and SiO_2-supported catalysts, pre-treatment of Pd/ZrO_2 by SO_2 enhances the activity substantially.

KEY WORDS: methane; heterogeneous catalyst; combustion; promotion/poisoning; SO_2

1. Introduction

Catalytically stabilised combustion of natural gas using Pd-based catalysts for power generation has seen great advances since the original proposal by Pfefferle [1] and patented systems have been reported [2]. There has been significant interest also in the application of catalytic combustion to natural gas powered vehicles [3]. However, in both cases sulphur-containing compounds either in the fuel, or as contaminants from the engine systems, are known to poison conventional Pd catalysts [4]. Conversely, exposure of platinum catalysts to SO_2 can have beneficial effects for the combustion of higher hydrocarbons [5–8]. This promotion has been variously ascribed to enhanced alkane adsorption on Pt [5], support mediated interactions [6] or the modification of the Pt site by interfacial interaction with an adsorbed sulfate species [7].

To investigate the possibility of a similar promoting effect for methane combustion on palladium we have examined the effect of SO_2 exposure on the activity of Pd/Al_2O_3, Pd/ZrO_2 and Pd/SiO_2.

2. Experimental

All catalysts were prepared by incipient wetness impregnation ($Pd(NO_3)_2$, Johnson Matthey) of the dried supports (Azko CK300 Al_2O_3, surface area 195 $m^2\,g^{-1}$, Grace 432 acid washed silica, 265 $m^2\,g^{-1}$ and ZrO_2, Melcat X20 632/03 $Zr(OH)_2$, 12 $m^2\,g^{-1}$). After impregnation all samples were dried at room temperature (24 h), and 120 °C (12 h) prior to calcination at 600 °C (12 h) in static air.

Catalyst testing was performed in a standard plug-flow microreactor with on-line analysis. The catalyst (50 mg) was heated in a Eurotherm 818p series controlled furnace and the bed temperature monitored by an *in situ* thermocouple. All reactant gases, supplied by BOC and used without further purification, were provided from mass flow controllers at a total flow rate of 200 $cm^3\,min^{-1}$ at the compositions listed. All reactor lines, fittings and valves were constructed in stainless steel. Product analysis was by Perkin–Elmer 8700 GC fitted with a Porapak Q-S column. Analysis of CO and CO_2 was achieved by the use of a methanator and FID.

NH_3 TPD was performed on pre-oxidised samples (150 mg, 5% O_2 for 1 h at 550 °C). 1% NH_3/N_2 was dosed at 150 °C for 1 h, the sample purged (30 min) and cooled to 100 °C prior to desorption at a rate of 20 °C min^{-1} in 103 $cm^3\,min^{-1}$ of He. Product analysis was by mass spectrometry (Fisons Gaslab). Note that when Pd is present some oxidation of NH_3(ads) can occur so we estimate the amount of ammonia adsorbed by summing all the desorption products (including NO, N_2 and N_2O as well as NH_3). In this way we can back calculate the amount of nitrogen adsorbed originally as NH_3 on acidic sites.

Dispersions were measured using standard H_2 chemisorption methods in a glass vacuum system. Pre-reduction was performed in H_2 for 30 min at 250 °C. The values obtained were 1% Pd/Al_2O_3, 9.9%; 1% Pd/SiO_2, 5.2%; and 1% Pd/ZrO_2, 21.1%.

TPR experiments were performed at a ramp rate of 10 °C min^{-1} on 20 mg samples in a flow of 10 $cm^3\,min^{-1}$ of 5% H_2/Ar (BOC) using a standard Wheatstone bridge/amplifier assembly linked to a PC-interfaced Perkin–Elmer Nelson integrator.

3. Results and discussion

3.1. Isothermal SO_2 poisoning studies

Figure 1 summarises the effects of 20 ppm SO_2 (introduced after 1 h SO_2-free combustion) on the activity of Pd supported on Al_2O_3, SiO_2 and ZrO_2 for CH_4 combustion at

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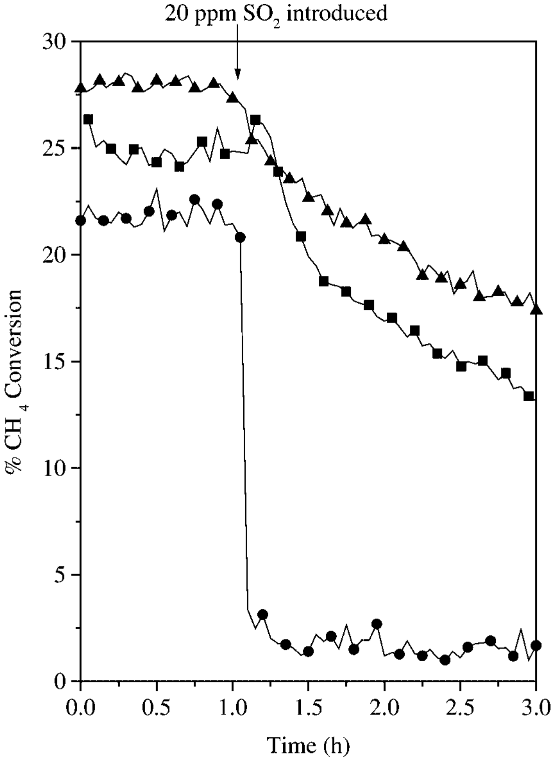

Figure 1. Effect of introduction of 20 ppm SO_2 on the steady state activity of PdO-based CH_4 combustion catalysts. Conditions: 2000 ppm CH_4, 5000 ppm O_2, 0.05 g catalyst, 400 °C. (▲) 1% PdO/Al_2O_3, (■) 1% PdO/ZrO_2 and (●) 1% PdO/SiO_2.

400 °C. These data reflect the competition between SO_2 and CH_4 for active sites and the expected cumulative poisoning effect due to SO_2 retention. In the case of 1% Pd/SiO_2 the loss of activity was almost instantaneous, reflecting the inability of this support to scavenge any SO_x species. The molar flux of SO_2 (ca. 1.79×10^{-7} mol min^{-1}) and molar concentration of exposed Pd atoms ($\sim 1.0 \times 10^{-7}$ mol) indicates that there is a sufficient amount of SO_2 to saturate the PdO in <1 min. In the case of the 1% Pd/ZrO_2 and 1% Pd/Al_2O_3 catalysts deactivation was much slower but similar in both cases. However, for 1% Pd/ZrO_2 introduction of SO_2 showed, before the onset of deactivation, a small initial increase in conversion which merited further study by varying the method of introducing SO_2 (see later).

TPR analysis (results not shown) gave large H_2 uptake peaks at 600–650 °C for 1% PdO/Al_2O_3 and 1% PdO/ZrO_2, consistent with sulphate reduction [7], in contrast to silica, where no such peak was observed in line with expectations [9–12].

3.2. Effect of SO_2 pre-treatment on activity

Figure 2 contrasts the effects of SO_2 pre-treatment (20 ppm SO_2, 5000 ppm O_2, 400 °C, 1 h) on the subsequent activities for the CH_4 combustion reaction of 1% Pd/Al_2O_3 and 1% Pd/ZrO_2. In the case of the alumina-supported catalysts the initial activity was lower after SO_2 pre-treatment and, while some recovery over ca. 2 h was evident, the final steady state conversion was still somewhat lower than for the untreated catalyst. The contrast with the 1% Pd/ZrO_2 catalyst is quite marked. This again exhibited an initial suppression of activity but over a comparable 2 h period displayed a dramatic increase in activity to a final steady state conversion which was more than 150% that of the untreated sample. Figure 2 also shows that the enhanced activity is not due to the sulphation of the ZrO_2 alone. Crittle [13] has shown that in the Pd case only a small quantity of SO_2 is required to get enhanced activity. Further exposure to SO_2 can result in poisoning of the active centres. Indeed, the gradual rise in activity with time after the cessation of the SO_2 treatment (see also figure 3) is attributed to a slow release of SO_x from the Pd since it is known that PdO is reversibly poisoned by SO_x.

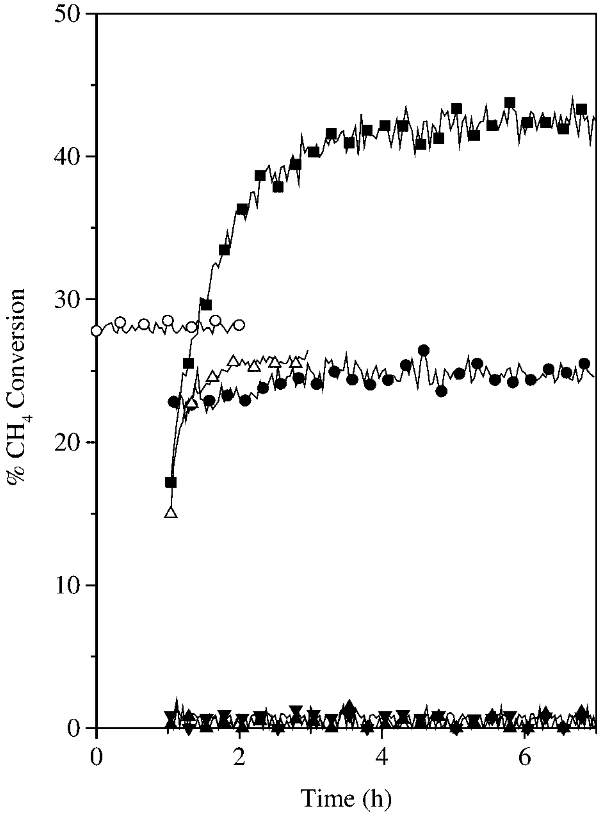

Figure 2. Effect of SO_2 pre-treatment (1 h 20 ppm SO_2, 5000 ppm O_2, 400 °C) on the activity of PdO-based CH_4 combustion catalysts. (■) 1% PdO/ZrO_2-ex SO_2, (●) 1% PdO/ZrO_2, (△) 1% PdO/Al_2O_3-ex SO_2, (○) 1% PdO/Al_2O_3, (▲) ZrO_2-ex SO_2 and (▼) ZrO_2.

To further examine this dramatic increase in activity of the 1% Pd/ZrO_2 catalyst NH_3 TPD analysis of various ZrO_2-based samples was performed (table 1). The SO_2-treated PdO/ZrO_2 showed a large increase in acidity relative to all other samples and is indicative of a strong synergy between the PdO particles and the sulphate formed via spillover at the PdO/support interface.

From these observations it would appear that the active sites for CH_4 activation are enhanced by the presence of the SO_4^{2-}. It could be postulated that by providing this interfacial acidic sulphate species the cleavage of the initial weakly

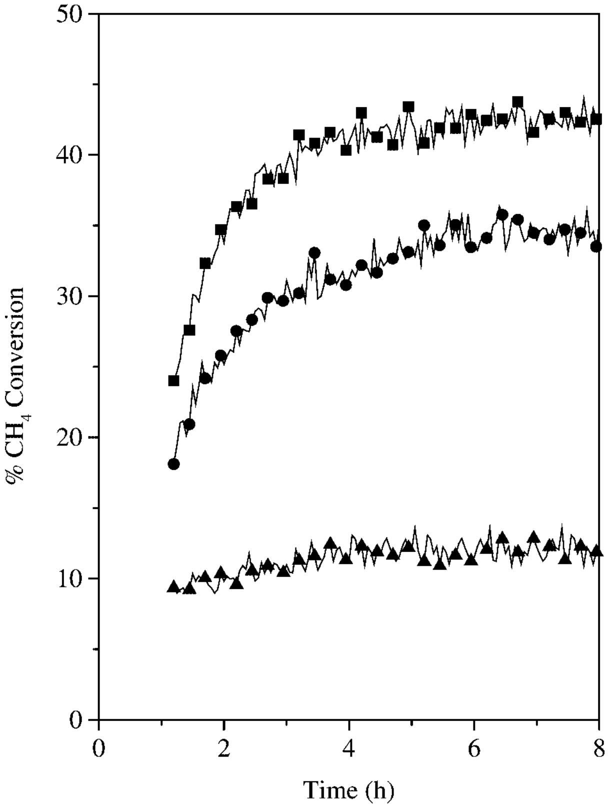

Figure 3. Effect of PdO dispersion on the SO_2 promotion of CH_4 combustion of 1% PdO/ZrO_2 catalysts. Conditions: pre-treatment 1 h 20 ppm SO_2, 5000 ppm O_2, 400 °C, followed by reaction of 2000 ppm CH_4, 5000 ppm O_2, 400 °C. Dispersions: (▲) 6.3, (●) 18.2 and (■) 26.9%.

Table 1
Amounts of nitrogen-containing species desorbed in NH_3 TPD experiments.

Sample[a]	Total amount of N-species desorbed (μmol g^{-1})
ZrO_2	97
S/ZrO_2	122
Pd/ZrO_2	106
$S/Pd/ZrO_2$	204

[a] S indicates sulphated samples.

basic C–H bond in CH_4 is facilitated by a polarisation of the C–H bond in a manner similar to that proposed by Burch et al. [7] for Pt-based propane combustion catalysts.

3.3. *Effect of particle size*

A further indication for the role of interfacial sites comes from the activity of samples of 1% Pd/ZrO_2 of varying dispersions (6.3, 18.2 and 26.9%) pre-treated for 1 h with 20 ppm SO_2. Figure 3 shows that the samples of higher dispersion display a significant activity enhancement. In contrast, figure 4 shows that the sample of low dispersion was hardly promoted by SO_2 under the conditions of these experiments.

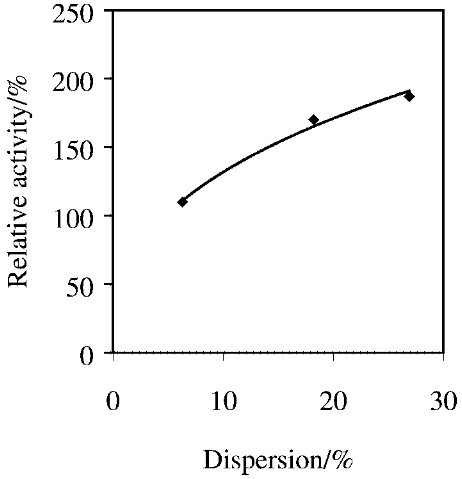

Figure 4. Relative activity of samples after treatment with SO_2 to activity before treatment as a function of Pd dispersion in Pd/ZrO_2 catalysts.

4. Conclusions

The activities of PdO-based CH_4 combustion catalysts are markedly affected by SO_2. The nature of the support determines the type of interaction observed. Non-interacting supports, e.g., SiO_2, display immediate deactivation due to formation of $PdSO_4$. Interacting supports delay this poisoning by the formation of support sulfates. However, in the case of PdO/ZrO_2, when the catalyst is *pretreated* in SO_2, there is a dramatic increase in activity which we associate with the formation of a composite site between the PdO and acidic sulphate at the PdO/support interface.

Acknowledgement

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References

[1] L.D. Pfefferrle and W.C. Pfefferrle, Catal. Rev. Sci. Eng. 129 (1987) 219.
[2] US Patents 5 425 632, 5 405 260, 5 326 253, 5 281 128, assigned to Catalytica Combustion Systems Inc.
[3] *Compressed Natural Gas as a Fuel*, Analysis series no. 5 (Centre of Energy Technologies, Sittard, 1991).
[4] D.D. Beck and J.W. Sommers, Appl. Catal. A 6 (1995) 185.
[5] K. Wilson, C. Hardacre and R.M. Lambert, J. Phys. Chem. 99 (1995) 13755.
[6] C.P. Hubbard, K. Otto, H.S. Ghandi and K.Y.S. Ng, J. Catal. 144 (1993) 484.
[7] R. Burch, E. Halpin, M. Hayes, K. Ruth and J.A. Sullivan, Appl. Catal. B. 19 (1998) 199.
[8] H.C. Yao, H.K. Stepien and H.S. Ghandi, J. Catal. 67 (1981) 231.
[9] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Ed. (Interscience, New York).
[10] S. Khairulin, B. Beguin, E. Garbowski and M. Primet, J. Chem. Soc. Faraday Trans. 193 (1997) 2217.
[11] J.K. Lampert, M.S. Kazi and R.J. Farrauto, Appl. Catal. B 14 (1997) 211.
[12] T.C. Yu and H. Shaw, Appl. Catal. B 18 (1998) 105.
[13] D.J. Crittle, Ph.D. thesis, University of Reading (1999).