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Sulphur poisoning and regeneration of precious metal catalysed methane combustion

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Abstract

In many of the applications of catalytic combustion small amounts of sulphur compounds are present in the feed gas. In the case of natural gas combustion, and solid fuel syngas, the sulphur compounds are in reduced forms. The present work investigates the influence of small quantities of reduced sulphur compounds on the combustion of methane over alumina-supported precious metal catalysts. The kinetics of the methane combustion in the presence of low concentrations of a mixture of sulphur compounds (ethyl mercaptan, methyl mercaptan, carbonyl sulphide and hydrogen sulphide) are compared with those in the absence of sulphur compounds. The ease of regeneration of the poisoned catalysts, via low temperature reduction with hydrogen, is also examined. In the conditions studied all catalysts have reduced activity in the presence of the sulphur-based gas mixture, but Pt/Al_2O_3 and Rh/Al_2O_3 are more strongly poisoned than Pd/Al_2O_3. Qualitative studies using gas chromatography with atomic emission detection of the exhaust gases, and FTIR spectroscopy of the spent Rh/Al_2O_3 catalyst, suggest that the catalysts experience a mixture of reduced and oxidised species under reaction conditions, and that sulphating of the support occurs. The regeneration step facilitates metal mobility and meets with varying success depending upon the metal. Pt/Al_2O_3 in particular is difficult to regenerate by reduction in hydrogen (400 °C for 0.5 h), and agglomeration is observed by TEM. Rh/Al_2O_3 regenerates well, and low metal particle size is maintained. A non-linear deactivation model is tested to separate sulphur-induced deactivation from 'natural' deactivation in the reaction mixture and preliminary results are presented.

Keywords: Methane combustion kinetics; Palladium; Platinum; Rhodium; Sulphur; Poisoning; Deactivation; Regeneration

1. Introduction

Applications for precious metal oxidation catalysts include catalytic burners fitted in gas turbines, domestic water heaters, industrial process heaters, exhaust gas after treatment such as odour control and 3-way catalytic converters. Emerging applications include catalytic partial oxidation in, for instance, integrated fuel cells. In all cases, the catalysts are exposed to variable concentrations of sulphur species in the gas streams. For example, in domestic gas supplies, hydrogen sulphide and odourants including alkylsulphides and mercaptans result in a sulphur concentration totalling approximately 5 ppm. The adverse impact of sulphur compounds on catalytic performance is well known and is the subject of much current research, particularly in the case of reforming and 3-way catalysts [1–15].

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Several factors have been identified which contribute to catalyst poisoning by sulphur compounds. Firstly, it is apparent that sulphur species bond very strongly to the active sites of the catalysts, usually the metal atoms, forming stable surface metal sulphides, and thereby prevent the reactants (oxygen, fuel, nitric oxide, depending on the catalyst selectivity) from adsorbing at the surface [2,4]. A second factor that may contribute to sulphur poisoning is sulphating of the support. For example, sulphation of CeO_2 or Al_2O_3 alters the crystalline structure and nature of the support [15–19]. This is expected to have an impact on the metal–support interaction, and, in addition, the ability to reverse this process varies with the catalyst. The changes in the support or the metal due to sulphur can sometimes be beneficial. Sulphur–oxygen species at the metal–support interface have been cited as promoting the catalytic combustion of some alkanes [15,18,20]. An increase in activity of Pt/Al_2O_3 catalysts in dehydrogenation has been reported, which was attributed to different sulphur–metal interactions depending upon the platinum salt used in the catalyst preparation [21]. A similar enhancement in activity of Pt/Al_2O_3 by H_2S in the catalytic combustion of methane has also been reported [12,14].

It is well established that palladium is the most active catalyst for the combustion of methane in lean conditions [22–24] but is poisoned by H_2S [10,12]. It is proposed that platinum possesses greater resistance to sulphur poisoning by H_2S because it has improved activity for the oxidation of SO_2 to SO_3, but has a lower activity in methane combustion [10,12]. Rhodium has intermediate activity and regenerates well after exposure to H_2S [10].

Most of the studies to date have examined the influence of SO_2 or H_2S on catalyst performance [5–14], and some kinetic measurements have been made [8–11]. The present study examines the influence of a mixture of sulphur compounds, more typical of the types of sulphur compounds experienced in solid fuel gasification syngas or in the odourant added to natural gas. The influence of a realistic sulphur-based mixture on the activity of alumina-supported precious metal catalysts in the combustion of methane performance is investigated, and the kinetics are evaluated over the temperature range 500–950 K. A comparison is made to published data concerning the kinetics in the presence of other sulphur species. The work also examines and compares the effectiveness of catalyst regeneration via treatment in hydrogen following the exposure to sulphur poisons. A preliminary attempt to separate natural and sulphur-induced deactivations is presented.

2. Experimental

2.1. Catalyst preparation

Three different catalysts of 2 wt.% Pt, Pd or Rh supported on γ-alumina were prepared using incipient wetness impregnation from solutions of Pt(II) acetylacetonate (in toluene), $Pd(NO_3)_2{\cdot}H_2O$ (aq), and $Rh(NO_3)_3{\cdot}2H_2O$ (aq). Calcination was achieved by heating at 4 °C/min to 475 °C for 240 min. The surface areas (determined by the BET method) of the catalysts, respectively, are 114 m^2/g (2 wt.% Pt/Al_2O_3), 124 m^2/g (2 wt.% Pd/Al_2O_3), 123 m^2/g (2 wt.% Rh/Al_2O_3), and 134 m^2/g (γ-alumina support). The calcined, freshly reduced and regenerated catalysts were examined by TEM using a Philips CM200 FEG-TEM and the average particle sizes were recorded. The BET surface areas of the reduced and regenerated catalysts were also recorded.

2.2. Activity in the catalytic combustion of methane

The activity of the catalysts in the catalytic combustion of methane was studied using an isothermal vertical tubular quartz micro-reactor at atmospheric pressure placed within a electrically heated furnace. Conversion, over a range of temperatures, of a 100 ml/min gas feed consisting of 4% methane diluted in air (GHSV $\approx 1\,s^{-1}$) was monitored using on-line gas chromatography. A Perkin Elmer Autosystem XL gas chromatograph fitted with an Alltech CTR 1 column in series with thermal conductivity and flame ionisation detectors was used to measure CH_4, O_2 and CO_2 in the feed and flue gases. Although this system was also capable of analysing CO, this gas was not detected in any of the experiments described, and 100% carbon conversion to CO_2 was seen in all experiments. All gas concentrations were calibrated against standard gas mixtures.

Approximately 100 mg of powdered catalyst, sieved to $\leq$150 μm, was reduced in situ at 400 °C for 0.5 h under flowing H_2, prior to the catalytic studies. After reduction the catalyst was cooled under flowing N_2 and then subjected to a number of comparative studies. The first study involved the combustion of methane as a function of temperature; this is referred to as the ‘freshly reduced’ case. The second study involved the combustion of methane in the presence of 10 ppm of a synthetic odourant mixture as a function of temperature; this is referred to as the ‘poisoned’ case. After the second study the catalyst was again reduced in flowing hydrogen at 400 °C for 0.5 h in an attempt to remove any chemisorbed sulphur species from its surface. After this step, the third study involved the combustion of methane as a function of temperature; this is referred to as the ‘regenerated’ case. In a separate experiment the catalyst activity was also measured over the catalysts in their calcined states. In this case the catalyst was pretreated in situ at 400 °C for 0.5 h in air, prior to the methane oxidation experiment.

In all cases, at each set-point temperature, the conversion of CH_4 to CO_2 was followed with time until approximately steady-state conversion had been achieved, and this is the conversion reported. The synthetic odourant mixture (totalling 10 ppm S) consisted of 34 vol.% ethyl mercaptan, 30 vol.% methyl mercaptan, 19 vol.% carbonyl sulphide and 17 vol.% hydrogen sulphide, and was introduced from a gas-tight syringe via a septum into the feed stream using a Cole-Parmer 74,900 series syringe pump. Multiple replicate studies were carried out in order to allow estimation of experimental errors. The estimates suggest that typical errors in the gas chromatographic analyses performed are in the region of 3–4%.

2.3. *Fate of sulphur-containing species*

In a separate experiment, the fates of the sulphur species in the synthetic odourant mixture were followed during the combustion of methane over the Rh/Al_2O_3 catalyst at 390 °C. The exhaust gases were sampled twice, after 10 min and after 16 h, into a tedlar bag and analysed off-line using a Hewlett Packard 5890 series II GC fitted with a HP 5921A Atomic Emission Detector. Separation was achieved on a 60 m GSQ porous-layer-open-tubular (plot) column. This and similar methods have been applied successfully for the analysis of sulphur species in landfill gas [25,26]. The method may be regarded as semi-quantitative only.

At the end of this experiment, the FTIR spectrum of the spent catalyst was obtained using a Nicolet-Magna 560 FTIR spectrometer at 4 cm^{-1} resolution. Approximately 5 mg of catalyst was mixed with 200 mg of spectroscopic grade KBr and pressed into a wafer, from which the transmission spectrum was obtained. The spectrum of the original, calcined Rh/Al_2O_3 catalyst was also recorded in the same manner for comparison.

3. Results

The activity–temperature curves of the freshly reduced catalysts, poisoned, and regenerated Pd/Al_2O_3, Pt/Al_2O_3 and Rh/Al_2O_3 catalysts in the combustion of methane are shown in Fig. 1. For comparison, the effect of the freshly reduced Rh/Al_2O_3 catalyst experiencing 3-temperature sweeps is shown in Fig. 2. For the freshly reduced catalysts, the activities over the 2 wt.% metal/alumina catalysts follow the order Pd > Rh > Pt, as can be seen from the temperature at which 50% conversion of methane is observed, T_{50}. When the combustion is conducted in the presence of the sulphur mixture, all the catalysts display decreased activity, with a shift in T_{50} of 36 K for palladium, 46 K for platinum and 50 K for rhodium. Thus alumina supported rhodium and platinum are more susceptible to poisoning by the sulphur mixture than supported palladium. Upon regeneration by reduction in hydrogen, all the catalysts recover some activity, but in the case of platinum this is very slight. In contrast, the rhodium catalysts is regenerated beyond the activity observed in its freshly reduced state. The activity of the regenerated catalysts follow the order Rh > Pd ≫ Pt.

The kinetics of methane combustion for all the three experiments were evaluated as described below and the results are presented in Table 1. This table also compares these results with those given by other authors, where available, and gives the kinetic parameters measured for the calcined catalysts. Table 1 also gives the temperature at 50% methane conversion, and the mass specific rate constant evaluated at 623 K. These latter two parameters enable a direct comparison of the catalysts to be made.

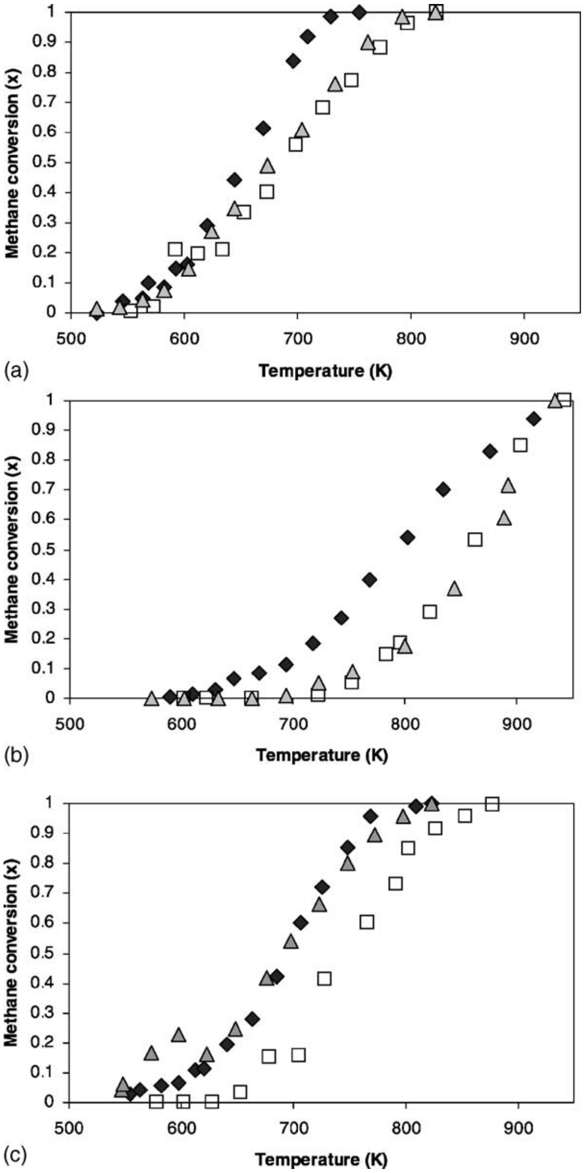


Fig. 1. Methane conversion with temperature over precious metal catalysts under different conditions: (◆) freshly reduced catalyst; (☐) poisoned; (▲) regenerated. (a) Pd/Al_2O_3; (b) Pt/Al_2O_3; (c) Rh/Al_2O_3. 4% methane, balance air; see text for further description of experimental conditions.

The kinetics of the catalytic combustion of very lean methane/air mixtures over precious metal and other metal catalysts have been established previously [11,27–29]. For alumina supported Pd and Rh catalysts, the rate is almost independent of oxygen [27,29]. In the case of alumina supported Pt catalysts, the reaction is zero order in oxygen when the CH_4:O_2 ratio is below stoichiometric (<0.5) [28]. With regards to reaction order in methane, there is general agreement that the kinetics are first order provided the oxygen is in excess [11,27–29]. This is the case here and a limited number of experiments also established a reaction order of 1 in methane, using the initial rate method. Further validation was obtained by applying chemical kinetic modelling using a commercial code that simulates an isothermal plug-flow reactor (SENKIN) [30]. This utilised the experimentally derived global Arrhenius parameters, and as shown in Fig. 3 gave good prediction of behaviour over the entire temperature range, even though kinetic parameters were derived at $<30\%$ conversion.

The mass-specific reaction rate constant (k_m) was calculated from the fractional conversion of methane (x) using the equation:

$$-\left(\frac{F}{m}\right)[\ln(1-x)] = k_m = A\exp\left(-\frac{E_a}{RT}\right)$$

where F/m is the temperature-corrected volumetric rate of methane/air feed divided by the weight of catalyst (i.e. the reciprocal of the space–time divided by a constant, catalyst density). The kinetic parameters, including the apparent mass-specific rate constant at 623 K (k_{m623}), are presented in Table 1 for comparison. It should be noted that there is expected to be a large error in the pre-exponential factor and this is provided only for completeness.

Table 1 also compares the values of the activation energies and pre-exponential factors for methane combustion over alumina-supported precious metal catalysts to those reported by other workers. A direct comparison is difficult, because of different pretreatment conditions, and also because the kinetic parameters are influenced by the support used [27]. Most kinetic studies have concerned Pd/Al_2O_3, and there has been very little published on platinum and still less on rhodium. Certainly, the present work indicates activation energies of approximately 80–90 kJ mol^{-1} for all three freshly reduced catalysts and these values are not inconsistent with the limited previous work. In addition, it is apparent that the activation energy for methane combustion increases in the presence of the sulphur mixture for all three catalysts. Some compensation is observed on the rates, since an increase

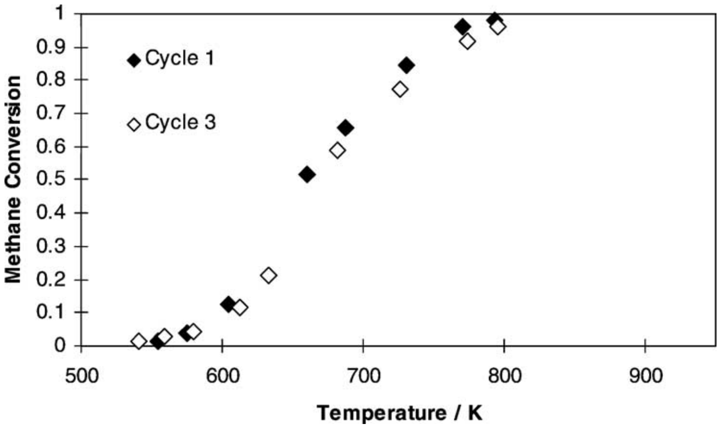


Fig. 2. Methane conversion with temperature over freshly reduced Rh/Al_2O_3. Influence on activity of three consecutive temperature cycles (4% methane, balance air).

Table 1

Kinetic rate data for the combustion of methane over precious metal catalysts under different conditions, and comparison with available published data[a]

Catalyst	Pretreatment/reaction conditions	E_a (kJ/mol)	A ($cm^3\,g^{-1}\,s^{-1}$)	k_{m623} ($cm^3\,g^{-1}\,s^{-1}$)	T_{50} (K)	Reference
Pd/Al_2O_3	Calcined	91	5×10^8	12.2	650	This work
	Reduced in H_2, 673 K	86	2×10^7	11.2	652	This work
	Sulphur mixture	113	2×10^{10}	6.2	688	This work
	Regenerated	89	3×10^8	8.4	675	This work
	2.2 wt.%, reduced in H_2 at 673 K	137			658	11
	2.0 wt.%, reduced in H_2 673 K	84			640	10
	2.0 wt.%, 100 ppm H_2S pretreatment	113			680	10
	2.0 wt.%, regenerated in H_2	83			660	10
	5 wt.% calcined	70–120				27
	6 wt.% calcined	74			∼575	9
	6 wt.% calcined, 0.9 ppm SO_2	105			∼740	9
	4% PdO calcined	128.8	7.02×10^{12}		∼568	8
	4% PdO, 80 ppm H_2S pretreatment	91.2	1.78×10^8		∼660	8
	4% PdO, regenerated in H_2	131.2	3.63×10^{12}		∼595	8
Pt/Al_2O_3	Calcined	62	5×10^5	3.5	775	This work
	Reduced in H_2, 673 K	87	2×10^7	1.0	794	This work
	Sulphur mixture	154	9×10^{10}	0.011	840	This work
	Regenerated	121	7×10^8	0.053	850	This work
	2.0 wt.%, reduced in H_2, 673 K	77			790	10
	2.0 wt.%, regenerated in H_2 after H_2S pretreatment	76			820	10
	Various wt.%	100–147				28
Rh/Al_2O_3	Calcined	59	5×10^5	5.0	720	This work
	Reduced in H_2, 673 K	83	5×10^7	5.4	695	This work
	Sulphur mixture	105	5×10^8	0.79	745	This work
	Regenerated	60	1×10^6	9.3	690	This work
	2.0 wt.%, reduced in H_2, 673 K	96			690	10
	2.0 wt.%, regenerated in H_2 after H_2S pretreatment	84			700	10

[a] E_a is the activation energy, A the pre-exponential factor, k_{m623} the evaluated mass specific rate constant at 623 K, and T_{50} is the temperature at which 50% conversion is achieved.

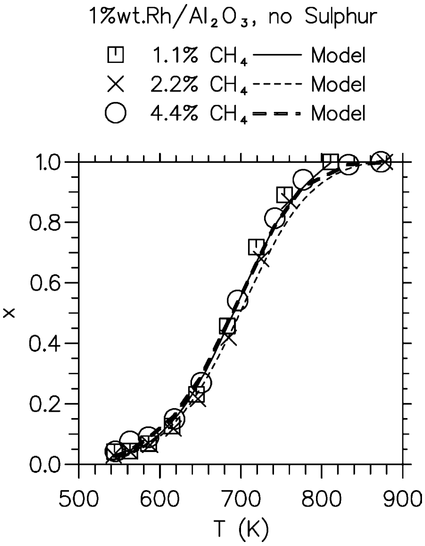


Fig. 3. Methane conversion with temperature over a 1 wt.% Rh/Al_2O_3 catalyst at various methane concentrations (symbols) and kinetic model fits assuming first order in methane and zero order in oxygen.

in the pre-exponential factor is also observed, but this is not enough to maintain the activity compared to the freshly reduced analogue. Comparing the mass specific rate constants at 623 K, it is seen that there is a 45% decrease in the rate of methane combustion over Pd/Al_2O_3, compared to 99 and 85% decreases in the combustion rates over Pt/Al_2O_3 and Rh/Al_2O_3, respectively.

Further insight into the fate of the sulphur-odourant poison species was sought using gas chromatography coupled with atomic emission detection, which is very sensitive to sulphur compounds. A gas mixture containing 10 ppm sulphur species from the synthetic odourant added into a 4% methane/96% air feed was passed over 0.1 g of the rhodium–alumina catalyst at 563 K and the gases were sampled after 10 min and 16 h and analysed off-line as described in Section 2.3. The species in the sulphur mixture were readily detected but unfortunately this approach was unable to detect any SO_2 or SO_3. It was noted that when the sampled flue gas was spiked with SO_2 no signal was detected by AES except when an excess amount was added (ca. 80 ppm); presumably this is because the SO_2 is lost by absorption in the sampling system and dissolution in the humid flue gas, etc.

While this method may be regarded as semi-quantitative only, nevertheless the study shows clear differences between the feed gas and flue gas measurements taken after the catalyst had been used for 10 min and after 16 h. These results are shown in Fig. 4. Compared with the sulphur components (H_2S, COS, MeSH, EtSH) found in the feed gas, all of these components and most notably H_2S were decreased in the flue gas sampled after 10 min and 16 h.

The FTIR spectrum of the catalyst from this experiment is given in Fig. 5 and compared with the fresh catalyst. Typical IR spectra for alumina catalysts were observed with absorbances associated with OH groups and adsorbed CO_2 at ~3400, 1520–1570 and 1350–1410 cm^{-1} [31]. In addition absorbances due to adsorbed hydrocarbons are clearly present in the spent catalyst as shown in Fig. 5(a) and an envelope of bands appears in the C–H stretching region with peak maxima at 2959, 2923 and 2851 cm^{-1}. This suggests the presence of methylene groups, which have characteristic asymmetric and symmetric stretches at 2926 and 2853 cm^{-1}. The S–H stretch of thiols appears at approximately 2550–2600 cm^{-1}, but is very weak and would not be expected to be detected even if such species were present on the catalyst. Bands are also present in the 1100–1200 cm^{-1} region and two distinct peaks are clearly seen at 1162 and 1115 cm^{-1} as shown in Fig. 5(b). Bands in this region have been attributed to surface sulphate and possibly sulphite species [32,33]. The BET surface area of this spent catalyst was 89 $m^2\,g^{-1}$ compared to a value of 125 $m^2\,g^{-1}$ in its freshly reduced state. This suggests that prolonged contact with the sulphur mixture does influence the surface area, which would be consistent with sulphate formation.

Table 1 also shows the kinetic parameters for methane combustion after an attempt to regenerate the catalyst by reduction in hydrogen. It is clear that regeneration by this method meets with varying success depending upon the catalyst. Regeneration results in a catalyst with a lower activation energy for methane combustion than that observed in the presence of the sulphur mixture. In the case of Pd/Al_2O_3 this is comparable to that observed over the ‘freshly reduced’ catalyst, and the activity is restored to approximately 75% of the original activity. In the case of Pt/Al_2O_3 the regeneration step is not very successful, the activation energy remains higher than that seen over the

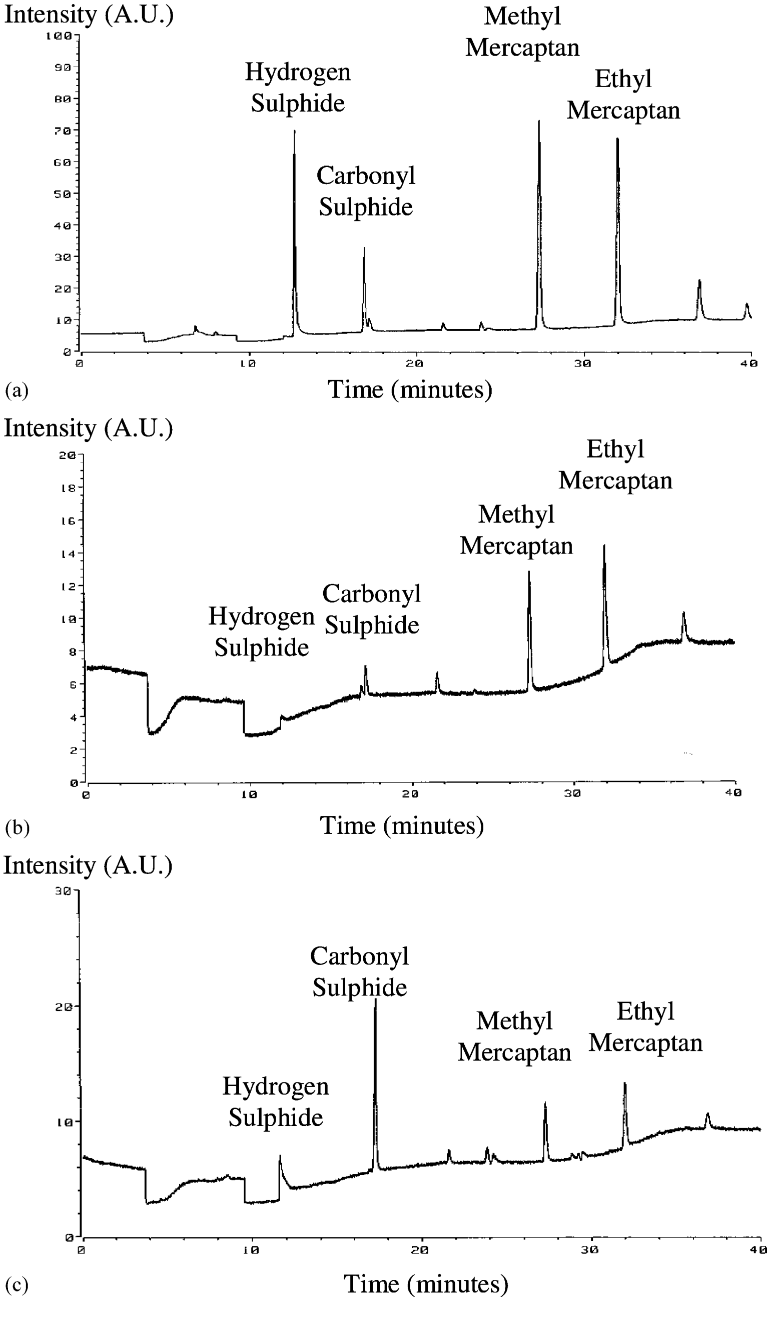


Fig. 4. GC/AED chromatogram of odourant poisoned methane/air feed (34 vol.% ethyl mercaptan, 30 vol.% methyl mercaptan, 19 vol.% carbonyl sulphide and 17 vol.% hydrogen sulphide): (a) feed, (b) exhaust gases 10 min after start of catalytic combustion, (c) exhaust gases 16 h after start of catalytic combustion over Rh/Al_2O_3 at 563 K.

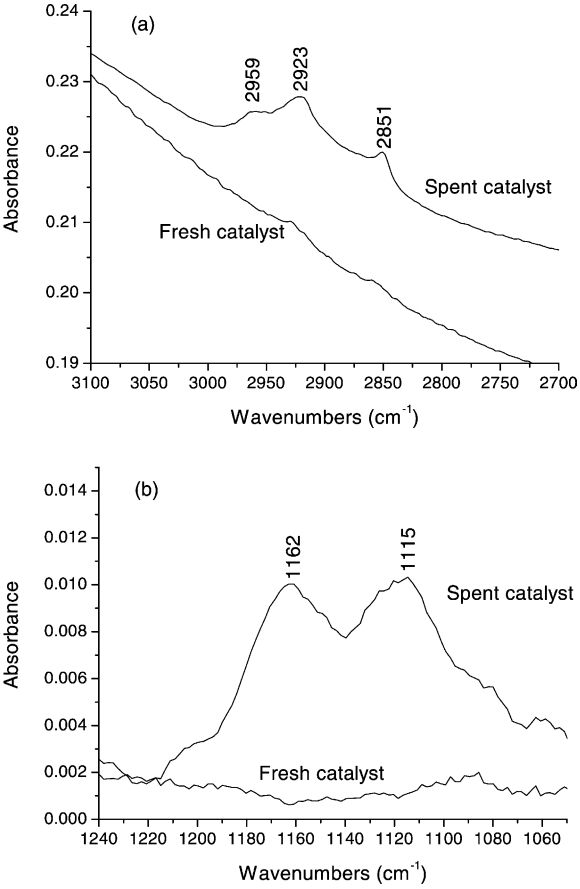


Fig. 5. FTIR spectra of calcined and 'poisoned' Rh/Al_2O_3: (a) C–H stretching region; (b) S=O stretching region.

catalyst in its freshly reduced state, and only 6% of the original activity is restored. Interestingly, there appears to be an improved activity of the Rh/Al_2O_3 catalyst upon regeneration compared to that seen in its freshly reduced state, and this is accompanied by a lower activation energy for the combustion of methane.

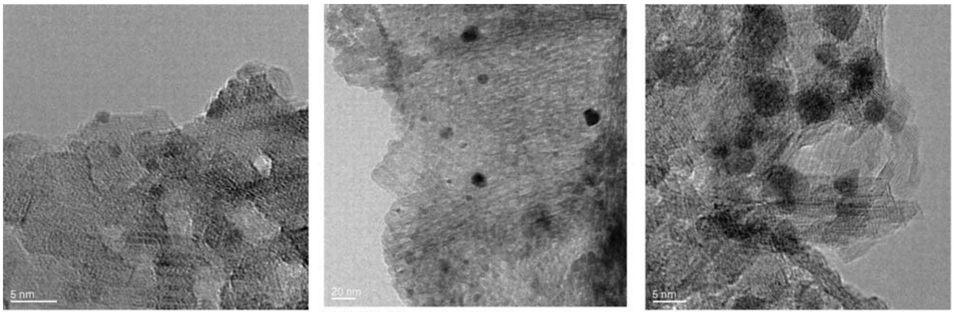
The calcined, freshly reduced and regenerated catalysts were examined by TEM and some of the results are given in Fig. 6. BET surface areas were also determined. The measured average metal particle sizes and standard deviations were 5.0 ± 1.3, 3.2 ± 2.1 and 2.7 ± 1.2 nm for the calcined Pd/Al_2O_3, Pt/Al_2O_3 and Rh/Al_2O_3, respectively. After reduction in hydrogen the average particle sizes increased for Pd/Al_2O_3 and Pt/Al_2O_3 to 6.0±2.5 and 8.0±3.1, respectively, while the dispersion of Rh/Al_2O_3 improved slightly, to an average particle size of 2.2 ± 1.0. After reduction the surface areas are very similar to their respective calcined values 120, 117 and 125 $m^2\,g^{-1}$ for Pd/Al_2O_3, Pt/Al_2O_3 and Rh/Al_2O_3, respectively. After regeneration, the BET surface areas are decreased to 89, 81 and 89 $m^2\,g^{-1}$, respectively. Compared to the reduced catalysts, the average particle sizes are larger still for Pd/Al_2O_3 and Pt/Al_2O_3 and only slightly larger for Rh/Al_2O_3, i.e. 9.8 ± 2.9, 18 ± 9.2 and 2.6 ± 1.0, respectively. In the case of the palladium and platinum catalysts these numbers are slightly misleading, since a wide range of particle sizes were observed, and particularly for palladium areas of very large agglomerations of particles were present.

It is clear that sulphur-induced deactivation (poisoning and/or sintering) is taking place, but 'natural' deactivation (surface rearrangement/sintering) may also take place under the reaction conditions. Fig. 7 shows the results of methane conversion over Pd/Al_2O_3 at 315 °C. A natural decrease in activity is seen in the reaction atmosphere (Fig. 7(a) and (b)). After approximately 1060 min, 80 ppm of H_2S was injected into the feed and the deactivation followed (Fig. 7(c)). As a first attempt to separate 'natural' and sulphur-induced deactivation, the data in Fig. 7 was fitted using a similar approach to the deactivation model proposed by Borgna et al. [3]. The deactivation is modelled by the sum of the terms (Model 1):

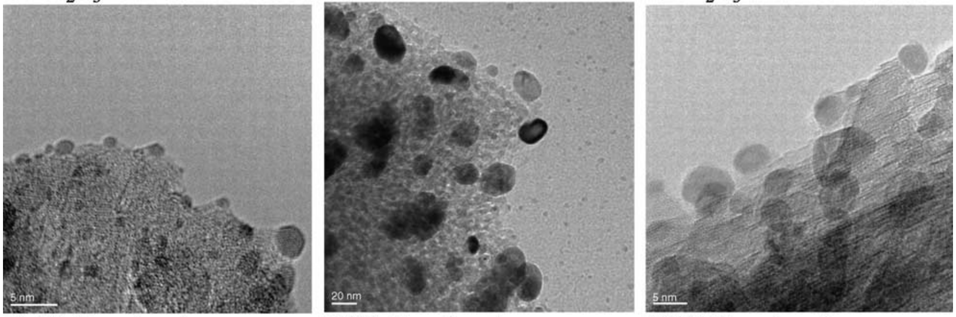
$$\frac{x}{x_0} = R(e^{-(s_n+s)(t-t_0)} + e^{-(k_{dn}+k_d)(t-t_0)}) + 1 - 2R$$

where x is the activity at time t, and x_0 is the activity at the initial time t_0. The coefficients s and k_d are deactivation coefficients that are found by running a program of least-squares non-linear regression. The additional subscript 'n' of the parameters s and k_d apply to the deactivation occurring in the absence of any sulphur component which we have termed as 'natural' deactivation. The lack of the subscript 'n' refers to the deactivation due to the presence of an S-containing dopant in the CH_4–air feedstream. The coefficient R is related to the steady-state conversion x_∞ by $x_0(1-2R) = x_\infty$.

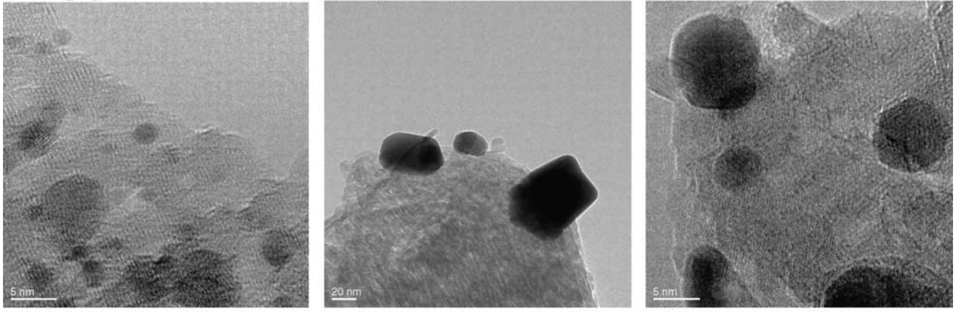
For the first part of the experiment, i.e. in the absence of H_2S (Fig. 7(a) and (b)), x_0 was 1 and t_0, the time of introduction of 4% methane in the air stream, was zero. The CH_4 conversion to CO_2 (x) was measured every 2 min, and therefore allowed



Rh/Al_2O_3 calcined Pt/Al_2O_3 calcined Pd/Al_2O_3 calcined



Rh/Al_2O_3 reduced Pt/Al_2O_3 reduced Pd/Al_2O_3 reduced



Rh/Al_2O_3 regenerated Pt/Al_2O_3 regenerated Pd/Al_2O_3 regenerated

Fig. 6. TEM images of precious metal catalysts: calcined (first row), hydrogen reduced (middle row); and regenerated by hydrogen reduction after exposure to the sulphur mixture (bottom row).

monitoring the deactivation with time-on-stream. In the second part of the experiment, i.e. in the presence of H_2S (Fig. 7(c)), the new initial conditions are $t_0 = 1095\,\text{min}$, $a_0 = 0.547$, and the methane conversion was monitored for a further ∼170 min.

A program based on the Levenberg–Marquardt method was developed to carry out the least squares fitting of the experimental deactivation for this two-part experiment. The method is iterative and necessitates gross starting estimates of the three parameters that need fitting in each part of the experiment. The first step consists in finding out the deactivation coefficients for natural deactivation (R, s_n and k_{dn}) by artificially setting to zero the relevant coefficients. Once the coefficients for natural deactivation are known, the program is run a second time with the set of deactivation data obtained in the presence of the S-dopant, this time in order to obtain s and k_d and the new value of R (hence x_∞).

The model chosen to represent the deactivation function of time-on-stream needs to verify the conditions $s < k_d$ and $s_n < k_{dn}$ in order to fit the shape of the experimental curves. The exponential term containing the smaller values of s and s_n describes

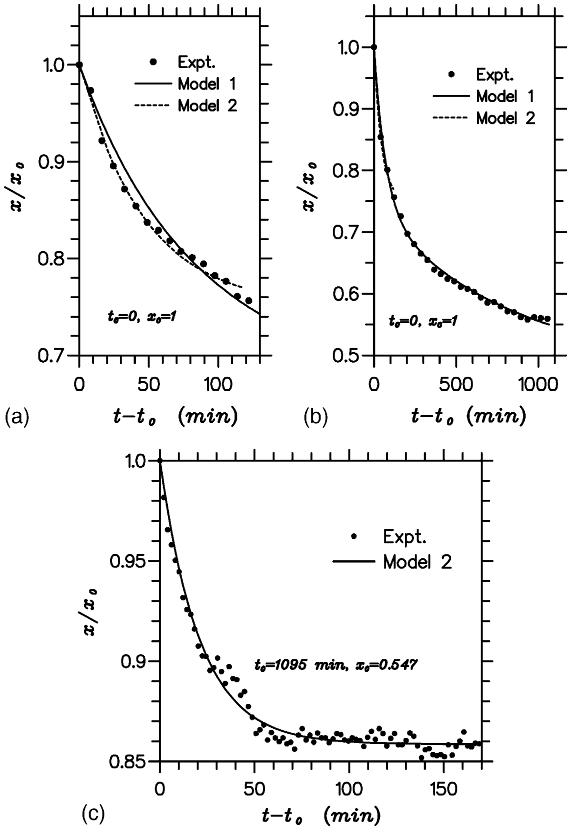


Fig. 7. Deactivation during methane conversion over the 2 wt.% Pd/Al_2O_3 catalyst at 315 °C and 4% CH_4–air. (a) Initial time-on-stream and (b) longer time-on-stream. (c) Deactivation after introduction of 80 ppm H_2S in the feed at the end of the experiment shown in (b). Symbols show experimental data and lines show model fits using the two models described in the text.

the activity at large time-on-stream, whereas the exponential term containing the larger order values of k_d and k_{dn} describe the activity for times nearer t_0. When $s + s_n \ll k_d + k_{dn}$, the deactivation function simplifies to Model 2:

$$\frac{x}{x_0} = R(e^{-(k_{dn}+k_d)(t-t_0)}) + 1 - 2R$$

Model 2 is essentially a first order deactivation model where the deactivation rate is described by

$$\begin{aligned}\frac{dx}{dt} &= -(k_{dn} + k_d)(x - x_\infty)\\ &= -k_{dn}(x - x_\infty)^1 - k_d(x - x_\infty)^1\end{aligned}$$

where the k_{dn} and k_d coefficients represent each a rate constant of deactivation (natural and caused by H_2S). The exponential terms with s and s_n are more difficult to incorporate in an equation for dx/dt and do not lend themselves to a first order reaction expression. The modelled curves shown in Fig. 7(a) and (b) corresponding to natural deactivation indicate that the more complex Model 1 yields an excellent fit over the entire experiment, while for short time-on-stream, the simpler Model 2 is sufficient to produce an excellent fit. The values obtained for the coefficients in these two cases were (by 8 and 5 iterations, respectively):

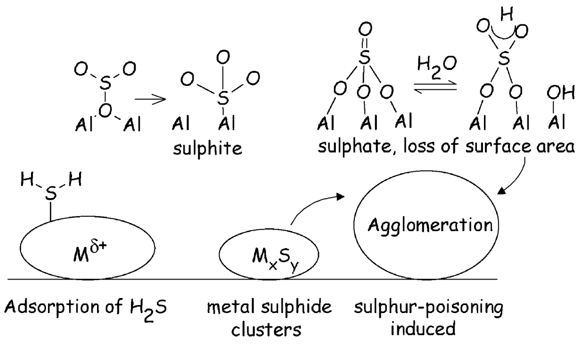
- Model 1: $x_\infty = 0.4791 \pm 0.04$, $s_n = (1.223 \pm 0.4) \times 10^{-3}$, $k_{dn} = 0.0142 \pm 0.002\,\mathrm{min}^{-1}$.
- Model 2: $x_\infty = 0.4994 \pm 0.05$, $s_n = 0$, $k_{dn} = 0.0214 \pm 0.005\,\mathrm{min}^{-1}$.

The modelled curve of Fig. 7(c) obtained with Model 2 shows an excellent fit for the whole run in the presence of the H_2S. The best-fit coefficients obtained by 8 iterations were: $x_\infty = 0.3921 \pm 0.007$, and $k_d = 0.0474 \pm 0.006\,\mathrm{min}^{-1}$. Consequently, Model 1 was not run for this second part of the experiment.

4. Discussion

4.1. Comments on sulphur poisoning and catalyst regeneration

Methane oxidation over precious metal catalysts in the presence of sulphur species is interesting because, depending upon the temperature, metal nature, loading, and dispersion, oxidation of H_2S and presumably other sulphur species to SO_2 occurs. The SO_2 can be further oxidised to form SO_3 which reacts with the support to form sulphates. The extent of the above reaction chemistry can be critical, since H_2S may react to form metal sulphides, with severe catalyst deactivation and sulphur poisoning induced agglomeration. Scheme 1 summarises the possible contributions of S-poisoning. Regeneration by reduction can convert sulphate to SO_2 which is removed, but metal sulphides are not regenerated. It is surprising therefore that there have been few studies of the oxidation of H_2S over precious metal catalysts. The activity order for oxidation of SO_2 has been given as Pt > Pd > Rh, but the order is sensitive to many fac-



Scheme 1.

tors such as dispersion or the presence of other gases [34].

Qualitative studies using GC–AED indicate that conversion of all S-components is occurring over Rh/Al_2O_3 at 563 K, and evidence for sulphate formation is seen in the FTIR spectrum of the spent catalyst. Thus, during the methane combustion studies carried out in the presence of sulphur compounds over all the catalysts, it is probable that a mixture of reduced and oxidised sulphur species are present, and the exact composition depends on the factors listed above. At this point, we are only able to speculate on the nature of the observed decrease in the methane combustion rates in the presence of the sulphur compounds, and on the subsequent ease of regeneration by low temperature reduction. We also note however that the extent of catalyst poisoning and ease of subsequent regeneration differs to that observed when H_2S alone is present in the methane/air feed [10].

The decrease in catalyst activity for the conversion of methane over Pd/Al_2O_3 can be attributed to Pd–S interactions as observed by Hoyos et al. [7,11] either in the form of sulphide or sulphate, arising from the interaction with either H_2S or SO_2/SO_3, respectively. Similar interactions are possible with platinum [34]. It is known that Pt is a superior catalyst for SO_2 to SO_3 conversion compared to Pd [12], and it is possible that sulphation of the support is the dominant influence of sulphur species over the Pt/Al_2O_3 catalyst. This would lead to agglomeration of palladium particles, loss of metal surface area, and a decrease in catalyst activity. Sulphation of the support is known to provide a promotional effect in the oxidation of propane over Pt/Al_2O_3, which has been attributed to the formation of new sites at the metal–support interface [20]. Promotion has sometimes been reported for the combustion of methane [12] but results are conflicting. Our work would suggest that at least at low temperatures, and using a mixture of sulphur compounds, there is catalyst poisoning for methane combustion, and sulphur-induced agglomeration is a key factor.

In the case of Rh/Al_2O_3, there is FTIR evidence of surface sulphates after the catalyst had been used in methane combustion in the presence of the sulphur mixture. Again, it is plausible to suggest Rh–S interaction as a source of catalyst poisoning, but whatever the poisoning effect it is clear that it is easy to reverse in the case of the Rh/Al_2O_3 catalyst.

Interpretation of the results is complicated by the fact that ‘natural’ deactivation, i.e. sintering and/or surface rearrangement under the reaction atmosphere, is taking place as well as any sulphur poisoning and sulphur-induced agglomeration. Using a simple non-linear deactivation model to fit deactivation data for Pd/Al_2O_3 it is apparent that the rate of deactivation in the presence of 80 ppm H_2S is more than twice as fast as any ‘natural’ surface rearrangement or sintering. The model approximates to first-order deactivation in both ‘natural’ and S-induced deactivation. This model needs to be extended to different temperatures, H_2S concentrations, and to other sulphur species, but this initial study demonstrates the insight that can be obtained of the deactivation phenomena, and provides an initial approach to quantify them.

As stated above, regeneration by low temperature reduction in hydrogen is very successful in the case of Rh/Al_2O_3, but is somewhat less successful in the case of Pd/Al_2O_3, and very poor in the case of Pt/Al_2O_3. The purpose of the regeneration step is to reduce oxidised sulphur species back to SO_2 which is subsequently desorbed from the catalyst. However, the temperature was kept relatively low (400 °C) in an attempt to minimise metal sintering as suggested by Wang et al. [35]. TEM studies indicate that during the catalyst lifetime of calcination, reduction, reaction/poisoning and regeneration, the precious metals have different tendencies to remain dispersed or to agglomerate. There is evidence of a large proportion of the platinum surface area being lost through the formation of large particles and the consequence of this is the severe catalyst deactivation observed in methane combustion. Some studies indicate that oxidation–reduction or oxychlorination–reduction cycles can be effective in redispersing platinum [35,36]. This was not attempted in the present work.

Pd/Al_2O_3 also tended to agglomerate after regeneration by reduction, but this effect was not uniform. In a few areas, this was very severe but this was not the norm.

Rhodium can form a number of oxide forms in oxidising environments, but can also move below the alumina surface to form sub-surface species that are difficult to reduce [37] and hence catalyst deactivation can occur. The nature of the species present is very much influenced by temperature, metal loading, and support surface structure [38]. Reduction of Rh/Al_2O_3 is known to restore or partially restore catalyst activity when sub-surface species exist, and can result in isolated rhodium atoms, two-dimensional rhodium islands and three-dimensional rhodium particles [39].

In the present work it is seen from the TEM results that the calcined catalyst has a good dispersion of rhodium on the support and this translates to a good activity in the combustion of methane, and a light-off temperature of ca. 720 K is observed. Upon reduction, TEM studies reveal improved rhodium dispersion and this is reflected in its lower light-off temperature of 695 K. The sulphur odourant mixture has an adverse effect on the catalyst behaviour and surface sulphate species were identified in the IR of the spent catalyst. Regeneration by reduction is very successful and restores the catalyst activity to slightly beyond that observed for the freshly reduced system. The TEM studies indicate that good dispersion is present. Hence it is clear that not only can sulphur poisoning of Rh/Al_2O_3 be reversed, but also that the second reduction step can be beneficial.

Aside from the preceding discussion, it is interesting to note the influence of metal particle size on catalyst activity. Fig. 8 shows the apparent effect for catalysts which have seen different pretreatments (calcined, reduced and regenerated). The intrinsic high activity of palladium in this reaction is clearly demonstrated, but the figure also illustrates the importance of particle size on activity. Since an increase in particle size is observed on regenerated catalysts, it is possible to speculate that sulphur-induced agglomeration is an important factor in the decreased activity of catalysts in the presence of the odourant mixture. Regeneration by reduction may also result in agglomeration (in the case of Pd and Pt).

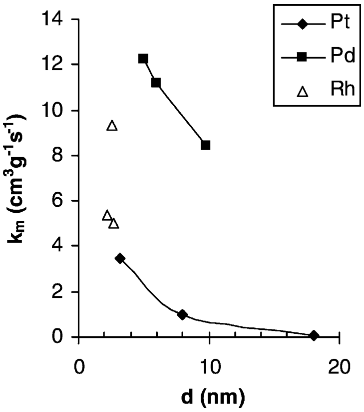


Fig. 8. Relationship between average metal particle size and catalyst activity in the combustion of methane. Activity is expressed as the mass specific rate constant at 623 K.

5. Conclusions

All alumina-supported precious metal catalysts are poisoned by the sulphur mixture for their activity in the low temperature combustion of methane. The kinetics of the reaction in the presence of the sulphur mixture can still be determined assuming first order in methane and zero order in oxygen. A simple deactivation model has been applied in a preliminary study to separate sulphur-induced deactivation from ‘natural’ deactivation in the reaction atmosphere. Low temperature reduction by hydrogen can restore the activity of precious metal catalysts but the extent of this regeneration is highly metal dependent. Presumably the sulphur species are reduced and removed as SO_2 during this process. However, at the same time, the metals can become mobile, which can lead to agglomeration of a portion of the dispersed metal, and this was particularly the case for platinum as well as palladium to a lesser extent. Thus the success of regeneration follows the order Rh $>$ Pd $\gg$ Pt.

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