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REMARKABLE ACTIVITY ENHANCEMENT IN THE CATALYTIC COMBUSTION OF METHANE ON SUPPORTED PALLADIUM CATALYSTS

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Pd; complete oxidation; supported catalyst.

The activity of supported palladium catalysts for the combustion of methane has been determined. It has been observed that the activity increases with time on stream irrespective of whether the catalysts are pre-calcined or pre-reduced. Careful re-reduction experiments have shown that the enhanced activity is maintained. It is concluded that the increase in activity with time on stream is not attributable to slow variations in the chemical state of the palladium particles, but to changes in the morphology of the palladium crystallites under reaction conditions. The possible role of dissolved carbon in stabilising the reconstructed crystallites against reduction is discussed.

1. Introduction

The catalytic combustion of methane has been known for over 150 years since the work of Davy with palladium and platinum wires [1]. In more recent years catalytic combustion has been explored for applications involving gas sensors, car exhaust emission control, space heaters and gas turbines. Palladium is generally known to be the most active metal for methane combustion [2]. However, little is known about the detailed mechanism of the reaction or the nature of the active catalyst. Because of the reaction conditions used, in which both an oxidant (air or oxygen) and a reductant (methane) are introduced simultaneously it is uncertain whether the active catalyst should be viewed as a metal on which oxygen is adsorbed, or a partially reduced metal oxide.

For reduced palladium catalysts a mechanism has been suggested [3] in which there is a surface reaction between adsorbed methane and oxygen with the methane and oxygen competing for surface sites. On the other hand, for palladium dispersed in 13X zeolite it was proposed that methane and oxygen could jointly adsorb and react on a single site [3]. Siemanides and Stoukides, on the basis of a study using solid electrolyte potentiometry, have proposed an Eley Rideal mechanism [4]. Other, even more complex reaction schemes have been proposed [5].

One reason for the variation in the results reported may be that the nature and oxidation state of the reactive surface is itself a function of the reaction conditions. Thus, oxidation could be occurring on palladium metal, on a Pd(II) oxide surface, or on a palladium surface partially covered with oxygen. Indeed, all three types of site could be present simultaneously if the catalyst contains a range of palladium particle sizes since it is known from XPS measurements that small palladium particles are more likely to exist in an oxidised state [6].

A further complexity in catalytic combustion of methane on palladium catalysts arises from the observation that there is no clear correlation between activity and palladium surface area or palladium particle size. In recent work, Hicks et al. have presented results which indicate that methane combustion is a structure sensitive reaction [7,8]. Moreover, they have found that the activity may increase with time on stream. We have obtained similar results for palladium catalysts supported on silica or alumina [9–11]. Although the experimental conditions used in these two pieces of work are different it is interesting that in both cases an activity increase is observed.

Hicks et al. postulate that the increase in activity with time on stream may be related to the time taken for the oxidation or partial oxidation of palladium crystallites. In contrast we have concluded that this increase is caused by morphological changes in the palladium particles. The purpose of the present work was to investigate whether these changes in activity are due to a slow oxidation of palladium particles, or to morphological effects.

2. Experimental

CATALYST PREPARATION

Alumina-supported palladium catalysts were prepared by wet impregnation of a Ketjen alumina (CK 300, surface area 206 $m^2\ g^{-1}$) with solutions of either palladium chloride or palladium nitrate. The metal loading was between 3 and 5%. The samples were dried overnight. To prepare samples with different dipersions, the catalysts were calcined in air for periods from 1 to 24 h at temperatures in the range 500–850 ° C.

CATALYST TESTING

The activity of the catalysts was tested for the combustion of methane in a flow microreactor operating at atmospheric pressure with a 1% methane/air mixture (B.O.C. Special Gases). The sample (120 mg) was placed in a 5 mm i.d. quartz tube and heated to the required temperature. The reaction mixture, at a flow rate of 120 cm^3 min^{-1} was passed downstream through the catalyst and the products analysed on a Perkin Elmer 8410 gas chromatograph with data acquisition facilities. Carbon dioxide was converted into methane by using a catalytic reactor on the inlet to the FID detector of the GC.

CATALYST REDUCTION EXPERIMENTS

To investigate the effect of prereduction on the catalytic properties we have performed the following experiment. The reactor was set to a (low) temperature to give a small methane conversion (267 ° C) and the activity of the calcined catalyst measured. The reactor was then flushed with helium and cooled to room temperature. Hydrogen was introduced and the reactor heated at 10 ° C min^{-1} to 120 ° C to totally reduce the palladium oxide to the metal. The reactor was again flushed with helium and the temperature raised to 267 ° C. The reaction mixture was introduced and the activity monitored over a period of 5 days. At this point the flushing, reduction and re-heating described above was repeated and then the activity was remeasured for a further 7 days.

CHEMISORPTION EXPERIMENTS

The average palladium particle size of the catalysts was estimated by measuring the amount of hydrogen chemisorbed using a conventional glass volumetric apparatus. Because of the high solubility of hydrogen in palladium, measurements were made at ambient temperature and low pressure ($<$ 10 Torr). The monolayer coverage was estimated by back extrapolation of the linear portion of the adsorption isotherm to zero pressure. Metal particle sizes were calculated assuming spherical geometry.

3. Results and discussion

Figure 1 shows the activity of the various catalysts as a function of the average palladium particle size calculated from the amount of hydrogen adsorbed. It is clear that the methane combustion reaction is structure sensitive. However, it is also apparent that the structure sensitivity is not related in any simple way to the average particle size.

Figure 2 shows the variation in activity of a typical catalyst as a function of time on stream either after calcination or after prereduction. The results show that the activity of both catalysts increases steadily with time on stream. This effect is similar to that reported by Hicks et al. for prereduced palladium catalysts. However, since we observe the same type of effect with oxidised catalysts it does not seem likely that the effect in our case can be due to a slow

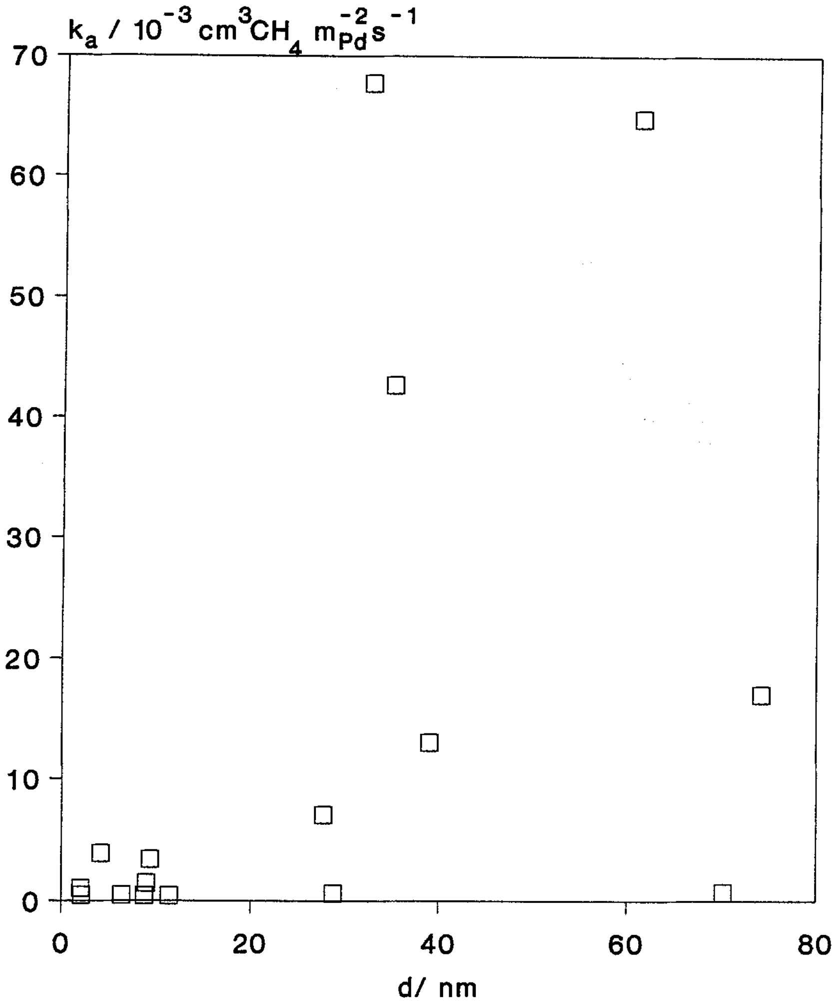

Fig. 1. Area specific rate constant as a function of the average Pd particle size for a variety of supported catalysts.

oxidation of palladium particles, which is the explanation suggested by Hicks et al.

The results of the experiment in which we investigated the effect of prereduction on the activity of one of our catalysts are summarised in fig. 3. The initial point corresponds to the activity of the calcined catalyst. The results shown after the first vertical bar on fig. 3 were obtained on a catalyst which was carefully reduced at low temperature to avoid sintering. The results show that the activity of this catalyst immediately after reduction is somewhat higher than the initial activity of the calcined catalyst. However, the different is not great. Of more significance is the fact that the activity of the prereduced catalyst increases

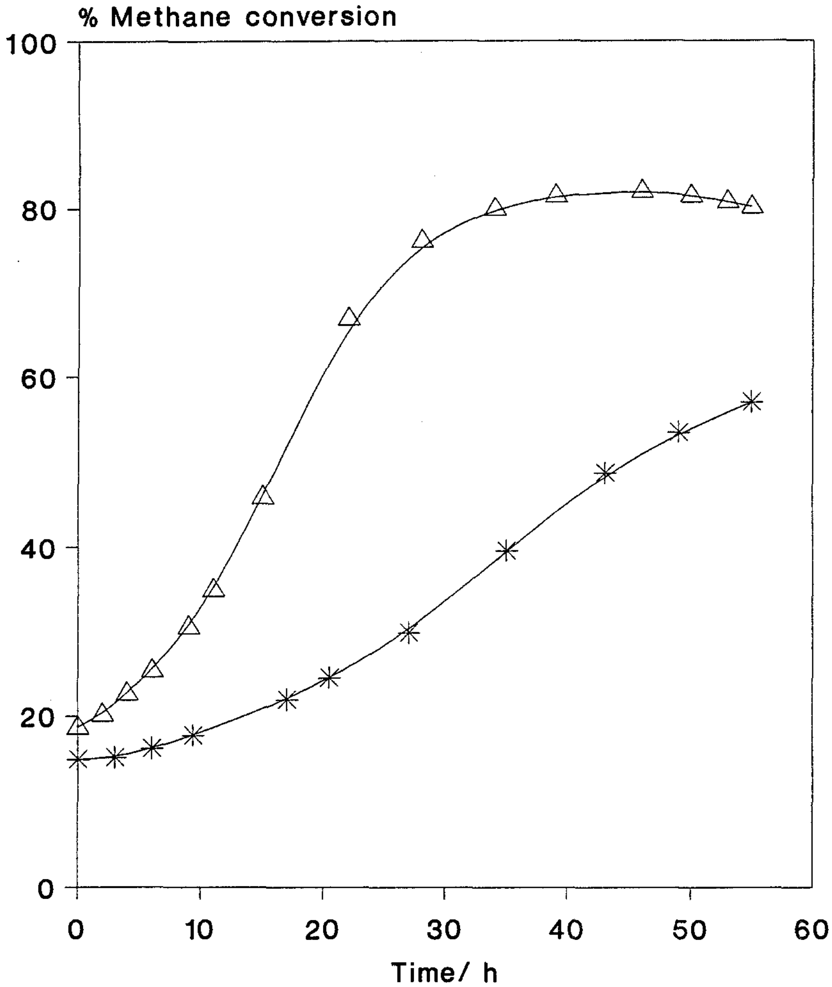

Fig. 2. Methane conversion as a function of time on stream for an alumina-supported Pd catalyst (*), calcined at 500 ° C for 16 h; (△), calcined at 500 ° C for 16 h and then reduced in hydrogen by heating at 10 ° C min^{-1} to 400 ° C.

steadily with time on stream until after about 120 h the activity has increased by about a factor of 4.

At this point the second low temperature reduction was performed to convert the palladium back to the metallic state. If the activation observed in the first part of the experiment was due to a slow oxidation of the palladium particles, then re-reduction should cause the activity to revert back to its original value. Figure 3 shows clearly that this does not happen. Indeed, the activity after the re-reduction treatment returns to precisely the value observed immediately prior to reduction. Further exposure to the reaction mixture results in a further continuous increase in activity over a period of about 200 h.

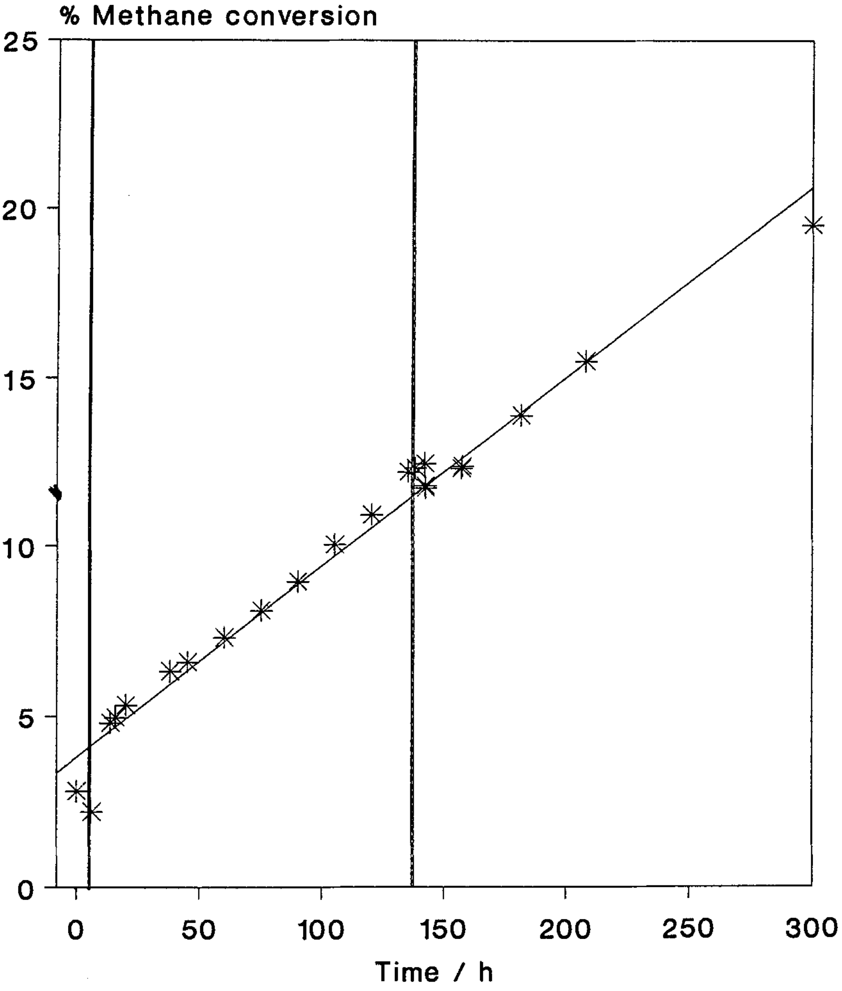

Fig. 3. Activity profile for an alumina-supported Pd catalyst originally calcined at 500 ° C for 16 h. Vertical lines indicate points at which reduction of the catalyst was performed (see text).

It seems clear from these experiments that the activity increase which we have observed cannot be due to a slow oxidation of palladium particles. Furthermore, since during the activation there is a small increase in the average particle size of the palladium, as measured by hydrogen chemisorption, we cannot explain the results on the basis of a change in dispersion. In any case, as fig. 1 shows there is no simple correlation between particle size and activity for the methane combustion reaction on our supported palladium catalysts.

We have suggested elsewhere [9–11] that the activity increase is caused by a change in the morphology of the palladium particles. Reconstruction of metal particles under reaction conditions has been proposed before to account for unusual catalytic results. Baddour et al. [12] have observed an induction period when studying silica-supported palladium catalysts for CO oxidation. Correlations with changes in the infrared spectrum of adsorbed CO led them to attribute the catalytic results to structural rearrangements which only occurred in the presence of CO and O_2. Gillet and Channakhone [13] have studied the decomposition of CO on model Pd/mica catalysts and found that the activity was dependent on the particle morphology.

There is good evidence from electron microscopy studies for structural rearrangements of small metal particles under the influence of different gaseous environments [14]. For example, Chojnacki and Schmidt [15] showed the exclusive formation of Pt cubes with (100) faces for supported catalysts heated in hydrogen, whereas heating in nitrogen or oxygen produced polyhedral or spherical particles. Chen and Ruckenstein [16,17] have studied Pd crystallites on alumina and shown marked variations in morphology after exposure to air at various temperatures.

We have confirmed that the activity increases are only observed when the catalyst is exposed to the reaction mixture. Various attempts to generate a more active catalyst, for example, by sintering in dry or wet air, were found to have no significant effect. We conclude from this that the crucial modifications of the palladium occur only in the presence of the reaction mixture. (We have not checked whether passing pure methane over the catalyst would result in a permanent change in activity.) We suspect that the deposition of a small amount of carbon on the palladium during the methane combustion reaction is a critical factor in generating the highly active catalysts. Separate temperature programmed reduction experiments on used catalysts have shown that carbon is deposited under reaction conditions, even though we use a large excess of oxygen. However, it is not possible to confirm that this carbon is actually deposited on the palladium. Some will certainly be laid down on the support.

The dissolution of carbon in palladium has been reported, and it is known that this carbon is very difficult to remove [18]. Some carbon dissolved in the palladium lattice would account for both the change in morphology, which we believe is necessary to explain our results for the calcined catalysts, and also be consistent with our observation that a mild re-reduction treatment does not destroy the enhanced activity.

In summary, we have demonstrated that the activity of supported palladium catalysts increases dramatically under reaction conditions. This increase in activity is not simply related to a change in the average particle size of the palladium crystallites. The effect is not eliminated by reduction of the used catalyst. We believe that the most reasonable explanation of our results, and possible also those of Hicks et al. [7,8], is that the reaction is structure sensitive and that under reaction conditions the morphology of the palladium particles is altered to give a more active surface. This could occur if specific crystal planes are either eliminated or created. Alternatively it is possible that the active centre is a surface defect, initially present in very low concentrations, but which is created under reaction conditions.

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