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Some aspects of hydrocarbon activation on platinum group metal combustion catalysts

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Abstract

The activation of different hydrocarbons on Pt and Pd catalysts has been investigated. The role of different forms of surface oxygen, and an explanation for the unusual order of activity (methane > ethane) is presented.

Keywords: Hydrocarbon activation; Platinum group metal combustion catalysts; Combustion

1. Introduction

The catalytic combustion of hydrocarbons is becoming of increasing importance both in the production of energy (e.g., gas turbines) and in emission control (e.g., car exhausts). The most commonly used combustion catalysts are alumina-supported platinum and palladium. Under oxidising conditions platinum has been found to be superior to palladium for the combustion of higher alkanes and olefins [1,2]. However, methane combustion is easier over palladium under similar conditions, although under reducing conditions platinum has again been found to be better [3,4]. The results seen under reducing conditions can be explained if one assumes the commonly accepted model that platinum is more efficient in the metallic state whereas palladium is most active in the oxidised state. Thus, conditions favouring reduction of the metal will favour platinum. The results seen under oxygen rich conditions for higher alkanes have been explained [2] in terms of an over oxidation of palladium preventing the adsorption of the hydrocarbon. A similar explanation has been proposed for methane oxidation in stoichiometric gas mixtures [3]. Platinum is less easily oxidised so will retain metallic sites for hydrocarbon adsorption. There is, however, little explanation for the apparent high reactivity of methane on palladium.

In order to explain the reasons for the high reactivity of methane on palladium it is first necessary to identify the active form of the catalyst. To date, however, there is no clear agreement on this matter. Whilst it is commonly agreed that the surface of palladium is more active in an oxidised form, the exact chemical state and morphology of the palladium particles is not known. Oxygen has been found to be bound less strongly to palladium oxide than to the metal [1] and thus bulk oxide has been proposed as the active species. However, Oh et al. [3] suggest that the formation of bulk oxide leads to a blocking of methane adsorption

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sites by oxygen. They conclude that the active species is a layer of palladium oxide supported on a metallic core. A similar conclusion has been reached by other workers [5,6]. It has also been found that small well dispersed particles of palladium oxide are less active than large oxidised particles [7–9]. Increases in activity with time for the methane combustion reaction have been attributed to a change in particle size [5]. However, this result could also be due to loss of chlorine from the catalysts. In addition, previous work from this laboratory [10] has found that the oxidation and reaction behaviour of palladium catalysts is very sensitive to the exact pre-treatment conditions, but that the apparent metal dispersion remained unchanged. Therefore, morphological effects are also important.

Another factor which must be considered is the effect of the reaction products on the catalyst. Water is well known to inhibit methane oxidation over palladium catalysts [9,11,12], possibly due to the formation of surface $Pd(OH)_2$. The case for CO_2 is less clear. Cullis et al. [11] found little inhibition whereas Ribeiro et al. [8] found a strong inhibition above 0.5% volume CO_2. Further studies from this laboratory [13] found inhibition from both CO_2 and water. However, the influence of water was much stronger and could reduce the activity by up to 50%. It is clear that the oxidation of hydrocarbons over platinum and palladium catalysts is complicated. This paper presents the results of experiments on hydrocarbon combustion on platinum and palladium catalysts.

2. Experimental

The catalysts used contained 2% Pt and 4% Pd supported on alumina and were prepared by dry impregnation using non-chlorine containing precursor salts. The catalysts were dried at 120°C and calcined in air at 500°C. Hydrocarbon combustion experiments were performed in a micro-reactor system operating at atmospheric pressure. In all cases analysis was performed using gas chromatography. The Pt catalyst was tested for methane combustion. 60 s pulses of reaction mixture (0.1% CH_4, 0.2% O_2, 100 cm^3 min^{-1}) were introduced at 300°C over 100 mg of catalyst which had been pre-reduced at 300°C for 30 min. Samples were taken at a different time during each pulse in order to build up a profile of activity across the pulse. Between pulses the catalyst was re-reduced at 300°C for 5 min. Pd catalysts were tested in the oxidation of methane, ethane and propane using a reaction mixture containing either 1% or 0.1% hydrocarbon in air. Flow experiments were performed using 100 cm^3 min^{-1} of the reactant mix over 50 mg catalyst. In one set of experiments the catalyst was pre-reduced at 300°C for 30 min and the activity measured at this temperature for 15 min after the introduction of the reaction mix. These experiments were performed using 1 and 0.1% methane, and 0.1% ethane. A second set of flow experiments was performed on samples which had been pre-oxidised for 1 h at 500°C and cooled to reaction temperature in N_2. The activity was measured for 1 h after the introduction of the reaction mix (0.1% hydrocarbon in air) both at 300 and 250°C. Pulse experiments were also performed on pre-oxidised samples. In this case 10 mg of catalyst was used and 0.5 cm^3 pulses of 0.1% hydrocarbon in air were injected over the catalyst in a stream of either air or N_2 (50 cm^3 min^{-1}) at 250°C. The effect of water on the methane combustion reaction was studied over the palladium catalyst. In this case 50 mg of catalyst was allowed to reach steady state at 300°C in 1% methane/air. Water was introduced by passing the air flow through a saturator containing water at room temperature to give a water concentration of 2.7%. The activity was measured prior to, during and after the addition of water. Oxygen uptake experiments were also performed on both Pt and Pd catalysts. These were carried out in a vacuum system. The catalysts were first reduced at 300°C for 30 min in H_2 before introducing 10 Torr of O_2, also at 300°C. The pressure decrease was measured with time and the oxygen uptake calculated.

3. Results

Fig. 1 and Fig. 2 show, for Pt and Pd, respectively, oxygen uptake and methane conversion with time for pre-reduced samples. For the platinum catalyst (Fig. 1) the methane conversion is initially zero but rises quickly, passing through a maximum about 10 s after the introduction of the reaction mixture. The activity declines rapidly over the next 15 s and has reached a steady value by the end of the 60 s pulse. The oxygen uptake on the reduced catalyst reaches a steady maximum value of about 65% of a monolayer within 20 s. Thus, the surface of the catalyst is not fully oxidised during the passage of the pulse. It is also of note that the maximum methane conversion is seen at a time before the oxygen uptake is complete.

The results of similar experiments on the palladium catalyst are shown in Fig. 2. As with platinum the initial activity is low. However, for palladium the activity continues to rise over a period of ca. 7 min before reaching a plateau. There is no activity peak. The oxygen uptake on the reduced palladium catalyst shows that a monolayer of oxygen is taken up almost immediately. The uptake of oxygen then increases continually over a period of 10 min at which point an equivalent of almost 4 monolayers has been taken up.

Fig. 3 shows the change in methane and ethane conversion with time for a pre-reduced palladium catalyst. For both hydrocarbons there is an increase in conversion with time before a plateau is reached within ca. 3 min. Note that the initial activity for ethane may be slightly higher than for methane. However, it is apparent that at steady state the activity for ethane is *lower* than that for methane. This is surprising since methane is expected to be the least reactive hydrocarbon.

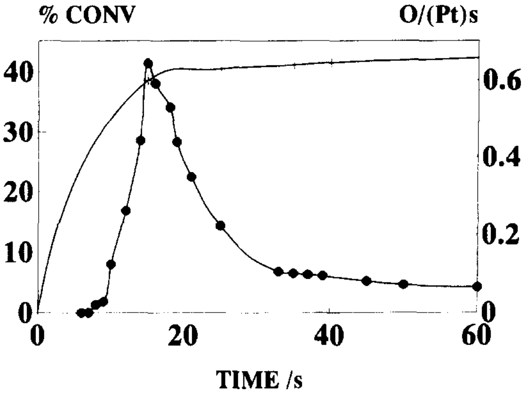

Fig. 1. Oxygen uptake (+) and CH_4 conversion (·) against time for a pre-reduced Pt/Al_2O_3 catalyst.

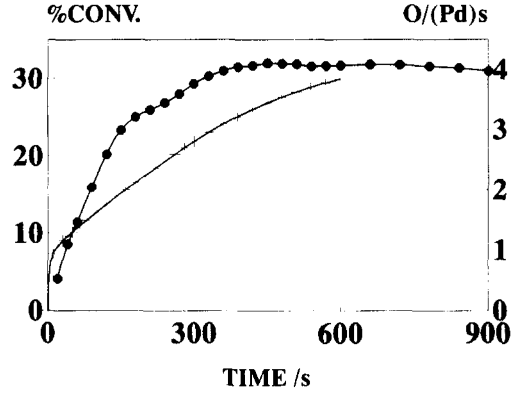

Fig. 2. Oxygen uptake (+) and CH_4 conversion (·) against time for a pre-reduced Pd/Al_2O_3 catalyst.

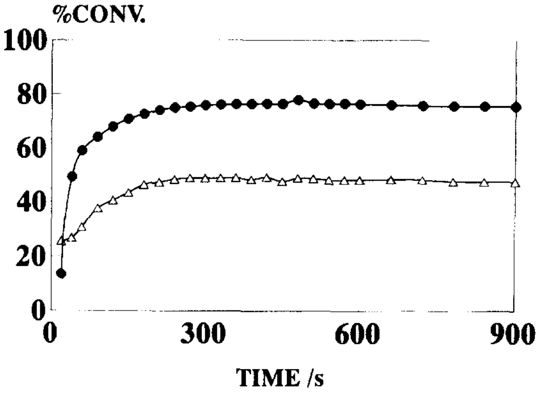

Fig. 3. Conversion against time for a pre-reduced Pd/Al_2O_3 catalyst. (·) methane; (△) ethane.

Fig. 4 shows the results of continuous flow experiments on a pre-oxidised palladium catalyst for methane, ethane and propane at both 250 and 300°C. For each hydrocarbon and at both temperatures the activity initially falls quickly before reaching a steady state. At both temperatures the activity towards ethane is again seen to be lower than for methane. Propane conversion is higher than that for ethane at both temperatures but at the lower temperature is seen to be less than methane conversion whilst at the higher temperature it is

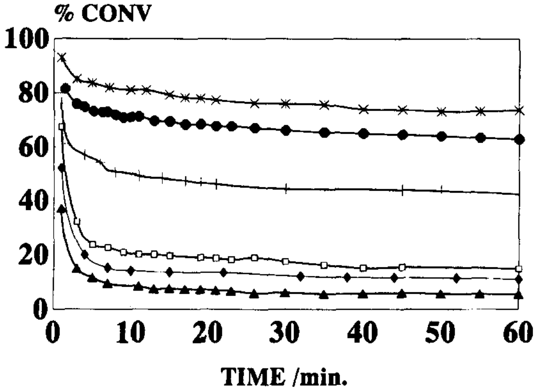

Fig. 4. Combustion of hydrocarbons with time for a pre-oxidised Pd/Al$_2$O$_3$ catalyst. (·) CH$_4$, 300°C; (+) C$_2$H$_6$, 300°C; (∗) C$_3$H$_8$, 300°C; (□) CH$_4$, 250°C; (▲) C$_2$H$_6$, 250°C; (♦) C$_3$H$_8$, 250°C.

higher than for methane. These results are again not consistent with the expected reactivity of the hydrocarbons.

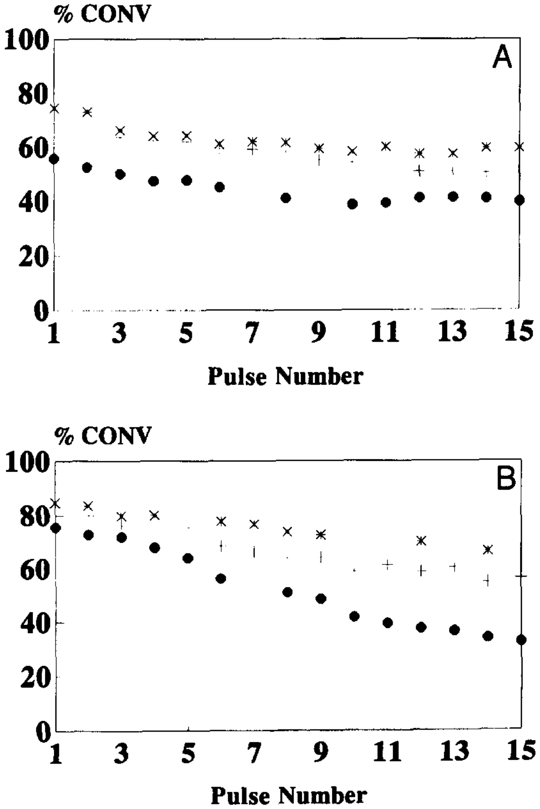

Fig. 5. (a). Combustion of hydrocarbons over a pre-oxidised Pd/Al$_2$O$_3$ catalyst. Change in activity with number of 0.5 cm^3 pulses of reaction mixture introduced into flowing air. (·) CH$_4$; (+) C$_2$H$_6$; (∗) C$_3$H$_8$. (b). Combustion of hydrocarbons over a pre-oxidised Pd/Al$_2$O$_3$ catalyst. Change in activity with number of 0.5 cm^3 pulses of reaction mixture introduced into flowing N$_2$. (·) CH$_4$; (+) C$_2$H$_6$; (∗) C$_3$H$_8$.

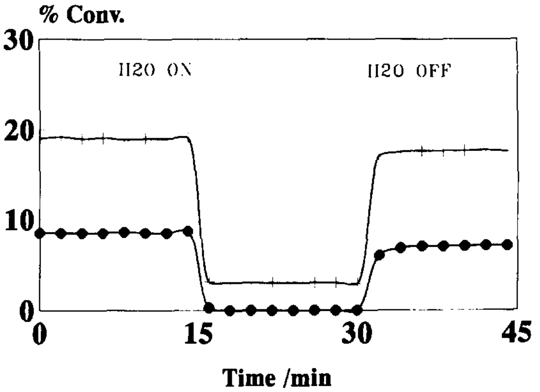

Fig. 6. Effect of water on the combustion of methane over Pd/Al$_2$O$_3$. (·) 275°C; (+) 300°C.

Fig. 5(a) and Fig. 5(b) show the results of experiments in which 0.5 cm^3 pulses of reaction mixture were injected over the pre-oxidised palladium catalyst kept in a stream of air and N$_2$, respectively. These experiments were designed to investigate the catalyst after very short exposures to the reaction mixture. In both cases the conversion of the hydrocarbons follows the expected trend, i.e., propane > ethane > methane.

Fig. 6 shows the results of experiments in which water was added to the reaction stream during methane oxidation over a palladium catalyst which had been allowed to reach steady state. It is clear that at conversion levels similar to those seen in the lower part of Fig. 4 water inhibits the reaction, although the effect is reversible, as when the water is switched off the conversion returns to its initial value. It is also of note that the extent of inhibition is greater at 275°C than at 300°C, i.e., conversion is zero at the lower temperature. A similar poisoning effect has previously been found for the high conversion levels seen in Fig. 4 and Fig. 5 [13]. In this study, the effect of water was again found to decrease with increasing temperature.

4. Discussion

The literature on catalytic combustion of hydrocarbons on platinum group metals is confused and many different active sites and surface oxygen species have been considered to be important. As summarised in the Introduction, earlier work has attributed special significance, for example, to chemisorbed oxygen, partially oxidised palladium, palladium oxide on a metallic core. Our results can be used to differentiate between these various alternatives.

The results shown in Fig. 1 and Fig. 2 illustrate clearly the differences between platinum and palladium catalysts, both in terms of the nature of the active surface and the oxidation capacity. It is clear that for both catalysts a clean metal surface shows low activity. For platinum, the maximum oxygen uptake corresponds to less than 70% of a monolayer. In addition, methane conversion reaches a maximum when the coverage of oxygen is ca. 50% of a monolayer but decreases upon further oxygen uptake. Although not shown in Fig. 1, it was also found [14] that the carbon balance was initially lower than 100% but rose to greater than 100% after the conversion maximum. It is clear, therefore, that maximum activity occurs at a time at which both oxygen and carbon are present on the surface. At later times the surface is poisoned by oxygen. This is in agreement with previous work [2–4] both for methane and higher hydrocarbons. Such a balance between adsorbed species has also been found when starting from an oxidised surface [14] and has been used to explain the light-off phenomenon on platinum catalysts which, under stoichiometric conditions, leads to a greater activity than on palladium catalysts.

The results obtained with palladium (Fig. 2) show that, unlike platinum, a monolayer of oxygen is taken up very quickly. At this point the methane conversion is low. This indicates that chemisorbed oxygen on palladium is not particularly active. As the oxygen uptake increases and bulk oxidation proceeds the methane conversion continues to rise, reaching a plateau when the oxygen uptake corresponds to ca. 3 monolayers. As oxidation continues the activity maintains a steady level. This indicates that bulk oxidation of palladium may not be detrimental to activity as has been suggested previously [3]. It seems more likely from our results that bulk palladium oxide is of comparable, or higher, activity than partially oxidised palladium particles. Moreover, we find no evidence of a special activity for palladium oxide on a metallic palladium core. Equally, our results suggest that earlier reports that small palladium oxide particles have low activity may be due to other effects, such as deactivation due to interaction with the alumina support.

The need for an oxidised palladium surface for methane combustion has been established. Fig. 3 shows that a similar surface is required for ethane combustion as the activity of the pre-reduced catalyst initially increases. However, whilst the initial activity for ethane is higher than that for methane, at steady state the methane conversion is higher. If the ease of activation of the hydrocarbon were the only important factor this would not be the case. The results shown for methane, ethane and propane over a pre-oxidised catalyst (Fig. 4) further indicate that other factors are present. Thus, at both temperatures the ethane conversion is the lowest. In addition, at 250°C propane conversion is also less than that for methane, although at 300°C propane conversion is higher. In addition there is an initial rapid deactivation on introduction of the reactants. Again it is clear that the ease of activation of the hydrocarbon is not the only factor operating in this system.

In order to investigate the behaviour of the catalyst at very short times on stream the pulse experiments shown in Fig. 5 were carried out. In this case the order of activity of the hydrocarbons is that which would be expected considering their ease of activation ($CH_4 < C_2H_6 < C_3H_8$). Thus it appears that the reaction is affecting the surface of the catalyst and changing its properties. As shown in Fig. 6, and previously mentioned [13], water can poison Pd catalysts at all the conversion levels reported in Fig. 4 and Fig. 5. Therefore, it is possible that water from the reaction is an important factor in determining the catalytic activity. This effect of water may be to influence the following equilibrium:

$$\underset{\text{(active)}}{PdO} + H_2O = \underset{\text{(inactive)}}{Pd(OH)_2}$$

If this is correct, and since the active site being poisoned will be the same in each case (PdO), the poisoning effect would be expected to be greater for higher hydrocarbons which will produce more water per mole of reactant converted. This could explain the results obtained for methane and ethane. However, propane shows higher conversion than ethane. It appears therefore that there is a balance between poisoning of the surface by water and the ease of activation of the hydrocarbon. For ethane, water is the most important factor: for propane the ease of activation dominates, but even this depends on the exact experimental conditions since at lower temperatures the activity for methane combustion is highest. This can be explained by the fact that the effect of water is greater at lower temperatures. Thus, at 275°C the effect of water is sufficient to pull the activity for propane combustion below that for methane.

In conclusion, the results of this study show that there are two possible explanations for the trend in activity of Pd and Pt catalysts towards alkanes. One is that the ease of oxidation of the palladium surface inhibits the adsorption of the hydrocarbon in all cases except methane. Another explanation is that water produced in the reaction poisons the Pd catalyst. Thus the apparent high activity of Pd towards methane is in fact a reflection of the low activity towards higher alkanes.

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