

# C–H bond activation in hydrocarbon oxidation on solid catalysts

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Received 1 June 1995

## Abstract

The activation of C–H bonds in saturated hydrocarbons is the crucial step in several different types of oxidation reaction on a variety of catalysts and could occur through homolytic or heterolytic mechanisms. From the available evidence it appears that the heterolytic mechanism, with the extraction of a proton, is the most likely process on oxide catalysts and this may also apply to metallic catalysts under typical (oxidising) reaction conditions. However, the state of oxidation of a metallic surface under reaction conditions is complex and the degree of oxidation will depend on the metal, the temperature, the oxygen partial pressure, the metal particle size, the support and the choice of hydrocarbon. The importance of coadsorbates in facilitating the dissociative adsorption of saturated hydrocarbons seems to be well established and could explain the unusual enhancement of activity observed for the oxidation of some saturated hydrocarbons when inorganic gases, such as SO<sub>2</sub>, are added to the reaction mixture. The inhibition by products of the oxidation reaction (CO<sub>2</sub> and H<sub>2</sub>O) can be quite severe, but H<sub>2</sub>O has by far the greatest effect. This is interpreted in terms of an equilibrium involving the formation of surface hydroxide ions which are considered to be inactive for activation of C–H bonds. As a consequence, it is possible, especially at low temperatures, that the rate determining step in C–H bond activation could be the regeneration of the active sites, through desorption of H<sub>2</sub>O, rather than C–H bond activation as is commonly assumed. The activation of C–H bonds by NO<sub>2</sub> is addressed in the context of selective reduction of NO<sub>x</sub> by hydrocarbons on various types of oxide catalyst and possible similarities with the promotion of the C–H bond activation process by SO<sub>2</sub> are discussed.

## 1. Introduction

The activation of C–H bonds in saturated hydrocarbons is a key step both in functionalisation and the combustion of many organic compounds. There is already considerable interest in the functionalisation of saturated hydrocarbons to manufacture valuable products such as synthesis gas (catalytic partial oxidation of methane), alkenes (oxidative dehydrogenation and methane coupling), oxygenates, eg., acids (partial oxidation of ethane to acetic acid), anhydrides (butane to maleic anhydride) and alcohols (ethane to eth-

anol). In addition, there is a need to find effective routes for upgrading lower hydrocarbons to manufacture liquid fuels (propane to higher hydrocarbons) or more easily transportable materials (methane to methanol). On top of these 'constructive' transformations, the total oxidation (combustion) of hydrocarbons is important as a way of generating heat and power. Catalytic combustion is being seriously considered as a clean technology approach to power (methane for gas turbines) and heat generation in various industrial processes.

In all these cases the key step in the catalytic reaction will be the activation of the first C–H bond in the saturated hydrocarbon. Once this bond

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has been broken, sequential reactions to intermediates or products will generally be relatively fast. It is important, therefore, to understand how C–H bonds in saturated compounds are activated. This is not an easy question to address given the wide range of hydrocarbons available, the variety of products formed, and the many different types of catalyst which may be used (metals, reducible oxides, nonreducible oxides, basic oxides, and acidic oxides including zeolite-based systems). The purpose of this contribution is to review C–H bond activation on various types of catalyst, to examine the evidence relating to the nature of the active sites and the reaction mechanism, to highlight trends and characteristic features for different types of catalyst, and to assess the effect of promoters/modifiers and poisons/inhibitors on hydrocarbon activation.

The scope of the presentation will be restricted since there is an enormous literature on hydrocarbon oxidation reactions. Therefore, we shall exclude any discussion of chemical processes involving oxygen insertion, such as propene to acrolein or acrylonitrile, butane to maleic anhydride, etc., since these are topics which have often been reviewed at great length in the past. Instead, we shall concentrate on hydrogen-abstraction processes such as: methane coupling; oxidative dehydrogenation; and total oxidation (combustion).

## 2. Oxide-based catalysts

Since the publication of the pioneering work of Keller and Bhasin [1] much research effort has been directed towards the development of oxide catalysts for the selective partial oxidation of methane to chemical products of higher value. Many hundreds of papers have been published in this area and thorough reviews of the relevant literature are also available. [2–6]

General agreement exists that the initial step in the activation of methane over these catalysts involves surface assisted hydrogen abstraction resulting in the formation of methyl radicals. [7–

11] Lunsford and co-workers have employed the technique of matrix isolation electron spin resonance (MIESR) to directly measure methyl radical production, [7–9] indicating that only one of the methane C–H bonds is broken in the initial dissociative adsorption.

There is still disagreement, however, regarding the nature of the C–H bond breaking step and also the nature and role of the active oxygen species. The most probable mechanisms for C–H bond breaking involve either heterolytic splitting, resulting in deprotonation and the formation of methyl carbanions ( $\text{CH}_3^-$ ) which undergo further reaction with oxygen to yield methyl radicals [12–14], or homolytic splitting involving abstraction of a hydrogen radical by a partially reduced oxygen species. [15,16]

Support for the heterolytic mechanism has been presented by Choudhary and Rane [13] who have monitored the acid and base strength distribution for a series of rare-earth metal oxides. It is concluded that the methane conversion of the catalysts is related to both the catalyst acidity and basicity. The relationship between the observed catalytic trends and the acid and base properties of the solid is thought not to be trivial. Table 1 shows the results obtained from an attempt to correlate activity for methane conversion with acidic or basic properties. Since no simple correlation was found it was proposed that both the acidic and basic properties were important simultaneously. The results were therefore rationalised by invoking the occurrence of a surface acid–base pair, comprising a metal cation (the acidic site) and an oxygen anion (the basic site). Such an acid–base pair of sufficient strength is thought to bring about heterolytic splitting of the C–H bond resulting in  $\text{CH}_3^-$  ions and protons which interact with the surface acid and base sites, respectively. Fig. 1 shows a representation of the heterolytic splitting mechanism as suggested by Choudhary and Rane [13].

Sokolovskii [14] has suggested that one of the necessary characteristics of a selective catalyst for hydrocarbon oxidation is its ability to provide nucleophilic oxygen to assist in the heterolytic

splitting of the C–H bond. It is suggested that the less polar the C–H bond the stronger the basic site required for its activation and the higher the optimum reaction temperature. Stone and co-workers [12] have previously presented convincing evidence from ESR, IR and UV studies for the heterolytic dissociative chemisorption of unsaturated hydrocarbons such as acetylene, propene and 1-butene on MgO. Electron transfer from the carbanion to O<sub>2</sub> leading to formation of O<sub>2</sub><sup>−</sup> and the corresponding hydrocarbon radical has also been suggested by this group. Recently, Finocchio et al. [17] have also concluded that C–H bond cleavage most likely occurs by heterolytic splitting at a cation–oxide anion couple, with the proton linking to the oxide ion.

Activation of methane by heterolytic splitting of the C–H bond has also been proposed by Ito et al. [18] on the basis of ab initio molecular orbital calculations and the chemisorption behaviour of CH<sub>4</sub> towards well-degassed MgO. The model of the active site proposed is similar to that suggested by Choudhary and Rane [13] and consists of an adjacent pair of low co-ordination Mg<sup>2+</sup> and O<sup>2−</sup> sites which can respectively accommodate the methyl anion and proton derived from heterolytically dissociated CH<sub>4</sub>.

Heterolytic splitting is *not* considered to be important by some authors, however. Since the C–H bond in methane is only very weakly acidic (pK<sub>a</sub> = 46) it follows in this case that sites capable of deprotonation must be very strongly basic. Consequently, it has recently been suggested by Lunsford and co-workers [19] that such strongly

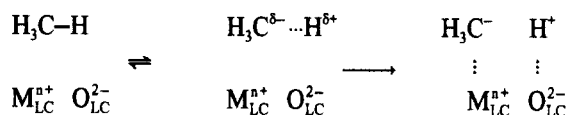


Fig. 1. Schematic representation of the formation of methyl radicals by heterolytic splitting of the methane C–H bond by a surface acid–base pair, after ref. [13]. M<sub>LC</sub><sup>n+</sup> and O<sub>LC</sub><sup>2−</sup> signify low co-ordination metal cation and oxygen anion sites which act as Lewis acid and Lewis base sites, respectively.

basic sites will more readily adsorb CO<sub>2</sub> (a by-product of the coupling reaction) and so may become quickly deactivated and therefore be of little relevance when considering the catalytic system operating at steady state. Evidence from H–D isotopic exchange reactions, which are known to occur via the heterolytic splitting of C–H and C–D bonds, over a Ba/MgO catalyst has shown that even a very low partial pressure of CO<sub>2</sub> is sufficient to cause almost complete poisoning of the exchange reaction. It is therefore concluded that there are very few surface sites on the surface of Ba/MgO which are sufficiently basic to deprotonate methane. These sites are highly susceptible to poisoning by catalytically produced CO<sub>2</sub> and are therefore thought to be unimportant when considering steady state reaction conditions.

Lunsford and co-workers [15] have also questioned the ability of the O<sub>2</sub><sup>−</sup> species formed during heterolytic activation to survive during the 500°C vacuum heating which their Li/MgO catalyst underwent prior to carrying out a matrix isolation EPR measurement. Their contention is that the CH<sub>3</sub> radicals produced on reaction of CH<sub>4</sub> with O<sub>2</sub> over MgO were formed by direct homolytic

Table 1  
Comparison of the surface and catalytic properties of the rare-earth metal-oxide catalysts, after ref. [13]

Catalyst	Surface area /m <sup>2</sup> g <sup>−1</sup>	CO <sub>2</sub> chemisorption (μmol g <sup>−1</sup> )		NH <sub>3</sub> chemisorption /μmol g <sup>−1</sup>	CH <sub>4</sub> conv./%
		323 K	773 K		
La <sub>2</sub> O <sub>3</sub>	3.8	91.2	55.9	1.69	24.8
CeO <sub>2</sub>	3.0	31.8	13.6	0.41	16.7
Sm <sub>2</sub> O <sub>3</sub>	3.9	39.2	4.5	0.38	24.0
Eu <sub>2</sub> O <sub>3</sub>	4.9	77.0	19.6	0.25	22.8
Yb <sub>2</sub> O <sub>3</sub>	1.8	37.5	11.7	1.09	12.9

Reaction conditions: 0.1 g catalyst. CH<sub>4</sub>/O<sub>2</sub> ratio = 4. Total gas flow rate = 180 cm<sup>3</sup> min<sup>−1</sup>. Temperature = 1123 K.

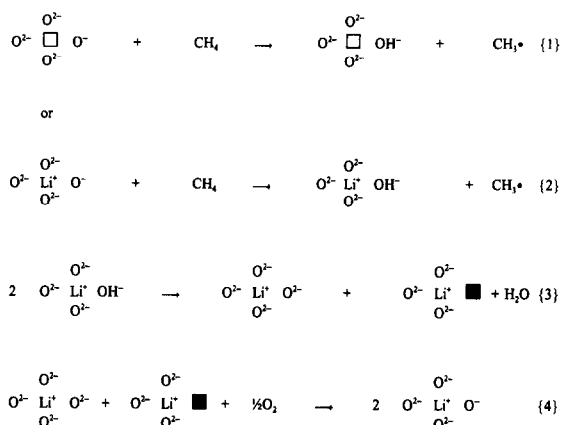


Fig. 2. Schematic representation of the catalytic cycle showing direct methyl radical production by H<sup>•</sup> abstraction from CH<sub>4</sub> by an O<sup>-</sup> species, after ref. [15] □ and ■ represent cation and anion vacancies respectively.

cleavage of the C–H bond by O<sup>-</sup> ions which are thermally formed at catalyst defect sites. The O<sup>-</sup> ions are thought to be present as [Li<sup>+</sup>O<sup>-</sup>] centres on the surface of the Li/MgO system. Fig. 2 shows a representation of their mechanism for C–H bond activation in CH<sub>4</sub>. Various groups [20–28] have used transient kinetic techniques to investigate the nature of the surface oxygen which is responsible for the activation of C–H bonds in methane and the role of lattice oxygen has been examined and it has been concluded that lattice oxygen may play an important role in the activation of the C–H bonds in methane.

Lapszewicz and Jiang [29] have also cast doubt on the activation of methane by a heterolytic mechanism. They argue that if activation occurs by heterolytic scission of a C–H bond then the rate of methane conversion should closely correlate with the rate of deuterium exchange. The results presented show that no such correlation exists and the conclusion is that the ability of the catalyst to effect heterolytic dissociation is not related to its ability to couple methane. The authors note that most selective coupling catalysts are strongly basic and conclude that dissociative adsorption of methane may be an important factor in a sequence of steps leading finally to the formation of methyl radicals. Clearly the situation concerning the key step in the mechanism for C–H bond activation is still confused.

Recent work carried out in our laboratory [30] on the effect of substituting a fluorocarbon for methane on the observed rate of conversion under methane coupling reaction conditions have clearly shown an increase in rate by up to an order of magnitude over basic oxides such as Sm<sub>2</sub>O<sub>3</sub> and 3% Li/MgO. Representative results are shown in Table 2. These results are consistent with the initial activation step being a deprotonation since the fluorine would be expected to have the effect of stabilising a transition state of the form FH<sub>2</sub>C<sup>δ-</sup>...H<sup>δ+</sup>. This lowers the energy barrier to reaction and is reflected as a large increase in rate. It would be expected that if the rate determining step for methane activation involved a homolytic abstraction of a hydrogen radical the rate of conversion would remain unaffected by the introduction of a fluorine atom into the molecule. Interestingly, no evidence for the production of coupling products (e.g. C<sub>2</sub>H<sub>4</sub>F<sub>2</sub>) is observed on substitution of CH<sub>4</sub> with CH<sub>3</sub>F over any of the oxides studied. This is consistent with the comment of Sokolovskii [14] that for compounds with more polar C–H bonds a shift towards less basic oxides is desirable to facilitate the coupling reaction.

### 3. Metal-based catalysts

The catalytic combustion of hydrocarbons has attracted much attention because on the one hand it offers the possibility of a ‘clean technology’

Table 2  
Comparison of the extent of conversion of CH<sub>4</sub> and CH<sub>3</sub>F on some oxide catalysts

	Conversion/%
Sm <sub>2</sub> O <sub>3</sub> (10 mg, 650°C)	
CH <sub>4</sub>	2.75
CH <sub>3</sub> F	14.7
3% Li/MgO (50 mg, 750°C)	
CH <sub>4</sub>	3.0
CH <sub>3</sub> F	33.6

Reaction conditions: 110 cm<sup>3</sup> min<sup>-1</sup> N<sub>2</sub>, 5 cm<sup>3</sup> min<sup>-1</sup> CH<sub>4</sub> or CH<sub>3</sub>F. 5 cm<sup>3</sup> min<sup>-1</sup> air, 1 bar pressure.

approach to the generation of heat and power while on the other hand it provides a means of removing hydrocarbons from exhaust gases. The high activity required at moderately low temperatures has meant that for such applications the choice of active catalyst has been restricted to the platinum group metals, and to Pt and Pd in particular. In general it is found that Pt is the most active catalyst although in the specific case of methane oxidation Pd oxide has a much higher activity than Pt. However, as we shall see later, Pd is also more susceptible to poisoning and so may not be the best choice even for methane oxidation in real situations. Additional factors in real emission conditions are the possibility of nitrogen oxides (NO<sub>x</sub>) being an oxidant (see later) and the effect of water, which is always present in exhaust gases, on the activity of the catalyst.

There have been many different studies on hydrocarbon combustion on platinum group metal catalysts but there is still not universal agreement about the nature of the active site, the role of the support, morphological effects, or the influence of anionic species such as halide or sulphate ions. It is generally concluded that the rate determining step is the activation of the first C–H bond and evidence for this has come from a comparison of the rate of oxidation of CH<sub>4</sub> versus CD<sub>4</sub> which shows a primary kinetic isotope effect [31]. However, this is not a unique interpretation since a kinetic isotope effect would also be observed in any step in the reaction process in which a bond to a hydrogen (deuterium) atom is broken. For example, the desorption of H<sub>2</sub>O, a product of the oxidation reaction, will involve breaking an O–H bond. As we shall see later for Pd catalysts this may be quite a slow step and could be rate determining especially at lower temperatures.

The activation of the first C–H bond is nevertheless a difficult process, especially for methane. The constraints on the active site required for this could be quite demanding which may be the reason why the activity of platinum group metal catalysts seems to be so sensitive to morphological effects [32–37]. Since there is no doubt about the relative difficulty of activating the first C–H bond

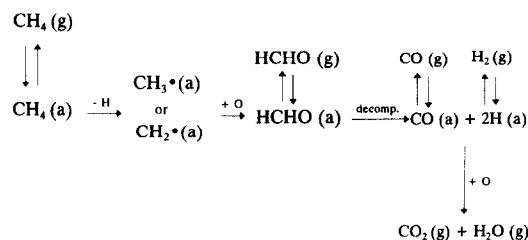


Fig. 3. Reaction scheme proposed for methane oxidation after ref. [38].

in saturated hydrocarbons (as compared to the activation of subsequent C–H bonds in the same molecule) the questions, of which there are many, which require attention all relate to the nature of the active surface. Is the active site a zerovalent metal atom, or a cluster of metal atoms? Is it a metallic surface covered with chemisorbed oxygen? Is it a fully oxidised metal particle? Is it a partially oxidised metal particle on a metallic core? Is it located on specific surface planes? Are there special active sites at the metal/support interface? Are active sites promoted by sulphur oxides and if so how does this occur? Is the active site different for different elements (Pd versus Pt, for example)? Do small metal particles contain more or less active sites per unit area than large particles?

Methane is not a typical hydrocarbon but because of the widespread availability of natural gas there has been much attention given to studying platinum group metal catalysts for methane combustion. Therefore, we first consider the information available on C–H bond activation in this reaction. On a metallic catalyst, in the absence of any adsorbed species, the only option for C–H bond activation is homolytic splitting with the fragments (H and CH<sub>3</sub> becoming adsorbed on adjacent metal atoms. Indeed, Oh et al. [38] have suggested just such a reaction scheme as shown in Fig. 3. In this model they envisage a preadsorption equilibrium involving undissociated CH<sub>4</sub>, from which various adsorbed CH<sub>x</sub> species are formed. This could be a feasible mechanism when there is very little oxygen in the reaction mixture but seems unlikely under oxygen-rich conditions since O<sub>2</sub> adsorption is so fast that the surface of

the metal particles will be covered with adsorbed oxygen species.

When electronegative adsorbed species such as oxygen are present, heterolytic splitting (to give  $H^+$  and  $CH_3^-$ ) also becomes possible, as discussed earlier for other types of bulk oxide catalyst. However, when a metal surface is fully covered with anionic species (e.g., at full monolayer coverage of oxygen) homolytic splitting again becomes the only option unless the partially positively charged metal ions are exposed at the surface. In view of the earlier discussion of C–H bond activation on oxide catalysts of various kinds it might be expected that heterolytic splitting would be favoured, in which case it would be expected that the activation of C–H bonds would go through a maximum as the surface coverage with oxygen increases from zero to monolayer coverage. We shall see later that this is indeed observed for Pt catalysts.

Since C–H bond activation, through a heterolytic mechanism, is likely to be relatively facile on metal surfaces containing *some* oxygen it is relevant to review what is known about the interaction between oxygen and metallic Pt or Pd, and also to consider whether different forms of surface oxygen might have different reactivities. Under dynamic reaction conditions in methane combustion Pt is likely to be present in the form of metallic particles covered to varying extents with adsorbed oxygen, which may take different forms and have different reactivities [35]. Single crystal studies illustrate the complexity of the interaction of oxygen with Pt surfaces. A Pt(100) single crystal surface [39] adsorbs oxygen very slowly on the  $(5 \times 2)$  surface but causes the surface to reconstruct to  $(1 \times 1)$  because of place exchange between Pt atoms in the first two surface layers. Oxygen penetration below the surface is *not* thought to be responsible for this structural transformation [40]. The different co-ordination numbers of Pt on the  $(5 \times 2)$  and  $(1 \times 1)$  surfaces is thought to account for the fact that oxygen adsorption on the  $(1 \times 1)$  surface is much faster [41]. At ca. 300°C, the uptake of oxygen is initially quite random and saturation is attained between 0.6 and

1 monolayer with two or three different states of adsorbed oxygen being observed, one of which may result from partial oxidation of the surface [40,42,43].

The Pt(111) surface is found to adsorb oxygen at low temperature resulting in a regular  $(2 \times 2)$  LEED pattern at a saturation coverage of 0.25 monolayers [44–49]. It has been proposed that the oxygen adsorption site is the f.c.c. hollow in the  $(2 \times 2)$  hexagonal surface layer [45]. The stoichiometry of oxygen chemisorbed on to (111) planes is  $Pt_2O$ , compared with PtO on (100) planes [50], which, interestingly, matches the stoichiometries suggested for real catalysts given mild [51] and severe [52] reduction treatments, respectively.

On Pt(110) surfaces oxygen adsorbs with a saturation coverage of 0.25 monolayers [53,54]. It is thought that the oxygen adsorbs first on  $[1\bar{1}0]$  rows between the (111) micro-facets and then at higher coverages adsorption occurs on 3 co-ordinate sites on the (111) micro-facets. The saturated surface shows LEED patterns for more than one type of surface structure [54]. Thus, on this particular surface the proportion of oxygen adsorbed on different sites, and thus the relative amounts of different forms of surface oxygen, changes with coverage.

Stepped surfaces composed of (100) or (111) terraces are generally found to adsorb more oxygen than non-stepped planes [44,47,55–58] and adsorption occurs preferentially on the steps. The saturation density for such surfaces is found to closely follow the density of steps sites [55]. The stoichiometry of the oxygen adsorbed at steps may vary from one oxygen atom for every alternate step Pt atom [56] to microdomains corresponding to  $PtO_2$  [57]. The structure of the adsorbed oxygen on the terraces may also change depending on the size of the terraces and whether or not these are separated by kinked steps [47,58,59].

Clearly, many different forms of adsorbed oxygen can be observed even on Pt single crystals and this complexity is further exacerbated by the variability of the structure of small metal particles on real catalysts. TEM analysis [51] of supported Pt

catalysts given a short or a long reduction at 500°C shows that a short reduction leads to particles with poorly defined shapes whereas a long reduction gives particles with regular geometric shapes having (100) and some (111) faces. Similar changes in the overall shape of Pt particles has been reported [60–63] although the exact detail of the final shape seems to differ from one study to another. In general, these studies show that a prolonged high temperature reduction causes some equilibration of the surface by allowing the formation of low index planes which have the least degree of surface anisotropy. Catalysts reduced at low temperatures may contain a bi-modal distribution of small and large Pt particles with the former being undetected by TEM [64]. Additional complexity comes from the fact that very small Pt particles may be strongly interacting with the support and may not therefore exhibit normal catalytic properties. For example, evidence has been presented [65] for a highly dispersed catalyst of 5 atom clusters of Pt in which four of the atoms are in contact with the support.

In summary, it would not be surprising to find that morphological effects, reflected in a variability in the form, and hence the reactivity, of adsorbed oxygen, could affect the efficiency of Pt catalysts for C–H bond activation, especially since it is very probable that this involves a dissociative adsorption which is very demanding of the nature of the active site. The active site required for C–H bond activation has been considered by a number of workers but little agreement has been reached. Some groups [33,34,66,67] have concluded that the *metal* is more active than the *bulk oxide*. Thus, Yao [66] has found a Pt/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst to be less active than a Pt wire for methane oxidation and concluded that Pt in an oxidised state is a less active catalyst. Hicks et al. [33] have suggested that their most active catalysts contain crystalline Pt whereas catalysts containing mainly dispersed phase Pt are up to two orders of magnitude less active. They conclude that the dispersed Pt can be fully oxidised to give PtO<sub>2</sub> particles whereas the large Pt particles only chemisorb oxygen, from which it is proposed that

bulk Pt oxide has a low activity whereas chemisorbed oxygen on Pt is active. Similarly, Drozdov et al. [68] have reported that the heat of adsorption of oxygen on Pt metal is lower than for adsorption on Pt oxide so that the metal would be expected to be more active. Support for this proposal comes from work of Niwa et al. [69] and Briot et al. [35] who have found that the most active catalysts contain the most reactive oxygen as determined by titration with hydrogen at low temperature.

The importance of Pt in the metallic state, as indicated by these results, is not entirely consistent with other kinetic data [66,68,70] which show that the methane combustion reaction is close to first order in methane but zero order in oxygen at high oxygen partial pressures but negative order in oxygen at low oxygen partial pressures. These kinetic results have been interpreted in terms of a competition between oxygen and methane for adsorption sites. At high oxygen partial pressures the methane cannot compete effectively and so the rate of reaction will be independent of the oxygen partial pressure. However, at low oxygen partial pressures, where methane can compete more effectively, both the oxygen and methane partial pressures will be important. This suggests that adsorption of both reagents simultaneously is favourable, a conclusion reached by Yao [66] and Trimm and Lam [71] who propose that the reaction occurs by a Langmuir–Hinshelwood mechanism involving adsorbed oxygen and adsorbed methane. Although this proposal involving co-adsorption of the reactants seems entirely sensible it does not clarify how the C–H bond is activated and it remains to be seen what type of active site is preferred for this crucial initial bond breaking step.

We have investigated this question using pulse and gas switching experiments, coupled with oxygen adsorption experiments, in order to determine whether metallic Pt, or fully oxidised Pt, or some intermediate state is optimum for the activation of C–H bonds in CH<sub>4</sub> [72]. Fig. 4 shows the variation in the methane conversion as a function of time on stream for a 2% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst pre-

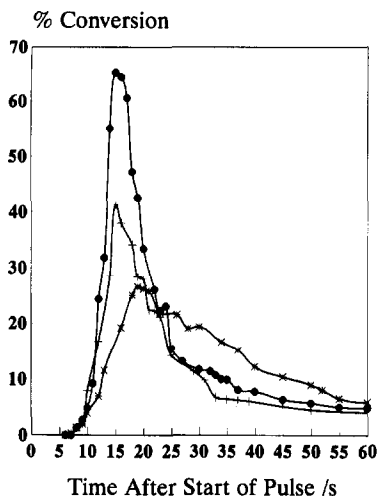


Fig. 4. Methane conversion during the passage of a reactant pulse containing 2000 ppm  $O_2$  and various concentrations of methane over a pre-reduced 2% Pt/ $Al_2O_3$  catalyst. (●) 400 ppm  $CH_4$ ; (+) 1000 ppm  $CH_4$ ; (\*) 2000 ppm  $CH_4$ , after ref. [72].

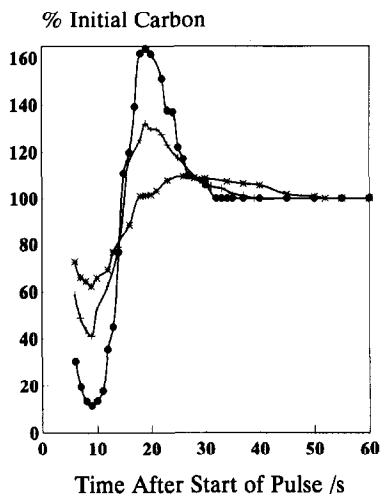


Fig. 5. Total carbon balance during the passage of a reactant pulse containing 2000 ppm  $O_2$  and various concentrations of methane over a pre-reduced 2% Pt/ $Al_2O_3$  catalyst. (●) 400 ppm  $CH_4$ ; (+) 1000 ppm  $CH_4$ ; (\*) 2000 ppm  $CH_4$ , after ref. [72].

reduced at 300°C and then exposed to a gas mixture containing 2000 ppm  $O_2$  and various concentrations of  $CH_4$ . The conversion is determined by the amount of  $CO_2$  detected and as Fig. 5 illustrates the carbon balance shows a carbon loss initially, followed by the detection of excess  $CO_2$  before the catalyst settles down to a steady state conversion and the carbon balance returns to normal. These results indicate clearly that *metallic* Pt is *not* active for  $CH_4$  oxidation but dissociative

adsorption of  $CH_4$  occurs under these conditions. This is not surprising, but what is more significant is that the amount of  $CO_2$  detected goes through a sharp maximum before dropping to a low steady state value. These results are interpreted as evidence that the optimum state for the activation of C–H bonds in  $CH_4$  corresponds to a partially oxidised Pt surface. The metallic Pt is not active because there is no adsorbed oxygen to react with the adsorbed  $CH_x$  species; the fully oxidised Pt surface has only a low activity because the dissociative adsorption of  $CH_4$  on a fully oxygen-covered Pt surface is a slow process. Heterolytic splitting of the first C–H bond, therefore, seems to be favoured.

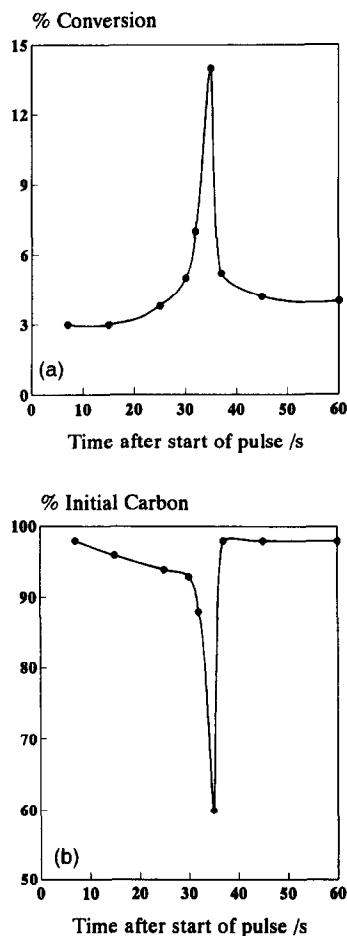


Fig. 6. (a) Methane conversion and (b) total carbon balance during the passage of a reactant pulse containing 2000 ppm  $CH_4$  over a 2% Pt/ $Al_2O_3$  catalyst pre-treated in air. Prior to the experiment the catalyst was reduced at 500°C for 16 h, after ref. [72].



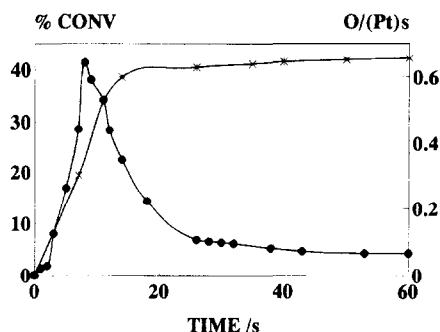


Fig. 7. Plot of oxygen uptake (\*) and  $\text{CH}_4$  conversion (●) against time at  $300^\circ\text{C}$  for a pre-reduced 2 wt.%  $\text{Pt}/\text{Al}_2\text{O}_3$  catalyst, after ref. [73].

When the catalyst is pre-oxidised and then exposed to a pulse of  $\text{CH}_4$  the results presented in Fig. 6(a) were obtained [72]. These results show that the fully oxidised Pt surface is not a very good catalyst for C–H bond activation in  $\text{CH}_4$ . However, with time, the activity increases dramatically to a sharp maximum before dropping back to a low level. The carbon balance through the pulse, shown in Fig. 6(b), shows that there is only a small amount of dissociative adsorption of  $\text{CH}_4$  on a fully oxidised Pt surface, but adsorption increases as the surface becomes partially reduced. These results again seem to confirm that a partially oxidised Pt surface is most active for C–H bond activation.

Fig. 7 [73] compares the oxygen uptake on a pre-reduced Pt surface exposed to 10 Torr of  $\text{O}_2$  at  $300^\circ\text{C}$  with the activity for  $\text{CH}_4$  oxidation at the same temperature. The maximum activity is observed after about 10 s on stream at which point the uptake of oxygen is about half the maximum observed. This is consistent with the ideas developed above and suggests that the preferred site for C–H bond activation comprises a combination of a Pt atom carrying a small positive charge in close proximity to an oxygen atom carrying a small negative charge. Heterolytic splitting of the C–H bond (see earlier discussion) then becomes a viable, and apparently favoured, option.

The activation of the C–H bond in  $\text{CH}_4$  on Pd catalysts is quite different because under normal circumstances the Pd will be in an oxidised state. Thus, PdO is thermodynamically stable in air up

to temperatures approaching  $800^\circ\text{C}$  and can be stabilised to even higher temperatures when promoters such as  $\text{CeO}_2$  are present. At lower oxygen partial pressures PdO decomposes to the metal at lower temperatures. These phase transformations greatly add to the complexity of methane oxidation on Pd catalysts. However, it is slowly becoming possible to identify some important features of the reaction although there is little agreement between published work especially where this relates to the identification of the active state of the catalyst. It is generally agreed that the active state is an oxidised form of Pd but the precise nature of the active site is not yet clear. Some of the confusion in the literature has arisen because it was not fully recognised until recently that catalysts made from chlorine-containing precursors may give anomalous results because chlorine is a severe poison of the combustion reaction. Furthermore, different forms of Pd oxide may have substantially different activities and the morphology of particle size may be critically important. However, confusion can again arise if catalysts with very different loadings of Pd are compared because at very low loadings (ca.  $<0.2\%$  Pd/100  $\text{m}^2$  of support area) the Pd may be fully dispersed on the support in an interacted form (surface 'palladium aluminate', for example) so that it is not appropriate to make comparisons with catalysts containing bulk PdO crystallites.

On the other hand, catalysts prepared using chlorine-free precursors generally contain quite large PdO particles (typically  $>4$  nm) so particle size and morphological effects may not be so important in this case. Nevertheless, several different forms of the active state of oxidised Pd have been proposed, including suggestions that chemisorbed oxygen is the active state, that PdO supported on a metallic Pd core is active, or that fully oxidised PdO is active.

We have undertaken some experiments [74] to try to establish the optimum state of Pd for methane combustion. Fig. 8 shows the variation in activity with time on stream for a 4% Pd/ $\text{Al}_2\text{O}_3$  catalyst pre-treated in different ways. These results show that a pre-reduced sample initially

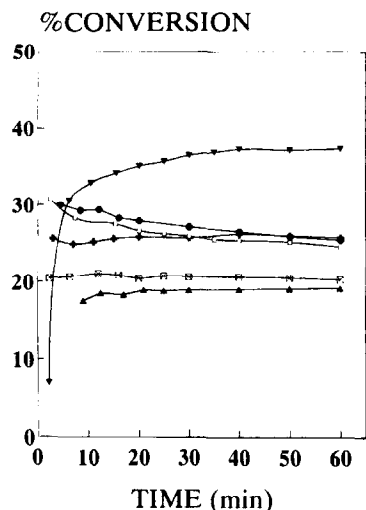


Fig. 8. Variation of the activity for methane combustion with time-on-stream for samples of the 4% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst exposed to various pretreatments for 1 h. (□) Dry air, (×) wet air, (●) nitrogen, (σ) hydrogen, (τ) 1% CH<sub>4</sub>/air, (+) oven, after ref. [74].

has a very low activity and this builds up to quite a high value after about 10 min on stream. In contrast, pre-oxidised samples show higher activities initially but some deactivate slightly with time on stream whereas others tend to be stable but at a somewhat lower activity. The complexity of the palladium system in this reaction is seen in the fact that the pre-reduced and the pre-oxidised catalysts do not end up with the same steady state activity. The effect of the pre-oxidation treatment is interesting. The results seem to show that when heated in a dry atmosphere the catalysts have a higher initial activity but tend to deactivate whereas when heated in wet air or in a 1% CH<sub>4</sub>/air mixture (which will generate water) the activity is lower but the catalyst tends not to deactivate. We shall consider the possible influence of water later.

Comparison with the curves in Fig. 9 show that the increase in activity with time on stream for a pre-reduced catalyst corresponds to the progressive oxidation of the metallic Pd. However, these results also show that the steady state activity, which is attained after 10 min, corresponds to a situation where the Pd has taken up the equivalent of almost 4 monolayers of oxygen (based on the hydrogen chemisorption on the pre-reduced cat-

alyst). Moreover, the activity for the reduced Pd and even for the reduced Pd covered with chemisorbed oxygen is low, showing that the most active form of the catalyst is neither the metallic state nor the metal covered with chemisorbed oxygen. The results also show that as the extent of oxidation of the Pd continues to increase to the point at which bulk PdO is formed the activity levels out and neither increases nor decreases. Clearly, PdO on a core of Pd metal is no more active than bulk PdO in these experiments. Also, a fully oxidised PdO does not deactivate, so other published results [38] which seem to indicate that PdO is not active must reflect some other effect, such as interaction with the support. Thus it seems quite possible that isolated Pd ions, coordinated by oxide ions from the alumina support, would have a very low activity for C–H bond activation, especially if after activation of a single CH<sub>4</sub> molecule at such a site the (relatively active) oxide ion is converted into an (inactive) hydroxide ion. Since this hydroxide ion will have more of the characteristics of aluminium hydroxide than of palladium hydroxide, it may be very stable and so self-poisoning of the ‘active’ site will have occurred. We shall return later to this whole question of the effect of water on the activity of PdO.

The results in Fig. 8 and Fig. 9 seem to show that the active site for C–H bond breaking in CH<sub>4</sub> is PdO, that is a site comprising a Pd<sup>2+</sup>–O<sup>2-</sup> couple (compare Fig. 1). Presumably exposure of the Pd<sup>2+</sup> does not occur when only chemisorbed oxygen is present on a metallic Pd surface. With a Pd<sup>2+</sup>–O<sup>2-</sup> metal ion/oxide ion couple, a heterolytic mechanism for C–H bond breaking once again becomes a possibility. It is interesting that on Pd this can occur for a fully oxidised material because Pd forms a distinct crystalline oxide whereas this state is only possible in Pt for a surface which is partially covered with chemisorbed oxygen, presumably because Pt does not form a comparable stable oxide phase.

Up to this point it has been assumed that the rate determining step in hydrocarbon combustion, especially of CH<sub>4</sub>, involves the breaking of the C–H bond. This indeed may be the case, and for Pt

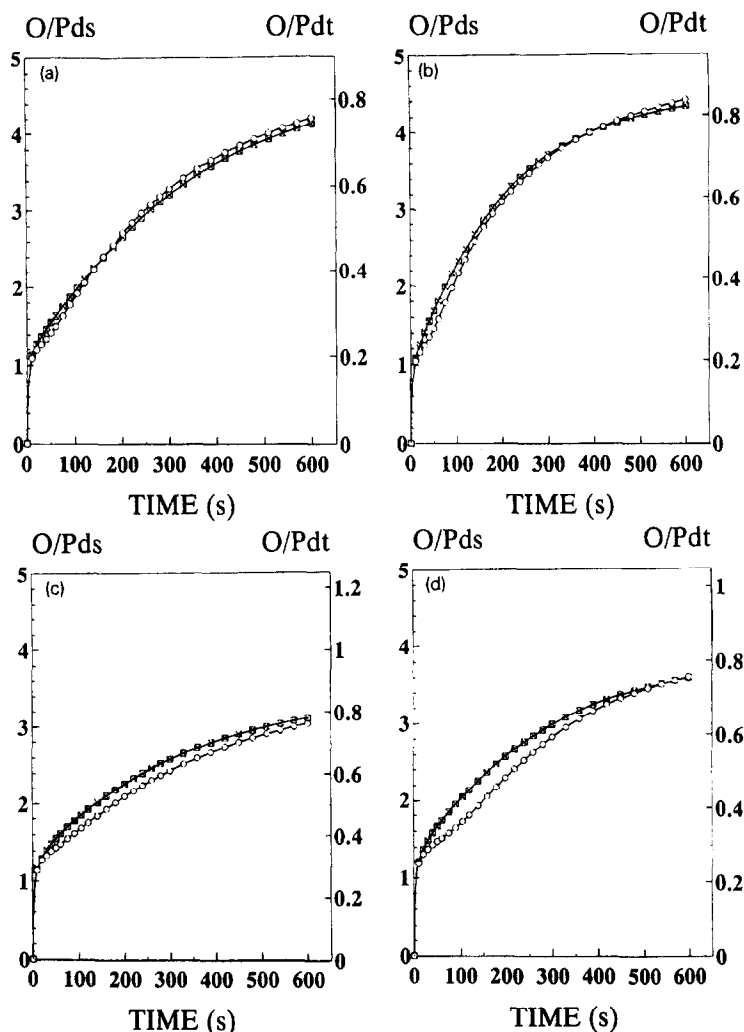


Fig. 9. Oxygen uptake experiments carried out on samples of the 4% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst exposed to various gaseous environments at 500°C. (a) Dry air, 1 h; (b) dry air, 16 h; (c) hydrogen, 1 h; (d) hydrogen, 16 h. (○) 1st run, (×) 2nd run, after re-reduction at 300°C, after ref. [74].

catalysts which do not form stable compounds (such as oxides or hydroxides) this may be the true rate determining step. However, as discussed earlier, for methane coupling, oxidative dehydrogenation, and partial oxidation reactions, where the catalysts are usually oxides, this may not be correct. The uncertainty arises because for oxide catalysts it is necessary to carefully consider the rate of removal of the products of combustion (CO<sub>2</sub> and H<sub>2</sub>O). Even in the case of CH<sub>4</sub> combustion on Pd catalysts the desorption of the products may be a slow step. Since catalysis involves *all* of the steps in adsorption, surface reaction, and desorption, any one of these steps can be rate determining in the catalytic reaction.

The influences of CO<sub>2</sub> or H<sub>2</sub>O on the activity of Pd catalysts for CH<sub>4</sub> oxidation have been considered and various groups have demonstrated that CO<sub>2</sub> and/or H<sub>2</sub>O will inhibit the combustion reaction [75–77]. Water is a particularly effective poison for the CH<sub>4</sub> combustion reaction on Pd catalysts especially at lower temperatures. Ribeiro et al. [77] have reported an order of reaction with respect to H<sub>2</sub>O of  $-1$  at concentrations between 0.03 and 0.15%.

We have examined [78] the effect of water vapour on the activity of Pd catalysts and typical results are shown in Fig. 10. These results show a very strong inhibiting effect of water vapour especially at low temperatures. Thus at 275°C the

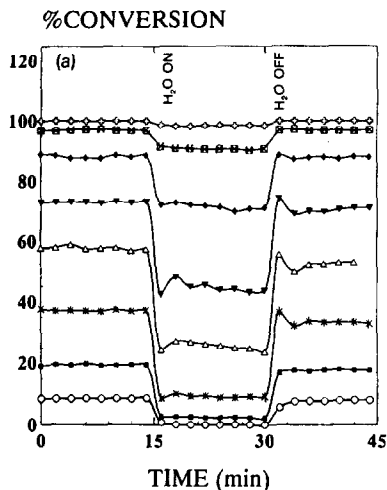


Fig. 10. Effect of water vapour at different temperatures on the activity for methane combustion over 4% Pd/Al<sub>2</sub>O<sub>3</sub>. (○) 275°C, (■) 300°C, (\*) 325°C, (△) 350°C, (τ) 375°C, (◆) 400°C, (×) 425°C, (+) 450°C, after ref. [78].

activity is almost completely destroyed. The effect is reversible, however, which led us to conclude that during normal reaction conditions the water formed in the combustion reaction might inhibit the reaction to the extent that the C–H bond activation step might no longer be rate determining. To explore this possibility we performed experiments in which very small pulses of 1% CH<sub>4</sub>/air were passed over a Pd/SiO<sub>2</sub> catalyst held in a flow of air. Fig. 11 shows some typical results [79]. There are a number of interesting aspects to these results. First, in a completely dry atmosphere at 300°C the catalyst has a very high, and stable activity. Second, at lower temperatures (e.g., 250°C) the catalyst shows some deactivation. Third, in normal cylinder air which is not further dried, the catalyst exhibits a much lower initial activity at 250°C. Fig. 11 also shows a result for a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst at 250°C in 'normal' air which again shows rapid deactivation. However, with this catalyst the experiment was temporarily interrupted after 12 pulses and the results show that on recommencing the experiment the catalyst had recovered much of its activity, but this then declined again.

We interpret these results as evidence that under reaction conditions the surface OH groups produced by the combustion of CH<sub>4</sub> are not easily

removed as gaseous H<sub>2</sub>O and so the initial high activity of the catalyst for activation of C–H bonds cannot be sustained under continuous flow conditions. Clearly for a fresh, dry, PdO catalyst the rate determining step is the breaking of the first C–H bond in CH<sub>4</sub>. However, as soon as this happens, the surface of the PdO is partially converted into a surface hydroxide which we assume is not active for breaking C–H bonds. Consequently, until this surface hydroxide decomposes to release H<sub>2</sub>O the active site is blocked and the rate of CH<sub>4</sub> combustion slows down. Since the desorption of H<sub>2</sub>O is an integral part of the catalytic cycle we suggest that on these catalysts the true rate determining step is not C–H bond activation but O–H bond decomposition on the catalyst surface.

This proposal concerning the rate determining step allows us to offer an explanation of the curious fact that on PdO catalysts CH<sub>4</sub> is more reactive than C<sub>2</sub>H<sub>6</sub>. This experimental fact has been known for a long time but has not, as far as we are aware, been satisfactorily explained previously. Fig. 12 shows [79] that at steady state our supported Pd catalysts are about twice as active for the combustion of CH<sub>4</sub> as for C<sub>2</sub>H<sub>6</sub>, which is not expected from the relative strengths of the C–H bonds in the two compounds, but is consistent with experimental observation. However, using our pulse

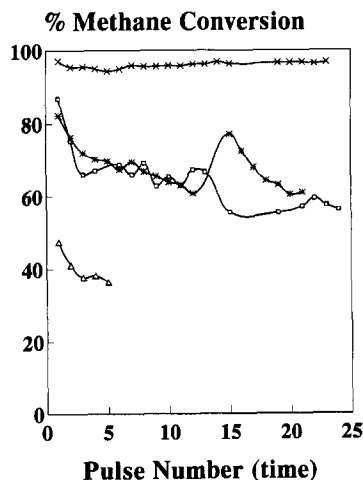


Fig. 11. Variation in the methane conversion for individual 50 μl pulses of 1%CH<sub>4</sub>/air introduced into a flow of either 'normal' cylinder air or into 'dry' air. 5%Pd/SiO<sub>2</sub> catalyst: (x), 300°C, dry air, (□) 250°C, dry air, (Δ), 250°C, normal cylinder air. 5%Pd/Al<sub>2</sub>O<sub>3</sub> catalyst: (\*), 250°C, normal cylinder air.

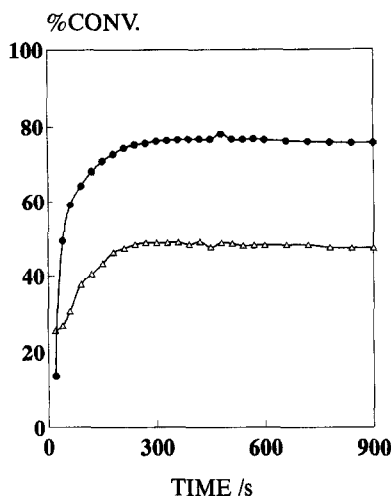


Fig. 12. Plot of conversion against time at 300°C for a pre-reduced 4% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst. (●) methane; (Δ) ethane, after ref. [73].

technique, Fig. 13 shows that *initially* the activity for C<sub>2</sub>H<sub>6</sub> combustion is *higher* than for CH<sub>4</sub> which is consistent with what would be predicted from the relative reactivities of the C–H bonds in these two saturated hydrocarbons. Our interpretation of these results is that for the fresh, dry PdO catalysts the activity reflects the relative reactivities of the C–H bonds in CH<sub>4</sub> and in C<sub>2</sub>H<sub>6</sub>. However, under steady state conditions, the C<sub>2</sub>H<sub>6</sub> generates more OH groups per molecule than does CH<sub>4</sub> so that the surface is more deactivated by C<sub>2</sub>H<sub>6</sub> than by CH<sub>4</sub>. This would seem to be entirely consistent with our proposal that the real rate determining step in the combustion of these small hydrocarbons on a PdO catalyst is *not* the activation of the C–H bond but the activation of the surface O–H bond. Isotopic labelling of the methane (CH<sub>4</sub> versus CD<sub>4</sub>) may not differentiate between these two possibilities since both C–H and O–H bond breaking will be susceptible to similar kinetic effects on substitution of hydrogen by deuterium.

The oxidation of higher hydrocarbons (ethane and upwards) is found to be faster on Pt than on Pd catalysts. We can now offer some explanation for this if it is accepted that a partially oxidised Pt surface is optimum for C–H bond activation. We suggest that for CH<sub>4</sub> oxidation on a fully oxidised Pt catalyst (covered with chemisorbed oxygen) C–H bond activation is very slow because there are very few sites which expose a Pt<sup>δ+</sup>–O<sup>δ-</sup> cou-

ple where heterolytic splitting of the C–H bond could occur. Moreover, when a single CH<sub>4</sub> molecule is oxidised it removes a limited number of surface oxygen atoms and the vacant sites left by their removal may be rapidly filled by migrating or adsorbing oxygen atoms. However, for large hydrocarbon molecules, once the molecule has adsorbed it will consume more oxygen atoms before it is oxidised and removed from the surface. During this period it may be the case that incoming hydrocarbon molecules can approach a *partially oxidised* patch on the Pt surface where C–H bond activation would be facilitated. In addition, of course, with larger hydrocarbon molecules there are many more ways in which the molecule can adsorb to a fully oxidised surface and this would certainly be expected to affect their activity since the initial molecularly adsorbed precursor state would be more stable for larger hydrocarbon molecules as compared with methane, for example. Nevertheless it would seem from our results that a partially oxidised surface would still present an especially favourable environment for the initial C–H bond activation in any saturated hydrocarbon.

Another interesting face of C–H bond activation on platinum group metal catalysts is the opposing roles of anionic species derived from halogens or sulphur. Here it is not appropriate to consider the effects of chlorine in much detail since the effects are generally negative, i.e., chlorine poisons combustion catalysts. However, it is worth just drawing attention to the problem of

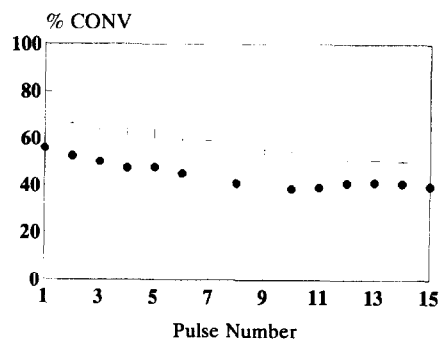


Fig. 13. Plot showing the change in activity for hydrocarbon combustion over a pre-oxidised 4% Pd/Al<sub>2</sub>O<sub>3</sub> catalyst with number of 0.5 cm<sup>3</sup> pulses of reaction mixture introduced into flowing air. (●) CH<sub>4</sub>, (+) C<sub>2</sub>H<sub>6</sub>, after ref. [73].

chlorine since a good proportion of the early work on palladium combustion catalysts was based on catalysts prepared from chlorine-containing precursors and many of these results may be open to question. Moreover, in some cases at least, activation effects seen for palladium catalysts may be due to slow release of chlorine although there are claims that is not the only reason for activation effects. [80] Note, however, that this work was performed using oxygen-rich conditions where the state of the Pd may vary from metallic Pd to Pd oxide depending on the temperature and the methane conversion.

Our own view now, and this is based on our experience with numerous batches of supported Pd catalysts, is that although we had observed extensive, and reproducible activation effects in some of our earlier work [81], since then we have never obtained catalysts in which these activation effects are observed. Indeed, as shown earlier in Fig. 8 we now routinely see small deactivation effects with time on stream for precalcined catalysts. We have no certain explanation for this but are inclined to the view that the earlier results could have been an artefact due to impurities, probably chlorine, even though the Pd precursor (Pd nitrate) was nominally chlorine-free. Attention has already been drawn to the fact that commercial samples of Pd nitrate may contain low concentrations of chlorine. [82] Since none of our current catalysts exhibit activation effects, we now suspect that our earlier work was affected by having an 'impure' sample of Pd nitrate. Furthermore, when we compare the activities of our present generation of chlorine-free catalysts with the final activated state of the previous 'chlorine-free' catalysts we find that the present catalysts have activities at least as high as the final 'activated' state of the earlier catalysts. Again, we have since shown that if we deliberately dope our present catalysts with chlorine we can observe a slow reactivation with time on stream.

We cannot comment in detail on the results of other workers who have observed similar activation effects and who attribute these to morphological effects, for example. However, as far as it is

possible to compare the results from different laboratories, we find that our present generation of 'clean' catalysts have higher activities as compared with the 'activated' state found in our own earlier work or in other published work ( $\text{CH}_4$  conversion ca. 40 mol/mol Pd/h in our 'clean' catalysts at steady state at 300°C, as compared with ca. 15 mol/mol Pd/h in our previous catalysts *after* activation [81], and with 6 mol/mol Pd/h in ref. [37] after activation). It does seem that 'activation' both in our own early work and in other published work is more accurately attributed to reversal of deactivation rather than to a true activation effect.

The effect of  $\text{SO}_2$  on the activity of Pt and Pd for the oxidation of saturated hydrocarbons is interesting. In the case of Pd the effect is inhibitory and even trace amounts of sulphur can seriously poison Pd catalysts [83,84]. In contrast, with Pt there is evidence that addition of  $\text{SO}_2$  to the gas stream can actually enhance the activity. We now consider the implications of this information in relation to the mechanism of C–H bond activation.

Early work by Yao et al. [85] has shown that propane oxidation on Pt catalysts is greatly enhanced by the formation of aluminium sulphate derived from the oxidation of  $\text{SO}_2$ . Thus the addition of 20 ppm  $\text{SO}_2$  lowers the light-off temperature for ethane (from 435°C to 305°C) and propane (from 290°C to 230°C) whereas for higher hydrocarbons the effect is small but in the opposite direction (hexane; temperature increases from 195°C to 210°C). This is consistent with our view that the activation of the lower hydrocarbons is rather difficult and demanding on the characteristics of the active site, and so the C–H bond in these molecules is much more susceptible to the effects of additives than the C–H bonds in higher hydrocarbon molecules. Ghandi and Shelef [86] proposed that new catalytic sites, active for propane oxidation, were created by the sulphate deposit. Yao et al., [85] from infrared studies, conclude that the presence of sulphate ion enhanced the dissociative adsorption of the hydrocarbon. Barbier and Duprez have commented on these results [87] and pondered how this might

Table 3  
Relationship between acid strength and propane conversion for oxide-supported Pt and Pd catalysts, after ref. [83] and [84]

Catalyst	Hammett function, $H_o^a$	Temp. at 50% $C_3H_8$ conv./°C
$\gamma-Al_2O_3$	4.8	550
$\gamma-Al_2O_3-SO_2$	1.1	525
0.05 wt.% Pt/ $\gamma-Al_2O_3$	4.8	390
0.05 wt.% Pt/ $\gamma-Al_2O_3-SO_2$	1.1	250
ZrO <sub>2</sub>	4.8	–
ZrO <sub>2</sub> -SO <sub>2</sub>	-5.6	–
0.04 wt.% Pt/ZrO <sub>2</sub>	4.8	283
0.04 wt.% Pt/ZrO <sub>2</sub> -H <sub>2</sub> SO <sub>4</sub>	-5.6	283
0.04 wt.% Pt/ZrO <sub>2</sub> -SO <sub>2</sub>	-5.6	275
SiO <sub>2</sub>	7.2	–
SiO <sub>2</sub> -SO <sub>2</sub>	7.2	–
0.10 wt.% Pt/SiO <sub>2</sub>	7.2	290
0.10 wt.% Pt/SiO <sub>2</sub> -SO <sub>2</sub>	7.2	290
0.05 wt.% Pd/ $\gamma-Al_2O_3$	4.8	390
0.05 wt.% Pd/ $\gamma-Al_2O_3-SO_2$	1.1	530

<sup>a</sup> The Hammett function,  $H_o$ , is defined as the inverse logarithm of the dissociation constant,  $K_a$ .

happen since they suggest that most of the sulphate would be on the support. They suggest that SO<sub>2</sub> should therefore act through an electronic effect. Hubbard et al. [83,84] have considered whether changes in the acidity of the support might account for the effects of sulphate. However, they have concluded that acid strength does not have a major influence on the activity of Pt for propane oxidation as can be seen from their results reproduced in Table 3.

A significant observation is that whereas alumina-supported Pt is very susceptible to an enhancement of activity for propane oxidation when SO<sub>2</sub> is present at low levels in the gas stream there is very little enhancement for silica or zirconia-supported catalysts. It seems that the support plays some role in affecting the activity of Pt in this reaction, a point to which we shall return.

In a very elegant surface science investigation Wilson et al. [88] have recently studied the promoting effect of SO<sub>2</sub> on the chemisorption and oxidation of propane on a Pt(111) surface. No propane adsorption was observed on a clean or on an oxygen pre-covered Pt surface. Similarly, no propane adsorption occurred on a Pt(111) surface pre-covered with SO<sub>2</sub>. However, when this surface was given a stepwise exposure to O<sub>2</sub> and then SO<sub>2</sub> at 27°C this produced a surface which was

very active for the dissociative adsorption of propane. The initial sticking probability increased from essentially zero on clean Pt to 0.02 on the modified surface. These results clearly indicate that in the presence of chemisorbed oxygen, SO<sub>2</sub> greatly enhances the chemisorption and oxidation of propane on Pt in the complete absence of a support phase.

Wilson et al. [88] rationalise their results in terms of the following reaction scheme:

- 1 initial dissociative adsorption of propane by abstraction of H by SO<sub>x</sub>  
 $SO_x + C_3H_8 \rightleftharpoons C_3H_y + HSO_x$
- 2 as the temperature is increased, C–C bond cleavage occurs to form CH<sub>x</sub> fragments which are oxidised to H<sub>2</sub>O, CO and CO<sub>2</sub>.
- 3 coincident desorption of SO<sub>2</sub> and CO<sub>2</sub> at ca. 170°C is taken to reflect the decomposition of a surface complex:  
 $CO-SO_x \rightleftharpoons CO_2 + SO_2 + xO_a$

It seems clear from these results that dissociative adsorption of propane, which is the rate determining step in C–H bond activation on Pt catalysts, is facilitated by adsorbed ‘sulphate-type’ species on the Pt metal itself in the absence of any support phase. It remains to rationalise these results with the results described earlier for

supported catalysts where, for example, it was seen that alumina-supported Pt is promoted and silica-supported Pt is not promoted by  $\text{SO}_2$  in the gas phase.

A number of explanations suggest themselves. First, the morphology or particle size distribution of Pt particles could be different on the two supports and if the results for Pt(111) single crystals is specific to this particular crystallographic plane then the supports could appear to have a direct influence on the effect of  $\text{SO}_2$  by creating Pt particles with different morphologies. A second possibility is that the effect is restricted to sulphate groups attached to the support at the periphery of a Pt particle. Since aluminium sulphate is much more stable than 'silica sulphate' the number of sulphate groups on the support would be very different in the two cases and the probability of finding a sulphate group adjacent to a Pt particle would be much higher for the alumina-supported catalysts. Furthermore, if the sulphate is only metastable under reaction conditions, the formation of more sulphate will come from oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  and this will obviously occur at Pt particles, from which it is a simple step for the  $\text{SO}_3$  to migrate to an oxide ion on an adjacent patch of the alumina surface. Thus, one way of combining the two sets of information would be to propose that sulphate on, or adjacent to, metallic Pt particles can facilitate the dissociative adsorption of propane. At low temperatures the  $\text{SO}_x$  may be directly, and even exclusively attached to the Pt, but as the temperature is increased and  $\text{SO}_x$  begins to desorb from the Pt some  $\text{SO}_x$  at the Pt/support interface could remain and continue to act as a promoter for propane adsorption at elevated temperatures.

These promoting effects may be unique to Pt because it forms relatively unstable bonds to sulphur oxides. Certainly, with Pd catalysts there is no promoting effect, quite the reverse. Table 3 shows that the temperature for 50% conversion of propane increases from 390 to 530°C when  $\text{SO}_2$  is introduced into a gas stream over Pd/ $\text{Al}_2\text{O}_3$  catalysts. The obvious explanation for this is that the *palladium oxide* reacts strongly with  $\text{SO}_2$  and

the surface Pd sulphate formed is inactive for the C–H bond breaking reaction.

#### 4. Hydrocarbon/nitrogen oxide(s) reactions

A subject of growing importance is the selective reduction of nitrogen oxides ( $\text{NO}_x$ ) by hydrocarbons in the presence of excess oxygen. As a result, some interesting new information has emerged which is relevant to C–H bond activation is saturated hydrocarbons. Moreover, in the reactions which may be involved in the treatment of the exhaust gas from natural gas vehicles it is feasible to consider direct  $\text{CH}_4/\text{NO}$  reactions since, at least for the present, these engines are operated close to the stoichiometric air/fuel ratio. Also, even in conditions where the exhaust gas contains a small amount of oxygen addition of a small balancing amount of methane could be an acceptable way to reduce  $\text{NO}_x$  emissions. Reactions of  $\text{CH}_4$  with  $\text{NO}_x$  are therefore of interest and the activation of the C–H bonds is again likely to be a slow step.

Demicheli et al. [32] have studied the  $\text{NO}/\text{CH}_4$  reaction on alumina-supported Pt and Pt–Au catalysts and concluded that the reduction of  $\text{NO}$  by methane (equivalent to the oxidation of methane by  $\text{NO}$ ) involves relatively large ensemble sites and occurs preferentially on flat planes exhibited by large Pt particles. The basis for this conclusion is that Au preferentially attaches to low coordination Pt atoms (edges and corners) and since the activity for the  $\text{NO}/\text{CH}_4$  reaction is unaffected by alloying, presumably these sites are not involved in the reaction. They conclude that the rate determining step is probably the dissociative adsorption of  $\text{CH}_4$  onto large ensembles of Pt atoms. Earlier work had suggested that dissociative adsorption of methane required an ensemble of 5–7 metallic atoms. Moreover, a kinetic isotope effect for the reduction of  $\text{NO}$  with  $\text{CH}_4$  or  $\text{CD}_4$  also supports the suggestion that cleavage of C–H bonds is the rate determining step in the reaction. [89]

Comparison of reactions of  $\text{CH}_4$  with  $\text{NO}$  and with  $\text{O}_2$  should be informative. We have per-



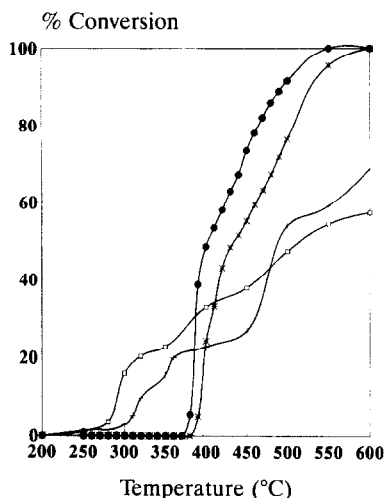


Fig. 14. Effect of temperature on  $\text{CH}_4$  conversion over  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ -supported 1% Pt catalysts in the presence of either  $\text{O}_2$  or NO as an oxidant. (●) 1% Pt/ $\text{Al}_2\text{O}_3$  ( $\text{CH}_4/\text{O}_2$ ), (+) 1% Pt/ $\text{Al}_2\text{O}_3$  ( $\text{CH}_4/\text{NO}$ ), (\* ) 1% Pt/ $\text{SiO}_2$  ( $\text{CH}_4/\text{O}_2$ ), (□) 1% Pt/ $\text{SiO}_2$  ( $\text{CH}_4/\text{NO}$ ), after ref. [90].

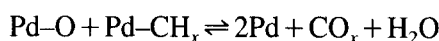
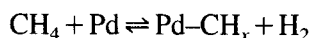
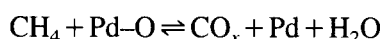
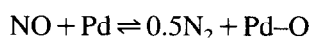
formed some preliminary experiments [90] on the relative reactivity of  $\text{CH}_4$  with NO or  $\text{O}_2$  and representative results are shown in Fig. 14 for 1% Pt/ $\text{SiO}_2$  and 1% Pt/ $\text{Al}_2\text{O}_3$ . In both cases the oxygen content was held constant (1000 ppm NO or 500 ppm  $\text{O}_2$ ) and the  $\text{CH}_4$  concentration was 1000 ppm, corresponding to methane-rich (overall reducing) conditions. There are some differences between the two catalysts but for these particular reactions there does not appear to be a strong support effect.

It is noticeable that the reaction between NO and  $\text{CH}_4$  commences at a much lower temperature (ca. 280–300°C) than the corresponding  $\text{O}_2/\text{CH}_4$  reaction (ca. 380–390°C). Since the sticking coefficient for oxygen on Pt is high and since we have shown elsewhere [72] (see also discussion above) that a *partially* oxidised Pt surface is most active for methane oxidation, one explanation for these results could be that when  $\text{O}_2$  is present the Pt is quite well covered with chemisorbed oxygen at steady state even though the gas mixture is methane-rich. On the other hand, since these same catalysts show a relatively low activity for NO decomposition it seems likely that in the  $\text{CH}_4/\text{NO}$  reaction the surface of the Pt will be at least partially reduced. The results discussed earlier would

indicate that such a surface would be closer to the optimum for  $\text{CH}_4$  oxidation.

These results are consistent with those reported by Demicheli et al. [32] who conclude that the relative activity of Pt, Pd, Rh and Ni for the  $\text{CH}_4/\text{NO}$  reaction reflects the ability of NO to *partially* oxidise the metallic surface. Thus in the  $\text{CH}_4/\text{NO}$  reaction the activation of the C–H bonds in methane will occur by dissociative adsorption either on regions of a fully reduced Pt surface or at mixed sites comprising  $\text{Pt}^{\delta+}-\text{O}^{\delta-}$ , whereas in the  $\text{CH}_4/\text{O}_2$  reaction the activation of the C–H bonds will have to take place at a Pt surface fully covered with  $\text{O}^{\delta-}$  sites. The fully oxidised Pt surface is less active than a partially oxidised surface.

Loughran and Resasco [91] have recently reported on the  $\text{CH}_4/\text{NO}$  reaction in the absence of  $\text{O}_2$  on Pd-ZSM-5 catalysts. They suggest that their results can best be interpreted in terms of a mechanism in which NO first dissociates, followed by a surface reaction between  $\text{CH}_4$  and the adsorbed oxygen. However, under certain conditions they also observe carbon deposition and so propose that two C–H bond activation processes can occur simultaneously:



To compare the relative rates of these two processes –  $\text{CH}_4$  decomposition on reduced Pd sites, and  $\text{CH}_4$  reaction with adsorbed oxygen – they conducted two sets of experiments, one with a sample pre-reduced in  $\text{H}_2$ , the other with a sample pre-treated in NO at 500°C. Pulses of  $\text{CH}_4$  were introduced and the  $\text{CH}_4$  consumption noted as a function of temperature. It was found that the NO-treated surface was active below 250°C whereas the pre-reduced surface was not active until the temperature was raised to 350°C.

A related area of hydrocarbon activation which has recently become of increasing importance is in the selective reduction of nitrogen oxides

(NO<sub>x</sub>) by higher hydrocarbons under oxygen-rich conditions. Interest in such reactions comes from the wish to develop catalysts suitable for the reduction of NO<sub>x</sub> in lean-burn gasoline or diesel engine emissions. In many practical situations the hydrocarbon present in the exhaust gas is unsaturated (ethene or propene, for example) and quite good progress has been made in developing suitable catalysts. However, for saturated hydrocarbons, and for methane in particular, this is a much more difficult challenge since the reactivity of the hydrocarbon is so much lower. Therefore, much higher temperatures are needed to initiate the reaction and, as is often the case with catalysed reactions, the selectivity for NO<sub>x</sub> reduction versus NO<sub>x</sub> oxidation is much lower at elevated temperatures.

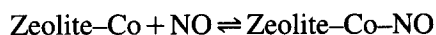
The purpose of this review is to examine the activation of C–H bonds in *saturated* hydrocarbons so we shall restrict our attention to these reductants. There are, of course, similarities with the activation of hydrocarbons for combustion reactions in NO<sub>x</sub>-free conditions. For example, it is likely that Ga-modified zeolites will activate saturated hydrocarbons as a preliminary step both for subsequent oxidation by oxygen and for oxidation by NO<sub>x</sub>. However, for some metal-loaded zeolites the view has also been expressed [92] that there may be a more direct interaction between a hydrocarbon and an NO<sub>2</sub> molecule so we shall address these aspects in particular.

The H-form of zeolites exhibit only a low activity for the activation of methane. Yogo et al. [93] have found that the NO–CH<sub>4</sub> reaction hardly proceeds at all even at temperatures up to 600°C, and the O<sub>2</sub>–CH<sub>4</sub> reaction is immeasurably slow below 500°C. In contrast, however, in the presence of *both* NO and O<sub>2</sub>, oxidation of CH<sub>4</sub> proceeds rapidly at any temperature above 300°C. When the zeolite is ion exchanged with an aqueous solution of gallium nitrate at 95°C, to a theoretical level of 92% exchange Yogo et al. [94] found that the conversion of CH<sub>4</sub> is about three times higher at 400°C than for the Ga-free zeolite but the differences become small at higher temperatures. Somewhat lower CH<sub>4</sub> conversions were reported

by Li and Armor [95] for comparable Ga-exchanged catalysts, but the same dependence on having NO and O<sub>2</sub> present simultaneously was noted.

The mechanism of this NO<sub>x</sub> reduction reaction is not certain but it seems that the key step involves the reaction between NO<sub>2</sub> and CH<sub>4</sub>. Thus, although Ga-modified zeolites are known to activate higher saturated hydrocarbons (see later) it is not known whether this is an important process for CH<sub>4</sub>. Li and Armor [95] have pointed out that there must be some synergistic effect between gallium species and H<sup>+</sup> sites since Ga-H-ZSM-5 is active whereas Ga-Na-ZSM-5 is not. However, since much of the Ga may be located outside the zeolite, this synergy may not necessarily arise from a direct interaction and may, therefore, not have a direct effect in the enhanced activation of C–H bonds in CH<sub>4</sub>. A plausible alternative has been suggested by Kikuchi and Yogo [96] who proposed that NO oxidation to NO<sub>2</sub> might occur on Brønsted acid sites, with the NO<sub>2</sub> then migrating to Ga sites where a direct NO<sub>2</sub>/CH<sub>4</sub> reaction would take place. On the other hand, Ga/Al<sub>2</sub>O<sub>3</sub> is not active for these reactions, but this could be due to a number of factors such as the Ga being in different forms in the two cases, the need for Brønsted acid sites for NO oxidation, the existence of unique sites involving both Ga and H<sup>+</sup>, etc. Clearly, it is difficult to differentiate between such alternatives. However, there seems to be a general consensus that the activation of CH<sub>4</sub> may arise from the reaction between an adsorbed NO<sub>2</sub> and a CH<sub>4</sub> molecule.

For zeolites loaded with reducible metal ions (Co, in particular, in the case of the CH<sub>4</sub>/NO reaction) a high activity has been reported, principally by Armor and co-workers [92,97]. They have proposed that the activation of CH<sub>4</sub> occurs through the following scheme involving adsorbed NO<sub>2</sub>:



leading to the formation of a CH<sub>3</sub> radical.

Cowan et al. [89] have made measurements of the relative rates of reaction of  $\text{CH}_4$  and  $\text{CD}_4$  over Co-ZSM-5 in the selective reduction of NO in excess  $\text{O}_2$ . They observe a difference in the rates of reaction ( $\text{CH}_4/\text{CD}_4$ ) of a factor of 2.8, close to the expected value for a primary kinetic isotope effect. They conclude that the activation of the C–H(D) bond is rate determining and, in common with Armor and co-workers, propose that the active surface site could contain adsorbed  $\text{NO}_2$ . Although hard evidence is difficult to obtain on this reaction mechanism, some direct interaction between an adsorbed  $\text{NO}_2$  species and an incoming  $\text{CH}_4$  molecule is plausible, especially if the adsorption of the  $\text{CH}_4$  is facilitated by the already adsorbed  $\text{NO}_2$ , leading to a Langmuir–Hinshelwood-type mechanism. What does seem clear is that activation of C–H bonds in  $\text{CH}_4$  is not easy even on redox ions in zeolites in the absence of a coadsorbate.

For the direct  $\text{CH}_4/\text{O}_2$  reaction on Cu-ZSM-5 Kucherov et al. [98] have concluded that the activation of an  $\text{O}_2$  molecule due to an interaction with a low-coordinated Cu(II) ion is more probable than that of the  $\text{CH}_4$  molecule. In view of the earlier discussion of the low activity of oxygen-free metallic surfaces this seems quite reasonable. It does appear that the activation of  $\text{CH}_4$  requires another adsorbed species to be present at the active site.

Activation of higher saturated hydrocarbons on acidic catalysts may involve different rate determining steps. Brønsted acid protons can activate hydrocarbons by protonation, giving an adsorbed carbonium ion which may, in turn, lose  $\text{H}_2$  to give an adsorbed carbenium ion. Subsequent reaction with  $\text{NO}_x$  can be relatively facile. Clearly, for higher saturated hydrocarbons, the acidity of the catalyst can be very important for C–H bond activation, as suggested by Hamada and co-workers [99].

Finally, the oxidation of  $\text{CH}_4$  by molecular oxygen on Pd/zeolite catalysts has been explored. This is relevant because it relates to the question which is often discussed concerning the nature of the active state of Pd in conventional (alumina-

or silica-supported) catalysts [33–37,81]. In the case of zeolite-based Pd catalysts it is inappropriate to think of the active species as bulk PdO, so the fact that these catalysts show very high activities is highly relevant [100–102]. Matsumoto [102], from a careful structural analysis, concludes that small clusters of Pd species formed on the zeolite could function as catalytic centres through a reversible redox mechanism between Pd and PdO. Ishihara et al. [101], using Pd-SAPO-5, find that 90% conversion of  $\text{CH}_4$  occurs some  $200^\circ\text{C}$  lower than for a conventional Pd/ $\text{Al}_2\text{O}_3$  catalyst. They conclude that this is only due to the high dispersion of Pd in the zeolite. Li and Armor [100] have also studied the combustion of  $\text{CH}_4$  on Pd-exchanged zeolites and find for comparable loadings of Pd that the zeolite-based catalysts give the same conversion some  $70\text{--}80^\circ\text{C}$  lower than for a Pd/ $\text{Al}_2\text{O}_3$  catalyst. They also note the high dispersion of Pd in the zeolite and suggest that the higher activity may be related to the reducibility of almost isolated Pd ions in the zeolite as compared with Pd in PdO crystallites on  $\text{Al}_2\text{O}_3$ . They interpret their results as evidence that methane combustion can take place on a single atom and that the Pd cations positioned in the zeolite sites are highly active. This is entirely consistent with the models we have tried to develop above in terms of the higher activity to be expected for active sites in which heterolytic splitting of the C–H bond in methane is possible. The high activity of some Pd catalysts for methane combustion seems to be more dependent on the existence of such sites than on the availability of specific morphologies.

In summary, while there is now broad agreement on the nature of the sites required in different types of catalyst for the activation of C–H bonds in saturated hydrocarbons, some questions are still not fully resolved and further research to elucidate the fine details of C–H bond activation on various types of metallic and oxidic catalysts is still required. C–H bond activation can occur through either homolytic or heterolytic splitting, but the latter seems to be more favourable, especially in the case of methane. The importance of coadsor-

bates in facilitating the dissociative adsorption of saturated hydrocarbons now seems well established and the extension of this idea could lead to the design of more active catalysts. On the other hand, inhibition by the products of the oxidation reaction ( $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) can be quite severe and needs to be taken into account when comparing the activities of catalysts tested under different reaction conditions, especially at lower temperatures.

## Acknowledgements

We are grateful to Dr. Sophia Chalker, Dr. Peter Loader, Dr. Garbine Guiu and Miss Anita Ramli for providing some of the unpublished results shown in this paper and for many fruitful discussions on the mechanism of C–H bond activation. We are grateful to Dr. R.M. Lambert for permission to refer to his unpublished work. We are grateful to the EPSRC for financial support for MJH, and to NATO for awarding a Collaborative Research Grant to RB Grant No. CRG 930652.

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