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C–H bond activation in hydrocarbon oxidation on heterogeneous catalysts

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Abstract

The activation of C–H bonds in different hydrocarbons on the surfaces of metal oxide and metal catalysts is considered. On oxides, it appears that the initial activation may occur through either homolytic or heterolytic scission of the C–H bond, but the reaction is surface-catalysed. The activation of methane requires highly basic sites which are susceptible to severe poisoning by carbon dioxide. With metal surfaces, the extent of oxidation of the surface can strongly affect the oxidation activity. For rhodium catalysts, it is shown that the intrinsic activity for methane combustion is high. However, rhodium is strongly deactivated under oxidising conditions when alumina is used as the support: deactivation is not observed when the support is zirconia. Transient effects on the activity of an alumina-supported palladium catalyst are reported and these show that the steady state is not easily established. Water severely inhibits the methane combustion reaction on palladium, and chlorine and sulphur dioxide are strong poisons. In contrast, for the combustion of propane on alumina-supported platinum catalysts, sulphur dioxide is a significant promoter of the reaction. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

C–H bond activation in saturated hydrocarbons is a crucial first step in the combustion of these compounds for power and heat generation. Once the first bond is broken, sequential reactions to CO_2 and H_2O are relatively facile. It is important, therefore, to understand how C–H bonds in saturated hydrocarbons are activated, and also to assess the influence of catalytic and process parameters on the rate and efficiency of catalytic combustion. Several different types of catalysts – nonreducible oxides, reducible oxides, metals – are capable of oxidising saturated hydrocarbons with varying efficiencies. Methane is the most difficult compound to activate, ethane, propane and butane are of intermediate difficulty and higher hydrocarbons are relatively easy to activate. This is partly related to the ease of adsorption of the different hydrocarbons on oxides, or on oxidised metal surfaces [1]. Strong adsorption of a saturated hydrocarbon is a prerequisite to combustion, but the strength of the C–H bond is not the only factor which influences the rate of combustion. Thus, although the adsorption of methane compared with ethane will reflect to some extent different C–H bond energies, the ease of adsorption of hexane, for example, compared to ethane cannot just be due to differences in

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bond energies. An important additional factor is the "stickiness" of a molecule to an oxidised surface. A larger molecule can be adsorbed much more effectively in a pre-dissociative state than would be possible for a small molecule. In this paper, we shall address a number of factors which influence the activation of C–H bonds in different saturated hydrocarbons on various types of oxidation catalysts. We shall also explore the influence of reaction products (CO_2 and H_2O) and of potential contaminants (chlorine and SO_2) in catalytic combustion.

2. Oxide-based catalysts

Combustion of methane on oxides requires relatively high temperatures. Under these circumstances evidence from work on methane coupling catalysts suggests that gas phase contributions to the combustion may be important [2]. For example, there is evidence that methyl radicals can be observed in the gas phase above oxides at temperatures as low as 500°C [3]. The initial activation of the C–H bond is however, a surface-catalysed process which could involve a homolytic or a heterolytic fission. At present there is no general agreement on the correct mechanism. Since the C–H bond in methane is only very weakly acidic ($pK_a=46$), it follows that surface sites capable of deprotonation of methane must be very basic. Such sites would be expected to strongly adsorb CO_2, and so they might be expected to be rapidly self-poisoned. Indeed, evidence from H–D isotopic exchange reactions, which are thought to occur by heterolytic splitting of C–H and C–D bonds, shows that even small traces of CO_2 cause almost complete poisoning of this reaction.

On the other hand several authors have proposed that C–H bond activation occurs through deprotonation, but the evidence in support of this proposal is not entirely clear. For example, Choudhary and Rane [4] have compared the activity of several oxides for methane conversion with the acid/base properties of the catalysts but found no simple correlation. They proposed that *both* acidic and basic sites were important and rationalised the results by proposing the occurrence of an acid–base pair as the active site, which comprised a metal cation (the acidic site) and an oxide anion (the basic site). Deprotonation would lead to the formation of an OH(ads) and a CH_3^- ion attached to a metal cation.

3. Metal-based catalysts

The rate of activation of C–H bonds on metal catalysts depends on the choice of hydrocarbon, the choice of metal, and the reaction conditions. Although it is a rather simple point, it is apparently not always fully appreciated that the state of the surface of a "metal" catalyst depends on the reaction conditions. Under oxygen-rich conditions the metal may be fully covered with oxygen because the competitive adsorption of oxygen and a *saturated* hydrocarbon strongly favours oxygen. On the other hand, under fuel-rich conditions, the surface could be fully reduced, and is likely to be covered with carbonaceous species, or it may only be partially reduced, and covered with both carbonaceous and oxygen species. The exact state of the catalyst under nominally reducing conditions will depend on factors such as the choice of metal, support effects, the hydrocarbon, the temperature, the stoichiometry of the reaction mixture, and the time of exposure to a particular reaction mixture. It is certainly the case that a catalyst exposed to a reactant mixture which has a fluctuating composition may not have a surface in the expected equilibrium state and may, in consequence, not have the expected catalytic activity.

Other factors of importance in C–H bond activation on metal catalysts are: inhibition by products (CO_2 and H_2O); poisoning effects (e.g. by chlorine or SO_2/SO_3); and promotion effects (e.g. by SO_2). We shall now describe examples of results which illustrate the significance of these various effects.

3.1. The optimum state of the surface for catalytic combustion

It is well established that Pd is the most active catalyst for the oxidation of methane but that Pt is a better catalyst for the oxidation of higher hydrocarbons. The rate of combustion of methane on Pt or Pd catalysts depends on the state of the catalyst surface. Because oxygen adsorbs much more effectively than methane, the metal surface will either be covered with chemisorbed oxygen (in the case of Pt) or be oxidised (in the case of Pd) under circumstances where there is either an excess of oxygen in the gas mixture or at low conversions with fuel-rich mixtures. Kinetic studies show that the order of reaction with respect to oxygen is 0 and with respect to methane is 1 except when there is insufficient oxygen for the reaction. Previous work carried out in our laboratory has shown that the rate of oxidation of methane on Pt increases to a maximum as the Pt is contacted with a methane/air mixture. The optimum activity occurs when the Pt is *partially* oxidised [5]. In contrast the combustion of methane on Pd increases steadily as the Pd is progressively and *fully* oxidised to PdO [5]. The difference between the two metals can be rationalised by the fact that the Pt surface, fully covered with adsorbed oxygen cannot readily activate the almost non-polar C–H bonds in methane (by a homolytic mechanism), whereas the $Pd^{2+}O^{2-}$ ions at the surface of the PdO can more easily activate the C–H bonds by a heterolytic mechanism.

When the oxygen content of the reaction mixture is decreased, Pt can be a more effective catalyst than Pd. This can be rationalised on the basis that a partially oxidised Pt surface will contain free metal sites, adjacent to adsorbed oxide ions, at which methane can dissociatively adsorb leading to a light-off of the combustion reaction. The active sites on PdO are less sensitive to oxygen partial pressure because of the greater stability of PdO as compared with Pt oxide.

The actual state of the metal or oxide surface is therefore important in determining the inherent activity of the system, so it is relevant to investigate the state of the surface under non-steady state reaction conditions. The transient exposure of Pd/PdO to changes in the gas composition provides information about the state of the catalyst surface under dynamic reaction conditions. Fig. 1 shows that when the gas composition is oscillated between lean and rich conditions the activity observed does not correspond to the steady state activity in either the lean or rich conditions, which are indicated in the figure. The activity of the dynamic state (results not shown) depends on the temperature of the reaction and can be a more active or a less active state than the expected steady state values.

Fig. 1 shows that at 400°C when the gas mixture is cycled and a measurement made at the end of the oxidation or the reduction cycle, the activity is very low compared to the steady state values. However, when the catalyst is then left continuously under either the oxidising or the reducing mixture, the activity begins to increase over a period of about 1 h. However, whereas the activity under oxidising conditions rises to about the steady state value, the activity under reducing conditions never attains the corresponding level. On returning to cycling conditions the activity in both cases falls again.

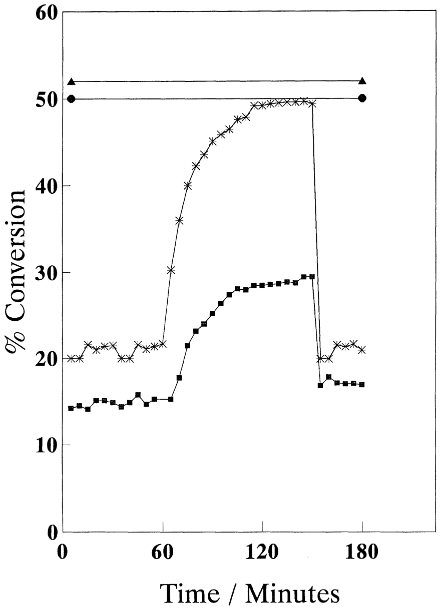

Fig. 1. The effect of 30 s cycling between oxidising (2000 ppm CH_4, 5000 ppm O_2) and reducing (2000 ppm CH_4, 3000 ppm O_2) gas mixtures on methane combustion activity over a 0.5% Pd/Al_2O_3 catalyst at 400°C: (∗) catalyst exposed to oxidising gas mixture after 1 h cycling; (■) catalyst exposed to reducing gas mixture after 1 h cycling; (▲) steady state for methane combustion in the oxidising gas stream; (●) steady state for methane combustion in the reducing gas stream.

This complicated behaviour is not yet understood, but it once again reflects the complexity of combustion catalysts in which the metal and the metal oxide are in a dynamic equilibrium and in which the influence of the support can be significant. Support effects are also important in the case of Rh catalysts for methane combustion. The activity of Pd and Pt for methane combustion is generally considered to be significantly higher than that of Rh. However, Fig. 2 shows that this is probably a result of deactivation of Rh by interac-

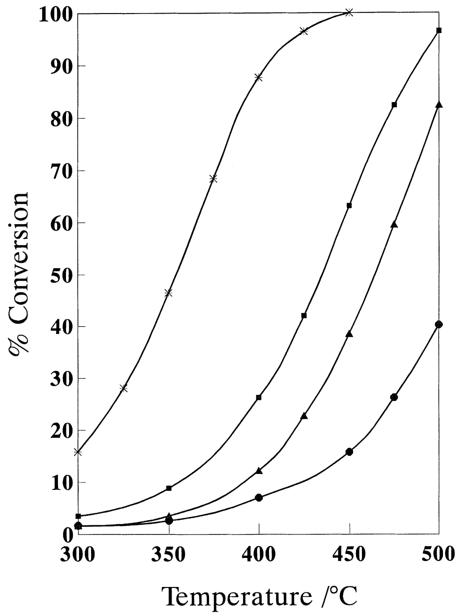

Fig. 2. Plot of CH_4 conversion against temperature for fresh 1% Rh/Al_2O_3 catalysts. Catalysts calcined at (∗) 300°C, (■) 500°C, (▲) 600°C, (●) 700°C.

tion with the alumina support under strong oxidising conditions at higher temperatures. By avoiding these strong metal/support effects it is possible to prepare a supported Rh catalyst (Rh/ZrO_2) which has a high activity for methane combustion. It seems highly probable that for Pd/Al_2O_3 catalysts some of the anomalous effects observed, and the lack of correlation between activity and particle size could be attributed to variations in the extent of metal/support interaction. This would be expected to be a particular problem for catalysts containing a low loading of PdO.

The products of combustion, CO_2 and H_2O, can also inhibit the reaction. Experiments show, however, that H_2O is a much stronger inhibitor than CO_2 and that in the presence of both, CO_2 has hardly any effect. An interesting point concerning H_2O is that the release of H_2O involves a dehydroxylation of the surface to re-create surface oxide sites, e.g. on PdO. If these oxide ions are required for C–H bond activation then it is apparent that the rate of dehydroxylation needs to be much faster than for C–H bond activation otherwise severe catalyst deactivation will occur because active sites are blocked. Experiments at very short contact time using very dry gas mixtures have shown that the *initial* activity of dry PdO/Al_2O_3 catalysts is significantly higher than that of catalysts exposed to the reaction mixture. The effect is reversible and therefore not due to permanent deactivation. We conclude from this that at moderate temperatures the breaking of a surface O–H bond is slower than the breaking of a C–H bond and so it is not safe to assume that the rate determining step, even for methane combustion, is C–H bond activation. There is a similarity here with the results mentioned above concerning C–H bond activation on methane coupling catalysts where again it has been proposed that the rate determining step may not be the breaking of the C–H bond but rather the dehydroxylation of the surface to re-create the active site. It should be noted that kinetic isotope experiments, which appear to support the breaking of the C–H bond as rate determining, may not be able to distinguish between breaking of C–H(D) and O–H(D) bonds, either of which will exhibit kinetic isotope effects.

3.2. *Poisoning and promoter effects*

Impurities, such as chlorine or SO_2, in gas streams, or introduced during catalyst preparation can significantly affect the activity of Pt and Pd for combustion of hydrocarbons. Chlorine is certainly a *poison* for methane combustion on Pd catalysts. Catalysts prepared from chlorine-containing precursors have higher metal dispersions, and hence a larger active surface area, but are much less active than catalysts prepared from chlorine-free precursors. When a catalyst prepared from a chlorine-containing precursor is used for a prolonged period of time, its activity gradually increases and approaches, but never quite attains that of the catalyst free from chlorine. There has been some debate in the literature concerning the role of chlorine but it now seems to be generally agreed that chlorine poisons metal catalysts for methane combustion and that the inadvertent presence of chlorine could account for some induction and activation effects with Pd catalysts.

SO_2 is in many ways more interesting since it can act both as a poison and as a promoter. For *alkene* oxidation, SO_2 is invariably a poison. For methane oxidation on Pd, SO_2 is also a poison. However, for *alkane* oxidation on Pt catalysts it is reported that SO_2

can promote the reaction. The poisoning by SO_2 is rather easy to understand. In the case of Pd the SO_2 will react with PdO to form a relatively stable Pd sulphate which is not effective for C–H bond activation. With alkenes, the surface will normally be almost covered with carbonaceous species with which oxygen will react very rapidly. SO_2 will block surface sites for adsorption and thus poison the activity.

The *promoting* effect of SO_2 for the oxidation of *alkanes* on Pt is intriguing. Recently, Lambert and coworkers [6] have shown that the adsorption of propane on a Pt single crystal surface is greatly facilitated if SO_2 and O_2 are co-adsorbed prior to the introduction of the propane. In the absence of the SO_2 the sticking probability for propane is almost zero. They conclude that the promoting effect of SO_2 can arise from a direct interaction on the metal surface and state that "support mediated effects are not necessary for SO_2 promotion of Pt-catalysed propane combustion". However, this would not explain why Pt/Al_2O_3 is promoted whereas SO_2 has no effect on Pt/SiO_2 [7].

We have investigated the SO_2 effect in propane combustion in some detail and some initial results are shown in Fig. 3. The results show that the pretreatment of a 1 wt% Pt/Al_2O_3 catalyst with 30:1 O_2:SO_2 at 500°C for 2 h leads to a dramatic enhancement of activity with sulphated catalyst being up to 15 times more active for propane combustion at 250°C. No equivalent effects are observed with Pt/SiO_2 catalysts. Fig. 4 shows that the effect of SO_2 is progressive with the activity being higher while the SO_2 is present in the gas phase but note also that the activity after the SO_2 is switched off is gradually rising.

Experiments to determine the orders of reaction with respect to propane and oxygen both in the absence and in the presence of SO_2 have shown that the order in *both* cases is 1 with respect to propane. The order of the reaction with respect to oxygen appears to be substantially more negative for the pre-sulphated catalyst. Further work is in progress to try to understand more fully the promoting effects of SO_2 in propane combustion.

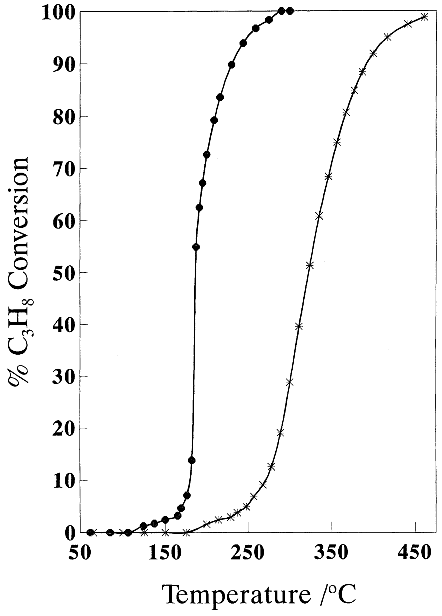

Fig. 3. The effect of a 2 h pre-treatment of 30:1 O_2:SO_2 at 500°C on the activity of a 1% Pt/Al_2O_3 catalyst for the combustion of propane ($[C_3H_8]$=4000 ppm, $[O_2]$=40 000 ppm). (●) SO_2 pretreated sample, (∗) SO_2-free sample.

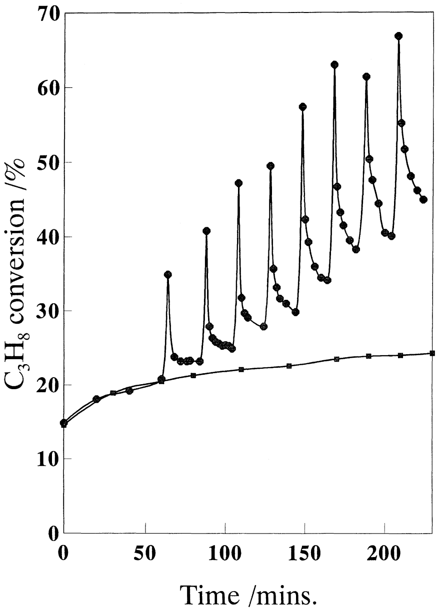

Fig. 4. Plot of propane conversion against time for a 1% Pt/Al_2O_3 catalyst which has been exposed to a series of 30 s pulses of 20 cm^3 min^{-1} 500 ppm SO_2/N_2 at 300°C (●). Steady state for propane conversion over the catalyst at 300°C in a 20:1 O_2:C_3H_8 gas mixture in the absence of SO_2 (■).

4. Conclusions

In surveying some aspects of catalytic combustion we can draw some general conclusions:

- The optimum state of the catalyst depends on the choice of hydrocarbon and metal. For example, with methane on Pt it is a partially oxidised surface, whereas for methane on Pd it is a fully oxidised surface.
- Alkenes adsorb strongly in competition with oxygen, giving a catalytic surface which is reduced and contains a high concentration of carbonaceous species.
- Alkanes adsorb weakly in competition with oxygen giving a catalyst surface which is close to fully oxidised.
- Metal/support interactions with alumina-supported catalysts can lead to severe catalyst deactivation.
- Induction effects may be due to poisoning by chlorine and/or support effects.
- For methane combustion on Pd catalysts the rate determining step could be the release of water from surface-OH groups rather than the initial C–H bond-breaking step because of the relative stability of Pd(OH).
- The Pd/PdO transition, which is dependent on temperature and the reaction mixture, is relatively slow and under conditions which oscillate from net oxidising to net reducing, the "average" state of the catalyst may not reflect either steady state value.
- SO_2 greatly enhances the activity of Pt/Al_2O_3 catalysts for the combustion of propane but has no effect on Pt/SiO_2 catalysts. This suggests that the role of SO_2 is to create new active sites, possibly having a lower activation energy, on the support. The most likely location of such sites would be at the interface between a metal particle and the oxide support. The fact that the influence of SO_2 is support-dependent indicates that under typical reaction conditions the enhancement of propane adsorption and oxidation is not a metal-only effect.

Acknowledgements

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