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Ignition in alkane oxidation on noble-metal catalysts

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Abstract

The ignition behavior in the oxidation of four simple alkanes (methane, ethane, propane and isobutane) with air on a platinum-foil catalyst, as well as that of ethane/air mixtures on four noble-metal foil catalysts (Pt, Pd, Rh, and Ir) was studied at atmospheric pressure over the entire range of fuel-to-air ratios. While, Pd showed the widest range of surface flammability, ignition temperatures for ethane/air mixtures were lowest on Pt. Both, Rh and Ir deactivated rapidly under fuel-lean conditions and ignited considerably higher than Pd and Pt. The surface ignition temperatures were found to correlate well with the C–H bond energy of the hydrocarbon and the metal-oxygen bond energy of the noble metal. A very simple analytical model was able to reproduce the dependence of surface ignition temperatures on fuel-to-air ratios, yielding apparent activation energies for the surface reactions and indicating an oxygen-covered surface before catalytic ignition due to strong site competition between the hydrocarbon and oxygen on the catalyst surface. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic hydrocarbon oxidation; Noble metal catalysts; Ignition/extinction; Homogeneous-heterogeneous reactions

1. Introduction

Catalytic oxidation of hydrocarbons has again become the focus of many basic and applied catalysis research because of its increasing importance for many industrial processes [1–3]. Catalytic partial oxidation under fuel-rich conditions (i.e. with over-stoichiometric hydrocarbon content in the reaction mixture) is the basis for the production of many important chemicals [4]. Catalytic abatement of waste gases (i.e. total oxidation of trace amounts of hydrocarbons in air-rich gas streams) has become of major importance on account of increasingly restrictive environmental legislation [5–7]. Finally, the total oxidation of lean and near-stoichiometric hydrocarbon/air mixtures has received great interest in the context of catalytically aided combustion for power generation [8–10]. The reasons for the use of catalysts in these processes vary from enhancing the selectivity towards the desired products within a network of parallel and consecutive reactions (in the case of partial oxidation reactions), to avoiding undesired side reactions (such as NO_x formation) by lowering the necessary reaction temperature and stabilising the reaction against fluctuations in the feed composition (in the case of total oxidation reactions). For all of these processes, a detailed knowledge of the ignition and extinction limits of both, the catalytic surface reactions as well as the homogeneous gas-phase reactions, are of prime importance due to both, economic and safety concerns.

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Despite this importance, very few studies have so far been conducted to investigate the ignition–extinction properties of hydrocarbon–air mixtures over typical oxidation catalysts. While the purely homogeneous ignition behaviour of fuel–air mixtures has been intensively studied since many decades [8,11,12], equivalent studies for catalytic reactions, as well as investigations of the mutual influence between catalytic and homogeneous reactions are still lacking. A few published studies on the ignition of different hydrocarbons on platinum catalysts differ widely in their experimental conditions and the reported behaviour, making a meaningful comparison between the reported results very difficult [13–15]. On the other hand, most studies of alkane oxidation on different metal catalysts typically focus on comparing the steady-state activity of these systems, ignoring the aspect of ignition of the catalytic reaction [16–18].

The present paper is part of a study that attempts to help to close this gap by investigating, in a systematic and easily reproducible manner, the complete ignition–extinction behaviour of different hydrocarbon–air mixtures over several catalytic noble metals. While the study is aimed at obtaining complete bifurcation diagrams for these systems (i.e. the complete curves for heterogeneous ignition and extinction as well as for homogeneous gas-phase ignition), this paper focusses exclusively on the ignition of the catalytic surface reaction. For more extensive reports on the complete heterogeneous and homogeneous ignition–extinction behaviour, the reader is referred to Refs. [19,20].

2. Experimental setup

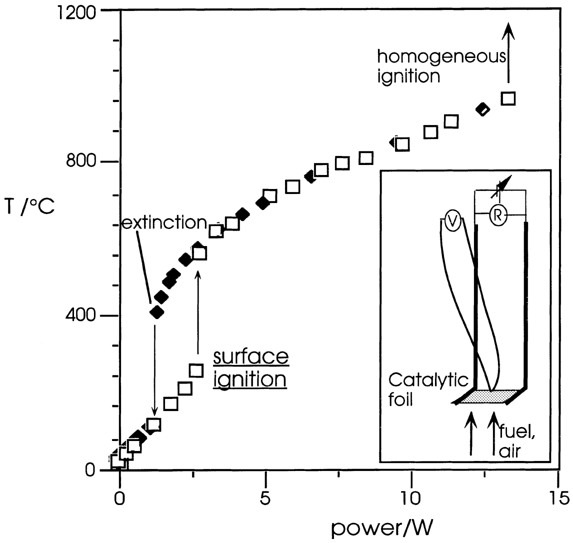

Fig. 1. Typical S-shaped ignition–extinction curve, showing an experimental temperature trace vs. external power input for one fixed fuel-to-air ratio. In addition, (a) surface ignition, (b) surface extinction and (c) ignition of the gas phase are also indicated. The inset shows the experimental setup.

The experimental setup was designed for simplicity and reproducibility. All experiments were conducted at atmospheric pressure in a quartz-glass flow tube reactor of 2.5 cm diameter and 20 cm length. The reaction gases were introduced through mass-flow controllers, premixed in a premixing zone, and flowed perpendicular to the catalytic foil in a stagnation-point flow configuration (inset Fig. 1). All experiments were conducted at a fixed 3 slpm air-flow rate with varying hydrocarbon-flow rates. Varying the total gas flow rate between 1 and 6 slpm did not influence the results within experimental error. The high-purity metal foils were resistively heated, which allowed calculation the external power input by measuring the current along with the voltage drop across the foil. The temperature of the foil was determined by a catalytically inactive chromel/alumel thermocouple spot-welded to the back of the foil. Temperature measurements were reproducible within ±20 K on the same foil and within ±50 K in independent runs with different foils. All data shown was reproduced on at least five different foils.

During an experiment, the gas flow was adjusted to a fixed hydrocarbon–air ratio and then the power input to the foil was increased, until a discontinuous jump in the foil temperature indicated the ignition (light-off) of the catalytic surface reaction (Fig. 1). On decreasing the power input, these reaction typically show a hysteretic behaviour, i.e. the extinction of the surface reaction occurs at a lower power input than the ignition due to the heat released by the catalytic reaction. Ignition and extinction are, thus, defined in this study by the occurrence of a hysteresis loop in the power–temperature diagram (Fig. 1). This data acquisition procedure was repeated with varying hydrocarbon content of the reaction mixture and, thus, determining the ignition–extinction behaviour over the whole range of (catalytic) flammability. To assure reproducibility of the results, data acquisition and the control of the power unit were computer controlled, strict criteria for a stationary point were applied, and the experiments were repeated with several different foils for each catalyst.

Throughout this paper, the experimental ignition curves will be shown as temperature vs. a corrected equivalence ratio. While the equivalence ratio, Φ, is usually defined in the combustion literature as:

$$\Phi \equiv \frac{(\%\,\mathrm{fuel}/\%\,\mathrm{air})}{(\%\,\mathrm{fuel}/\%\,\mathrm{air})_{\mathrm{stoich.}}}$$

we prefer to depict the data vs. a modified equivalence ratio, $\Phi/(1+\Phi)$. This modification has the advantage that it puts equal weight on the fuel-lean and fuel-rich sides of the ignition curve, i.e. while the usual Φ maps fuel-lean mixtures on a scale from 0 to 1 and fuel-rich mixtures on a scale from 1 to ∞, the corrected ratio maps fuel-lean mixtures from 0 to 0.5 and fuel-rich mixtures from 0.5 to 1. Therefore, independently of the specific fuel (hydrocarbon) used in the study, the stoichiometric point for total oxidation to CO_2 and H_2O is at 0.5 on this axis, with typical partial oxidation reactions occurring on the fuel-rich side of this axis ($\Phi/(1+\Phi)>0.5$) and catalytic combustion typically occurring under fuel-lean ($\Phi/(1+\Phi)<0.5$) conditions. Throughout this paper, the term ‘equivalence ratio’ will be used to refer to this modified equivalence ratio, unless stated otherwise.

3. Results

The investigation was aimed at studying both, the influence of the specific fuel (hydrocarbon) as well as that of the catalyst on surface ignition temperatures. To determine the influence of the fuel on catalytic ignition, we studied the ignition of four different simple hydrocarbons, namely methane, ethane, propane and isobutane, on platinum. For comparison of fuels, Pt was chosen as a catalyst due to the fact that it constitutes the most investigated and best understood oxidation catalyst, and exhibits the simplest behaviour showing neither oxide nor coke formation under the conditions of our experiments.

Fig. 2 shows the results for the catalytic ignition of the four simple saturated hydrocarbons on a platinum foil. All four ignition curves show essentially the same trends: they start at an equivalence ratio at the lower surface ignition limit of 0.2 for methane to 0.27 for ethane and extend to an upper limit of 0.88 for

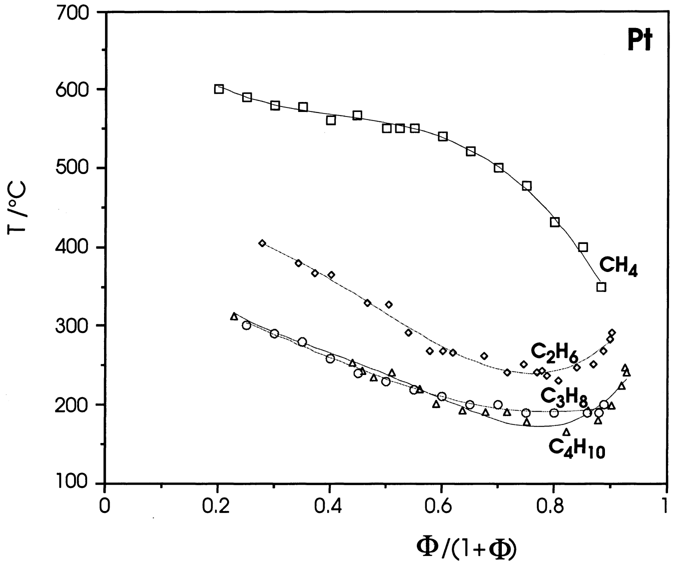

Fig. 2. Ignition curves for the four alkanes on platinum-foil catalyst. Depicted is the ignition temperature vs. (modified) equivalence ratio. (Not all experimental data points are shown.)

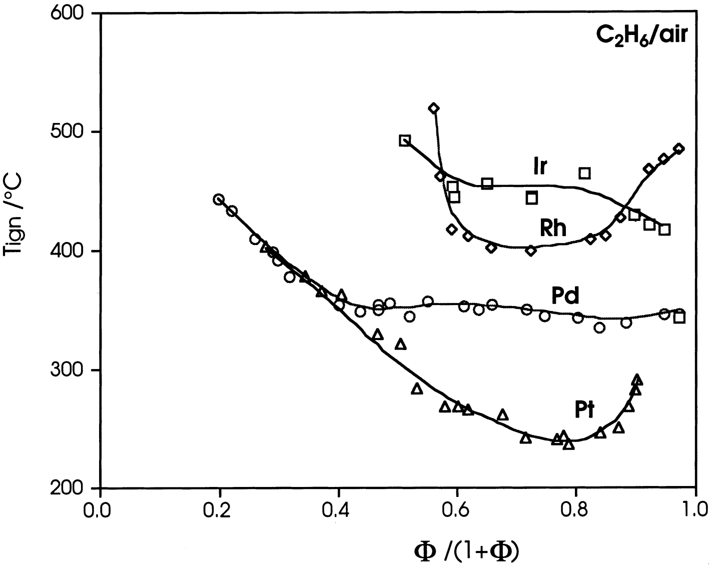

Fig. 3. Ignition curves for ethane/air mixtures over four noble-metal foil catalysts. Depicted is the ignition temperature vs. (modified) equivalence ratio. (Not all experimental data points are shown.)

methane to 0.93 for isobutane. For all hydrocarbons, the ignition temperatures drop continuously over almost the entire range from the lean ignition limit to an equivalence ratio of ca. 0.8. Beyond that, the ignition curves for all fuels, except methane, bend towards somewhat higher temperatures before reaching the fuel-rich limit of surface ignitability. At any fixed equivalence ratio, the ignition temperature drops with increasing chain length of the hydrocarbon. On account of the slight increase in ignition temperature for the C2–C4 hydrocarbons at the fuel-rich end of the ignition curves, this trend is somewhat less pronounced for fuel-rich than for fuel-lean mixtures.

The results for catalytic ignition over four different noble metals, i.e. platinum, palladium, rhodium and iridium, are shown in Fig. 3. For this set of experiments, ethane was chosen as 'representative' hydrocarbon. From the above results (Fig. 2), it can be seen that ethane shows a more 'typical' alkane ignition curve than methane, yet, it is still a very simple hydrocarbon molecule.

Obviously, the ignition curves for Pd and Pt are very similar as are those for Rh and Ir. While both, Pd and Pt show catalytic ignition over a wide range of fuel-to-air ratios from very lean to extremely rich mixtures, ignition on Rh and Ir is restricted to fuel-rich mixtures. Also, ignition temperatures on Pt and Pd lie ca. 100°–200°C below those on Rh and Ir. For fuel-lean mixtures, the ignition temperatures on Pd and Pt are essentially identical, showing the above-mentioned decreasing trend with increasing equivalence ratio. This trend continues on Pt well into the fuel-rich regime, while ignition temperatures on Pd remain essentially constant for fuel-rich mixtures. In contrast, the trends on Rh and Ir are quite dissimilar: on Rh, the ignition temperature shows an increase towards both limits of surface ignitability, while on Ir, ignition temperatures drop continuously with increasing fuel content. Both ignition curves show a plateau between equivalence ratios of ca. 0.6 and 0.85, with ignition temperatures of ca. 450°C on Ir and 400°C on Rh. As a consequence of their dissimilar behaviour towards both limits of surface ignitability, the ignition curves on Rh and Ir intersect near stoichiometric and at extremely fuel-rich ethane/air mixtures.

While the ignition temperatures for all hydrocarbons on Pt and ignition on Pd were highly reproducible (to ca. ±10 K between independent runs) and independent of the 'history' of the catalytic foil, ignition temperatures on Rh and Ir showed a considerably greater scatter (up to ±40 K) and were strongly dependent on previous runs with the same catalytic foil when switching between fuel-lean and fuel-rich conditions. Under lean conditions, Rh and Ir deactivated quickly after initial ignition (within >1 h) and could not be re-ignited, until after reactivation by running under highly fuel-rich conditions.

4. Discussion

The most obvious result of this investigation is that catalytic ignition for all hydrocarbons studied and on all catalysts occurs at much lower temperatures and over a much wider range of fuel-to-air ratios than homogeneous ignition. While homogeneous ignition temperatures for these fuels lie well above 1000°C, catalytic ignition occurs at temperatures of 600°C and below, and while homogeneous ignition is confined to a relatively narrow flammability range (between an equivalence ratio of 0.33–0.6 for methane and 0.37–0.73 for isobutane), this range can be extended significantly by using a catalyst.

The most versatile catalysts in these respects are Pd and Pt, which not only show the lowest ignition temperatures, but also the widest range of surface ignitabilities. While ethane ignition extends over an even broader range of equivalence ratios on Pd than on Pt (0.2–0.97 on Pd vs. 0.27–0.9 on Pt), ignition occurs at considerably lower temperatures for fuel-rich mixtures on Pt. Also, while no coke formation was observed on Pt under any conditions and with any of the fuels used, deactivation due to coke formation could be observed on Pd for very fuel-rich mixtures (equivalence ratio >0.65). Thus, for catalytic combustion, where one essential criterion for catalyst selection is ignition at as lean as possible equivalence ratios and as low as possible temperatures, Pd seems to be the best catalyst. For the ignition of partial oxidation reactions, which occur typically under highly fuel-rich conditions, Pt is clearly better suited, since it ignites at lower temperatures and does not coke.

In the following, we will discuss the influence of the specific hydrocarbons on catalytic ignition and the influence of the different noble-metal catalysts separately in more detail.

4.1. Influence of fuel

The ignition curves for the four different hydrocarbons show two distinct qualitative trends: (1) a decrease of the ignition temperature with increasing fuel-to-air ratio over a wide range of equivalence ratios; and (2) a decrease in ignition temperature with increasing chain length of the hydrocarbon. The correlation of the ignition temperature with the chain length of the hydrocarbon can be traced back to correlation of the activation of the hydrocarbon with the C–H bond strength. This is depicted in Fig. 4, which shows the ignition temperatures for the four alkanes near the stoichiometric point vs. the weakest C–H bond energy of the corresponding alkane. Similar correlations of alkane oxidation activity with the C–H bond energy have also been reported recently in single crystal UHV-studies during dehydrogenation and combustion of aromatic hydrocarbons on Pd(100) [21]. As we find a strong correlation between surface ignition and C–H bond strength, the deviation from a simple linear dependence also indicates that the C–H bond strength is not the only factor determining surface ignition temperatures. Obviously, a realistic picture of the mechanistic processes during catalytic ignition will be more complex, taking into account additional factors such as differences in the sticking coefficients between the different hydrocarbons, site competition between the surface adsorbates, and others.

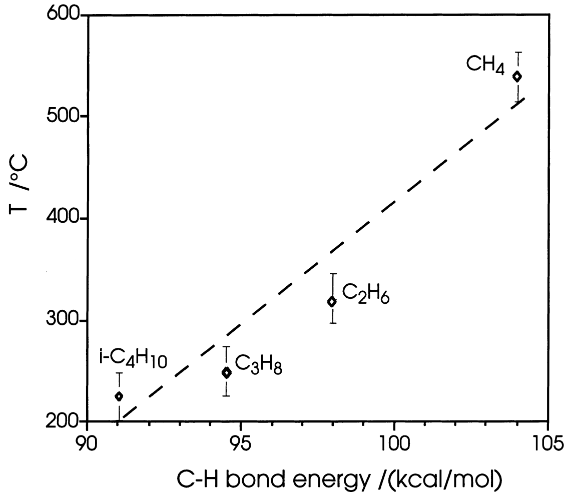

Fig. 4. Ignition temperatures for four alkane/air mixtures on platinum vs. C–H bond energy of the corresponding alkane. Ignition temperatures were taken at the stoichiometric point for total oxidation of the hydrocarbon ($\Phi/(1+\Phi)=0.5$).

The decrease in ignition temperature with increasing fuel content of the reaction mixture, on the other hand, is strongly indicative of site blocking by oxygen on the catalyst surface, poisoning the catalyst for the reaction. This assumption was tested with a highly simplified model for the catalytic surface reaction [19], assuming a simple first-order Langmuir–Hinshelwood (LH) mechanism, in which the hydrocarbon (HC) and oxygen adsorb competitively and non-dissociatively on the surface (S) according to:

$$\mathrm{HC} + \mathrm{S} \rightleftharpoons \mathrm{HC} - \mathrm{S}$$

$$\mathrm{O_2} + \mathrm{S} \rightleftharpoons \mathrm{O_2} - \mathrm{S}$$

$$\mathrm{HC} - \mathrm{S} + \mathrm{O_2} - \mathrm{S} \rightleftharpoons 2\mathrm{S} + \text{products}$$

Obviously, the assumption of non-dissociative adsorption as well as the reaction being of the first order in both reactants are gross simplifications, since both, the hydrocarbon and oxygen will obviously dissociate before reaction on the surface, and the further reaction will involve several consecutive and parallel reaction steps. Nevertheless, the model should allow for a qualitative test of the assumption that site competition between the hydrocarbon and oxygen accounts for the observed trend in ignition temperature with fuel-to-air ratio.

The standard kinetic rate equation for the mentioned LH mechanism can be further simplified by assuming that the adsorbate coverages are determined by adsorption–desorption equilibrium, since we are only interested in the ignition behaviour of the surface reaction. This assumption also allows us to disregard any mass transport limitations in the gas phase above the catalyst surface, since these only become relevant *after* ignition of the surface reaction. If we, finally, take into account the hypothesis that a higher oxygen sticking coefficient is responsible for the observed trend and, thus, assume a mostly oxygen covered surface (for fuel-lean conditions), we obtain the following overall rate expression which yields a direct proportionality of r with Φ:

$$r = k_{\mathrm{r},0}\frac{K_{\mathrm{HC},0}}{K_{\mathrm{O_2},0}}\exp\left\{-\frac{E_{\mathrm{app}}}{RT}\right\}\Phi$$

where $k_{\mathrm{r},0}$ denotes the kinetic pre-exponential factor, $K_{\mathrm{i},0}$ the pre-exponential factors of the adsorption/desorption equilibrium constant for the hydrocarbon and oxygen, respectively, and Φ denoting the (standard) equivalence ratio. E_{app} sums the activation energies for the surface reaction, as well as the desorption of the hydrocarbon and oxygen by $E_{\mathrm{app}} = E_{\mathrm{R}} + \Delta H_{\mathrm{ad,HC}} - \Delta H_{\mathrm{ad,O_2}}$.

A heat balance, including conductive heat losses ($\alpha(T-T_0)$), resistive heating (VI) and the heat evolved by the surface reaction ($r\ \Delta H_{\mathrm{R}}$) yields, after applying the ignition criterium and substituting the above rate equation, an analytic expression for the equivalence ratio as a function of temperature:

$$\Phi = aT^2\exp\left\{\frac{E_{\mathrm{app}}}{RT}\right\}$$

where 'a' is a proportionality factor that lumps several pre-exponential and geometrical factors. This function can be fitted to the measured ignition curves for all alkanes between equivalence ratios of ca. 0.2 and 0.75, yielding apparent activation energies that drop with increasing chain length from $E_{\mathrm{app}}\approx 110$ kJ/mol for methane and $E_{\mathrm{app}}\approx 95$ kJ/mol for ethane to $E_{\mathrm{app}}\approx 80$ kJ/mol for propane and isobutane. These values are very reasonable for surface reactions and yield an almost perfect fit between calculated and experimentally measured ignition temperatures (Fig. 5), which strongly supports our hypothesis that site competition between the hydrocarbon and oxygen during adsorption is mainly responsible for the observed trend of decreasing ignition temperatures with increasing fuel content in the gas phase. This trend has recently also been observed in UHV studies of methane dissociation on Pt(111), where Valden et al. [22] found a decreasing methane dissociation activity with increasing oxygen pre-coverage of the catalyst.

Finally, it is also interesting to note that a plot of these fitted apparent activation energies vs. the C–H bond energies of the corresponding hydrocarbons (Fig. 6) reflects again the close correlation between ignition and C–H bond strength as shown in Fig. 4. Despite the fact that we did not assume dissociative adsorption of the hydrocarbon, the dissociation step is obviously contained implicitly in our model in the lumped surface reaction step.

4.2. *Influence of catalyst*

The most striking feature in comparing surface ignition on the four different noble metals is the range

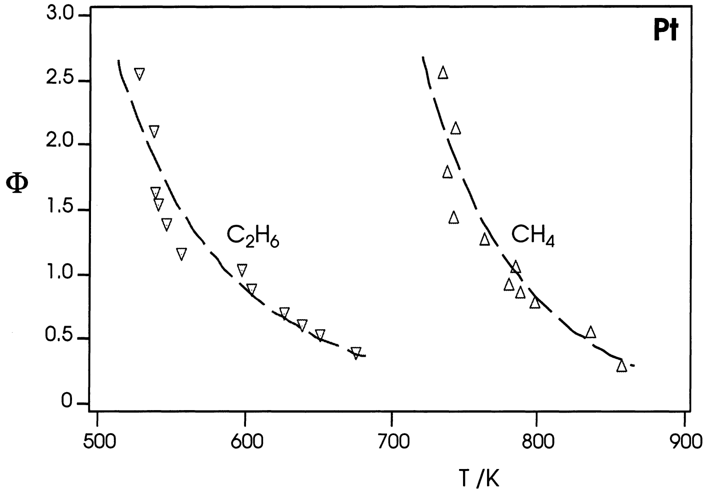

Fig. 5. Model fit (- - -) and experimental data points for the ignition temperatures of ethane/air (▽) and methane/air mixtures (△) over platinum foils. A two-parameter fit produces the right curvature and an almost perfect quantitative fit. (Note that this graph depicts the unmodified equivalence ratio vs. absolute temperatures.)

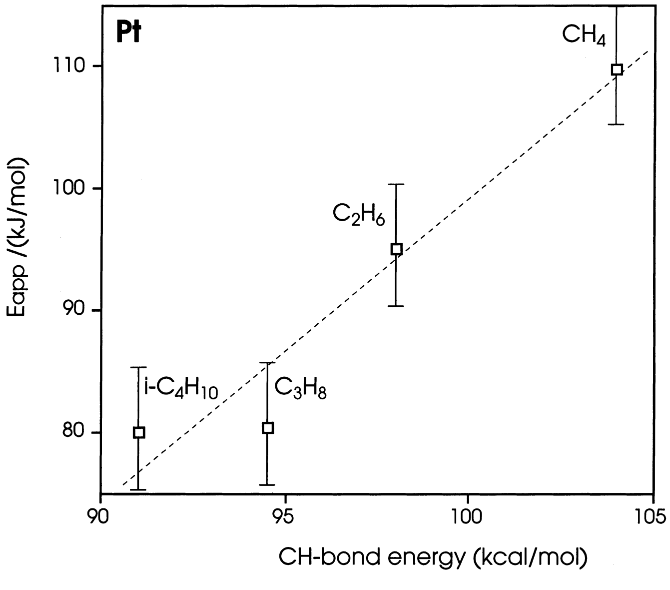

Fig. 6. Apparent activation energies for alkane/air oxidation on platinum foils vs. C–H bond energy of the corresponding alkane. The activation energies were obtained from a two-parameter model fit to the experimental ignition curves. C–H bond energies are taken from [27].

of fuel-to-air ratios over which they exhibit surface ignition. Whereas Pd and Pt support the surface reaction over a very wide range of equivalence ratios from very fuel-lean to extremely fuel-rich mixtures, Rh and Ir only show surface ignition in a fuel-rich atmosphere. Also, ignition on these metals was strongly dependent on the history of the foil, i.e. on the conditions under which the previous experiment on a specific foil had been conducted. Under fuel-lean conditions, Rh and Ir foils deactivated rapidly and could only be reactivated by running in a fuel-rich mixture (i.e. reducing atmosphere). Obviously, oxida-

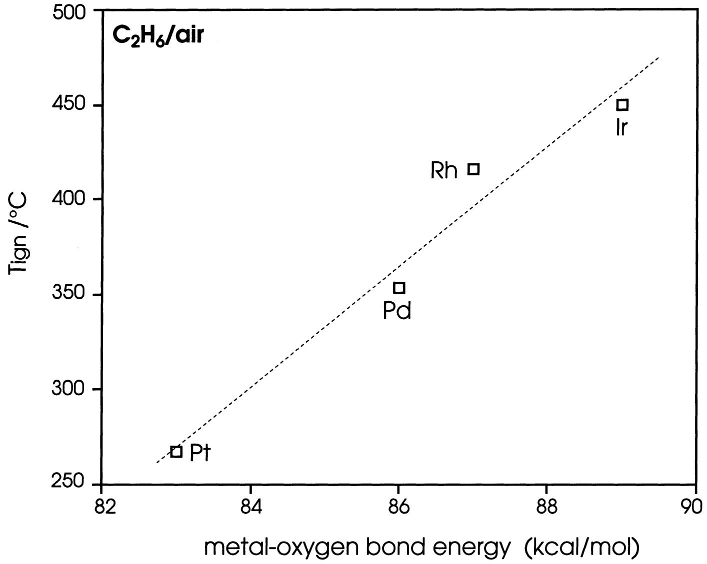

Fig. 7. Ignition tempeartures of ethane/air mixtures on four noble-metal foil catalysts vs. metal–oxygen bond energy of the corresponding noble metal. Ignition temperatures were taken at $\Phi/(1+\Phi)=0.6$, metal–oxygen bond energies are from [28].

tion and reduction of the catalyst plays an important role for the catalytic activity of these metals in that the oxidised state of the foil seemed to be inactive for ignition of the surface reaction.

This observation suggests, along with the fact that the ignition temperatures increase in the order Pt<Pd<Rh<Ir, that the metal–oxygen (MO) bond strength might be a determining factor for the reactivity of the catalytic foils. To test this hypothesis, we plotted the measured ignition temperatures vs. MO-bond strengths, taken from the literature (Fig. 7). Obviously, there seems to be a very close correlation between these two quantities which indicates that indeed the MO-bond strength is a decisive factor during ignition of the surface reaction. Based on the results of the ignition studies for the different alkanes on a platinum foil, the correlation with the MO-bond energies can be rationalised with the site competition between the hydrocarbon and oxygen on the catalyst surface: If we assume that, as on platinum, we again have a largely oxygen-poisoned surface up to ignition, then oxygen desorption, which creates free sites for the surface reaction, will be the decisive step for catalytic ignition. This desorption step is obviously determined by MO-bond energies.

Following this reasoning, we also conclude that deactivation on Rh and Ir is most likely a result of the formation of a relatively stable surface oxide under fuel-lean conditions. This can also explain the higher degree of scatter in the measured ignition temperatures on these catalysts: both, Rh and Ir form oxides with different stoichiometries, which will most likely also show different activities, thus making ignition temperatures very sensitive to the oxidation state of the metal surface prior to ignition.

From the foregoing argument, it logically follows that the lean ignition limit should also show some correlation with the MO-bond strength, since a strongly bonded surface oxygen should lead to a rapid poisoning of the catalyst surface in excess air. While this holds for the difference in lean ignition limits for Rh and Ir, on the one hand, and Pt and Pd, on the other, the lean ignition limits of Rh vs. Ir and of Pt vs. Pd are in reversed order of their MO-bond strength (see Fig. 3): Ir ignites somewhat leaner than Rh, and Pd ignites significantly leaner than Pt. Thus, while the simple dependence from MO-bond energies can explain the increasing ignition temperature on the different catalytic foils for a fixed fuel-to-air ratio, this model is too simple to fully explain the difference in the fuel-lean limits between the four metals.

In this respect, the extremely lean ignition limit of Pd is of particular interest for lean catalytic combustion applications. Palladium as a combustion catalyst has been intensively studied in recent years due to its unusual behaviour in an oxygen-rich atmosphere. Many researchers have noted a hysteresis in the oxygen uptake and release curves during heating and cooling cycles of Pd in oxygen or air, and reported an unusually high combustion activity of oxidised Pd catalysts [21,23–26]. Yet, no conclusive explanation for this behaviour has been found so far. We are currently extending our experiments to further investigate this surprising phenomenon.

5. Summary

The present report is part of a study which aims at obtaining a consistent set of data for the ignition–extinction behaviour of hydrocarbons during catalytic oxidation over noble-metal catalysts. By comparing the behaviour of four different alkanes over a platinum catalyst, and of ethane/air mixtures over four different metal foils, we attempted to isolate essential mechanistic steps in the catalytic ignition behaviour of hydrocarbon/air systems.

Three main correlations in the ignition behaviour of saturated hydrocarbons over noble-metal catalysts could be identified:

1. the surface ignition temperature decreases with increasing chain length of the hydrocarbon, which can be explained by the decreasing C–H bond strength of the alkanes;
2. surface ignition temperatures generally decrease with increasing fuel-to-air ratio due to site competition between oxygen and hydrocarbon on the catalyst surface and the higher sticking probability of oxygen on these surfaces; and
3. surface ignition temperatures increase with an increasing metal–oxygen bond energy in the order Pt<Pd<Rh<Ir.

The same correlation of the lean ignition limits with metal–oxygen bond energy, while expected, did not hold for all the metals. Obviously, in this case, a more complex model has to be setup to explain the ignition behaviour.

Finally, a highly simple model of the surface reaction was able to reproduce the dependence of the ignition behaviour of the fuel-to-air ratio surprisingly well. This suggests that, despite the fact that catalytic oxidation reactions typically involve an extremely complex set of parallel and consecutive reaction steps, only a few of these steps can suffice to describe the behaviour of these systems in specific situations.

Acknowledgements

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References

[1] F. Cavani, F. Trifirò, Appl. Catal. A88 (1992) 115.
[2] D.L. Trimm, Appl. Catal. 7 (1983) 249.
[3] B.K. Warren, S.T. Oyama, Heterogeneous Hydrocarbon Oxidation, American Chemical Society, Washington, DC, 1996.
[4] L.D. Schmidt, M. Huff, S.S. Bharadwaj, Chem. Eng. Sci. 49 (1994) 3981.
[5] J.A. Cusunamo, Chemtech, August (1992) 482.
[6] G. Eigenberger, U. Nieken, Int. Chem. Eng. 34 (1994) 4.
[7] J. Villermaux, D. Schweich, Ind. Eng. Chem. Res. 33 (1994) 3025.
[8] A. Linán, F.A. Williams, Fundamental Aspects of Combustion, Oxford University Press, Oxford, 1993.
[9] H. Ikeda, P.A. Libby, F.A. Williams, J. Sato, Combust. Flame 93 (1993) 138.
[10] L.D. Pfefferle, W.C. Pfefferle, Catal. Rev. -Sci. Eng. 29 (1987) 219.
[11] B. Lewis, G. von Elbe, Combustion, Flames and Explosions of Gases, Academic Press, New York, 1987.
[12] C.K. Law, F.N. Egolfopoulos, Twenty Fourth Symposium (International) on Combustion, 1992, p. 137.
[13] P. Cho, C.K. Law, Combust. Flame 66 (1986) 159.
[14] T. Griffin, L.D. Pfefferle, AIChE J. 36 (1990) 861.
[15] L. Hiam, H. Wise, S. Chaikin, J. Catal. 9 (1968) 272.
[16] L. van de Beld, M.P.G. Bijl, A. Reinders, B. van der Werf, K.R. Westerterp, Chem. Eng. Sci. 49 (1994) 4361.
[17] P.M. Torniainen, X. Chu, L.D. Schmidt, J. Catal. 146 (1994) 1.
[18] M. Huff, P.M. Torniainen, L.D. Schmidt, Catal. Today 21 (1994) 113.
[19] G. Veser, L.D. Schmidt, AIChE J. 42 (1996) 1077.
[20] M. Ziauddin, G. Veser, L.D. Schmidt, in preparation, (1996).

[21] X.-C. Guo, R.J. Madix, J. Chem. Soc. Faraday Trans. 91 (1995) 3685.

[22] M. Valden, N. Xiang, J. Pere, M. Pessa, Appl. Surf. Sci. 99 (1996) 83.

[23] R.J. Farrauto, M.C. Hobson, T. Kennelly, E.M. Waterman, Appl. Catal. A81 (1992) 227.

[24] P. Salomosson, S. Johansson, B. Kasemo, Catal. Lett. 33 (1995) 1.

[25] J.G. McCarty, Catal. Today 26 (1995) 283.

[26] X.-C. Guo, R.J. Madix, J. Am. Chem. Soc. 117 (1995) 5523.

[27] S.W. Benson, J. Chem. Educ. 42 (1965) 502.

[28] R.J. Madix, J.T. Roberts, in: R.J. Madix (Ed.), Surface Reactions, Springer, New York, 1994, p. 5.