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Catalysis of H_2, CO and alkane oxidation–combustion over Pt/Silica catalysts: evidence of coupling and promotion

N.D. Hoyle, P. Kumarasamy, V.A. Self, P.A. Sermon*, M.S.W. Vong

Catalysis, Fractal Solids and Surfaces Research Group, Department of Chemistry, School of Physical Sciences, University of Surrey, Guildford GU2 5XH, UK

Abstract

Results are presented on the oxidative–combustion reactions of H_2, CO, methane and propane over polycrystalline-powdered silica-supported catalysts containing Pt (and possibly oxide promoters, e.g. MnO_2, etc.) and the *coupling* of different combustion processes and also heterogeneous–homogeneous reactions. The Pt/silica catalysts appear to mature with use. Catalysed combustions take place, as expected, at far lower temperatures and with smaller activation energies than the homogeneous reactions. The role of added or intermediate (i.e. produced by alkane partial oxidation or steam reforming) H_2 in accelerating and lowering the temperatures of catalysed alkane combustions and hence minimising NO_x emission is considered with regard to the dispersion of the Pt, as is bifurcative–hysteretic combustion in the catalysed reaction, prevalent for CO, but less certain for H_2 or alkanes. CO decelerates the catalysed combustion of hydrogen on supported Pt (and may also do this for alkane combustion). Whether the acceleration due to intermediate H_2 in alkane combustion exceeds the deceleration due to intermediate CO remains to be seen, but it may be that the water–gas shift reaction moves the advantage to H_2. Further study by in situ methods will be needed to optimise and understand this coupling so that it can be used to maximise efficient alkane-catalysed combustion with minimum NO_x production. This should also lead to higher turnover numbers (which are at present quite low for propane-catalysed combustion). © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The 9th International Symposium on Combustion in Ithaca in 1963 [1] contained *no* catalytic papers, and by the 23rd meeting in the series held in Orleans, France in 1991 [2] there were just *two*:

1. a flow tube study of catalytically stabilised combustion of CH_3Cl over Pt (and MnO_2) at 800–1350 K in which there was evidence of coupling of heterogeneous–homogeneous reaction mechanisms [3].
2. a study of bifurcative behaviour in the oxidation of hydrocarbons (HC: methane and propane) over Pt [4].

In the *former* work, the catalysed conversion took place at 150 K lower temperatures than the non-catalysed process and rose exponentially at about 1000 K, producing CO_2 extensively as the temperature rose and smaller extents of CO at high temperature along with small amounts of C_2 species (e.g. C_2H_3Cl, *trans*/*cis*-$C_2H_2Cl_2$, etc). There was a suggestion that the

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*Corresponding author.

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catalyst did more than simply provide a hot surface, in that catalysed product distributions were different from those for the homogeneous reaction, where CO was more dominant. As with the oxidative coupling of methane, there was evidence of CH_3 radical coupling, although the Pt was a *deep-oxidation* catalyst, and *also of a heterogeneous–heterogeneous reaction mechanism coupling*. In the *latter* case the activation energy for the heterogeneous reaction was (as expected for catalysed processes) significantly lower than that for the homogeneous reaction, and the relevant rates (in mol/cm^2/s or mol/cm^3/s; where activation energies were in kcal/mol) were higher at a given temperature for catalysed combustion than for the non-catalysed one:

CH_4

Homogeneous	$2.5 \times 10^{12} \cdot \exp(-48.4/RT)[HC]^{0.2}[O_2]^{1.3}$
Heterogeneous	$1.3 \times 10^{11} \cdot \exp(-32.2/RT)[HC]^{1.0}[O_2]^{0.5}$

CH_4

Homogeneous	$8.6 \times 10^{11} \cdot \exp(-30.0/RT)[HC]^{0.1}[O_2]^{1.6}$
Heterogeneous	$1.1 \times 10^{9} \cdot \exp(-17.0/RT)[HC]^{1.0}[O_2]^{0.5}$

Interestingly, in this latter case the ratio of orders of reaction were very different for the homogeneous and heterogeneous reactions and the catalyst surface had a dramatic effect on the ignition of the homogeneous reaction, possibly as a result of surface radial desorption.

Some of the present authors have recently reported [5] on the use of Zr–O-based and Fe–Cr alloy-based catalysts in combustion technologies for a cleaner environment, where on wants to maximise the extent of efficient fuel oxidation, but minimise NO_x production. Of course at low air : fuel ratios λ (i.e. rich conditions relevant to a petrol engine) the levels of CO and hydrocarbons are relatively high, while at $\lambda > 1$ CO_2, H_2O and NO_x levels rise. Water injection can lower NO_x levels [6], but in lowering combustion temperatures catalysts also do this effectively. Methane can be an emission product from boilers and space heaters [7] and so can be minimised by catalytic combustors for methane [8]. Catalysts are also effective at catalysing CO oxidation [9]. In both contexts, then (i.e. improved fuel usage and lower pollutant emissions) catalysts are beneficial. Here, however, the authors were *also* interested in oxidative–combustion reactions of H_2, CO, methane and/or propane over polycrystalline-powdered silica-supported catalysts containing Pt (and possibly oxide promoters, e.g. MnO_2) and the coupling of heterogeneous reactions and exhibition of bifurcative–bistable behaviour and the role of intermediate H_2 and CO in the oxidation of alkanes. The following results are presented at this Amsterdam meeting which is solely dedicated to catalytic combustion. It was of course realised that the average ignition temperatures for homogeneous combustion rise from H_2 to CO to CH_4 and then decrease with increasing alkane carbon number (and the degree of hydrocarbon unsaturation) at 101 kPa, e.g.

H_2	856 K
CO	907 K
CH_4	964 K
C_2H_6	824 K
C_2H_4	789 K
C_2H_2	646 K [10]

and that they should be even lower for the catalysed oxidations–combustions of these reductants. This sequence is broadly that which is presented here.

2. Experimental

0.5 and 1% Pt/Silica were prepared by impregnation of Aerosil 200 (non-porous; 200 m^2/g total surface area; Degussa) with H_2PtCl_6 solution and then dried, calcined and in one case high-temperature reduced at 773 K in hydrogen (101 kPa). The total surface area of the latter catalyst (247 m^2/g) was a little higher than for the support alone. The average Pt particle size (d_{pt}) in this catalyst determined by chemisorption was 13.7 nm, which corresponded to a 7% dispersion of the group VIII metal. 3% Pt/Silica was prepared with an average Pt particle size (d_{pt}) of 18.6 nm, which corresponded to a 5.8% Pt dispersion. 6.3% Pt/Silica (EuroPt-1) [11] was used as received [5]; it had an average Pt particle size (d_{pt}) of 1.1 nm. These catalysts are denoted S1/2, S1, S3 and S6. Samples of S1/2 subsequently had TiO_2, CeO_2 or MnO_2 intentionally introduced as solutions of soluble salts and then transformed to the oxides by drying and calcination.

The catalysed combustions were followed by gas chromatographic, FTIR, IR emission and calorimetric methods, which have been described previously [5,9]. Oxidation of mixtures (e.g. 0.1% propane in air [SIP Analytical] or 0.1% propane and 0.5% H_2 in air [SIP Analytical; Air Products]) were also investigated by the same methods at 101 kPa in a flow microreactor.

3. Results and discussion

These are best considered in sequence of increasing difficulty of combustion: H_2, CO, CH_4 and C_3H_8.

3.1. H_2 (and CO)

Hydrogen oxidation occurred even at 295.4 K over S6 (a temperature much lower than the 856 K for the ignition of the homogeneous reaction [10]) and then suddenly accelerated (as seen by water production or temperature rises) after some 55 min reaction time. This induction period was not seen at 349.6 or 427.1 K, where the steady state rates were higher. It may be that the water slowly generated *in* the low-temperature combustion accelerated the oxidation of hydrogen when it reached a sufficiently high coverage. Almost as importantly, when CO was introduced into the reactant $H_2/O_2/N_2$ stream, the rate of heat generation by the H_2–O_2 reaction dropped quickly. Thus it seems that adsorption of the more difficult to oxidise CO suppresses the oxidation of the more easily oxidised H_2. This is possibly not surprising given the strength of adsorption of CO on a Pt surface [12].

3.2. CO (and H_2)

Catalysed combustion of CO over S6 exhibited activity–temperature bistability (which has been shown to be stable with time at any position in the loop [9]), but required higher temperatures for catalysed ignition than did the catalysed combustion of hydrogen. Calorimetry (see Fig. 1) during this hysteretic catalysed combustion over S3 revealed [9] a switch from a predominantly heterogeneous combustion to a predominantly homogeneous combustion at about 500 K. This *coupling* of heterogeneous and homogeneous combustions is a matter of some importance, as highlighted by others [3]. Calorimetric and chromatographic data from Fig. 1 indicated activation energies for the catalysed combustion of CO (59–79 kJ/mol) which are, as expected, lower than for homogeneous combustion (i.e. 157 kJ/mol). With catalyst S6 when hydrogen was introduced into the $CO/CO_2/N_2$ stream the temperature of ignition was lowered and the temperature width of the hysteresis loop exhibited was decreased. Also, as the dispersion of Pt decreased so the temperatures required for catalysed combustion increased. For the lowest temperature combustion of CO one needs to take advantage of (i) the highest Pt dispersions and (ii) promotion by hydrogen (which in nature may be thermal or chemical, i.e. causing changes in θ_{CO} or θ_O or enhancing the spill-over of surface species), and of course hydrogen may act in this way because its catalysed combustion is faster than of CO. Thus in Fig. 1 gas chromatography showed increasing levels of CO_2 production (and calculated rates of heat evolution in mJ/s) as the temperature of 25 mg of S3 rose to 700 K in a stream of $CO/O_2/N_2$=3 kPa CO/3 kPa O_2/95 kPa N_2. However, calorimetry of the heat flow from the powdered catalyst was modest in comparison and passed through a maximum at the temperature of the mechanistic switch (500 K).

3.3. Alkane (and H_2)

S1 *matured* in propane oxidation with reaction time at 603 K. The addition of hydrogen accelerated propane oxidation, but the promotional effect of added hydrogen was only beneficial for the Pt/SiO_2 *not* subject to a high temperature pre-treatment. This seems to indicate that the combustion of propane is not promoted by H_2 over poorly dispersed Pt, but only when the metal is more highly dispersed. In the catalysis of the oxidation of methane over the poorly dispersed S1/2 the addition of hydrogen is *not* beneficial in accelerating its catalysed combustion. Furthermore, the addition of reducible oxides did *not* enhance methane combustion over S1/2. The beneficial effects of hydrogen in propane addition were only seen for highly dispersed Pt on silica (where they are even seen at a meagre level at 367 K, which is

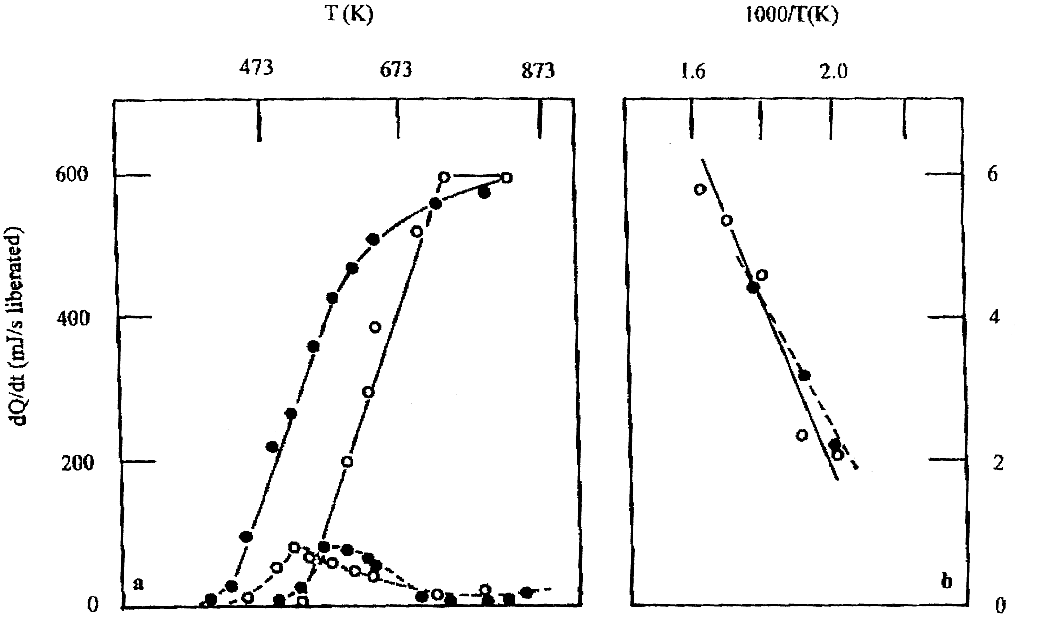

Fig. 1. (a) Rate of heat liberation in the catalysed combustion of CO over 3% Pt/SiO_2 detected by DSC (- - -) or gas chromatography (———) with increasing (○) and decreasing (●) temperature when $CO + O_2$ flowed at 40 cm^3/min. (b) Psuedo-Arrhenius plots of DSC (- - -) and gas chromatographic data (———) for the combustion of CO catalysed by 3% Pt/SiO_2.

a temperature far lower than for homogeneous reaction):

T (K) for various percentages of propane combustion

	20%	50%	80%
No H_2	708	757	818
Added H_2	609	654	723

and whether this is true for the oxide additives remains to be seen. Analysis of the data suggested an activation energy of 46 kJ/mol even in the absence of added hydrogen, which is much lower than the value (126 kJ/mol) for its homogeneous combustion [4] and may approach diffusion-limited regimes, This low activation energy may also relate to the lower turnover number seen (i.e. 19.5×10^{-3} molecules/Pt_s/s^{-1}) here.

4. Conclusions

Catalysed combustions take place, as expected, at far lower temperatures and with smaller activation energies than homogeneous reactions. Pt/silica combustion catalysts mature with use. The catalysed combustion of CO and H_2 is important in sensor technology and pollution control and the catalysed combustion of alkanes is important in increasing the efficiency of energy conversion processes based on the extraction of enthalpy changes (i.e. fossil fuel combustion, not fuel cells). CO and hydrogen *may* be produced as intermediates in alkane combustion [3], the balance of concentrations between the two possibly being modified by the water–gas shift reaction. It seems clear (and certainly for higher dispersed Pt on silica where the temperatures of catalysed combustion are lowest) that more readily oxidised fuel H_2 enhances the rates of alkane (and CO) combustion (and hence the efficiency of their transformation). However, the less readily oxidised and more strongly adsorbed CO retards the combustion of the more easily oxidised fuel H_2 and possibly the more difficult alkanes. The balance between the acceleration by H_2 and the deceleration by CO will depend upon their relative concentrations, and hence on the water–gas shift reaction and the nature of the Pt catalysts (dispersion and pre-treatment). The nature of the overall promotion: retardation of combustions by *reaction coupling* could be thermal-, coverage- or spill-over-controlled; obviously more highly dispersed Pt would benefit from their combustion at lower temperatures than more poorly dispersed Pt. This *reaction coupling* will only be resolved by in situ characterisation (e.g. transient FTIR [12], XPS, etc.), but it should lower the temperatures of alkane combustion and as a result minimise NO_x emissions at $\lambda > 1$. The *coupling between the heterogeneously/homogeneously catalysed combustions* (seen here for CO) will also be unraveled by calorimetry as a function of real time. It is not yet clear what is the cause (thermal or chemical) of activity–temperature hysteresis [13] in the polycrystalline-supported catalysts, and how the activity of such crystallites is synchronised. Nor is it yet understood whether the other combustions show the same bistability as CO oxidation. These must be matters for future investigation, which should ease alkane combustion on catalysts (thereby lowering NO_x emissions) and raise the modest turnover numbers seen here for propane combustion of supported Pt.

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