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Products and intermediates in propane hydrogenolysis on supported Pt

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Propane hydrogenolysis on Pt catalysts did not show serious deactivation over periods of 8 h below 630 K, but Arrhenius analyses were complicated. Selectivities to methane (S_1) and ethane (S_2) remained constant at 1.00 ± 0.02, with S_1/S_2 just above 1, when less than 10 mmol propane were converted per g catalyst per hour. However, S_1/S_2 rose as CH_4 was formed more selectively at higher conversions as the temperature increased. Thus at lower temperatures propane hydrogenolysis occurred by single C–C bond rupture, before switching to multiple bond rupture at higher temperatures. Transient analysis on Pt/SiO_2 using alternating H_2 and C_3H_8 pulses, similar in size to the adsorption capacity of the catalyst, enabled study of the surface at close to its working coverages of $\underline{H}$ (θ_H) and H-deficient hydrocarbon species, such as $\underline{C_m}\underline{H_n}$ ($\theta_{C_mH_n}$). C_3H_8 pulses at 573–773 K (to a catalytic surface that had just seen hydrogen) resulted in H_2 emergence as a result of dehydrogenation rather than displacement. H_2 pulses under the same conditions (onto the silica-supported Pt that had just seen C_3H_8) released C_3H_6 and C_2H_4 from previously accumulated surface $\underline{C_m}\underline{H_n}$ on the Pt, even though these are less favourable products than alkanes. Such observations may suggest a relationship between catalysed hydrogenolysis and dehydrogenation and a potential for catalytic fine-tuning through reaction coupling. Pulse work shows that hydrogenolysis activity at intermediate temperatures can involve multiple C–C scission initially, but that the build-up of carbonaceous deposits deactivates such sites only leaving those able to support single C–C bond rupture in propane. Such maturation effects on hydrogenolysis selectivity need to be better understood by a combination of pulse and steady-state experiments.

Introduction

Cleavage of C–C[1] (and C-heteroatom[2–6]) bonds in $H_{2(g)}$ on metal catalysts is important in petroleum processing (where its rate must be minimised along with C deposition[7]), pollution control, organic synthesis and catalyst preparation.[8–10]

Surface metal atoms (*e.g.* Pt_s or _) as larger ensembles[11–13] or in special coordinations[14] (representing only a small fraction of the total[8–10]) are required for catalysis of alkane C–C hydrogenolysis (HLS) more than for facile alkane dehydrogenation (DEH). For propane HLS[15–32] C_2H_6 and CH_4 can be produced by α and β reaction paths:[14,33]

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6 \qquad \alpha$$

$$C_3H_8 + 2H_2 \rightarrow 3CH_4 \qquad \beta$$

Catalytic studies have investigated C_3H_8 adsorption[32] and whether C–C bond rupture is rate-determining[11–13] and whether this defines the high activation energies (*i.e.* 120 kJ $mol^{-1} < E_a < 174$ kJ mol^{-1} [34]) seen in alkane HLS.

In early studies the hydrogenolysis rate r_{HLS} was observed[11–13] to *increase* with reaction time (t), ${p_{C_3H_8}}^{+0.90-+0.94}$ and $1/{p_{H_2}}^{+2.43-+2.70}$ producing more CH_4 than C_2H_6. This has been supported by work on Ru[34] showing propane orders of +0.54 to +1.00 and H_2 orders of −1.22 to −2.07. That h (in $r_{HLS} \propto p^h_{H_2}$) should be −2.5[7] at moderate p_{H_2} is not surprising, since on Group VIII metals hydrogen is more strongly chemisorbed than an alkane[35] and often h increases negatively at moderate p_{H_2} with increasing E_a.[35] However, at *lower* p_{H_2} h is positive.[7] Not only does p_{H_2} affect r_{HLS}, but also selectivities to C_2H_6 (S_2) and CH_4 (S_1).[36]

By-product carbonaceous deposits also affect the activity and selectivity.[37] They complicate kinetic studies,[35] and so accumulation of carbonaceous deposits[11–13] at higher temperatures can cause maxima in psuedo-Arrhenius plots.[14,38] Molecular surface intermediates (on the left in the scheme below) are preferred at high p_{H_2} and low temperature, while ultimately $\underline{C}$ can be the product of DEH and HLS processes at low p_{H_2} and high temperature:

$$\begin{tikzcd}
C_3H_8 \arrow[r] \arrow[d] \arrow[dd, bend right] & \underline{C_3}\underline{H_8} \arrow[r, "\text{DEH}"] \arrow[d] & \underline{C_3}\underline{H_7} \arrow[r, "\text{DEH}"] \arrow[d] & \underline{C_3}\underline{H_6} \arrow[d, "\text{HLS}"] & & \\
C_2H_6 \arrow[r] \arrow[d] & \underline{C_2}\underline{H_6} \arrow[r] \arrow[d] & \underline{C_2}\underline{H_5} \arrow[r] \arrow[d] & \underline{C_2}\underline{H_4} \arrow[d, "\text{HLS}"] & & \\
CH_4 \arrow[r] & \underline{CH_4} \arrow[r] & \underline{CH_3} \arrow[r] & \underline{CH_2} \arrow[r, "\text{DEH}"] & \underline{CH} \arrow[r, "\text{DEH}"] & \underline{C}
\end{tikzcd}$$

Pt *is* active in propane DEH at 823 K[39] yielding propene with a selectivity of 47–94% and its dissociative adsorption[40] may lead to significant coverages of hydrogen-deficient species (*via* a sequence predominantly from left to right in the above scheme). For example, C_2H_6 at 360 K gives ethylidene[41] and vinylidene on Pt[41–44] and so propane/H_2 [34,43] may produce surface propylidene on Pt(111) (more than on Ir[15–32]), $\underline{C_3}\underline{H_4}$, $\underline{C_3}\underline{H_3}$, $\underline{C_2}\underline{H_y}$ and $\underline{CH_x}$ species depending on the reactant ratio. It may be relevant in this context to note that the formation of such *surface* dehydrogenated species is surprisingly exothermic (*e.g.* $\Delta H_f = -102.1$ kJ mol^{-1} for CH_3–Pt_s and −97.4 kJ mol^{-1} for $CH_2<(Pt_s)_2$).[45,46] Even if such DEH/HLS-derived surface intermediates did not reach the gas phase,[47] they could be mechanistically important. Their formation would be consistent with widely assumed mechanisms of alkane activation through dissociative adsorption, C–H scission and

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DEH.[35] Certainly r_{DEH} exceeds r_{HLS} at short reaction times.[48] One assumes that the balance between alkene and alkane product evolution will depend on the Pt_s chemistry, H_2/propane ratio,[48] $\theta_H : \theta_{C_mH_n}$, temperature and reaction time.

Despite the above discussion, some C–C HLS models[33,34,49–52] do not require knowledge of the H-deficiency of intermediate surface hydrocarbons, although others assume DEH is a pivotal process in CH_4[53–56] reactions and alkane HLS on Pt surfaces.[57–60] In general dissociative adsorption of an alkane on $\_$ surface sites leads to an equilibrium $C_mH_{n+x} + (1 + x)\_ \leftrightarrow \underline{C_mH_n} + x\underline{H}$ defined by K_{DEH} $(\theta_{C_mH_n}\,\theta_H^x/(p_{C_mH_{n+x}}\,\theta_\_^{1+x})$, where θ_m, θ_H, $\theta_\_$ and $p_{C_mH_{n+x}}$ are coverages of $\underline{C_mH_n}$, $\underline{H}$ and free sites ($\_$) and the partial pressure of the alkane). Dehydrogenated surface species can then react with $\underline{H}$ to form fragments that rapidly desorb (or remain for further fragmentation).[35]

Here the activity and selectivity of Pt catalysts in propane HLS have been measured and related to catalyst properties, pre-treatments and to reaction intermediates seen transiently over a model Pt/SiO_2, for which the hydrocarbon is predominantly Pt-held and bound sufficiently long prior to hydrogenolysis to liberate measurable concentrations of critical reaction intermediates from its surface.

Experimental

Catalyst preparation

6.3% Pt/SiO_2 (EuroPt-1; a standard catalyst of long standing)[61–62] was used. Other Pt catalysts listed in Table 1 were prepared by: (i) *impregnating* Al_2O_3 (Degussa C; 100 m^2 g^{-1}) to give Pt/A, TiO_2 (P-25; 55 m^2 g^{-1}) to give Pt/T and graphite (Fluka; 11 m^2 g^{-1}; 99.9% purity) to give Pt/C with an aqueous solution of hexachloroplatinic acid (HCPA; $H_2PtCl_6 \cdot 2H_2O$; Johnson Matthey), drying in air at 373 K to give 3% Pt after reduction (5 K min^{-1}, 543 K, 1 h) in flowing H_2 (30 cm^3 min^{-1}) or (ii) *adsorbing* 0.45% mono-dispersed colloidal Pt[63] (prepared by reducing an aqueous solution of HCPA (50 mg dm^{-3}) with a 1% trisodium citrate solution at 373 K) onto Al_2O_3–C.

Adsorptive characterisation

The extent of H_2 (99.9998%; BOC) chemisorption was measured at 298 K using a conventional Pyrex volumetric apparatus on samples (0.5 g) of pre-reduced (16 kPa H_2, 573 K, 1 h) catalysts after outgassing (298 K, 1 h and then 573 K, 1 h), reducing *in-situ* in H_2, evacuating (to 0.13 mPa, 573 K, 16 h), purging with N_2 (16 kPa, 473 K, 1 h), oxidising in air (16 kPa, 473 K, 1 h), purging in N_2, (16 kPa, 473 K, 15 min), reducing in H_2 (16 kPa, 573 K, 1 h) and finally evacuating (to 0.13 mPa, 573 K, 16 h). Linear portions of n_{H_2}–p_{H_2} adsorption isotherms were extrapolated to zero pressure intercepts (n_m in mmol H_2 (g-cat)$^{-1}$) by the ASTM method.[64] Values of n_m were converted to Pt surface areas (S_{Pt} in m^2 (g-Pt)$^{-1}$) and average particle sizes (d_{Pt} in nm) assuming $\underline{H}/Pt_s = 1.00$,[64] that there are 1.25×10^{19} Pt_s/m^2 and that $S_{Pt} = 6000/\rho_{Pt}d_{Pt}$, where ρ_{Pt} is the density of Pt (21.45 g cm^{-3}).

Catalyst pre-treatment

In reductive pre-treatment A the sample (0.2 g) was purged in N_2 (573 K; 1 h), reduced in H_2 (573 K; 1 h) and purged in N_2 (423 K; 16 h). In oxidative–reductive pre-treatment B the sample was purged in N_2 (473 K; 1 h), oxidised in air (473 K; 2 h), purged in N_2 (573 K; 15 min), reduced in H_2 (573 K; 1 h) and finally purged in N_2 (423K; 16 h).

Steady-state catalytic activity-selectivity

Hydrogenolysis of propane (99.0%; Argo International Ltd.) was studied in a continuous flow Pyrex microreactor using a $H_2 : C_3H_8$ ratio of 10 : 1 produced with H_2 (100 cm^3 min^{-1}), C_3H_8 (10 cm^3 min^{-1}) and N_2 (30 cm^3 min^{-1}). Oxidative dehydrogenation[65] of propane by contaminant $\underline{O}$ was avoided by gas purification with water and oxygen removal on 4A molecular sieve and MnO_x/celite beds. Samples (0.2–1.0 g) were tested at 101 kPa total pressure by increasing (and then decreasing) the temperature (10 K min^{-1}) between 563 and 673 K. Products were analysed using a Perkin Elmer 8500 with an FID and a 3% squalane/Al_2O_3 column (100–120 mesh; 3 mm × 4 m) at 363 K). The HLS rate r_{HLS} was expressed in mmol propane converted (g-cat)$^{-1}$ h^{-1}. The product selectivities to methane (S_1) and ethane (S_2) were related through $S_1 + 2S_2 = 3$. The turnover frequency (TOF in h^{-1}) was deduced from r_{HLS} (in mmol C_3H_8 converted (g-cat)$^{-1}$ h^{-1}) divided by $2n_m$ (the number of active sites (mmol H_2 adsorbed (g-cat)$^{-1}$ at 298 K)).

Pulse activity

Short reaction pulses (SRP) have been used to study alkane hydrogenolysis reactions over 6.3% Pt/silica EuroPt-1.[37] In that study the pulse of alkane could have saturated the Pt surface at least twelve times. Here the authors have chosen smaller reactant pulses (22 μmol H_2 and 4.4 μmol C_3H_8) that were injected into a flowing Ar stream (30 cm^3 min^{-1} at 101 kPa). Specifically, the size of H_2 and C_3H_8 pulses was similar to or a little less than the adsorption capacity of the EuroPt-1 (182 μmol H_2 (g-cat)$^{-1}$; 18.2 μmol Pt_s in the reactor; see Table 1) sample. However, it was felt to be important to choose a $H_2 : C_3H_8$ ratio of pulse sizes (5 : 1) to keep the surface close to the conditions used in the reaction and not

Table 1 Characterisation and hydrogenolysis data for Pt catalysts

Catalyst[a]	Pretreatment[b]	n_m/μmol H_2 (g-cat)$^{-1}$ [c]	d_{Pt}/nm from H_2 adsorption[c] /TEM	S_{Pt}/m^2 (g-Pt)$^{-1}$ [c]	Rate (r_{HLS}) /mmol (g-cat)$^{-1}$ h^{-1} [d]	E/kJ mol^{-1} [d]	ln A /nmol (g-cat)$^{-1}$ h^{-1} [d]	TOF /h^{-1} [d]	S_2
0.5% Pt/A	A	4.31	1.52	185	0.4	202	38.72	46.4	0.990
3.0% Pt/C	A	11.93	3.63/3.84	77	0.46	210	40.28	19.3	0.989
3.0% Pt/A	A	31.50	1.40/1.66	203	3.25	191	38.61	51.6	0.996
6.3% Pt/S	A	182.35	1.88/2.00	149	8.25	136	28.55	22.6	0.987
3.0% Pt/T	B	18.21	2.39	117	1.3	105	20.81	35.7	0.993
3.0% Pt/T	A	22.73	1.92	146	0.76	113	21.88	16.7	0.993

[a] Pt/A, Pt/C, Pt/S and Pt/T denote Pt/alumina, Pt/graphite, Pt/silica and Pt/titania samples, where 6.3% Pt/S is the EuroPt-1 sample. [b] Pre-treatments are described in the Experimental section but A was reductive and B was oxidative–reductive. [c] Average measured by H_2 chemisorption (with data extrapolated to zero pressure)[64] and TEM. [d] Measured at 594 K as defined in the Experimental section.

'clean', when dehydrogenation would be expected. The times (t) to the maximum residual gas analyser (RGA) response (t_{max}) in the absence of the catalyst were 28 s. With Ar flowing over a sample (50 mg) of EuroPt-1, the t_{max} of H_2 and C_3H_8 pulses were 26 and 21 s respectively. Dividing the time after injection (t) by t_{max} normalised the timescales of the responses. Again, to avoid the complication of oxidative dehydrogenation of propane[65] there was careful gas purification of Ar using an Alltech purification system that lowered the p_{O_2} to a level that would have required 140 min for Pt_s surface sites in the reactor to be O-covered. No detectable O-modification of Pt_s reactivity was seen. The RGA peaks chosen were at $m/z = 2$ (H_2), 28 (C_2H_4), 29 (C_3H_8) and 41 (C_3H_6). Duplicate pulse results over the catalyst were always compared to blank data in the absence of the catalyst.

Catalytic results and discussion

Monolayer extents of adsorption (n_m) at 298 K determined[64] for EuroPt-1 (see Table 1) were close to those previously reported.[61] Average particle sizes of Pt derived from n_m values compared moderately well with those from transmission electron microscopy (TEM).[66]

Steady-state rates (r_{HLS}) of propane conversion at 594 K (see Table 1) were much faster after oxidative–reductive pre-treatment B of 3% Pt/TiO_2, as SMSI effects may have been overcome.

Observed turnover frequencies (TOFs) for propane hydrogenolysis at 594 K (see Table 1) were similar to those seen for diffusion-moderated liquid-phase hydrogenation reactions.[67] It would be unusual for a structure-sensitive reaction like propane HLS for TOFs to increase as the average Pt particle size decreased, but there is insufficient data on this point in Table 1 to clarify this.

The formation of carbonaceous deposits is known to affect the activity and selectivity seen[37] in HLS and to complicate its Arrhenius analyses.[35] Curvature in Arrhenius-type plots in propane hydrogenolysis has been seen over Ni catalysts.[14] Here, pseudo-Arrhenius plots (see Fig. 1) were not linear at any temperature used for conversions between 0.1 and 20% over Pt/SiO_2 or Pt/Al_2O_3, presumably due to mass-transport limitation external to the catalyst particles, deactivation[14,37,68] even at these moderate temperatures *or* a change in the nature of the active Pt_s sites. Non-linearity persisted during reaction cooling on Pt/Al_2O_3, but disappeared for the reaction-aged Pt/SiO_2. It was this catalyst that was chosen for pulse studies and one assumes that the nature of the support will minimise the laydown of deactivating carbonaceous deposits. E_a and ln A values in Table 1 were determined at 594 K. In compensation[14,68,69] or Constable[70] plots there is good linearity if there is a common type of surface site and reaction intermediate on a family of Pt catalysts.[14,38] Data in Fig. 2 lead one to assume that this is the case here for present catalysts in propane HLS. This is relevant to the discussion about the number and type of Pt_s sites required for the reaction.[8–14]

The nature of dissociative adsorption of alkanes may affect the apparent activation energy for their HLS.[35] Here such activation energies (see Table 1) were, within the uncertainties set by non-linearity in Fig. 1, consistent with previous findings. E_a values rose a little with decreasing d_{Pt}, if one separates out the activation energy for Pt/C as being unusually high. Activation energies were unusually low for Pt/TiO_2 after both reductive (A) and oxidative–reductive (B) pre-treatments (see Table 1), emphasising the absence of SMSI in what is still a good hydrogenolysis catalyst,[11–13] not suffering from too much TiO_x decoration of Pt_s.

In propane HLS the selectivity ratio S_1/S_2 is normally $\geqslant 1$. However, it decreases as p_{H_2} rises[15–32] and is independent of reactant residence time or % conversion (c).[15–32,34] It has, however, a dependence on temperature that is more variable (increasing with $T^{15-33,49-52,68}$ or $1/T^{71}$ or passing through a minimum at intermediate T^{36}). Here, Fig. 3 shows no significant temperature-dependence of this reaction selectivity ratio nor an effect of pre-treatments A or B or changes in d_{Pt} or

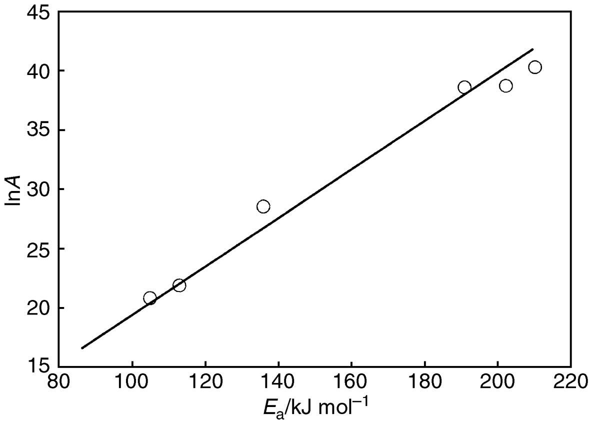

Fig. 2 Compensation plot for C_3H_8 hydrogenolysis over Pt catalysts (including Pt/TiO_2 after pre-treatments A and B).

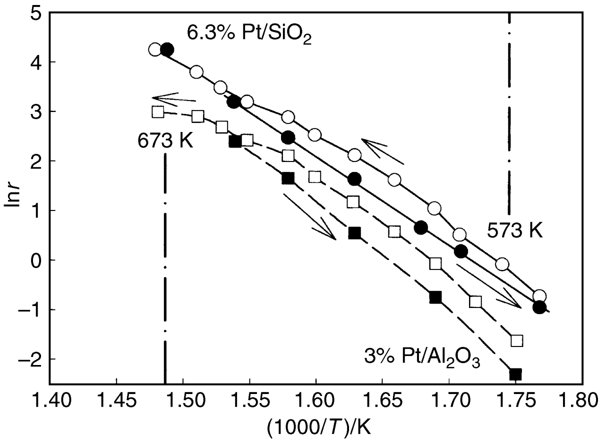

Fig. 1 Pseudo-Arrhenius plots for C_3H_8 hydrogenolysis over a Pt/SiO_2 and a Pt/Al_2O_3 catalyst during heating and cooling.

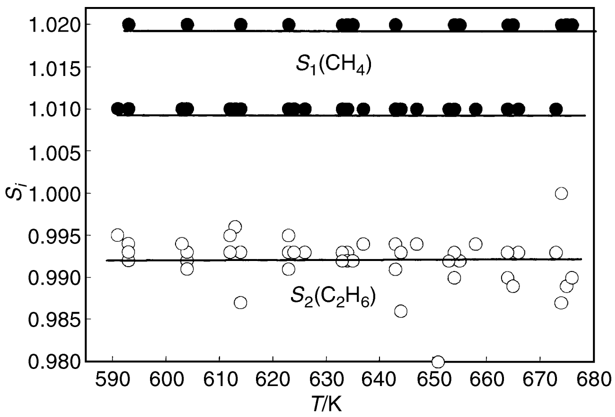

Fig. 3 Absence of an effect of reaction temperature in the range 590–678 K on the selectivities (S_i) in C_3H_8 hydrogenolysis over all Pt catalysts in Table 1.

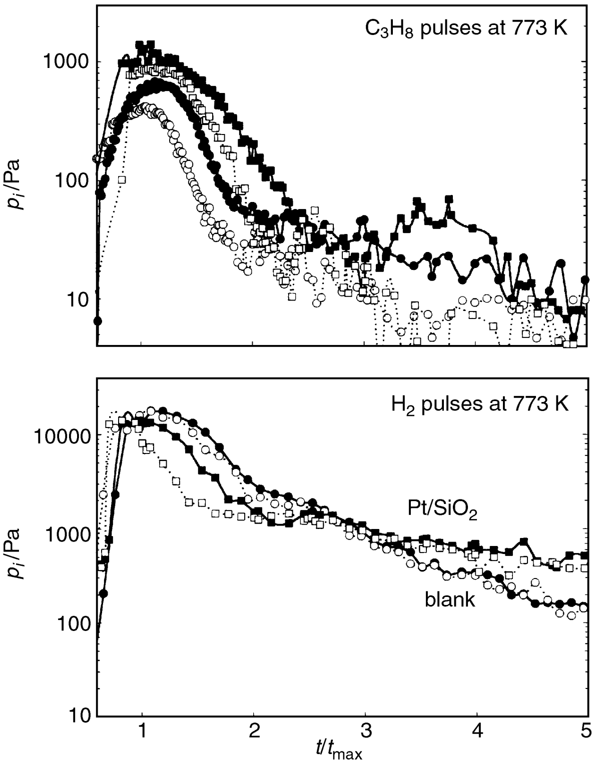

Fig. 4 H_2 and C_3H_8 pulses to the blank reactor (○, ●) and Pt/SiO_2 at 773 K (□, ■). Filled symbols with solid lines denote duplicate data for open symbols with dotted lines.

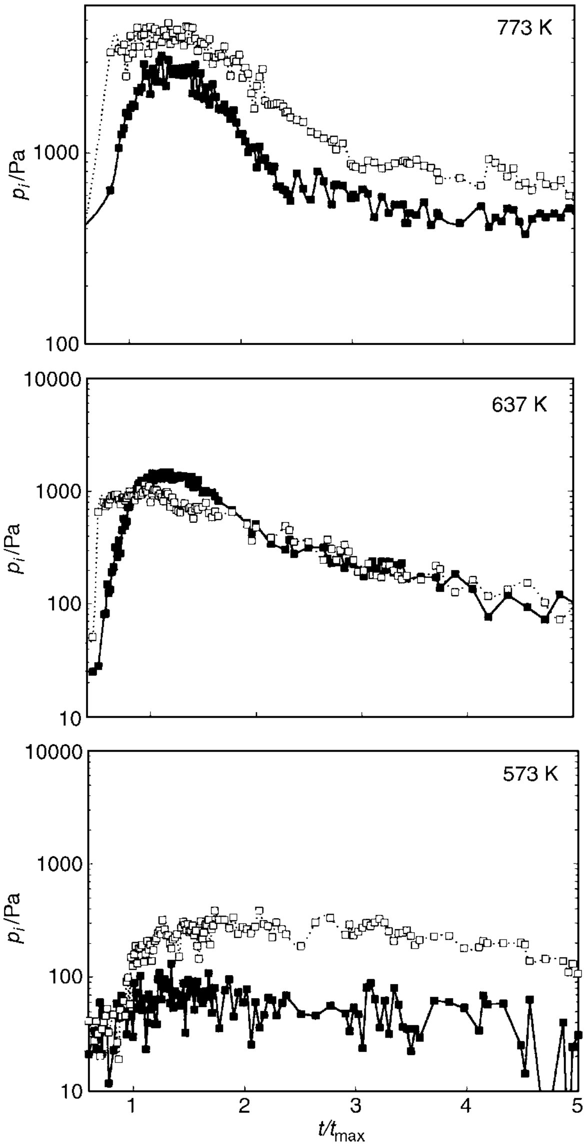

Fig. 5 H_2 production over a Pt/SiO_2 hydrogenolysis catalyst at 573, 673 and 773 K during C_3H_8 pulsing.

support type, when measured at intermediate C_3H_8 conversions (*i.e.* $2\% < c < 70\%$). The preference for single C–C bond scission, over multiple sequential C–C scission, is revealed with all catalysts by the near equivalence of S_1 and S_2 in Fig. 3 (*i.e.* $S_1 \approx S_2 \approx 1.00 \pm 0.02$). Others have defined this in terms of a fission parameter (M_f)[72] that is 1 if there is a preference for single C–C bond breakage, but <1 when multiple C–C scission[72] is preferential. Single C–C bond HLS[15–32] of propane may thus be taking place on these surfaces (which Fig. 2 suggested contained similar Pt_s sites) with a high $\alpha : \beta$ reaction path ratio at 573–673 K. At higher temperature and conversions, S_1 rose further above S_2, consistent with previous investigations.[15-32]

The steady-state selectivities in Fig. 3 unfortunately do not reveal much information about initial selectivities at short reaction times. It is also possible that some catalysts initially possessed sites capable of giving multiple hydrogenolysis at short times, low intermediate conversions and temperatures, but that these then become poisoned with time of use or as the reaction temperature is raised, leaving those only giving single C–C bond rupture. It is most likely that surface $\underline{C}_2$ species undergo further HLS at higher temperatures on the Pt_s sites to $\underline{C}_1$, as frequently encountered with other metals.[68,73] Alternative methods of rationalising this selectivity shift with increasing temperature exist.[15–32]

Of course, the formation of CH_4 by total hydrogenolysis is much more favourable than C_2H_6 at all reaction temperatures here, but the present 6.3% Pt/SiO_2 catalyst[11–13,15–32,37] has an activation energy E_a (199–210 kJ mol^{-1}) for ethane HLS that is higher than that of propane (181–189 kJ mol^{-1}) and butane (114–142 kJ mol^{-1}). This observation is consistent with suggestions[15–32,74,75] that the reactivity sequence over most catalysts in alkane hydrogenolysis is $n\text{-}C_4H_{10} > C_3H_8 > C_2H_6$. Hence kinetics are expected to limit S_1/S_2 in Fig. 3 *below* the thermodynamic value.

Consider now the nature of adsorbed intermediates in HLS arising from any combination of DEH and HLS processes depending on the conditions prevailing at individual Pt_s sites.[15–33,37,76] *If* these are partially dehydrogenated then qualitatively this relates well to some earlier HLS mechanisms.[11–13,34,77]

It is certainly known that alkenes can be formed on surfaces and desorbed prior to HLS (*e.g.* Guczi *et al.*[22,23]), but here propene and ethene were not measured in significant levels in continuous steady-state catalysis under present conditions.

Pulse results and discussion

Pulse results obtained over Pt/SiO_2 at 573, 673 and 773 K are shown in Figs. 4–7, where filled symbols denote duplicate runs. The lowest temperature was set by the range of the pseudo-Arrhenius plot in Fig. 1, suggesting that on this catalyst deactivation was less serious than on Pt/Al_2O_3 (*i.e.* 573 K) when there is single C–C bond scission (see Fig. 3). The upper temperatures were selected as being those where deactivation and multiple C–C bond scission would probably be significant (*i.e.* >673 K) in continuous propane hydrogenolysis. Fig. 4 shows that clean 22 μmol H_2 pulses and 4 μmol C_3H_8 pulses were just large enough for surface reactions not to consume

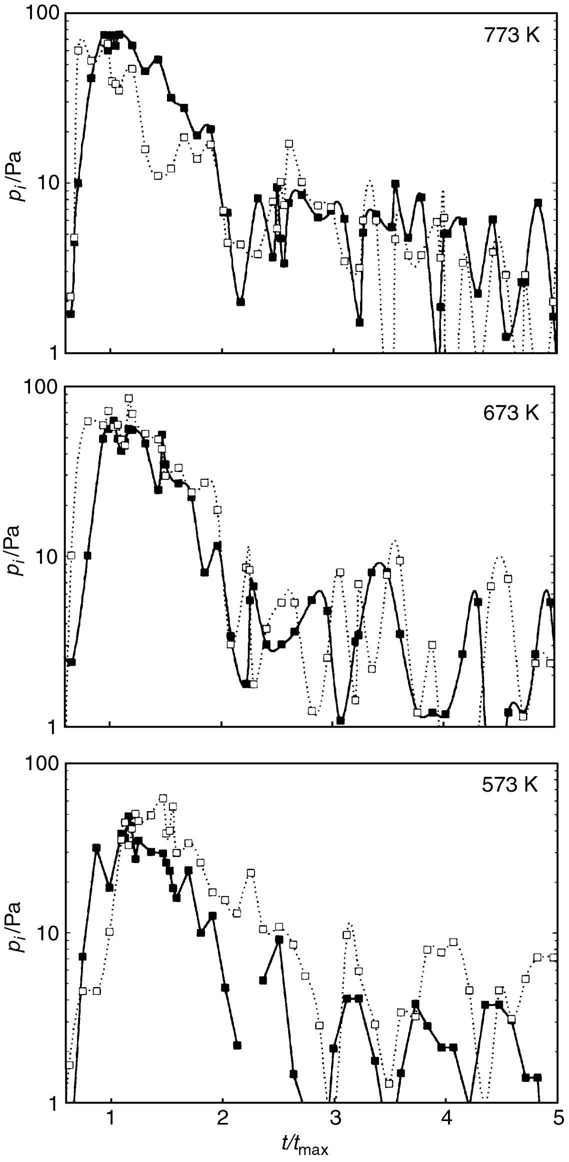

Fig. 6 C_3H_6 production over a Pt/SiO_2 hydrogenolysis catalyst at 573, 673 and 773 K during H_2 pulsing.

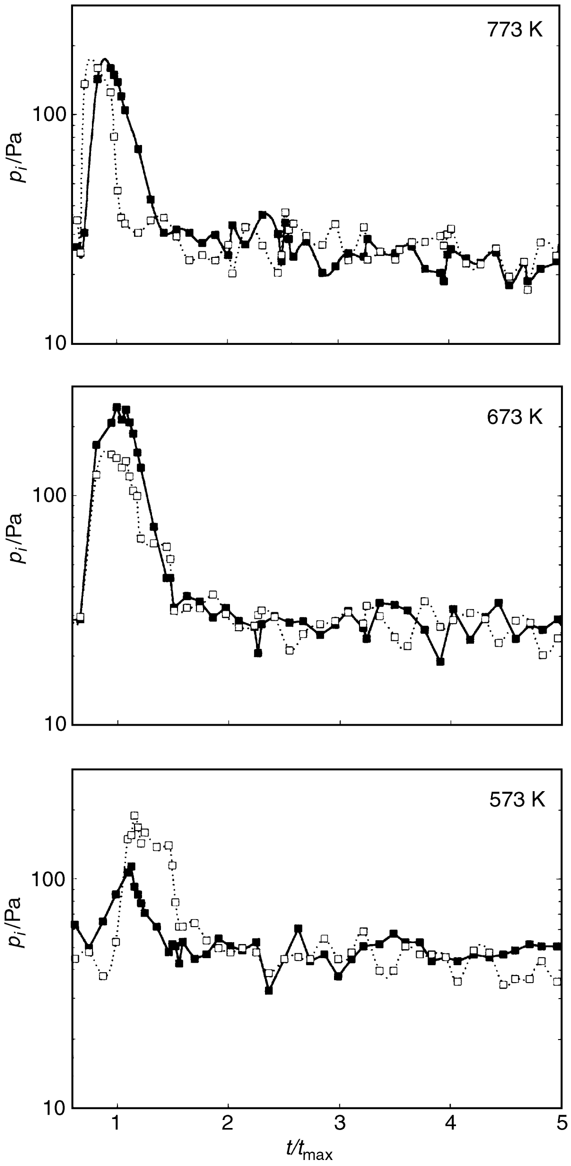

Fig. 7 C_2H_4 production over a Pt/SiO_2 hydrogenolysis catalyst at 573, 673 and 773 K in H_2 pulsing.

these significantly when they were injected alternately onto a 50 mg sample of 6.3% Pt/SiO_2 at 773 K (or 673 K, or 573 K, although for brevity these are not shown). Hence θ_H and $\theta_{C_mH_n}$ must have been close to those on the working catalyst surface under these pulse conditions, especially since repeated pulses were identical and did not change with maturation of the catalyst surface. Some broadening of the H_2 pulse in Fig. 4 arises from adsorption–desorption at these temperatures.[78,79]

Fig. 5 shows that DEH processes liberated H_2 during propane pulses (even though these alternated with H_2 pulses) onto the Pt/SiO_2 catalyst that had a significant θ_H. The extent of H_2 release increased as the temperature rose. No H_2 was, however, seen in the absence of the catalyst. Of course C_3H_8 adsorption with the formation of C_3 species could simply displace pre-adsorbed $\underline{H}$ to yield H_2, but it is more likely that H_2 is produced by $\underline{C}_3$ (and $\underline{C}_2$) dehydrogenation.

Fig. 6 reveals that H_2 pulses (alternating with C_3H_8 ones) then produced propene to an extent that was temperature-independent in the range tested. Again this was not produced in the absence of the catalyst. The H_2 pulse must therefore titrate surface $\underline{C}_3$ species (that may be more H-deficient than propene (*e.g.* propylidene)) off the surface. Such species would indeed be unusual in the presence of $H_{2(g)}$.

Fig. 7 shows that ethene production on H_2 pulsing to the catalyst (that had seen alternating C_3H_8 ones) occurred in parallel to C_3H_6 production to an extent that *rose* when the temperature rose above 573 K. This suggests that the activation energy for DEH processes is smaller than for hydrogenolysis (even if followed by DEH). There was no parallel C_3H_8 desorption during H_2 pulsing that could have complicated C_2H_4–C_3H_6 RGA analysis. Gaseous C_3H_6 and C_2H_4 were not seen in the absence of the catalyst or in the continuous steady-state catalysis experiments at these temperatures.

Even at significant θ_H, C_3H_8 then adsorbs to produce H_2 and a pool of H-deficient species.[34,43–44] Raising θ_H by H_2 pulsing then releases C_3H_6 and C_2H_4. At all temperatures ethene production during H_2 pulses is much *faster* than propene.

What do pulse studies reveal about hydrogenolysis activity–selectivity? Fig. 8 shows that H_2 pulses (alternating with those of C_3H_8) to the Pt/SiO_2 catalyst at 673 K also produced CH_4, but not C_2H_6 as a result of HLS paralleling DEH (seen in Figs. 6 and 7). CH_4 concentrations were more modest than those of C_3H_6 and C_2H_4 in Figs. 6 and 7, but were not seen in the blank reactor. Neither was CH_4 seen during the C_3H_8 pulsing. Hence it seems that Pt_s (or _) surface sites do indeed *initially* possess activity in multiple hydrogenolysis at intermediate temperatures. That this is not shown in Fig. 3 must

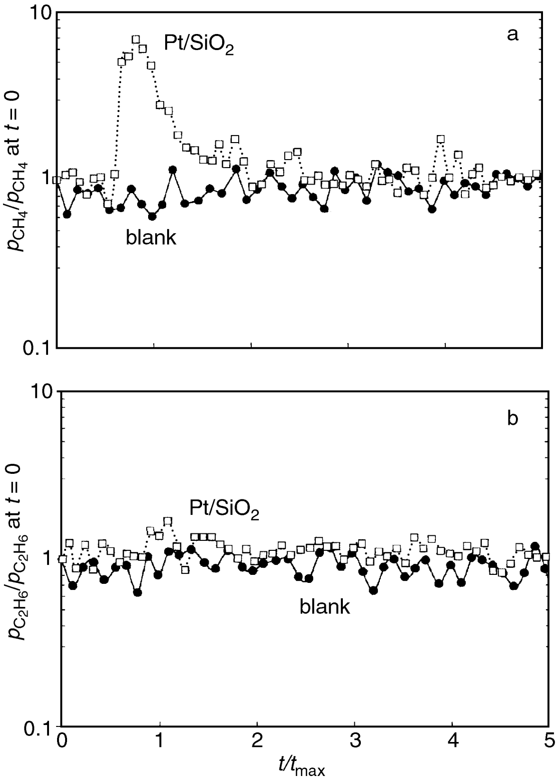

Fig. 8 Production of CH_4(a) but not C_2H_6 (b) in H_2 pulsing to a Pt/SiO_2 hydrogenolysis catalyst at 673 K onto which C_3H_8 had just been adsorbed. Such data are compared to the effect of pulsing into the empty reactor.

mean that these sites become *poisoned* with time of use, leaving those only giving single C–C bond rupture.

Conclusions

Hydrogenolysis certainly occurs on as yet poorly defined Pt_s ensembles or special sites,[14] provided these are not poisoned by carbonaceous species. Whether kinetic models of this need to define the H-deficiency of surface intermediates depends entirely on any improvement in their ability to predict r, S_1 and S_2 trends on a particular catalyst system that could acrue as a result.

Mechanistically, neglect of DEH processes in hydrogenolysis is probably not justified. The relationship and balance between DEH and HLS processes may in time be fine-tunable by catalyst design and reaction conditions.[80] What is seen here for intermediates on Pt/SiO_2 may be even more significant for catalysts subject to even greater rates or extents of laydown of carbonaceous deposits (*e.g.* Pt/Al_2O_3).

The extent of dissociative adsorption of alkanes (and resulting $\theta_{C_mH_n}$ or C/Pt_s values) seen on Pt[81] will change (i) for propane with temperature rises (as H_2 desorbs[78]), (ii) if one uses different alkanes[82,83] or (iii) as one moves from Pt to other metals.[84] Studies [85,86] have shown that such carbonaceous overlayers are not always detrimental to catalytic activity.

Experimental and theoretical studies should certainly proceed in parallel to define the HLS and DEH surface species (and their concentrations) under selected conditions, in order to define when these are positive intermediates in hydrogenolysis and when they become reaction poisons. Much more, therefore, needs to be known about $m : n$ ratios in such surface C_mH_n species. Here the different experimental approaches of RGA and continuous catalysis are shown to complement one another, and would now benefit from the use of isotopically labelled reactants.[24] Pulse work, where reactant–intermediate surface coverages are close to those of the working catalyst or when $\theta_{C_mH_n}$ can be incrementally increased in a manner not possible in steady-state studies, are likely to be one part in our analytical armoury. Pulse work also shows that hydrogenolysis activity at intermediate temperatures can *initially* involve multiple C–C scission (see Fig. 8). Then maturation of the catalyst (as a result of the build-up of carbonaceous deposits deactivating surface sites) occurs leaving only those able to support single C–C bond rupture in propane (see Fig. 3).

For the moment alkane hydrogenolysis (and the role of dehydrogenation processes in this) remains an intriguing and important area of heterogeneous catalysis. Pulse studies hint at reaction intermediates that are also available as building blocks of carbonaceous deposits,[85,86] which form even on catalysts such as EuroPt-1[51,87] under conditions such as those used here. These surface species may however be different at high and low p_{H_2}.

Sinfelt *et al.* compared the effect of modifiers of Ni catalysts on the relative rates of cyclohexane dehydrogenation and ethane hydrogenolysis at 589 K,[88] but is it surprising that DEH and HLS occur on Pt surfaces under the present conditions? Probably not. For example, sol–gel, mono-, bi- and trimetallic Pt catalysts promote 20–50% propane DEH at $H_2 : C_3H_8 = 0.9$ and 853–700 K.[39,89,90] They also facilitate simultaneous HLS and DEH of n-heptane (in a ratio of 2 : 1 at 773 K) over Pt/Al_2O_3[91] and Pd acts in the same way for hexane at 573–673 K.[48] Of course the balance of the two types of reaction will depend (and order of reaction rates with respect to $H_{2(g)}$ will vary smoothly from negative to positive[69]) on the H_2 : alkane ratio. A low value will produce alkenes (and irreversibly bound surface hydrocarbonaceous species), but a high H_2 : alkane ratio will produce more hydrogenolysis.[92] It may be that in future exothermic HLS will be found to compensate for endothermic DEH (in a manner similar to that in oxidative DEH[65]).

Catalysis of hydrogenolysis reactions[74,93–95] is important and may become more so as it is even better understood.

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