

## Temperature Programmed Titration of Silica-supported Platinum

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When operated under temperature-programmed conditions, the alkene titration of hydrogen chemisorbed on silica-supported platinum estimates the active surface area of platinum *and* the quantities of support- and metal-held hydrogen.

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The surface area of supported platinum may be determined by selective chemisorption, desorption, and titration.<sup>1</sup> Isothermal

titrations of Pt saturated with chemisorbed hydrogen by gaseous oxygen and alkenes (and titrations of chemisorbed

oxygen by gaseous hydrogen and carbon monoxide) at 290–373 K have allowed<sup>2</sup> characterisation with greater accuracy than that attainable by direct chemisorption; integration of the titration process with time allowing determination of metal dispersion. Only the alkene–H titrations, which monitor the rate of formation of product alkane as a function of time, differentiate support- and metal-held hydrogen partially. Desorption methods, on the other hand, may involve temperature programming (t.p.d.) of a catalyst pre-saturated with adsorbate at a low temperature and monitor the adsorbate concentration in an inert gas stream as temperature rises, allowing the population of different energetic states on the Pt surface to be determined (*e.g.* up to five states for hydrogen and two for ethene on Pt<sup>3</sup>). Thus no adsorptive method exists for measuring the surface area *and* the relative populations of different adsorbed states *simultaneously*. The present work was undertaken to ascertain whether the temperature programmed alkene titration of hydrogen chemisorbed on silica-supported Pt could provide a greater resolution of adsorbate populations and a better estimate of Pt surface areas than that attainable by the titration undertaken isothermally. The alkene titration was selected because of its relationship to rates of product formation, rather than titrant consumption, and its utility in measuring active Pt surface areas rather than total metal areas.<sup>3</sup> Cyclohexene was chosen as the titrant for hydrogen chemisorbed on Pt since, after extracting adsorbed hydrogen at low temperature, it could donate hydrogen to the catalyst by dehydrogenation at elevated titration temperature.

Silica-supported Pt catalysts of varying metal loading and dispersion (see Table 1) were used and their preparation is described elsewhere.<sup>4</sup> A sample (0.4 g) of one of these pre-reduced catalysts was placed in a Pyrex flow reactor at 290 K and was flushed first with N<sub>2</sub> (B.O.C., purity >99.9% with total oxygen removal by prior passage over manganese oxide<sup>5</sup>) and H<sub>2</sub> (B.O.C., purity >99.9% with total oxygen removal by prior passage over alumina-supported palladium). With the sample in flowing H<sub>2</sub>, its temperature was raised to 373 K and then lowered to 263 K using an ice-salt slurry. After flushing with N<sub>2</sub> at this temperature until no further gaseous H<sub>2</sub> was detectable by gas chromatography, the temperature programmed alkene titration (t.p.t.) was commenced by introducing N<sub>2</sub> saturated with cyclohexene (B.D.H., purity >99.8% with impurities removed by agitation with activated alumina) at 243 K to give a reactant gas stream (15.00 ± 0.10 cm<sup>3</sup> min<sup>-1</sup>, 460 Pa cyclohexene and 101 kPa N<sub>2</sub>) which flowed as the sample temperature was raised at 0.33 K min<sup>-1</sup> using a linear temperature programmer and low mass furnace (LVPCA4R and LMVS-100, Stanton Redcroft). Rates of hydrogen extraction by cyclohexene (corrected for rates of cyclohexene disproportionation) and rates of desorption to

gaseous molecular hydrogen were estimated from measurements of the concentrations of gaseous benzene, cyclohexane, cyclohexene, and hydrogen as a function of titration temperature (and time) using an F11 gas chromatograph fitted with a 5% PEG-400M on Celite column at 353 K and a flame ionisation detector, and an F17 gas chromatograph fitted with

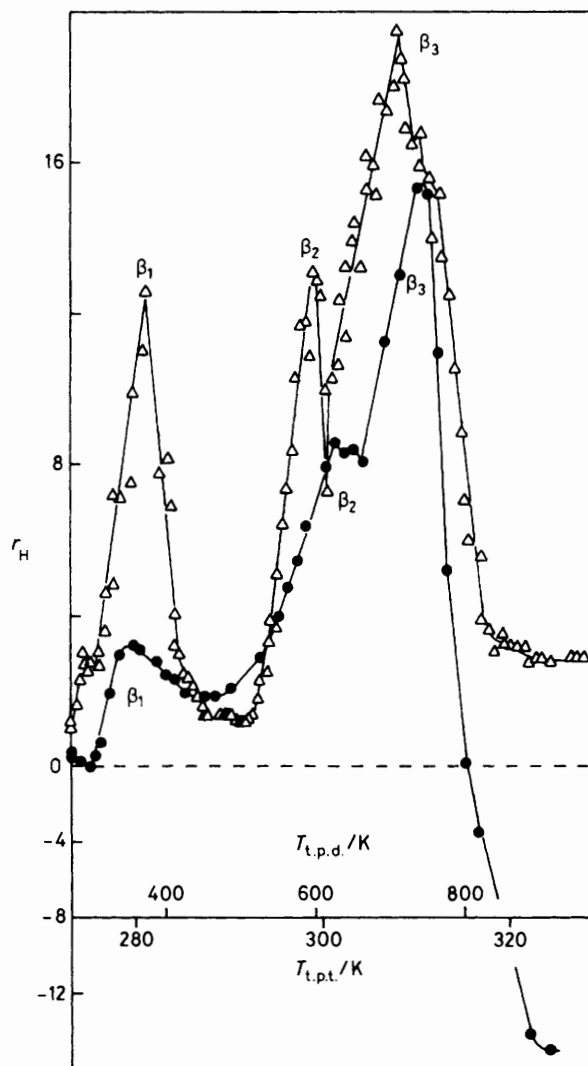


Figure 1. The rate of release of H atoms from Pt/SiO<sub>2</sub> (sample D) ( $\times 10^{19}$  atoms per g cat. per min) during temperature programmed desorption ( $\Delta$ ) and temperature programmed titration ( $\bullet$ ) using an alkene.  $T_{t.p.d.}$  and  $T_{t.p.t.}$  denote the catalyst temperature measured during these techniques.

Table 1

Catalyst <sup>a</sup>	No. H atoms ( $\times 10^{19}$ ) <sup>b</sup> /g cat						
	t.p.t. (H <sub>M</sub> )		t.p.t. (H <sub>T</sub> )		t.p.d.		t.p.d. <sub>T</sub>
				No. H atoms titrated from		% H atoms desorbed from Pt	
				Pt	t.p.t. (D <sub>T</sub> )	t.p.d. <sub>M</sub>	
A (5.0% Pt)	2.03	5.26	39	4.22	3.43	9.22	37
D (5.0% Pt)	3.61	6.82	53	4.30	5.10	12.78	40
H (2.4% Pt)	3.74	5.75	65	3.12	5.28	6.20	85
J (2.4% Pt)	8.40, 9.43	10.87, 13.76	72	7.00, 7.00	10.20	15.00	68
K (6.2% Pt)	9.37, 8.02	11.95, 10.60	77	7.33, 9.70	16.23	20.60	79

<sup>a</sup> These were pre-reduced and pre-treated in H<sub>2</sub> (101 kPa) at 423 K for 1 h and in N<sub>2</sub> (101 kPa) for 0.5 h at 573 K. <sup>b</sup> t.p.t. (H<sub>M</sub>) denotes metal-held hydrogen ( $\beta_1 + \beta_2$ ) titrated during hydrogenation, t.p.t. (H<sub>T</sub>) the total hydrogen ( $\beta_1 + \beta_2 + \beta_3$ ) titrated during hydrogenation, t.p.t. (D<sub>T</sub>) the total hydrogen ( $\beta_1 + \beta_2 + \beta_3$ ) titrated during dehydrogenation, t.p.d.<sub>M</sub> metal-held hydrogen ( $\beta_1 + \beta_2$ ) desorbed, and t.p.d.<sub>T</sub> the total hydrogen desorbed.

Table 2

	$S/m^2$ (g Pt) <sup>-1</sup> <sup>a</sup>		$S_{t.p.t.}(H_M)/S_{H_2(chem.)}$ <sup>b</sup>
	t.p.t. ( $H_M$ )	t.p.d. <sub>M</sub>	
A	32.4	54.8	2.03
D	52.6	81.6	0.98
H	124.8	176.0	0.70
J	280, 314	340	1.36
K	103.5, 121.0	198.7, 209.4	0.44

<sup>a</sup> Assumed  $H/Pt_s = 1$ . <sup>b</sup> Monolayer coverage was estimated by extrapolation of the volumetric adsorption data at ambient temperature and 0–4 kPa to zero pressure.

a molecular sieve column at 323 K and a hot-wire detector. Peak areas were estimated using a Minigrator (Spectra Physics). Rates of isothermal alkene titration of hydrogen on silica-supported Pt at 373 K rapidly declined from an early high value, associated with titration of metal-held hydrogen, to a low plateau value attributed to titration of hydrogen which had spilled over onto the support and which has migrated slowly back to the Pt for titration.

Temperature programmed desorption (t.p.d.) of hydrogen was achieved by flushing the sample (0.5 g) at 290 K with  $H_2$  (101 kPa, 60 cm<sup>3</sup> min<sup>-1</sup>, 15 min) and then saturating it with  $H_2$  (101 kPa, 60 cm<sup>3</sup> min<sup>-1</sup>, 1 h) while it was taken through the thermal cycle 295–423–273 K. At the last temperature, the sample was flushed with  $N_2$  (101 kPa, 60 cm<sup>3</sup> min<sup>-1</sup>, 30 min) until no gaseous hydrogen was detectable chromatographically. With the  $N_2$  flow rate adjusted to 15.00 ± 0.10 cm<sup>3</sup> min<sup>-1</sup>, the sample was then heated at 4 K min<sup>-1</sup> from 273 to 900 K.

Figure 1 shows the t.p.t. and t.p.d. profiles obtained for catalyst D and the similarities between these. Naturally, the thermodynamics and kinetics of titration and desorption are very different and the absolute temperatures for t.p.d. processes are substantially higher (100–200 K) than those required for t.p.t. and yet the relative populations of the different states of hydrogen chemisorbed upon these catalysts are remarkably similar. This is confirmed in Table 1; indeed, t.p.d. and t.p.t. were similar for all these catalysts. Therefore when operated in a temperature programmed mode the alkene titration is as good as t.p.d. in ascertaining the relative populations of different states of chemisorbed hydrogen on supported Pt. Interestingly both techniques indicate that as the dispersion of Pt increases so the percentage of hydrogen extracted, which is assumed to be metal-held, increases from 39 to 77%. Thus increasing the Pt dispersion does not increase the extent of hydrogen spillover to the support (or its reversal for extraction).

In addition the temperature programmed titration and t.p.d. methods were also used to estimate the specific surface area of the Pt assuming that only the first and second peaks ( $\beta_1$  and  $\beta_2$ ) in both profiles involved the extraction of metal-held hydrogen and that this had been held with a stoichiometry of  $H/Pt_s = 1$ . Table 2 shows that t.p.t. gives Pt surface areas

which are 55–87% of those derived from t.p.d. and which are greater than those derived from hydrogen chemisorption at low dispersions (catalyst A) but lower than those derived from hydrogen chemisorption at high dispersion. That traditional hydrogen chemisorption measurements do not agree well with those of t.p.d. and t.p.t. is attributed to its well known deficiencies.<sup>4</sup> Surface areas derived from t.p.t. show a linear relationship with the turnover number for these catalysts in cyclohexene hydrogenation at 295 K and there is reason to believe that t.p.t. produces a better estimate of the *active* rather than the *total* surface area of silica-supported Pt.<sup>6</sup>

At high titration temperature thermodynamics favour dehydrogenation of cyclohexene rather than hydrogenation and Figure 1 shows hydrogen donation to the catalyst rather than extraction-titration. The temperature at which hydrogenation flips over to dehydrogenation decreases with increasing metal dispersions (A: 315 K, D: 310.5 K, H: 312 K, J: 307.5 K, K: 290 K). Since dehydrogenation was never completed within any titration time, this upper minima could not be accurately converted into an estimate of Pt surface area as had been hoped. However it is clear from Table 1 that as the Pt dispersion increases the number of hydrogen atoms donated to the catalysts increases broadly in line with the number of hydrogen atoms which had earlier been extracted by cyclohexene titration, despite the absolute number donated being only 61–80% of the number extracted. The low temperature at which cyclohexene starts to dehydrogenate provides an upper limit on the t.p.t. with this titrant and could be one reason why surface areas estimated by t.p.t. were lower than those estimated by t.p.d. With other alkene titrants this might not be so, and the titration could provide still further information.

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## References

- 1 R. L. Moss, in 'Catalysis' (Specialist Periodical Report), vol. 4, eds. C. Kemball and C. A. Dowden, The Royal Society of Chemistry, 1981, p. 33.
- 2 J. E. Benson and M. Boudart, *J. Catal.*, 1965, **4**, 704; P. Wentreck, K. Kimoto, and H. Wise, *ibid.*, 1973, **33**, 279; G. C. Bond and P. A. Sermon, *React. Kinet. Catal. Lett.*, 1974, **1**, 3; P. A. Sermon and G. C. Bond, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 745; G. Leclercq, J. Barber, C. Betizeau, R. Maurel, H. Charcosset, K. Frety, and L. Tournayan, *J. Catal.*, 1977, **47**, 389.
- 3 S. Tsuchiya, Y. Amenomiya, and R. J. Cvetanovic, *J. Catal.*, 1970, **19**, 245; 1971, **20**, 1; Y. Amenomiya, *ibid.*, 1971, **22**, 109; R. Komers, Y. Amenomiya, and R. J. Cvetanovic, *ibid.*, 1969, **15**, 293; J. P. Candy, P. Fouilloux, and A. J. Renouprez, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 616.
- 4 A. R. Berzins, P. A. Sermon, M. S. W. Vong (née Lau), and A. T. Warie, *Adsorption Sci. Tech.*, in the press.
- 5 C. R. McIlwrick and G. S. G. Phillips, *J. Phys. E*, 1973, **6**, 1208.
- 6 M. S. W. Vong (née Lau), Ph.D. thesis, Brunel University, 1982.