Unexpectedly Low Yields of Water from Hydrogen–Oxygen Titrations on Platinum at 293 K

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Despite expected extents of hydrogen–oxygen and oxygen–hydrogen titrations, the rates of heat and water vapour release from unsupported and silica-supported platinum at 293 K and 101 kPa surprisingly suggest that water may not be the primary major product of these widely used methods of surface characterisation under these conditions.

Despite their extensive use in the characterisation of metal surfaces, including those of Pt, there is much uncertainty concerning surface stoicheiometries,[1] the importance of surface OH groups,[2] and unreactive surface oxygen,[3] in the titrations of preadsorbed oxygen by gaseous hydrogen (HT) and the titration of preadsorbed hydrogen by gaseous oxygen (OT). The preliminary work described here was undertaken to elucidate these important processes on Pt and used two catalysts: (A) unsupported Pt-black (Johnson Matthey) and (B) silica-supported Pt (6.3% Pt, EuroPt supplied by Council of Europe).[4]

Unlike sample (B), the total metal surface area of sample (A) could be estimated by Brunauer–Emmett–Teller analysis of the extents of adsorption of Kr and nitrogen at 77 K and also HT and OT titrations at 293 K, although measurements of hydrogen and oxygen chemisorptions were prevented by the ease of sample sintering during pretreatment. Table 1 indicates that the areas deduced by such methods were in reasonable agreement. Table 1 also shows that the ratio of the extents of hydrogen chemisorption (q_{HC}) : oxygen chemisorption (q_{OC}) : hydrogen titration of preadsorbed oxygen (q_{HT}) : oxygen titration of preadsorbed hydrogen (q_{OT}) at 293 K and 5.3 kPa measured volumetrically for sample (B) after reduction in hydrogen (1 h, 13.3 kPa) and desorption at 673 K to 100 mPa is similar to that seen previously[1] (*i.e.* 2 : 1 : 4 : 2). However, the adsorption stoicheiometries for hydrogen and oxygen for sample (B) are different from those for sample (A) and this may in part be due to its differing dispersion.

A Dupont 990 differential scanning calorimeter was used with a flow (40 ml/min, 101 kPa) of reactive gases (6% H_2 in N_2 or 6% O_2 in N_2 from BOC Special Gases) above the catalysts to measure enthalpies of chemisorption or titration at 293 K. Between measurements catalysts were flushed with N_2 (BOC) for which great care was taken to reduce concentrations of oxygen impurities to <1 part in 10^9 by passage through celite-supported MnO_x.[5] Thermokinetic profiles of dQ/dt *vs.* time, t, for HT and OT show induction times, maxima (at about 180 s), and slow returns to baselines (achieved in 5 min with HT and >15 min with OT) as reported previously,[6] and are characteristic of Langmuir–Hinshelwood mechanisms. Integration of such thermokinetic profiles, as described previously, gave the enthalpies of titration given in Table 1. Such titration enthalpies are greater than those for chemisorption,[7] but are at variance with those for HT and OT obtained after vacuum pretreatment,[8] and therefore surprisingly suggest that, in the absence of effects of oxygen impurities, at 293

Table 1. Hydrogen–oxygen and oxygen–hydrogen titrations on (A) unsupported Pt and (B) Pt—SiO_2.

Sample	Extent of adsorption[a] q (μmol/g Pt)	Enthalpy of adsorption[a] Q (kJ/mol titrant or adsorbate)	Pt Surface area[b] (m^2/g Pt)
(A)	249(HT)	85.8±3%(HT)	8.9(HT)[c] 4.0(N_2)
	100(OT)	501 ±3%(OT)	7.2(OT)[c] 7.0(Kr)
(B)	2556(HC)	[d]	
	1000(OC)	[d]	
	3984(HT)	113 ±3%(HT)	
	1587(OT)	700 ±3%(OT)	

[a] Titration at 293 K and 5.3 kPa. [b] Estimated by various methods of adsorption. [c] Assume 11.2 Pt atoms occupy 1 nm^2 of surface, H/Pt = 1, sample (A), or 2, sample (B), see Renouprez *et al.* in ref. 1. [d] Q_{HC} and Q_{OC} found (ref. 7) to be 67.2 and 263.6 kJ/mol adsorbate.

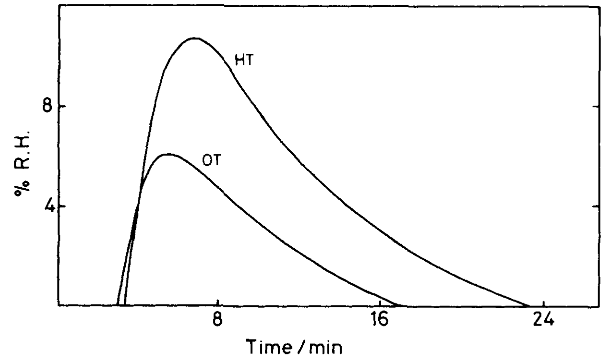

Figure 1. Concentrations of water vapour released in titrations over 0.5155 g Pt-black at 293 K.

K and 101 kPa water may not be the major product of such titrations.

Using a flow microcatalytic reactor containing a sample (*ca.* 1 g) of either (A) or (B) at 293 K and a humidity detector (Kane and May model 2001 precalibrated against saturated aqueous solutions of LiCl and NaCl at known temperatures which was unaffected by either H_2 or O_2), the percentage relative humidity (R.H.) was monitored as a function of time (on a 20 mV full scale deflection chart recorder) as one of the above gases flowed (40 ml/min, 101 kPa). No fluctuations in gas temperatures were noted. Integration of the % R.H. (or rate of release of water vapour)–time curve allowed the total number of moles of water released to be calculated. Figure 1 shows such traces for the release of water vapour from catalyst (A) at 293 K and 6 kPa reactant partial pressure, and integration confirms that only about a third of the water expected by normal titration stoicheiometries and values of q_{HT} and q_{OT} is found to be released experimentally (*i.e.* 33% for HT and 34% for OT). Equivalent experiments with samples of catalyst (B) detected no water vapour released under these conditions. Recent results[9] have found that HT–OT titrations on alumina-supported Pt only released water at about 500 K. Therefore, since water vapour adsorbed on (A) and (B) at 293 K was readily found to desorb at 387 K, the small fraction of titrants consumed and released as water vapour must reflect a slow rate of water formation rather than a slow rate of water desorption. This is surprising since it is normally assumed that water is rapidly produced but subsequently scavenged by any support present.

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References

1. J. E. Benson and M. Boudart, *J. Catal.*, 1965, **4**, 704; D. E. Mears and R. C. Hansford, *ibid.*, 1967, **9**, 125; G. R. Wilson and W. K. Hall, *ibid.*, 1970, **17**, 190; A. Renouprez, J. M. Tejero, and J. P. Candy, 8th International Congress on Catalysis, 1984, vol.3, p. 47.
2. M. A. Akhtar and F. C. Tompkins, *Trans. Faraday Soc.*, 1971, **67**, 2454; B. A. Morrow and P. Ramanurthy, *J. Phys. Chem.*, 1973, **77**, 3052; J. L. Gland, G. B. Fischer, and E. B. Kollin, *J. Catal.*, 1982, **77**, 263.
3. D. D. Eley, D. M. Moran, and C. H. Rochester, *Trans. Faraday Soc.*, 1968, **64**, 2168.
4. EuroPt-1 Handbook (Council of Europe Group on Catalysis 1981).
5. C. R. McIlwick and C. S. G. Phillips, *J. Phys. E*, 1973, **6**, 1207.
6. E. R. A. Mills, P. A. Sermon, and A. T. Wurie, 8th International Congress on Catalysis, 1984, vol. 3, p. 131.
7. I. Toyoshima and G. A. Somorjai, *Catal. Rev.*, 1979, **19**, 105; A. Linares-Solano, F. Rodriquez-Reinoso, O. P. Salinas-Mahajan, and P. L. Walker, *Carbon*, 1982, **20**, 177.
8. S. M. Basset, A. Theolier, M. Primet, and M. Prettre, 5th International Congress on Catalysis, vol. 2, p. 915.
9. D. Duprez and A. Miloudi, *J. Catal.*, 1984, **86**, 441.