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NOTE

The Form of Hydrogen Chemisorption Isotherms on a Pt/SiO$_2$ Catalyst (EUROPT-1)

Estimation of the degree of dispersion of the active phase in supported metal catalysts is still most often and most economically performed by measuring the H$_2$ chemisorption isotherm and then relating the derived monolayer volume to the number of surface metal atoms M_s, assuming an H/M_s ratio of unity. The popularity of this method continues, despite increasing evidence that the chemisorption process can have a complex character (1) and that the H/M_s ratio can frequently exceed unity for small particles (2). Regrettably too, publications often give only the scantiest details of how the measurements are made and how the monolayer volume is derived from the observed uptakes: estimates of accuracy are also only rarely provided. Experience teaches that, whatever the range of equilibrium pressures covered, there is always a quasilinear portion of the isotherm that can be extrapolated to zero pressure to afford a value for "monolayer volume;" however, the wider the pressure range covered, the larger the intercept (1) because the uptake is at no point linearly dependent on equilibrium pressure. Instead the slope decreases continuously as the equilibrium pressure tends towards the limiting high-pressure uptake. Moreover, such an extrapolation involves an element of personal judgement.

A preferable method would be to plot the results according to the linearized form of the appropriate equation relating uptake to equilibrium pressure; unfortunately the literature reveals some disagreement as to what this is. Early results based on H$_2$ desorption reported by Frennet and Wells (1) appear to obey the Temkin equation, at least over some part of the equilibrium pressure range, and especially at low temperatures, but Berzins *et al.* (3) find the Langmuir equation more suitable, although the linearized plots (see Fig. 8c of Ref. (3)) are not convincingly straight. Resolution of the question is not helped by conflicting results concerning variation of the enthalpy of adsorption with coverage (4): one laboratory has reported enthalpies independent of coverage, as required for the Langmuir equation to hold, while another has spoken of decreasing values, as befits the Temkin equation.

We have recently re-investigated the form of the H$_2$ chemisorption isotherms obtained with EUROPT-1 (6.3% Pt/SiO$_2$) at room temperature, following pretreatments which mimic those used before making catalytic measurements (5, 6): these were (i) high-temperature reduction (HTR), viz. 2 h in H$_2$ at 750 K, and (ii) low-temperature reduction following an oxidation step (O/LTR), viz. 1 h in air at 620 K, then (after purging with N$_2$) 2 h in H$_2$ at 520 K. Samples were then outgassed for 30 min at 750 K, in a system evacuated by an Hg-diffusion pump backed by a rotary pump; residual pressures were about 10^{-5} Torr. Measurements have also been made with EUROPT-1 modified by the addition of either TiO$_2$ or Al$_2$O$_3$ (6).

Figure 1 shows the isotherms obtained with EUROPT-1 after these pretreatments and the corresponding results for the material containing 9.1% TiO$_2$; in both cases, but especially with unmodified EUROPT-1, the O/LTR treatment results in somewhat higher H$_2$ uptakes at all pressures. This form of treatment had been devised to see whether, as with Ru/TiO$_2$ and Ru/Al$_2$O$_3$ catalysts (7), oxidation followed by low-temperature reduction might lead to a change in turnover frequency or product selectivities in consequence of an alteration in particle size or surface roughness. Furthermore, with modified catalysts (6), such a treatment might have been expected to reverse any SMSI-like effect produced by the modifiers in a high-temperature reduction, although such an effect, if indeed present here, is scarcely observable. Values for monolayer volumes obtained by extrapolation to zero pressure are shown in Table 1.

Figure 2 shows the H$_2$ uptakes shown in Fig. 1 plotted according to the Langmuir equation for dissociative chemisorption, linearized as

$$P_e^{0.5}/n = (K^{0.5}n_m)^{-1} + (P_e^{0.5}/n_m),$$

where P_e is the equilibrium pressure, n and n_m are the molar quantities of H$_2$ adsorbed respectively at any pressure P_e and in the monolayer, and K is the adsorption coefficient. Excellent straight lines are obtained (correlation coefficients > 0.9999), from which n_m and hence K may be calculated with high accuracy (Table 1). Assuming one H per surface Pt atom in the monolayer, the

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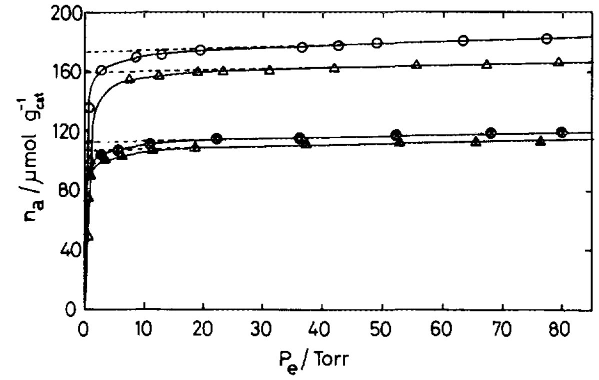

FIG. 1. H_2 chemisorption isotherms for EUROPT-1 (open symbols) and for EUROPT-1 modified with 9.1 wt.% TiO_2 (filled symbols): circles, O/LTR treatment; triangles, HTR treatment (see text for details).

H/Pt_{tot} ratios are readily obtained, as the Pt content is accurately known (8) (see also Table 1).

Since the amounts adsorbed in the range where the Langmuir equation is seemingly obeyed are a large fraction of the total uptake, and are not changing much with equilibrium pressure, it was possible that the results might also agree with the Temkin equation, the range of validity of which is between 30 and 70% coverage. Plots of uptake versus log (equilibrium pressure) were indeed linear for pressures greater than about 5 Torr, but since this corresponded to coverages well in excess of 70%, based on the estimate of monolayer capacity using the Langmuir equation, we conclude that such plots are of no real significance, and they cannot of course be used to estimate a monolayer volume.

A number of other modifications of EUROPT-1 have also been examined, and have given results of broadly similar quality: values of the H/Pt ratios have been published (6). Values of *K* obtained from the slopes and intercepts of the linearized Langmuir plots show considerable variation; thus, for example, addition of up to 3 wt.% of TiO_2 or of Al_2O_3 to EUROPT-1 lowers *K* by 40 to 65%, the lowering being somewhat greater after HTR than after O/LTR. This suggests that the modifiers may lower the strength of H_2 chemisorption, but in view of the doubts over the applicability of the Langmuir equation it would be unwise to press the analysis further.

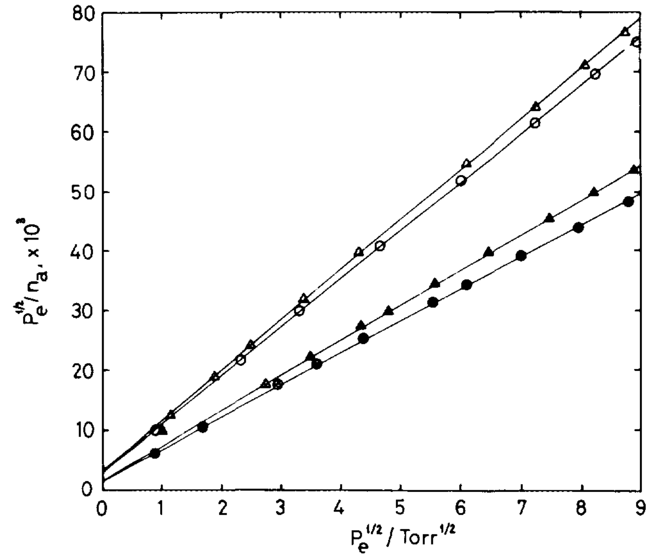

FIG. 2. Plots of the results shown in Fig. 1 according to the Langmuir equation for dissociative chemisorption (symbols as in Fig. 1).

We have also established that it is possible to obtain close reproducibility of results in duplicate measurements. Thus, for example, EUROPT-1 modified by 0.5-wt.% Al_2O_3 gave H/Pt values of 0.883 and 0.878, the corresponding values of *K* being 2.62 and 3.38.

Finally, it is of interest to compare our results for EUROPT-1 with literature values (1, 3); this is done in Table 2. Our HTR treatment leads to an H_2 uptake, however estimated, that is slightly smaller than those reported previously: this is unlikely to be due to sintering because the catalyst is remarkably stable on heating in a reducing atmosphere (9), and the O/LTR treatment raises the uptake so that it equates to the literature values. The most likely explanation is that the HTR carbonizes traces of organics absorbed from the atmosphere and that the adsorption capacity is in consequence slightly lowered; the O/LTR treatment cleanses the surface and the ad-

TABLE 1

H_2 Chemisorption Isotherms Plotted According to the Langmuir Equation: Parameters and Derived Quantities

Catalyst	Pretreatment	Intercept	Slope ($\times 10^3$)	n_m/νmol g_{cat}^{-1}	*K* ($Torr^{-1}$)	H/Pt_{tot}
EUROPT-1	HTR	1.804	5.858	170.7	10.12	1.060
	O/LTR	1.814	5.311	188.3	8.57	1.170
EUROPT-1 + 9.1% TiO_2	HTR	2.963	8.455	118.3	8.15	0.737
	O/LTR	2.783	8.121	123.1	8.51	0.768

TABLE 2

Monolayer Capacities (μmol g_{cat}^{-1}) for H_2 on EUROPT-1 Derived in Various Ways

Pretreatment	n_m^o	n^{40}	n_m^L	H/Pt^L	Reference
—	166	174	—	—	1
—	166±4	168	~192	1.19	3
HTR	159.5	162	171	1.06	This work
OLT/R	173.5	178	188	1.17	This work

Note. n_m^o: monolayer capacity by extrapolation to zero pressure; n^{40}: H_2 uptake at 40 Torr equilibrium pressure; n_m^L: monolayer capacity according to Langmuir equation; H/Pt^L: the corresponding H/Pt ratio.

sorption capacity is raised. The improved linearity of the Langmuir equation plots (Fig. 2) over those shown before (3) may also be attributed to better outgassing of the material through the use of a higher temperature.

We are aware that the original work on EUROPT-1 (1) revealed that the H/Pt ratio exceeded that expected on the basis of a mean particle size of 1.8 nm as deduced by TEM, from which it was concluded that not all the H_2 taken up formed H–Pt bonds, and that some might be used to break Si–O–Pt bonds fixing the metal particles to the surface. For this reason we have declined to use H_2 uptakes to calculate turnover frequencies (5, 6), but instead have contented ourselves with using them in a qualitative way to monitor changes in the number of available Pt atoms (6). Thus if only part of the uptake titrates exposed Pt atoms, the extent of coverage of the metal surface of a modifier (Table 1 and Ref. (6)) may be considerably greater than appears at first sight. The chief purpose of this note, however, is to show that application of the Langmuir equation to H_2 uptakes on supported metals can give very accurate and reproducible estimates of monolayer capacities. Further work is needed to elucidate the processes responsible for the uptake.

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REFERENCES

1. Frennet, A., and Wells, P. B., *Appl. Catal.* **18,** 243 (1985).
2. Kip, B. J., Duivenvoorden, F. B. M., Koningsberger, D. C., and Prins, R., *J. Catal.* **105,** 26 (1986).
3. Berzins, A. R., Lau Vong, M. S. W., Sermon, P. A., and Wurie, A. T., *Adsorp. Sci. Technol.* **1,** 51 (1984).
4. Bond, G. C., and Paál, Z., *Appl. Catal. A: Gen.* **86,** 1 (1992).
5. Bond, G. C., and Lou, Hui, *J. Catal.* **132,** 462 (1992).
6. Bond, G. C., and Lou, Hui, *J. Catal.* **142,** 512 (1993).
7. Bond, G. C., Rajaram, R. R., and Burch, R., *in* "Proceedings, International Congress on Catalysis, 9th Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1130. Chem. Institute of Canada, Ottawa, 1988.
8. Bond, G. C., and Wells, P. B., *Appl. Catal.* **18,** 225 (1985).
9. Geus, J. W., and Wells, P. B., *Appl. Catal.* **18,** 231 (1985).

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