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Chemisorption measurements on polymer-stabilized colloidal platinum and rhodium nanoclusters in liquid dispersion

John S. Bradley * and Wilma Busser

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

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A simple method is reported for the precise and accurate differential barometric measurement of gas adsorption into liquid dispersions of colloidal metal catalysts. Using both hydrogen adsorption and hydrogen/oxygen titration the fraction of the total surface of polyvinylpyrrolidone-stabilised Pt and Rh colloids available for adsorption is found to be approximately 44%. This method is also applicable to supported metal catalysts in liquid slurries.

Keywords: chemisorption, colloidal metal, nanoclusters, platinum, rhodium, catalysis, surface area, hydrogen–oxygen titration

1. Introduction

Among the methods used for the characterization of supported metal catalysts, gas adsorption techniques are the most common. Quantitative chemisorption of gases such as hydrogen or CO is used to determine the metal surface area of supported metal catalyst particles, with the assumption of a certain generally accepted stoichiometry for the metal-adsorbate site [1]. In addition, reactive adsorption probes such as hydrogen/oxygen titration are sometimes used [1–3]. These methods are carried out on solid catalyst samples by adsorption from the gas phase to determine the number of available surface atoms per unit mass of catalytic metal. Other surface characterization techniques such as vibrational spectroscopy also rely on chemisorption measurements in order to correlate, for example, spectra of adsorbed molecules with coverage.

In the course of an ongoing investigation of the spectroscopic and catalytic properties of colloidal metal nanoparticles in liquid dispersions we had a need for a method for determining the available surface area of the dispersed metal in order to make rational comparisons of catalytic activity data among several catalysts. Estimations of available surface area for colloidal metals based on techniques such as transmission electron microscopy require the assumption that the entire surface of the metal particles is available for adsorption or catalysis, and this is an extremely unlikely state of affairs. The presence in colloidal metal dispersions of stabilizing species such as polymers or surfactants, which presumably interact with the surface in some manner, raises the possibility that the surface area available for adsorption of reactant molecules is less than the geometric surface area due to occlusion by the stabilizers, but to date no physical measurements of metal surface area in colloidal metal dispersions are to be found in the literature. Even in the case of supported metals used catalytically as slurries, chemisorption methods are routinely carried out by gas adsorption into an evacuated solid sample prior to dispersion in the dispersing liquid, in which form the surface may be partially occluded with solvent molecules.

We report here a simple method for the precise and accurate barometric measurement of gas adsorption into liquid dispersions of either supported or colloidal metal catalysts. The method relies on the high precision attainable from pressure transducers coupled with a differential mode of measurement between the neat dispersant liquid and the liquid catalyst dispersion. By developing a method for gas adsorption measurement for colloidal metal catalysts we have also provided a means of characterization for supported metal catalysts in liquid slurries.

2. Experimental

Colloidal rhodium [4] and platinum [5], stabilized with polyvinylpyrrolidone (MW 40,000), were prepared by heating $RhCl_3{\cdot}3H_2O$ or H_2PtCl_6 in aqueous alcohol mixtures in the presence of the stabilising polymer. Particle sizes were determined by transmission electron microscopy.

2.1. 2.5 nm Rh/PVP

A solution of $RhCl_3{\cdot}3H_2O$ (240 mg, 0.91 mmol) and PVP (40,000 MW, 3.5 g, 32 mmol monomer equivalents) in 480 ml 1-butanol/water (5 : 2) was stirred under hydrogen (2 bar) for 2 h at 70 °C. Evaporation to dryness under reduced pressure gave a solid polymer containing Rh particles with a mean diameter of 2.5 nm.

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* Present address: Department of Chemistry, University of Hull, Cottingham Road, HU6 7RX Hull, UK.

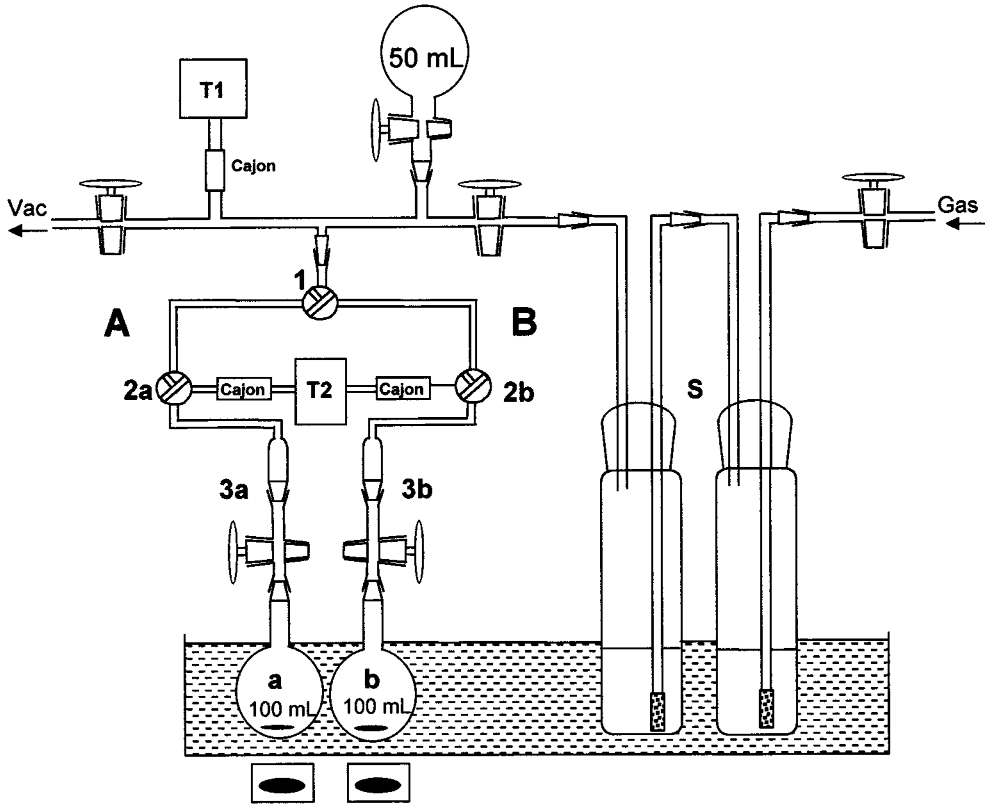

Figure 1. Differential barometric measurement of gas absorption into liquid catalyst. See text for an explanation.

2.2. 1.5 nm Pt/PVP

$H_2PtCl_6{\cdot}6H_2O$ (500 mg, 0.97 mmol) was heated in a mixture of methanol (50 ml) and water (50 ml) containing PVP (40,000 MW, 5.9 g, 54 mmol monomer equivalents) to reflux for 4 h. Evaporation to dryness gave a solid polymer containing platinum particles with a mean diameter of 1.5 nm.

2.3. Gas adsorption measurements

Barometric gas adsorption measurements were conducted in a differential gas adsorption manifold, shown schematically in figure 1. The method relies on the precise measurement of the pressure differential which develops between two volumetrically calibrated bulbs, one containing a polymer-stabilised colloidal suspension, the other a solution of the polymer stabiliser, when each previously degassed and quiescent liquid is stirred under an identical pressure of an adsorbent gas. The following procedure, which is essentially identical to that used for subsequent hydrogen adsorption measurements, describes the measurement of the solubility of hydrogen in 1-butanol. The absorption manifold was connected to a vacuum manifold fitted with a pressure transducer **T1** (MKS Baratron 225AD) and a calibrated 50 ml bulb. Each arm, **A** and **B**, of the manifold from stopcock **1** to the absorption bulbs **a** and **b** was calibrated. The essential volumes are those from each side of the diaphragm in the differential pressure transducer **T2** (MKS Baratron 225AD) up to and including the gas absorption bulbs **a** and **b**, each of which were of 100 ml nominal volume. Bulbs **a** and **b** were evacuated and removed from the manifold at **3a** and **3b** and weighed, to allow subsequent gravimetric measurement of liquid sample quantities. To the two preweighed bulbs were added volumes of 1-butanol differing by approximately a factor of four (ca. 15 and ca. 65 ml), magnetic stirring bars were added to each, and the two bulbs were attached to the manifold with three-way stopcocks **2a** and **2b** open to the transducer **T2**. Both the absorption bulbs and the saturators were immersed in a thermostated water bath at 23.0 °C. The pressure in the system was reduced to the vapour pressure of 1-butanol, and each sample was stirred at this pressure for several minutes and allowed to reach thermal equilibrium. Argon was added to 1 bar, and the system evacuated again. This cycle was repeated three times. The manifold was then isolated from the vacuum system, stirring was stopped and, after the liquid samples had remained quiescent for several minutes, hydrogen was added to both sides of the manifold via **1** through a double bulb saturator, **s**, filled with 1-butanol.

The absorption bulbs were then isolated from the manifold and connected via **2a** and **2b** to each side of the differential pressure transducer, which was nulled. Stirring was begun and continued until no further change in pressure difference was observed. The actual volumes of 1-butanol present during the absorption experiment were determined by introducing argon into the system, removing, stoppering and weighing the absorption bulbs.

For adsorption experiments on colloidal metal dispersions, approximately equal volumes of solvent were used in each absorption bulb, one of which contained a weighed quantity of previously dried polymer-stabilised colloidal metal sample, the other a quantity of polymer equal to that in the colloidal metal sample. The experiment was then carried out, as described in section 2.3, the respective volumes of solvent in each bulb being determined gravimetrically after each barometric measurement.

In addition to simple hydrogen chemisorption measurements, hydrogen–oxygen titration measurements [2,3] were also performed, in which the colloidal metal dispersion was first stirred in air for 12 h at 535 K and then subjected to hydrogen chemisorption measurement at 298 K.

3. Results and discussion

The addition of a gas to a dispersion of a colloidal metal in a closed system results in a pressure drop corresponding to the volume of gas dissolved in the liquid plus the volume adsorbed on the dispersed metal particles. It is only necessary to be able to subtract the volume dissolved in the liquid alone to make a valid measurement of the adsorbed gas. In principle this is possible by a sequence of two experiments, one on the pure liquid, one on the colloidal dispersion. However, imprecision in thermostating (and thus liquid vapour pressure as well as measured gas pressure) coupled to the precision limit of the pressure measuring device make this a less than ideal method. The precision of the measurements carried out as described in this paper depends on isothermal operation, which is ensured by immersion of all significant parts of the system in a thermostat bath, and the fact that gas–liquid mass transfer is negligible across a quiescent liquid–gas interface, allowing a null point to be achieved before the adsorption experiment is begun. If comparable volumes of liquid are used in each side of the differential apparatus, the pressure difference measured in the experiment will be reasonably close to the actual $\mathrm{d}P$, which arises from gas adsorption on the catalyst surface, and the precision of the pressure transducer may be applied in full to the measurement of chemisorption on the colloidal metal surface, since the additional $\mathrm{d}P$ due to gas solubility is practically nulled. It is not even necessary for equal volumes of liquid to be added to each of the two absorption bulbs, so long as the headspace volume in each side of the apparatus (bulb **a** or **b** to each side of the transducer diaphragm) is accurately known. Ideally the pressure differential at the end of the experiment would reflect only the quantity of gas adsorbed on the colloidal metal surface, but accurate measurement of the headspace volume, the liquid volumes used and the gas solubility in the liquid are all that is needed to calculate the quantity of adsorbed gas. It is not necessary to control the stirring speed in each flask – only the initial null value and the final $\mathrm{d}P$ are needed for the measurement.

The reliability and precision of the experiment is seen by a comparison of the values obtained by this method for the solubility of hydrogen and of carbon monoxide in 1-butanol with those reported in the literature. For this measurement, volumes of approximately 16 and 65 ml 1-butanol were placed in the two bulbs, giving rise to a $\mathrm{d}P$ of approximately 50 Torr at approximately 760 Torr initial hydrogen pressure. Over a series of six measurements values for Henry's constant for hydrogen in 1-butanol of $3.89 \pm 0.05 \times 10^8$ Pa were obtained (3.79×10^8 Pa [6]) and corresponding values for CO in 1-butanol of $1.85 \pm 0.13 \times 10^8$ (1.88×10^8 Pa [7]).

The solubility of hydrogen in butanol was used in the following determinations of hydrogen chemisorption and hydrogen/oxygen titration for samples of colloidal platinum, palladium and rhodium, each stabilised in 1-butanol dispersion with polyvinylpyrrolidone.

In a typical experiment, in which the hydrogen chemisorption capacity of a 2.5 nm Rh/PVP colloid was measured, 3.725 g of a solid sample of a PVP-stabilised rhodium colloid containing 95 mg Rh was dissolved in approximately 50 ml of 1-butanol and attached to one side of the apparatus. A similar quantity of 1-butanol containing 3.630 g PVP was attached to the other side of the apparatus. After three degassing cycles and thermal equilibration, as described above, hydrogen was added to both sides of the apparatus to a pressure of 751.2 Torr, the adsorption bulbs isolated to each side of the differential pressure transducer, and stirring begun. The development with time of the pressure differential between the polymer solution and the colloid is of no kinetic significance, being a function only of the relative gas–liquid diffusion rates into the two liquids, but is of use in determining whether equilibrium has been reached in the chemisorption process. Approximately 3 h was required in this experiment for a equilibrium $\mathrm{d}P$ of 19.3 Torr (9545 Pa). The actual volumes of liquid in each absorption flask during the experiment were determined gravimetrically to be 52.4 ml for the polymer solution and 63.7 ml for the colloid dispersion, and thus the gas volumes in each side of the apparatus (previously calibrated to be 130.4 and 155.4 ml, respectively) of the apparatus before absorption was begun were determined at 78.0 and 91.8 ml, respectively. Using the value for Henry's constant determined earlier to determine the quantity of gas dissolved in the liquid in each bulb at equilibrium, the quantity of hydrogen adsorbed on the colloid is calculated to be 0.103 mmol/mg atom Rh. Thus, assuming a stoichiometry of $\mathrm{Rh : H} = 1 : 1$ [1], the sample contained 0.206 surface Rh atoms/total Rh available for hydrogen chemisorption. In order to express this in terms of a fraction of surface atom available, a theoretical dispersion for the Rh colloid was calculated, assuming close-packed cuboctahedral particles with a diameter equal to the mean observed by TEM. The assumed morphology is a better assumption than spherical morphology for particles in the 1–4 nm size range. Accordingly we have adopted the statistics for closed fcc cuboctahedra over this size [8,9] shown in table 1. For a 2.5 nm Rh particle this gives a dispersion of 0.46, and so the resulting fraction of the surface on the Rh colloid avail-

Table 1
Calculation of dispersions for colloidal Rh and Pt.

Metal	Mean diam. (nm)	Atoms[a] Total	Atoms[a] Surface	Dispersion
Rh	2.5	586[b]	272	0.46
Pt	1.5	201[c]	122	0.61

[a] Calculated from [9].
[b] Assuming an fcc cuboctahedron with 4 atoms on an edge.
[c] Assuming an fcc cuboctahedron with 3 atoms on an edge.

Table 2
Hydrogen chemisorption results.

Metal	Diam. (nm)	Dispersion	H_2/total M[a]	Available surface (%)
Rh	2.5	0.46	0.10	45
Pt	1.5	0.61	0.14	46

[a] Calculated on the basis of $0.5H_2$ per surface metal atom.

Table 3
Hydrogen/oxygen titration results.

Metal	Diam. (nm)	Dispersion	H_2/total M[a]	Available surface (%)
Rh	2.5	0.46	0.29	42
Pt	1.5	0.61	0.41	45

[a] Calculated on the basis of $1.5H_2$ per surface metal atom.

able for hydrogen chemisorption, based on this differential barometric experiment, is 45%.

The results from hydrogen chemisorption and hydrogen/oxygen titration for a 2.5 nm Rh colloid and a 1.5 nm Pt colloid are summarized in tables 2 and 3. The usual stoichiometries of $0.5H_2$/surface metal atom for the former method and $1.5H_2$/surface metal atom for the latter are assumed, although for particles of this size in supported metal systems higher ratios have been reported and variously ascribed to “spillover” onto the support, dissolution of hydrogen into the metal particle or multiple adsorption on the low coordination number metal atoms on the edges and vertices of the particles, which at small particle sizes become a significant fraction of the total metal surface [10].

It is clear from these results that a significant fraction of the surface of these PVP-stabilized colloidal metal particles are available for hydrogen adsorption. If we make the usual correlation between hydrogen adsorption capacity and hydrogenation activity for metal particles, a comparison can be made with data we obtained earlier for the catalytic hydrogenation of ethyl pyruvate using a platinum/PVP colloidal catalyst [11]. A comparison with a simple supported Pt/Al_2O_3 catalyst, where, in the absence of any polymer, the surface is all presumably available, will provide information concerning the fraction of the colloidal catalyst surface which is available, since for the polymer-stabilized platinum the activity will be reduced by a factor reflecting the surface occupancy of the polymer. If we assume that the interaction of PVP with colloidal platinum particles in that system is similar to that in the Pt/PVP sample on which we have measured hydrogen chemisorption and hydrogen–oxygen titration, an activity ratio of 0.46 would be expected, reflecting the fraction of free surface available on the surface of the PVP-stabilized Pt. An activity ratio of 0.41 was observed. Thus we have supporting evidence for the assertion that PVP occupies approximately 40–50% of the surface of the Pt/PVP sols studied. This is the first measurement of surface adsorption of a polymer stabilizer on a metal colloid.

The method we have described is, of course, applicable to the determination of the chemisorption capacity of supported metal catalysts in liquids, i.e., under the actual conditions of use. Such studies are now underway and will be reported separately.

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