Surface Characterization of Polymer-Stabilized Colloidal Metal Catalysts

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SUMMARY: A new method for measuring hydrogen chemisorption on polymer-stabilized metal colloids, in conjunction with variable coverage infrared spectroscopy of adsorbed CO, is applied to analyse the surface of Pt/polyvinylpyrrolidone colloids. The results correlate well with the measured activity of Pt/PVP as a hydrogenation catalyst.

Introduction

For the purpose of this lecture we will be considering the chemistry and catalytic properties of small, polymer stabilized metal particles in liquid dispersions, having diameters of from 1.5 nm to 2.5 nm and thus containing between 150 and 500 metal atoms. Transition metal particles in this size range on solid supports have found a wide range of applications in traditional heterogeneous catalysis, and the principal focus in this paper is the surface chemistry and catalytic properties of these small particles in liquid dispersions, in which state they are known as *colloidal metals* or *sols.*

A common means by which colloidal metal particles are stabilized in liquid dispersions and prevented from aggregating is by the adsorption of polymers at the surface of the particles, thus providing a protective layer.[1] Vinyl polymers with polar side groups such as poly(vinylpyrrolidone) and poly(vinyl alcohol) are especially useful in this respect. We will focus in this paper on the nature of the interaction of a stabilizing polymer with the surface of a colloidal metal cluster in a poly(vinylpyrrolidone) (PVP)/Pt sol. In particular we will attempt to estimate how much of the available particle surface is occupied by the polymer, how the polymer perturbs the available surface of the metal particle, and how the surface chemistry and thus the catalytic properties of the polymer-stabilized colloidal metal clusters are affected by the presence of the polymeric stabilizer.

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Experimental Section.

Colloidal platinum stabilized with PVP was prepared by literature methods. [2,3]

Gas Adsorption Measurements.

Barometric gas adsorption measurements were conducted in a differential gas adsorption manifold, shown schematically in Figure 1.

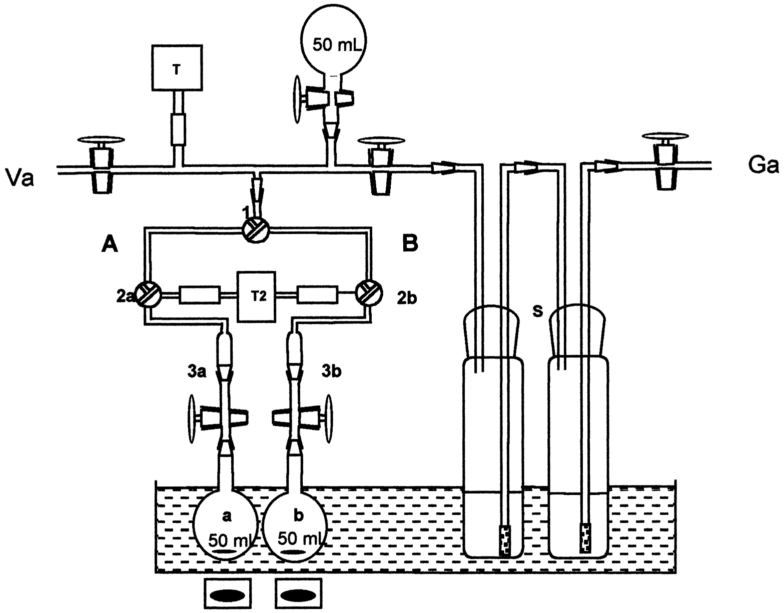


Fig. 1. Differential barometer for gas absorption measurement into liquid catalyst dispersions.

The method relies on the precise measurement of the pressure differential which develops between two volumetrically calibrated bulbs, **a** and **b**, one containing a polymer-stabilised colloidal suspension, the other a solution of the polymer stabiliser, when each previously degassed and quiescent liquid sample is stirred under an identical pressure of an adsorbant gas. The bulbs, which are isolated from each other, are connected to the two sides of the diaphragm of a pressure trasducer, $\mathbf{T_2}$, by 3-way taps at **2a** and **3b**, and gas is added via the saturator **S**, through **1**, **2a** and **2b** to both the absorption bulbs. Both bulbs and the saturator were immersed in a thermostatted water bath at 23.0°C. Stirring under an atmosphere of the adsorbing gas was continued until no further change in pressure difference was observed. The actual volumes of solvent present during the absorption experiment were determined by introducing argon into the system, removing and stoppering and weighing the absorption bulbs at **3a** and **3b**. The experimental procedure will be described in detailelsewhere.

Both hydrogen chemisorption measurements and hydrogen-oxygen titration measurements were performed. For the latter the colloidal metal dispersion was first stirred in air for 12 h at 535K and then subjected to hydrogen chemisorption measurement at 298K. In this experiment the hydrogen consumed corresponds to a re-reduction of the metal surface plus adsorption of hydrogen on the reduced metal particle.

FTIR Spectroscopic analysis of adsorbed carbon monoxide

Infrared spectra during addition of CO to a liquid dispersion of colloidal Pt/*PVP* were obtained as previously described. [2,4] The colloidal suspension, (using ca. 200 mg of solid Pt/PVP in 20mL of dry dichloromethane) was passed through through a flow cell (CaF_2 windows, pathlength variable from 0,05 - 2 mm) at a rate of 300mL.min^{-1}. Spectra were obtained at 8 cm^{-1} resolution and accumulated at 10 s^{-1} using a remote MCT detector. Addition of CO in a slow stream to the colloid suspension was made via a saturator containing dichloromethane, so that during the course of the experiment the concentration of the colloid remained constant. This allowed the precise subtraction of the relatively intense solvent and polymer overtone and combination bands in the region 2200 - 1800 cm^{-1} of the initial spectrum from all subsequent spectra during CO addition. The resulting spectra thus contained only absorptions due to adsorbed CO on the colloidal metal particles, and dissolved CO.

Results and Discussion.

The first question we will address is how much of the geometric surface area of the colloidal metal is occuppied by the polymer stabilizer in liquid dispersion? Measurement of metal particle surface areas for supported metal particles in the solid state is commonly performed by hydrogen chemisorption measurements. [5] In addition, reactive adsorption probes such hydrogen/oxygen titration are sometimes used. [5-7] Since an understanding of the nature of the surfaces of colloidal metal particles is important in the context of their liquid phase catalytic application, it is necessary that the surfaces of colloidal metal catalysts be investigated in the liquid phase, that is to say in the same environment in which their catalytic properties are evaluated. Accordingly we made hydrogen chemisorption and hydrogen/oxygen titration measurements on liquid dispersions of 1.5 nm Pt/PVP in 1-butanol using the apparatus shown in Figure 1. The reliability and precision of the differential barometric experiment is seen by a comparison of the value obtained using this apparatus for the solubility of hydrogen in 1-butanol with that reported in the literature. For this measurement, volumes of approximately 16 mL and 65 mL 1-butanol were placed in the two bulbs, giving rise to a dP 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 $3.89\pm.05\mathrm{x}10^{-8}$Pa were obtained (lit. $3.79\mathrm{x}10^{8}$Pa). This value for the solubility of hydrogen in butanol was used in the determinations of hydrogen chemisorption and hydrogen/oxygen titration for samples of colloidal platinum, shown in Table 1.

Table 1. Hydrogen Chemisorption and Hydrogen/Oxygen Titration Results for 1.5 nm Pt/PVP

Metal	Method	Dia. (nm)	Dispersion	$H_{2\,ads}$/total metal	% M surface available
Pt	H_2-chemisorption	1.5	$0.61^{a,b}$	0.14	46^{c}
Pt	H_2/O_2 Titration	1.5	$0.61^{a,b}$	0.41	46^{d}

a. Assuming an f.c.c. cuboctahedron with 3 atoms on an edge [8]. b. Calculated from ref. 8 c. H/M=1 d. H/M=3

Thus of the total geometric surface area provided by a Pt particle of 1.5nm diameter 46% was found to be available for hydrogen adsorption or for oxygen/hydrogen titration. The close agreement of the hydrogen chemisorption and hydrogen/oxygen titration results establishes the usefulness of this method.

Having demonstrated that in the system under study the stabilizing polymer occupies approximately half of the particle surface, we will next address the question of how the polymer arranges itself on the surface. Although the chemisorption results allow a measure of the amount of free surface, they do not give any information on whether the free surface atoms are isolated from each other or whether they form islands or domains on the surface.

Vibrational spectroscopy has been widely applied to structural studies of adsorbed molecules on the surfaces of small metal catalyst particles, and the use of adsorbed CO in vibrational spectroscopic methods of surface analysis has played an important role in the elucidation of the surface chemistry of transition metals. Colloidal metals are particularly amenable to IR spectroscopic study,[1] since even at relatively high concentrations the liquid suspensions do not scatter IR radiation, and the resulting spectra contain relatively high absorbance bands. CO adsorbed on colloidal metal clusters has been analysed by infrared spectroscopy on aqueous colloids of platinum, palladium and rhodium, and on organosols of palladium, platinum ruthenium, nickel and palladium-copper alloys.[4] The observation of IR absorptions due to adsorbed CO demonstrates that CO can occupy at least some of the surface of the colloidal metal particles even in the presence of high concentrations of organic molecules (i.e. neat liquid), and the spectra of CO adsorbed on colloidal metals in liquid dispersion, where the surface might be occluded or otherwise perturbed by solvent and stabiliser, often resemble those observed for CO adsorbed on nominally much cleaner supported metals under controlled atmosphere conditions.

For our present purpose of demonstrating whether a stabilizing polymer leaves areas of the metal particle surface free or whether it breaks up the free surface into isolated metal atoms, we use the observation of vibrational coupling between adsorbed CO molecules when they are present in islands or domains on the metal surface, which increases the infrared absorbance frequency of the CO molecules. [9] Isolated CO molecules, remote from each other, do not couple in this way. In Figure 8(a) are shown the spectra obtained when CO is added slowly to colloidal nanoclusters of 1.5nm Pt/PVP. The sequence of spectra show increasing surface coverage of CO. Calculated spectra[10] for CO at increasing coverage on a hypothetical metal surface are shown in Figure 8(b). The change in frequency of the absorption maximum at 2046 cm^{-1} with increasing coverage is a consequence of vibrational coupling between the CO molecules on the colloidal metal particle, and this implies that CO molecules can arrange themselves in interacting domains on the surface despite the presence of the stabilizing polymer.

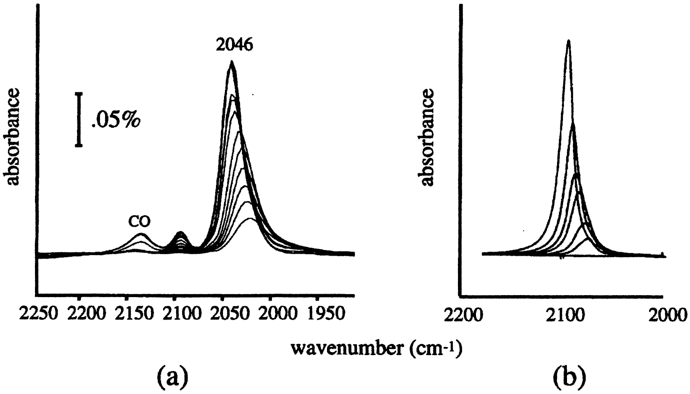
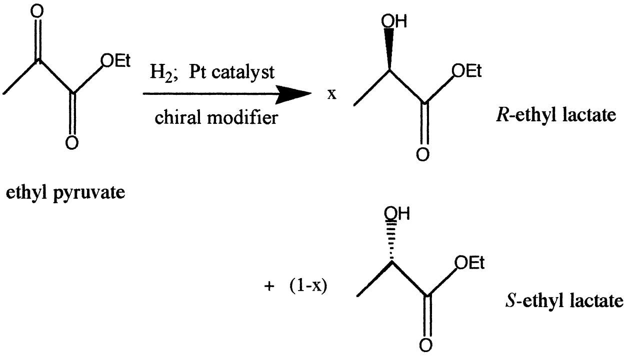


Fig. 8(a) Infrared spectra of increasing coverages of CO on colloidal 1.5nm Pt/PVP nanoclusters;[2,4] (b) Theoretical spectra for vibrationally coupled CO molecules on a hypothetical metal surface.[10]

The results obtained by hydrogen chemisorption implies that that PVP occludes approximately 50% of the surface of the Pt/PVP colloid, and the infrared spectroscopy results imply that the free remaining surface comprises islands of platinum atoms. It is of interest to compare these results with some catalytic data for another similar Pt/PVP colloidal catalyst, in a reaction which is thought to require not only free surface atoms of platinum but that they be available in domains of adjacent atoms. That reaction is the enantioselective hydrogenation of ethyl pyruvate by platinum catalysts on which are adsorbed molecules of the cinchona alkaloid, cinchonidine[11] Eq. 1. The reaction is catalyzed by supported platinum catalysts, such as Pt/Al_2O_3, but in order to make the reaction occurr asymmetrically the catalyst must be modified with an asymmetric additive, such as the naturally occuring alkaloid, cinchonidine, or a related compound. The modifier, cinchonidine, is a large, highly asymmetric molecule which not only induces enantioselectivity (that is to say the formation of a product enriched in one enantiomeric form, in this case ethyl *R*-lactate) but also accelerates the reaction.



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These phenomena are central to our current argument and, since they occur by the adsorption of the modifier molecule onto the catalyst surface, the reaction can be used to probe the surface environment of colloidal platinum stabilised with polyvinylpyrrolidone since free domains of platinum atoms are required for the adsorption of the modifier.[12,13] The very observation of enantioselectivity by the colloidal catalyst will confirm the availablity on the surface of the platinum particles of arrays of platinum atoms. In addition comparison with a simple supported platinum catalyst, where the surface is all 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.[12] 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.

Conclusion

On the basis of chemisorption measurements, infrared spectroscopy of adsorbed CO and activity measurements for catalytic hydrogenation, we conclude that the interaction of the stabilizing polymer with the stabilized metal particles in Pt/PVP colloidsresults in the occlusion of approximately half of the total geometric surface area of the metal particles.

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