

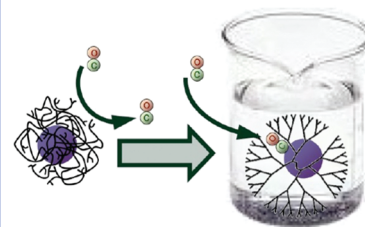
Adsorption of Carbon Monoxide on Dendrimer-Encapsulated Platinum Nanoparticles: Liquid versus Gas Phase

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ABSTRACT The ability of dendrimer-encapsulated platinum nanoparticles (Pt DENs) to adsorb carbon monoxide was contrasted in the gas versus liquid phases by using in situ infrared absorption spectroscopy. It was found that while only limited, weak, and reversible adsorption is possible in the gas phase, extensive and stronger adsorption occurs in the liquid phase, even when the Pt DENs are dispersed inside of the pores of a high surface-area solid. It is speculated that the dendrimer structure may collapse in the gas phase, blocking access to the Pt surface, but may expand and open up in the presence of a proper solvent.

SECTION Surfaces, Interfaces, Catalysis



Because of their versatility and great potential in many applications, dendrimer-encapsulated nanoparticles (DENs) have gained some notoriety in recent years.^{1,2} DENs are particularly promising in catalysis, where size and shape control of metal particles can help improve reaction selectivities.^{3–6} Metal DENs can be used to prepare dispersed heterogeneous catalysts,^{7–9} or be used directly in the gas phase or in solution.^{5,10,11} Since in all of those cases the metal is encapsulated within the dendrimer,^{12,13} the transport of reactants and products through the organic framework is a key issue.⁷ Indeed, there is some evidence that the dendrimers contract both in poor solvents and in the gas phase, thereby passivating the surface of the encapsulated nanoparticles.^{7,14} It is therefore desirable to understand the effect of the environment on the adsorption property of DEN-based catalysts. Here, we provide direct experimental evidence of the key role that the dendrimer plays during catalysis. Using in situ infrared absorption spectroscopy, we show that accessibility of carbon monoxide to the encapsulated metal nanoparticles is a strong function of its environment. Specifically, much greater accessibility is possible in good solvents such as ethanol compared to that seen in the gas phase, presumably because the solvent helps in the expansion of the dendrimer structure.

The key results from our infrared (IR) absorption spectroscopy CO titration experiments are summarized in Figure 1. The left panel shows the C–O stretching region of spectra obtained during exposures of dry Pt DENs to three different pressures of CO in the gas phase, all in the mbar range. In addition to the two main broad features around 2120 and 2170 cm^{-1} due to gas-phase CO,¹⁵ a sharper peak is also detected at $\sim 2060 \text{ cm}^{-1}$, easily assigned to CO adsorption on on-top sites within the Pt particles.^{8,16} This indicates that CO adsorption is possible on dry Pt DENs. On the other hand, two observations point to the weak nature of this adsorption;

(1) the peak intensity of the CO IR peak is approximately proportional to the CO gas-phase pressure, as expected in the low-coverage limit of Langmuir equilibrium isotherms, and (2) the adsorption is reversible; no peak assignable to adsorbed CO is detected once the gas is pumped out of the IR cell.

In contrast, CO adsorption on Pt DENs suspended in a liquid solvent is stronger and more extensive. Indeed, the right panel of Figure 1 shows how the IR band for CO adsorption on Pt DENs suspended in ethanol (the 2063 cm^{-1} peak) is more intense than that in the gas phase, even though the estimated concentration of CO in the solvent is quite low, several orders of magnitude lower than those used in the gas-phase experiments ($X_{\text{CO,Sat}} \sim 0.0005$).¹⁷ Also, the adsorbed CO is retained by the Pt surface after purging the system with hydrogen gas for several hours (data not shown). Another observation worth noticing from Figure 1 is that no significant shifts in frequency are observed for the C–O stretching frequency of adsorbed CO between the gas and liquid phases, suggesting that perhaps the solvent itself does not extensively infiltrate the inside of the dendrimer structure, into the volume surrounding the Pt particles.¹⁸

The accessibility of the platinum surface in Pt DENs to CO is not affected by dispersion of those nanoparticles onto a high-surface-area sol–gel silica support. This is indicated by the data provided in the left panel of Figure 2, which correspond to the IR spectra obtained after bubbling CO into a suspension of a 0.25 wt % Pt DEN/SiO₂ catalyst in ethanol as a function of catalyst pretreatment. Data after the following treatments are reported: (1) none (second trace from top); (2) reduction in 300 mbar of H₂ at 525 K for 2 h. (third trace); and (3) calcination at 575 K in O₂ followed by reduction (bottom

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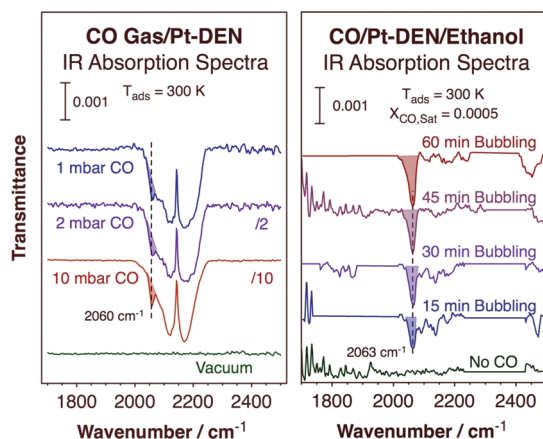


Figure 1. Infrared (IR) absorption spectra of CO adsorbed on Pt DENs at room temperature. Left: Data for adsorption on dry Pt DENs, under vacuum (bottom) and in the presence of 1, 2, and 10 mbar of gas-phase CO. Only a small amount of reversible adsorption is detected. Right: Spectra for Pt DENs suspended in ethanol before exposure to CO (bottom) and after bubbling CO at atmospheric pressure. A significant uptake of CO on the Pt surface is seen in this case, saturating after exposures on the order of 1 h.

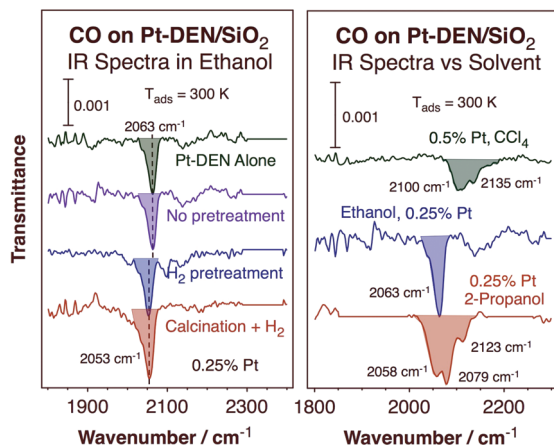


Figure 2. IR absorption spectra of CO adsorbed on Pt DENs dispersed on a sol-gel silica support. Left: Data for CO adsorption in ethanol as a function of the pretreatment of the catalyst. Access of CO to the Pt surface is virtually unhindered even before any pretreatment of the catalyst on Pt DENs where the dendrimer structure is still intact. Right: Spectra for silica-supported Pt-DENs suspended in different liquids. CO adsorption is greatly affected by the nature of the solvent.

trace). The low temperature used for the reduction and oxidation was chosen to preserve the structure of the Pt DENs; electron microscopy studies indicated that treatments above 625 K lead to particle sintering (data not shown). Also, IR data indicate that the organic matter is removed by the latter (oxidation) treatment (data not shown). Other than a slight red shift in the C–O stretching peak upon reduction, the data in Figure 2 obtained after all pretreatments show a similar degree of CO uptake, pointing to the high activity of the untreated supported Pt DENs, comparable to that of the free particles (the data from which is reproduced in the top trace of Figure 2, left frame). The dendrimer network does not appear to block CO adsorption on the platinum surfaces when in

solution, even when the Pt DENs are placed within the constrained environment of a porous material. In contrast, no CO adsorption could be detected on similar Pt DENs/SiO₂ catalysts in the gas phase unless full calcination of the dendrimers was performed beforehand (data not shown). Also to note is the high CO uptake observed after calcination, which indicates minimum sintering of the Pt particles.

Finally, the right panel of Figure 2 shows results for CO adsorption on silica-supported Pt DENs suspended in three different solvents: carbon tetrachloride (top trace), ethanol (middle), and 2-propanol (bottom). Adsorption is observed in all three cases, but with very different characteristics. Specifically, the uptake of CO from CCl₄ is less extensive (hence the use of a 0.50 wt % Pt loading instead of the 0.25 wt % value used in the other experiments) and results in higher C–O stretching frequencies. Adsorption in the more polar 2-propanol solvent, on the other hand, leads to extensive adsorption but also to the appearance of several states. We do not at present fully understand these differences but suggest that they may be associated with the dielectric properties of the solvent and the changes that they may induce to the local field at the Pt surface.¹⁹

In summary, the results presented here indicate that PAMAM dendrimers encapsulating Pt DENs are strongly affected by their contacting ambient. Specifically, in the gas phase or in poor solvents for the dendrimer such as CCl₄, little adsorption of CO is observed. In contrast, in good solvents such as ethanol, CO saturates the encapsulated nanoparticles. These results are fully consistent with a model in which the dendrimer contracts against the encapsulated nanoparticles when it is not adequately solvated. This finding suggests that Pt DENs may be highly sensitive to their environment and may thus function as chemically sensitive catalysts.

The experiments were carried out using particles containing an average of 40 platinum atoms encapsulated in a fourth-generation hydroxyl-terminated poly(amidoamine) (PAMAM) dendrimer [G₄–OH(Pt₄₀)]. These DENs were prepared by mixing together appropriate aliquots of aqueous solutions of K₂PtCl₄ and G₄–OH (Aldrich) followed by reduction of the metal with a 10-fold excess of NaBH₄.^{20,21} Transmission electron microscopy (TEM) images indicated a Pt DENs average size of 1.5 ± 0.3 nm. CO adsorption on those particles was assessed in situ in both the gas and liquid phases using a Bruker Tensor 27 Fourier-transform mid-infrared (IR) spectrometer set to a resolution of 4 cm⁻¹. In the case of the gas-phase studies, the Pt DENs were mixed with a KBr powder, dispersed onto a KBr window, and placed in the middle of a gas cell designed for in situ transmission IR absorption experiments.^{22–24} The experiments in solution were performed by trapping a thin film of a liquid suspension of the Pt DENs in a single-reflection cell limited by a gold mirror on one side and a calcium fluoride prism, used to allow the IR beam in and out of the cell, on the other.²⁵ CO (Matheson, research purity) was admitted directly into the gas cell and bubbled in the solution prior to the acquisition of the spectra in the liquid-phase studies. Both types of experiments were carried out at room temperature. The supported catalysts were prepared by dispersing either 0.25 or 0.50

wt % of Pt DENs on a homemade sol–gel silica²⁶ via wetness impregnation. TEM data suggested that the Pt DEN particles were incorporated inside of the pore structure of the support and not just deposited on the outside surfaces.

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