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Prominent Electronic and Geometric Modifications of Palladium Nanoparticles by Polymer Stabilizers for Hydrogen Production under Ambient Conditions

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Metallic nanoparticles are common active components in catalysts, electrocatalysts, and sensors.[1] Recent studies have revealed that their catalytic or sensing properties can be size and shape (crystallographic plane) dependent, giving new tuneable parameters for optimization.[2] Moreover, their electronic and structural properties can also be altered by alloying,[3] core–shell,[4] and templating (strain introduction)[5] approaches using inorganic modifiers. In particular, the strong metal support interactions (SMSI) stemming from electronic and geometric effects exerted by the solid supports on the metallic nanoparticles have been well documented.[6] Recently, there have been increasing efforts to assemble metallic nanoparticles into tailored sizes and shapes in solution through the use such soft materials as surfactants, stabilizers, organic templates, and structural directing agents,[7] for use as catalyst/sensor precursors. However, the electronic perturbation, if any, of these materials with regards to the metallic particles still remains obscure. For example, activity and selectivity do not always follow the electron-promoting/-withdrawing ability of the pendant groups. Furthermore, new opportunities for using active organic-metal hybrids with ultraselectivity for low temperature catalysis and sensing may arise, for example, in the areas of fine chemicals and pharmaceuticals, which would complement the traditional inorganic-based supported metallic particles for high temperature applications (where thermal stability is one prime issue). As a result, we attempted to elucidate the interaction(s) of the pendant groups of polymeric modifiers with Pd nanoparticles with or without a carbon support under ambient conditions. The selective catalytic decomposition of formic acid to supply hydrogen gas (and carbon dioxide) in situ for Proton Exchange Membrane (PEM) fuel cells over Pd nanoparticles has been reported to proceed at room temperature, hence the focus of this study. This in situ generation of hydrogen could overcome the hydrogen storage issue that currently prevents the widespread use of hydrogen PEM fuel cells in small portable devices. The majority of recent work in this important area is concentrated on the development of new Pd alloys, core-shell bimetallic nanoparticles, and metal-on-oxide supports for higher activity.[8–10]

Herein, we report a remarkable effect from the modification of electronic and geometric properties of Pd nanoparticles by the use of polymer pendant groups bound to the surface of palladium nanoparticles. The degree of electron promotion to the Pd nanoparticles is dependent on the availability of the lone pair electrons of the pendant groups; this can be assessed by the red-shift of the adsorbed CO molecule, as determined by IR spectroscopy. This is due to electron back bonding, which matches well with our Density Functional Theory (DFT) calculations and materials characterization. The prominent IR shift and greatly enhanced turnover frequency of Pd modified with polyallylamine (PA amine) indicate that electron promotion by a typical organic stabilizer is more favorable than conventional alloy or core-shell particles of Pd with another metal. It is interesting to observe that the activity for hydrogen production is also dependent on the binding mode of the pendant groups. Typically, poly(4-styrenesulfonic acid) (PSSA), poly(acrylic acid) (PA acid), and dissociated poly(vinylpyrrolidone) (PVP), which possess a carbon attached to two oxygen atoms (or an oxygen and a nitrogen) containing more than one lone pair of electrons, favor a bridging binding mode and exhibit a strong electron promotion effect. However, such adsorption also competes for the same terrace sites on the Pd surface with formic acid, hence reducing the rate of decomposition of formic acid to CO_2/H_2. On the other hand, modifiers with single nitrogen lone pairs, such as poly(allylamine) (PA amine) and poly(ethyleneimine) (PEI) bind on unselective high-index sites, thus exerting beneficial electronic and geometric effects for this reaction.

The syntheses of colloidal and supported Pd nanoparticles in the presence of polymers were conducted (see the Supporting Information). The electronic effects of the polymers were probed by ATR-IR spectroscopy (ATR = attenuated total reflectance) of the adsorbed bridging CO (dominant form) on polymer-stabilized colloidal Pd nanoparticles, as shown in Table 1 and Figure 1 a. The red-shift of the stretching wavenumber of adsorbed CO (linear and bridged forms) is well accepted as a method to interrogate the electron density of transition metal surfaces.[11] A lower CO wavenumber is indicative of a weaker C=O bond, owing to

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Table 1: Correlation of the basicity of the pendant groups with electron promotion (CO shift on Pd) supported by DFT modeling.

Entry	Monomer (pK_a)	Bridging CO [cm^{-1}]	
		Colloidal Pd	Calculated[a]
1	no polymer	N/A	1847 (0)
2	PSSA (−2.8)	1956	N/A
3	PA acid (4.4)	1948	1838 (+0.02)
4	PA amide (5.5)	1949	1828 (+0.03)
5	PVP (6.8)	1936	1828 (+0.03(5))
6	PA amine (9.7)	1915	1825 (+0.04)

[a] Bader charge difference after modifier coadsorption is shown in parentheses (see the Supporting Information). N/A = data not available.

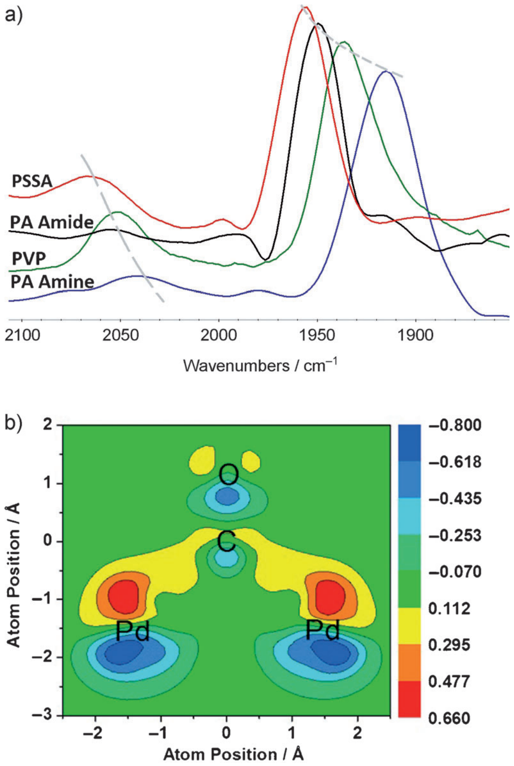

Figure 1. a) ATR-IR of CO on polymer-stabilized colloidal Pd. b) Calculated electron density difference contour of CO after adsorption on Pd(111). For detailed effects of the pendant groups, see the Supporting Information.

increased electron donation from the metal surface into the π* C=O orbital (supported by our DFT calculations, see Figure 1 b and the Supporting Information). For all polymers tested, the addition of the polymer to Pd results in a lower CO wavenumber than for the bare metal. Notice that the degree of red-shift follows with the basicity (pK_a) of the pendant group (Table 1). The results also agree well with our DFT calculations of electron gains in adsorbed CO on a 4 × 4 Pd(111) slab with coadsorption of the corresponding pendant groups. Moreover, a good correlation is obtained between measured and calculated CO wavenumbers (calculated by placing CO and monomer on the same surface, but with almost no spatial interaction), see Table 1 and the Supporting Information. There was about a 1.05x variation between experimental and calculated data, which is similar to those reported by Rösch et al.[12] and is consistent with the overestimation of interatomic distances in gradient-corrected DFT calculations. Thus, we conclude that there is a strong electronic effect from the polymers to Pd nanoparticle, according to the basicity of the pendant groups.

It has been reported that the adsorbed formate in bridging mode (from the dissociative adsorption of formic acid) on Pd is the key surface intermediate for this catalytic reaction (see the Supporting Information). A more electron-rich Pd surface favors the rate determining C−H activation of the bridging formate on terrace metal sites to give hydrogen and carbon dioxide, whereas the linear formate adsorption on high-index sites gives rise to water and carbon monoxide.[9] The most active PVP stabilized core-shell bimetallic catalyst reported, Ag@Pd nanoparticles, which exhibit electron donation from Ag to Pd, only gave a red shift of 11 cm^{-1} for CO compared to PVP-stabilized Pd.[9] By using PA amine polymer on Pd, a shift of about twice this value is achieved (Figure 1 a), demonstrating a remarkable electronic promotion to Pd nanoparticles simply by using a polymer stabilizer. However, electron donation to the metal surface by organic groups may not be the only factor affecting activity, as their surface coverage might deny substrate molecules access to the active sites.

It is also known that CO molecules would bind on terrace sites preferentially in bridging mode (1910–1960 cm^{-1}), but in a linear fashion on high-index Pd sites (2040–2070 cm^{-1}) with low surface coverage.[13] Thus, they can be used as a chemical marker to examine the Pd surface features embraced by the pendant groups. Indeed, Figure 1 a shows that there are variations in the relative areas of bridging to linear modes with different polymers, especially for the PA amine polymer. For example, an area ratio of 5 is obtained for PVP, in contrast with 8.5 for PA amine. Without taking these numbers too literally because of background and integration problems, PA amine clearly binds more favorably on the high-index Pd sites than the terrace sites, whereas the other polymers behave in the opposite manner. It is unfortunate that there were large variations in the Pd colloidal nanoparticle size synthesised in the presence of different polymer stabilizers (see the Supporting Information). To overcome the size effects we turned to the study of the deposition of polymers onto a commercial carbon-supported Pd (1:5 Pd/pendant groups) to further analyze the effects of electron promotion and selective coverage of Pd sites on hydrogen production activity.

Table 2 shows that the addition of polymer results in a general decrease in activity for gas production (H_2/CO_2), except in the cases of PA amine and PEI. The attenuation in activity is related to the loss of metal surface area owing to the adsorption of the polymers, but it is not a linear effect. It is surprising to find that there were still lower TOF (turnover frequency) values per metal site than for unmodified catalyst, which clearly suggests that active sites and/or ensembles for gas production were unfortunately passivated (terrace sites) by these polymers, which overrode their beneficial electron-promotion effect. Interestingly, the PA amine displaying the strongest electron promotion effect (Table 1) clearly shows the highest gas production rate, despite the loss in metal surface. We believe that the preferential binding of the PA

Table 2: Catalytic activity for hydrogen production.

Entry	Polymer additive[a]	Gas evolved [L g^{-1}(Pd)][b]	Metal SA [m^2 g^{-1}(Pd)][c]	TOF [h^{-1}][d]
1	no polymer	27.12	85.1	359.67
2	PSSA	3.10	52.3	38.00
3	PA acid	4.44	60.6	73.46
4	PA amide	8.12	71.5	157.40
5	PVP	9.51	60.8	212.53
6	PEI	36.33	63.5	836.29
7	PA amine	81.97	70.4	1352.57

[a] Polymer added to 10% Pd/C catalyst (JohnMatthey 87L). [b] Total gas produced in 2 h, using Pd (4.25 mg) in formic acid (10.575 mL, 1.44 M). [c] Metal surface area calculated from CO chemisorption. [d] Turnover frequency (TOF) = [moles H_2/moles Pd surface sites]; evaluated in the first 15 min. SA = surface area.

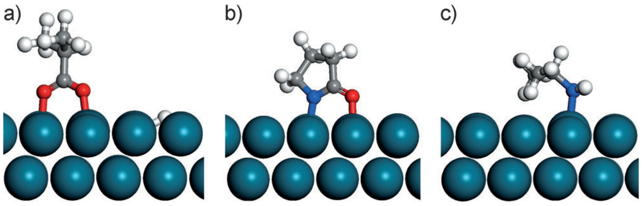

Figure 2. Calculated adsorption structures (side view) of a) acrylic acid, b) *N*-vinylpyrrolidone, and c) acrylic amine on Pd(111). For other groups, see the Supporting Information.

amine to high-index sites over terrace sites must play a role in the promotion of activity. From the DFT calculations, we also note that different pendant groups gave different adsorption geometries at their stable configurations on the same Pd(111) slab (Figure 2, also see the Supporting Information).

Figure 2 a shows that the pendant groups of PA acid (also PSSA and PA amide, see the Supporting Information) take an upright C_{2v}-like position, wherein the terminal carboxyl group binds to the surface in a bridging configuration. This adsorption geometry is similar to a bridging formate, hence competition with the substrate molecules for terrace sites, is envisaged. Thus, this can account for the lower TOFs of PA acid, PSSA and PA amide coadsorption systems, despite their electron promotion ability. On the other hand, modifiers with amine groups with single lone pair electrons, such as PA amine, can only allow a linear mode of attachment on single metal site, according to our calculations. Figure 2 c shows this adsorption mode (Table 1) on a terrace site on the same 4 × 4 (111) slab. It is also expected that the amine groups would preferably bind on higher index sites at low coverage, as these sites are energetically more favorable for adsorption, as reflected by our IR results (see Figure 1 a). PVP polymer was found to give good electron promotion, but with a lower measured TOF than unmodified Pd (Tables 1 and 2). PVP adsorbed on a metal surface can undergo a degree of dissociation to pyrrolidone at slightly elevated temperature, but it is difficult to estimate the extent[14] (the calculated Bader charge differences and CO wavenumbers in Table 1 were based on 50% dissociation). As shown in Figure 2 b, the dissociated pyrrolidone also gives a similar C_{2v}-like species, where the carbon atom attaches to one nitrogen and one oxygen (electron promoting), thus offering competition to the sites owing to the bridging configuration. We also attempted to study polyethyleneimine as another single lone pair donor, which appeared to match with the expected promotion effect. Lee et al. have recently modeled the ligands binding on a Pt cluster and the associated change in geometry.[15] They attributed the single lone pair from NH_2 to low coordination sites, whereas the SH ligands (with two lone pairs) show no site preference. Our experimental results echo with this insight and clearly suggest that not only electronic, but also geometric factors exerted by surface modifiers are keys to tailoring catalytic activity and selectivity, as exemplified by this reaction. We do not have further information to assess the degree of site selectivity, as the rigidity of polymer backbone, spatial arrangement of pendant groups, solvent, and coverage are not easily fixed and should be taken into account.

As a single lone pair donor, PA amine, which is the most basic, is established as a good promoter for this terrace-site-favored reaction. Figure 3 shows the effect of increasing the molar ratio of Pd relative to this pendant amine group, it is found that the TOF increases with increasing amine content (TOFs of 1438, 3189, 6061 h^{-1} for ratios of 1:5, 1:10, 1:20, respectively). We found that a ratio of 1:10 gave the optimum performance for hydrogen production per gram of Pd. However, the amount of gas produced in two hours actually decreased for the 1:20 ratio. This is due to the large loss of metal surface area, as some of the active terrace sites may also be poisoned at high coverage. Changing the solvent from water to ethanol gave a decrease in TOF (1352 h^{-1}), suggesting that fewer PA amine groups are bound to the metal surface owing to its higher solubility in ethanol. However, there was an increased activity per gram of Pd, which is indicative of selective desorption of amine from some poisoned terrace sites. When the polymer-modified catalyst was extensively washed with large quantities of water, a slight decrease in activity was observed (Figure 3, ▲). This is due to

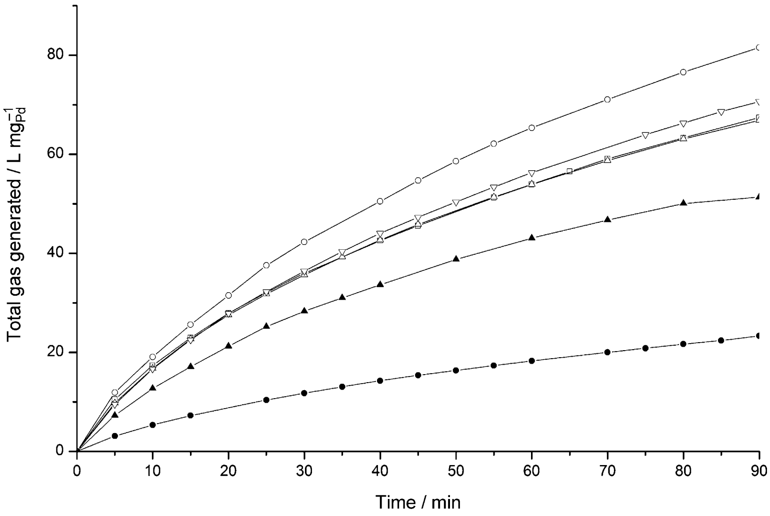

Figure 3. Activity plots of various ratios of Pd modified by PA amine; amine/H_2O 1:20 (□), amine/H_2O 1:10 (○), amine/H_2O 1:5 (△), amine/EtOH 1:5 (▽), amine/H_2O 1:5 with H_2O wash (▲), 10% Pd/C (JohnMatthey 87L; ●). Reactions conducted with Pd (ca. 4.25 mg) in formic acid (10.575 mL, 1.44 M).

some, but not all, weakly bound polymer molecules being washed from the catalyst, thus demonstrating that the total removal of this polymer stabilizer is more difficult than reported for poly(vinyl alcohol).[16]

In summary, the recent assembly of nanometals to a specific morphology by organic surfactants/stabilizers is an attractive direction in catalysis, but there are conflicting views on the potential effects of these stabilizers if retained on the metal surface. At one extreme, some researchers have ignored or greatly underestimated their impact on the physicochemical properties of nanoparticles in early work.[17] Also, their total removal could be challenging, as more strongly binding groups are required to displace them without particle agglomeration. Herein, we have shown that some adsorbed organic groups can clearly impose prominent electronic and geometric effects on small transition metal nanoparticles under mild conditions, hence this direction should be approached with caution when the catalytic performance of specific sizes and shapes of prepared nanometals are compared. The high proportion of surface atoms and the characteristic properties of small nanoparticles are very different from those of bulk metals, and are expected to be much more sensitive to electronic and geometric perturbations by organic adsorbates. On the positive side, for low temperature catalytic applications where organic adsorbates can be sustained, as exemplified by hydrogen production from formic acid, simple polymeric amine deposition on commercial Pd/C is clearly effective for rate enhancement. As far as we are aware, the TOFs of Pd catalysts modified by PA amine are higher than all reported solid counterparts and some of the best homogeneous catalysts at room temperature (see the Supporting Information), but without major separation issues. It can also overcome the problem of using small amines for gold particles[10] and homogeneous catalysts,[18] where the promotion mechanism is not yet clear, and the volatile amines can contaminate the gas stream. The electronic promotion, adsorption site preference of pendant groups, and spatial interactions of the polymer with the substrate and the nanoparticle may also open up exciting new designs for organic–metal hybrid nanocatalysts to tackle complex substrates in the fields of fine chemical and pharmaceutical catalysis.

Experimental Section

Polymer-stabilized colloidal nanoparticles were synthesized by a modification of a reported method.[9] Monomer units of the desired polymer (2.25 mmol) were dissolved in ethylene glycol (30 mL) and [Pd(NO$_3$)$_2$] (0.15 mmol) was added with stirring under N_2 for 15 min before being heated to 120 °C for 2 h. After cooling, the particles were precipitated and washed using acetone or a 2:1 mixture of acetone/hexane.

Pd/C (10%; type 87L) was also modified with polymer, this involved stirring the catalyst with the desired polymer in water or ethanol for 48 h. The solvent was then evaporated and the catalyst was dried for 12 h at 85 °C. Alternatively, after stirring, the catalyst was filtered using a 0.2 μm membrane filter, and washed extensively with water before drying for 12 h at 85 °C. All calculations were performed by DFT, using the Vienna ab initio simulation package (VASP).[19–22] Projector-augmented wave (PAW) potentials[23,24] were used for the core-electron interactions. The Perdew-Burke-Ernzerhof (PBE) functional,[25,26] based on the generalized gradient approximation (GGA), was employed to evaluate the non-local exchange-correlation energy. A plane wave basis set with a cutoff energy of 350 eV and a $2\times2\times1$ k-point grid, determined by the Monkhorst-Pack method, were used. For structure optimization, the ionic positions were allowed to relax until the forces were less than 0.05 eV Å^{-1}. The Pd(111) surface was modeled using a periodic slab model with a 4×4 surface unit cell (11.171×11.171 Å^2) and the bottom layer was fixed during all geometry optimizations. A vacuum layer of 15 Å along the z direction perpendicular to the surface was employed to prevent spurious interactions between the repeated slabs. Poly(allylamine) was modeled as poly(vinyl amine) to simplify calculations, as the differences between the two are expected to be minor. More experimental details on synthesis, testing, characterization, and DFT simulation can be found in the Supporting Information.

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[1] G. G. Wildgoose, C. E. Banks, R. G. Compton, *Small* **2006**, *2*, 182.
[2] R. Narayanan, M. A. El-Sayed, *J. Phys. Chem. B* **2005**, *109*, 12663.
[3] R. Ferrando, J. Jellinek, R. L. Johnston, *Chem. Rev.* **2008**, *108*, 845.
[4] N. Toshima, T. Yonezawa, *New J. Chem.* **1998**, *22*, 1179.
[5] T. Ressler, B. L. Kniep, I. Kasatkin, R. Schlögl, *Angew. Chem.* **2005**, *117*, 4782; *Angew. Chem. Int. Ed.* **2005**, *44*, 4704.
[6] S. J. Tauster, S. C. Fung, R. T. K. Baker, J. A. Horsley, *Science* **1981**, *211*, 1121.
[7] Y. Sun, Y. Xia, *Science* **2002**, *298*, 2176.
[8] X. Zhou, Y. Huang, W. Xing, C. Liu, J. Liao, T. Lu, *Chem. Commun.* **2008**, 3540.
[9] K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. J. Bagot, E. A. Marquis, G. D. W. Smith, S. C. E. Tsang, *Nat. Nanotechnol.* **2011**, *6*, 302.
[10] Q.-Y. Bi, X.-L. Du, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *J. Am. Chem. Soc.* **2012**, *134*, 8926.
[11] M. Hoffmann, *Sur. Sci. Rep.* **1983**, *3*, 107.
[12] I. V. Youdanov et al., *J. Phys. Chem. B.* **2003**, *107*, 255.
[13] J. S. Bradley, E. W. Hill, S. Behal, C. Klein, A. Duteil, B. Chaudret, *Chem. Mater.* **1992**, *4*, 1234.
[14] Y. Borodko, S. M. Humphrey, T. D. Tilley, H. Frei, G. A. Somorjai, *J. Phys. Chem. C* **2007**, *111*, 6288.
[15] J. H. Ryu, S. S. Han, D. H. Kin, G. Henkelman, H. M. Lee, *ACS Nano* **2011**, *5*, 8515.
[16] J. A. Lopez-Sanchez, G. J. Hutchings, *Nat. Chem.* **2011**, *3*, 551.
[17] R. Narayanan, M. A. El-Sayed, *J. Am. Chem. Soc.* **2004**, *126*, 7194.
[18] B. Loges, A. Boddien, H. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 4026; *Angew. Chem. Int. Ed.* **2008**, *47*, 3962.
[19] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558.
[20] G. Kresse, J. Hafner, *Phys. Rev. B* **1994**, *49*, 14251.
[21] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* **1996**, *6*, 15.
[22] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, *54*, 11169.
[23] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953.
[24] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.
[25] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
[26] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396.