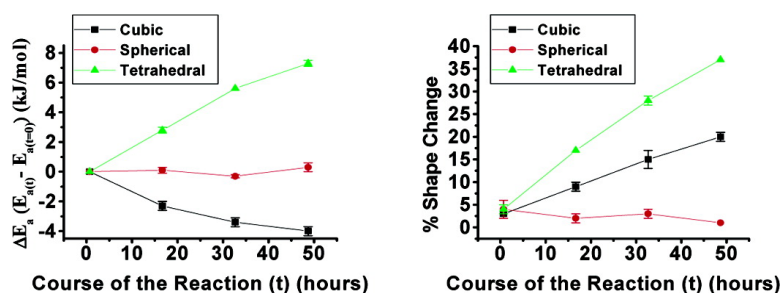


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Changing Catalytic Activity during Colloidal Platinum Nanocatalysis Due to Shape Changes: Electron-Transfer Reaction

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A great interest at this time in the field of nanoscience is the dependence of the different properties of nanoparticles on their shape.^{1–4} Platinum nanoparticles have been synthesized with different shapes.⁵ Since it is known that catalysis on transition metal crystal surfaces depends on the crystal face used⁶ and that different nanoparticles with different shapes have different facets and different ratios of the number of atoms on corners and edges to those on the facets, one would expect catalysis to be greatly dependent on the nanoparticle shape used.

The field of catalysis using transition metal nanocatalysts in colloidal solution has been active lately with many review articles^{7–14} published in the past decade. In this type of catalysis, the focus has been on the use of spherical or undetermined shaped nanoparticles to catalyze reactions. There are very few studies in which catalysis is conducted with nanoparticles of known shapes, e.g. using truncated octahedral Pt nanoparticles to catalyze the electron-transfer reaction¹⁵ and using cubic Pt nanoparticles for the decomposition of the oxalate capping agent.¹⁶

Being small and with surface atoms of different unsaturated valencies, nanoparticles of specific shape are more liable to change their shape in the harsh medium of chemical reactions. Surface reconstruction or dissolution of active atoms on corners or edges by one or more of the reactants or even the solvent is expected to take place during “catalysis”. We have already shown that the size of spherical nanoparticles changes during the catalysis process.^{17–18} It is thus possible that not only the size but also the shape of the nanoparticle could change during catalysis. This would screen any accurate conclusions regarding the shape dependence of the catalytic process.

In the present communication, we have determined the activation energies for the electron-transfer reaction between hexacyanoferrate (III) ions and thiosulfate ions in a colloidal solution in which tetrahedral, cubic, or spherical nanoparticles are dominant. This reaction is selected because it is very “gentle” reaction that is catalyzed around room temperature. It is found that the activation energy of the reaction changes continuously during the reaction. Using TEM, it is shown that the observed change in the reactivity of the nanoparticles is accompanied by changes in their shape distribution.

The PVP-stabilized dominantly tetrahedral Pt nanoparticles and the polyacrylate-stabilized dominantly cubic Pt nanoparticles are prepared by using the H₂ reduction method described previously⁵ with a few modifications.¹⁹ The dominantly spherical PVP–Pt nanoparticles are synthesized by the reduction of the Pt²⁺ ions with ethanol as described previously.¹⁸ For all three types of nanoparticles, the initial Pt ion concentration used is 8×10^{-5} M. All three nanoparticle solutions are adjusted to a pH = 7 by the addition of either NaOH or HCl as appropriate. The activation energy¹⁸ (see Supporting Information for details) is determined at four different time periods during the reaction (0–0.67 h, 16–16.67 h, 32–32.67

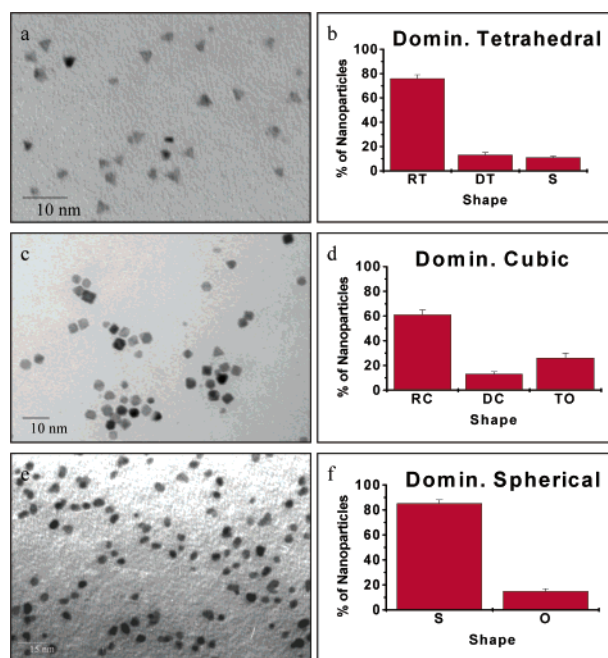


Figure 1. TEM images and shape distributions of the nanoparticle solutions used in the catalysis: a and b are for dominantly tetrahedral, c and d are for dominantly cubic, and e and f are for dominantly spherical platinum nanoparticle solutions. (RT = regular tetrahedral, DT = distorted tetrahedral, S = spherical, RC = regular cubic, DC = distorted cubic, TO = truncated octahedral, O = other.)

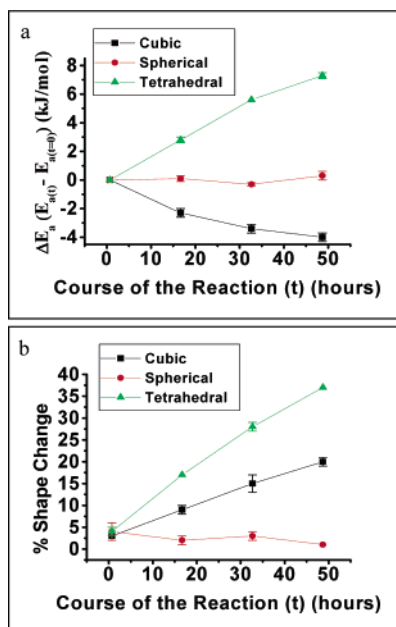
h, and 48–48.67 h). The shape distributions are obtained before the reaction, after 0.67 h at 45 °C, after 16.67 h at 45 °C, after 32.67 h at 45 °C, and after 48.67 h at 45 °C using JEOL 100C TEM. The spotting conditions and verification of internal and general reproducibility of the shape distributions are conducted by counting 1800 nanoparticles from nine enlarged TEM images. The shape distributions are determined for three shapes: specific, distorted, and spherical shapes. Size distributions are determined for the initial samples of tetrahedral, cubic, and spherical nanoparticles. Panels a–f of Figure 1 show typical TEM images and shape distributions for the three types of nanoparticles. Table 1 summarizes the initial shape and size distributions for the three different types of nanoparticles.

From Figure 2a and Table 1, it can be seen that the activation energy of the tetrahedral Pt nanoparticles increases during the course of the reaction, while the activation energy of the cubic nanoparticles slightly decreases. Tetrahedral nanoparticles are composed of (111) facets and are known to be the most catalytically active due to a large fraction of the surface atoms being present on edges and corners.^{20–21} As can be seen in Figure 2b and Table 1, the percentage of distorted tetrahedral nanoparticles increases during the course of the reaction. The rapid dissolution and surface

Table 1. Summary of Average Size and Change in the Shape Distribution^a (%D) for the Dominantly Tetrahedral, Cubic, and Spherical Platinum Nanoparticles and the Activation Energies (E_a) (kJ/mol) during the Course of the Catalytic Reaction

nanoparticle shape	average size (nm)	initial %D	after 0.67 h %D and E_a	after 16.67 h %D and E_a	after 32.67 h %D and E_a	after 48.67 h %D and E_a
tetrahedral	4.8 ± 0.1	76 ± 3 RT	72 ± 2 RT	59 ± 3 RT	48 ± 4 RT	38 ± 3 RT
		13 ± 1 DT	13 ± 2 DT	28 ± 3 DT	39 ± 3 DT	51 ± 4 DT
		11 ± 1 S	15 ± 3 S	13 ± 2 S	13 ± 3 S	11 ± 2 S
cubic	7.1 ± 0.2		14.0 ± 0.6 (E_a)	17.4 ± 0.8 (E_a)	20.2 ± 0.8 (E_a)	21.9 ± 0.6 (E_a)
		61 ± 4 RC	58 ± 4 RC	52 ± 3 RC	46 ± 2 RC	41 ± 3 RC
		13 ± 2 DC	16 ± 3 DC	24 ± 2 DC	29 ± 4 DC	33 ± 2 DC
		26 ± 4 TO	26 ± 4 TO	24 ± 3 TO	25 ± 2 TO	26 ± 3 TO
			26.4 ± 1.3 (E_a)	24.1 ± 1.6 (E_a)	23.0 ± 1.6 (E_a)	22.4 ± 1.0 (E_a)
spherical	4.9 ± 0.1	85 ± 2 S	81 ± 4 S	83 ± 3 S	82 ± 3 S	84 ± 2 S
		15 ± 2 O	19 ± 3 O	17 ± 2 O	18 ± 4 O	16 ± 3 O
			22.6 ± 1.2 (E_a)	22.7 ± 1.0 (E_a)	22.4 ± 1.1 (E_a)	22.9 ± 0.9 (E_a)

^a RT = regular tetrahedral, DT = distorted tetrahedral, S = Spherical, RC = regular cubic, DC = distorted cubic, TO = truncated octahedral, and O = other.

**Figure 2.** Time-dependent changes in the activation energy of the electron-transfer reaction (a) and time-dependent changes of the initial shape of the platinum nanocatalysts of different shapes (b).

reconstruction of the edge and corner atoms results in a greater percentage of distorted tetrahedral Pt nanoparticles with less sharp edges and corners and thus with higher activation energies. The cubic nanoparticles are larger in size (7 nm vs 5 nm) and are composed of (100) facets with small fractions of their surface atoms on the edges and corners. Among other factors, the dissolution and surface reconstruction of atoms on the (100) facets of the cubic nanoparticles could take place during the reaction and thus, creates defective and more active sites. This might explain the decrease in the activation energy observed when using the cubic nanoparticles. In the case of spherical nanoparticles composed of some (100) and (111) facets, the shape distribution, as well as the values of the activation energy, remains constant during the course of the reaction.

This is consistent with the fact that the surface energy of the spherical shape is the lowest. Thus, both the tetrahedral and cubic shapes strive to become spherical, the thermodynamic reason for their shape changes during the catalytic reaction.

The above results suggest that, indeed, nanocatalysis is shape dependent. However, the shape of the nanoparticles could change and try to assume the most stable (spherical) shape during the catalytic function.

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Supporting Information Available: Procedure for conducting the electron-transfer reaction and the resulting kinetics and examples of raw data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) El-Sayed, M. A. *Acc. Chem. Res.* **2001**, *34*, 257.
- (2) Link, S.; El-Sayed, M. A. *Int. Rev. Phys. Chem.* **2000**, *19*, 409.
- (3) Pileni, M. P. *Supramol. Sci.* **1998**, *5*, 321.
- (4) Yacamán, M. J.; Ascencio, J. A.; Liu, H. B.; Gardea, T. *J. Vac. Sci. Technol., B* **2001**, *19*, 1091.
- (5) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.
- (6) Bradley, J. S. *Clusters Colloids*; VCH: Weinheim, Germany, 1994.
- (7) Duff, D. G.; Baiker, A. *Stud. Surf. Sci. Catal.* **1995**, *91*, 505.
- (8) Toshima, N. *NATO Adv. Study Inst. Ser., Ser. 3* **1996**, *12*, 371.
- (9) Boennermann, H.; Braun, G.; Brijoux, G. B.; Brinkman, R.; Tilling, A. S.; Schulze, S. K.; Siepen, K. *J. Organomet. Chem.* **1996**, *520*, 143.
- (10) Fugami, K. *Organomet. News* **2000**, *1*, 25.
- (11) Mayer, A. B. R. *Polym. Adv. Technol.* **2001**, *12*, 96.
- (12) Bonnemann, H.; Richards, R. *Synth. Methods Organomet. Inorg. Chem.* **2002**, *10*, 209.
- (13) Moiseev, I. I.; Vargaftik, M. N. *Russ. J. Chem.* **2002**, *72*, 512.
- (14) Li, Y.; Petroski, J.; El-Sayed, M. A. *J. Phys. Chem. B* **2000**, *104*, 10956.
- (15) Fu, X.; Wang, Y.; Wu, N.; Gui, L.; Tang, Y. *Langmuir* **2002**, *18*, 4619.
- (16) Narayanan, R.; El-Sayed, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 8340.
- (17) Narayanan, R.; El-Sayed, M. A. *J. Phys. Chem. B* **2003**, *107*, 12416.
- (18) Narayanan, R.; El-Sayed, M. A. *J. Phys. Chem. B*, published online March 2, <http://dx.doi.org/10.1021/jp037169u>.
- (19) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; Wiley: New York, 1994.
- (20) Falicov, L. M.; Somorjai, G. A. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 2207.
- (21) Somorjai, G. A.; McCrea, K. R.; Zhu, J. *Top. Catal.*, **2002**, *18*, 157.

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