Effect of Pd Nanoparticle Size on the Catalytic Hydrogenation of Allyl Alcohol

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We report that the rate of hydrogenation of allyl alcohol is a function of the diameter of the Pd nanoparticles (1.3–1.9 nm) used to catalyze the reaction. Furthermore, kinetic data indicate that this effect is electronic in nature for particles having diameters <1.5 nm, but for larger particles it depends primarily on their geometric properties. This is a significant finding, because it represents a particle size effect for hydrogenation over unsupported Pd nanoparticle catalysts in a size range that has not been widely studied.

Dendrimer templates have been used to exert a high degree of control over the size, composition, and structure of catalytically active nanoparticles in the <3 nm size range. 1 Because of this, dendrimer-encapsulated nanoparticles (DENs) are well-suited for studying the effect of particle size on catalytic function. 1 We have previously briefly noted a qualitative link between the size of DENs and their catalytic properties. 2,3 This paper represents our first quantitative analysis of the origin of these trends.

The procedure used to prepare Pd DEN catalysts has been previously reported. 2 For the experiments reported here, the total moles of Pd used for each hydrogenation reaction was maintained constant for all experiments, but the Pd/dendrimer ratio was varied to yield DENs having different sizes. Specifically, sixth-generation, hydroxyl-terminated polyamidoamine dendrimers (G6-OH) were used to synthesize Pd DENs containing an average of 55, 100, 147, 200, or 250 Pd atoms (G6-OH(Pd)), where n is the average number of atoms per particle). These particles have measured (by TEM, Figures S1 and S2, Supporting Information) numbers of surface, defect, and face atoms for each particle size. The data are normalized to the largest number of each type of atom.

Figure 1. (a) Plot of the rate of hydrogen consumption as a function of particle diameter. (b) Plot of the total, calculated (Table S2, Supporting Information) numbers of surface, defect, and face atoms for each particle size. A5300, Austin Texas 78712-0165, and Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

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Based on the measured hydrogenation rates, we report a trend of decreasing rate with increasing particle size. Differences in reaction rates as a function of catalyst size arise from either electronic or geometric effects. 9 For example, as the size of a nanoparticle decreases, its electronic properties change from those of a metal to an insulator and then to something akin to a molecule.10,11 These changes modulate the catalytic properties of nanoparticles. Geometric effects are most evident when a reaction requires a specific type of surface atom, because the ratio of defect (vertex and edge) to face atoms changes dramatically as a function of size for <5-nm-diameter particles. While geometric effects have been observed for homogeneous colloidal Pd catalysts for both the Heck 12 and Suzuki 13 coupling reactions, literature reports pertaining...
to size effects in hydrogenation reactions focus almost exclusively on supported (heterogeneous) Pd catalysts. In addition to catalyst size, the preparation and structure of nanoparticles are also important factors that must be taken into account when comparing catalytic activity. This is because preparation methods, stabilizing ligands, and polydispersity can lead to activity changes that may mask true particle size effects. For example, Pd nanoparticles having similar diameters, but stabilized by either poly(vinylpyrrolidone) or 1,10-phenanthroline, exhibit very different catalytic activities for the hydrogenation of 1,3-cyclooctadiene.17

To determine the origin of the size effect shown in Figure 1a, we calculated the number of moles of surface, defect, and face atoms (Tables S2 and S3, Supporting Information), as well as the total number of face atoms in solution increases. From this result shown in Figure 1b, which shows that, as the particle size increases, only three of the four plots, there is a monotonic increase in the TOF as the particle size increases. This indicates that, if the size effect shown in Figure 1a is due to geometric factors, the active site does not correlate to the number of surface atoms, defect atoms, or nanoparticles. However, when only face atoms are considered, the plot attains zero slope for particle diameters \( \geq 1.5 \) nm. Because this TOF is calculated in terms of the number of face atoms (mol \( \text{H}_2/\text{mol face atoms-h} \)), it means there is a 1:1 correspondence between the rate of hydrogen uptake and the number of face atoms for particles in this size range. This result is related to that shown in Figure 1b, which shows that, as the particle size increases, only the total number of face atoms in solution increases. From this result we conclude that, for Pd DENs having diameters in the range of 1.5—1.9 nm, the hydrogenation of allyl alcohol occurs preferentially on the face atoms. Previous work focusing on ethene hydrogenation on model catalysts has indicated that the reaction is structure-insensitive and depends only on the number of Pd surface atoms available.19 Doyle et al. reported similar results for hydrogenation of ethene on Pd/Al_2O_3 catalysts in UHV, but catalyst size did affect the hydrogenation rate of trans-2-pentene under identical conditions.14 The latter observation was attributed to preferential hydrogenation of trans-2-pentene on face atoms. In our experiments, it is likely that changes in TOFs for smaller catalysts (diameters \(<1.5 \) nm) are dominated by differences in their electronic properties rather than the relative numbers of particular types of surface atoms.9

To summarize, we have shown a correlation between catalyst size and TOF for the hydrogenation of allyl alcohol. This structure/function relationship is a direct consequence of the nanoscale size of the catalysts. The hydrogenation reaction is sensitive to both the electronic and geometric properties of the catalytic Pd nanoparticles, both of which change quickly in the 1.3—1.9 nm diameter size range. Our analysis indicates that the hydrogenation kinetics are dominated by electronic effects for the smallest particles (\(<1.5 \) nm diameter) and by geometric effects for larger particles (1.5—1.9 nm diameter). Results of the type described here are enabled by the high degree of monodispersity resulting from the dendrimer templating approach to nanoparticle synthesis. We recently discovered that this same templating approach can be used to control the composition\(^{20,21}\) and structure\(^{21}\) of metal nanoparticles, and therefore we are presently studying the effect of these variables on catalyst performance.

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Supporting Information Available: Data tables, reaction rate, and TOF plots. This material is available free of charge via the Internet at http://pubs.acs.org.

References


Figure 2. Plots of normalized TOF (mol \( \text{H}_2/\text{mol active site-h} \)) as a function of particle diameter for three different types of possible active sites and for the total number of nanoparticles.