

Structure Sensitivity of Carbon-Nitrogen Ring Opening: Impact of Platinum Particle Size from below 1 to 5 nm upon Pyrrole Hydrogenation Product Selectivity over Monodisperse Platinum Nanoparticles Loaded onto Mesoporous Silica

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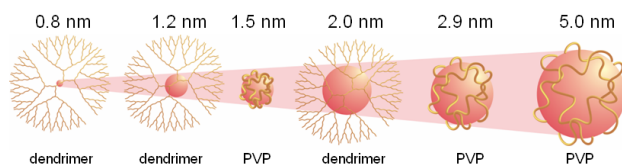
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The ability to control fundamental properties (e.g., particle size, surface structure, and metal-oxide interface) in order to design highly selective heterogeneous catalysts would greatly reduce energy intensive separations. Particle size dependence (i.e., structure sensitivity) upon selectivity can now be examined with well defined nanoparticles (NPs) because of advances in synthetic chemistry. Colloidal chemistry has provided means for synthesizing monodisperse Pt NPs as small as ~2 nm.^{1,2} Using a dendrimer templated approach, Pt NPs smaller than 1 nm – a new size regime for studying size induced effects in heterogeneous catalysis – can be synthesized (Scheme 1).^{3,4} In this contribution, we report that ring opening for pyrrole hydrogenation is distinctly different for Pt NPs smaller than 2 nm. This insight has not been demonstrated for hydrogenation of cyclic heteroatom bonds to the best of our knowledge. This finding adds fundamental insight into hydrodenitrogenation (HDN) chemistry, which is important for fuel processing and involves removal of N-containing organics. Advances in HDN catalysis are needed to meet new fuel quality regulations because N-containing organics inhibit hydrodesulfurization (HDS) through competitive adsorption⁵ and poison acid catalysts⁶, which are used for downstream processing and as supports for HDS catalysts. Pyrrole was selected as the reactant because organics with 5-member N-containing rings are the most common components in fuel.^{7,8}

Scheme 1. Strategy for Pt NP size control.



Pt NPs between 0.8 and 5.0 nm were synthesized by two techniques. For ultrasmall NPs, fourth generation hydroxyl terminated polyamidoamine (PAMAM) dendrimers were used as the templating and capping agent.⁴ Synthesis and characterization of Pt₂₀ and Pt₄₀ NPs (subscripts denote the average number of metal atoms per NP) have been described.^{4,9} The average number of metal atoms per NP is controlled by the Pt ion to dendrimer ratio. Due to difficulties in obtaining accurate size distributions from TEM, sizes were calculated from the average number of metal ions added per dendrimer, which was proven as accurate by X-ray absorption studies.¹⁰ Sizes of Pt₂₀ and Pt₄₀ NPs were calculated to be 0.8 and 1.0 nm, respectively.¹¹

A TEM image (Figure 1a) of the Pt₆₀ NPs showed that the Pt size was 1.95 ± 0.27 nm. This size is larger than that expected

from the Pt ion to dendrimer ratio and is caused by formation of interdendrimer complexes because the number of Pt atoms per dendrimer approached the number (62) of available internal tertiary amine groups. Pt NPs (1.5, 2.9, and 5.0 nm) were synthesized with polyvinylpyrrolidone (PVP) by existing procedures^{1,2} with a TEM image in Figure 1b for 5.0 nm Pt NPs.

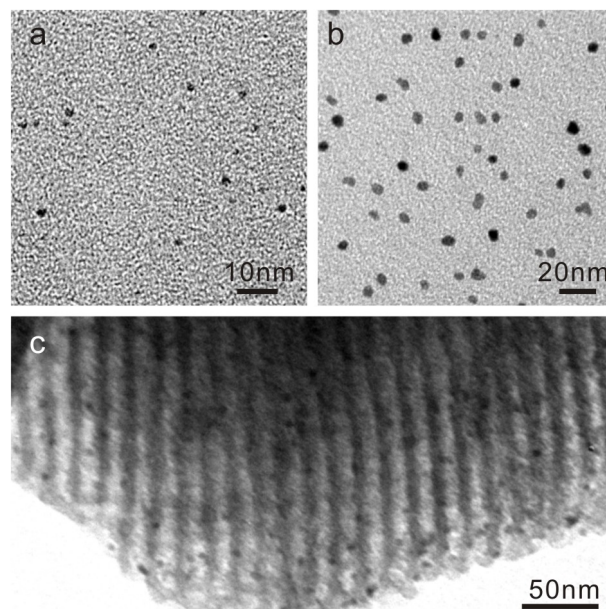


Figure 1. TEM images for (a) dendrimer-templated 2.0 nm Pt, (b) PVP capped 5.0 nm Pt, and (c) PVP capped 1.5 nm Pt loaded onto SBA-15.

Pt NPs were loaded onto SBA-15 silica (TEM image in Figure 1c for 1.5 nm Pt NPs). For PVP capped NPs, H₂ chemisorption indicated that Pt dispersion decreased as the NP size increased (Table S1). However, reliable dispersion measurements could not be obtained by this method for dendrimer encapsulated Pt NPs so ethylene hydrogenation, a structure insensitive reaction¹²⁻¹⁵, was performed to demonstrate an available catalytic surface (Table S1). Although the TOFs of smaller Pt NPs were comparable to results acquired over model Pt surfaces, these values were lower than those of the larger Pt NPs. This effect was attributed to reduction being more difficult for smaller NPs, which led to less metallic character necessary for activity, and may be caused by the dendrimer covering more of the Pt surface than PVP.¹⁶

As shown in Table S2, steady-state TOFs for hydrogenation of pyrrole (Scheme 2) are presented at equal pyrrole conversions ($11 \pm 2\%$), which is necessary for selectivity comparisons. TOFs

for pyrrolidine formation pyrrole were $\sim 70 \text{ ks}^{-1}$ except for the smallest Pt size. The lower activity was again attributed to reduction difficulty. Hence, we report that this step is structure insensitive, which was in agreement with results¹²⁻¹⁵ that report formation and scission of C-H bonds as structure insensitive.

Scheme 2. Pyrrole hydrogenation reaction network.

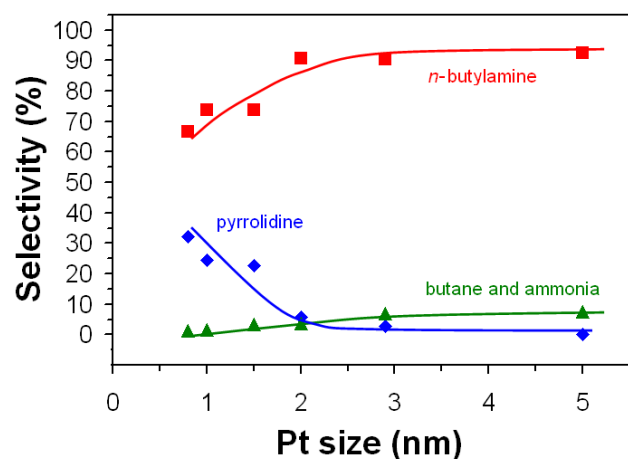
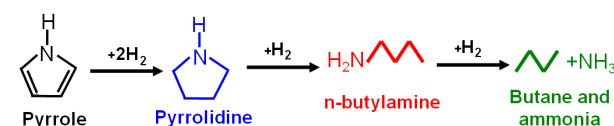


Figure 2. Pyrrole hydrogenation selectivity (color coordinated to Scheme 2) as a function of Pt NP size ($T = 413 \text{ K}$ and $11 \pm 2\%$ conversion). Feed was 4 torr of pyrrole and 400 torr of H_2 with a He balance.

For *n*-butylamine formation, TOFs increased as the Pt NP size increased. This structure sensitivity for the ring opening led to differences in product selectivity (Figure 2). This finding is important because ring opening was identified as the rate determining step for pyridine HDN over Pt.¹⁷ For NPs smaller than 2 nm, selectivity was a strong function of size as pyrrolidine formation occurred more easily over smaller sizes. As NP size increased above 2 nm, behavior became independent of size with *n*-butylamine selectivity approaching 100%. Since the largest dendrimer encapsulated NP (2.0 nm) was larger than the smallest PVP capped NP (1.5 nm), differences in capping agent and activation protocols did not appear to influence the catalytic behavior. TOFs for the cracked products (butane and ammonia) also increased as the NP size increased. It is difficult to comment on the structure sensitivity of this step because this amount was proportional to *n*-butylamine formation.

The reaction results demonstrated that the ring opening was more facile over larger Pt NPs, leading to almost entirely *n*-butylamine, compared to smaller ones, which formed both pyrrolidine and *n*-butylamine. We believe that these findings are caused by *n*-butylamine product poisoning. The N of *n*-butylamine is more electron-rich than its counterparts in pyrrole (lone electron pair shared with ring) and pyrrolidine (fewer N-H bonds than *n*-butylamine) and thus can form stronger bonds with the surface and consequently inhibit turnover. The same principle has been observed with butane formation occurring more easily over Pt supported catalysts for pyrrolidine hydrogenation than *n*-butylamine hydrogenation.¹⁸ Since *n*-butylamine is electron-rich, it bonds more strongly onto surfaces of smaller NPs because the

surfaces of smaller NPs contain more unsaturated surface sites compared to surfaces of larger ones. The higher degree of unsaturated bonds leads to rougher surfaces (more steps and kinks compared to smoother surfaces of larger NPs) and/or electronic effects (decreased metallic character).^{14,15} Either factor can explain product poisoning by *n*-butylamine.

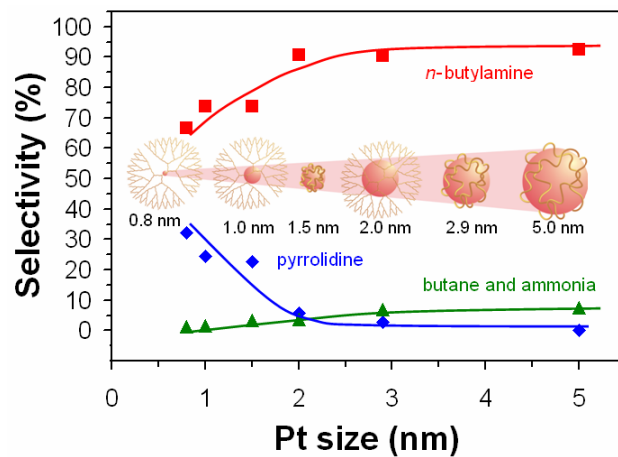
To conclude, we studied pyrrole hydrogenation over mesoporous SBA-15 supported Pt NPs between 0.8 and 5.0 nm. Ring hydrogenation was demonstrated as structure insensitive while ring opening to *n*-butylamine was structure sensitive. Selectivity differences were believed to occur because the N of *n*-butylamine is more electron rich than its counterpart in pyrrolidine and pyrrole and can therefore form stronger adsorbate-surface interactions. These interactions became stronger over smaller NPs, which possess more unsaturated surface bonds. Our observations of different behavior as a function of Pt size indicate new chemistry is achievable for ultrasmall NPs. The effects of temperature and support upon selectivity are under investigation.

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Supporting Information Available: Experimental details, characterization results, and additional catalytic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Well-defined platinum nanoparticles between 0.8 and 5.0 nm were prepared using dendrimer and polymer capping agents and supported onto mesoporous SBA-15 silica. Using these model catalysts, pyrrole hydrogenation was demonstrated to be structure sensitive because ring opening occurred more easily over larger particles compared to smaller ones. The phenomenon is caused by surface roughness or electronic effects that change with particle size.