

Figure 1: Transition Electron Microscope photo of unsupported NanoSelect palladium colloids. Reproduced with permission. © 2008 BASF.

Pd and Pt NanoSelect catalysts, available from Strem, are unique nanoparticle catalysts for the **selective hydrogenation** of **acetylenes** to cis-olefins and **substituted nitroarenes** to anilines, respectively, with low catalyst loadings.

These unimodal metal particles have crystallite sizes of approximately 7 nm when deposited onto various supports. Prepared via reduction-deposition in water, these catalysts exhibit very high activities and selectivities for hydrogenation reactions.

The reduction-deposition method

In the reduction-deposition method, unlike in conventional reductive precipitation, nanoparticles of a metal are formed via reduction in solution in the presence of a stabilizer, and then the particles are deposited onto a heterogeneous support. The reduction

of the metal prior to deposition on the support is the key feature of this method. Notably, this approach enables the formation of nanocatalysts with a narrow metal crystallite size distribution.

The NanoSelect Process

Unlike typical reduction-deposition methods, **NanoSelect** catalysts are produced in water rather than organic solvents. The commercially available ammonium surfactant hexadecyl(2-hydroxyethyl) dimethylammonium dihydrogenphosphate (**HHDMA**) is used as the stabilizer and reductant in a process that is readily scalable. The colloidal nanoparticles are thought to be stabilized by a double layer of HHDMA.

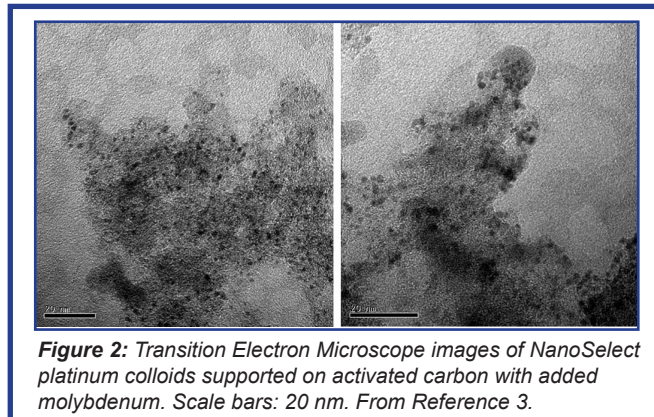


Figure 2: Transition Electron Microscope images of NanoSelect platinum colloids supported on activated carbon with added molybdenum. Scale bars: 20 nm. From Reference 3.

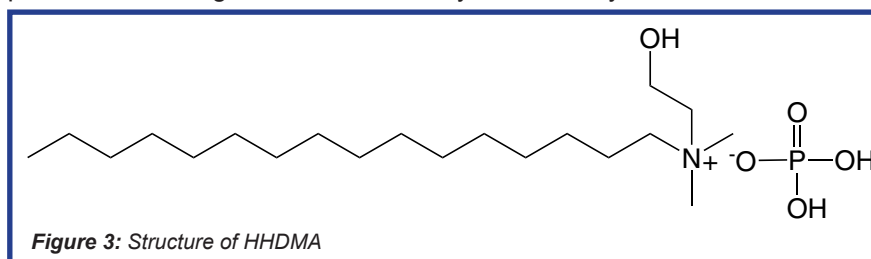


Figure 3: Structure of HHDMA

NanoSelect Catalysts from Strem: Typical Properties

Catalog No.	Name	Active Metal	Metal Content	Support	Quantities
46-1710	NanoSelect LF 100	Palladium	0.60%	Activated carbon	5g, 25 g
46-1711	NanoSelect LF 200	Palladium	0.50%	Titanium silicate	5g, 25 g
78-1630	NanoSelect Pt-100	Platinum	0.80%	Activated carbon	5g, 25 g
78-1635	NanoSelect Pt-200	Platinum	0.80%	Activated carbon (Mo promoted)	5g, 25 g

*All NanoSelect catalysts are reduced, 50% water-wet pastes with a mean particle size of 25 microns.

Pd and Pt NanoSelect catalysts are sold in collaboration with BASF for research purposes only.

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NanoSelect LF 100 and LF 200 are selective hydrogenation catalysts that are environmentally friendly, lead-free alternatives to Lindlar catalysts. Although they contain just 0.5-0.6 wt% palladium on a support of either carbon or titanium silicate powder, in various hydrogenation reactions, these **NanoSelect** catalysts exhibit similar activity and selectivity to Lindlar catalysts that contain 5 wt% palladium. As a result, it is possible to achieve the same results using a 10-fold reduction of precious metal.

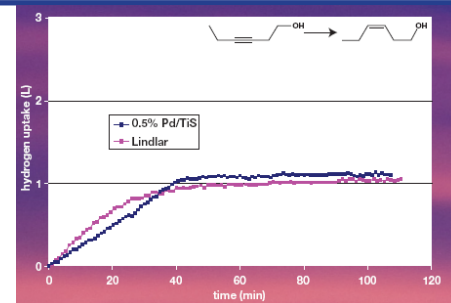


Figure 4: NanoSelect LF 200 versus Lindlar Catalyst. Reproduced with permission. © 2008 BASF.

NanoSelect palladium catalysts are ideally suited for the partial hydrogenation of functional groups, and are particularly effective in the selective hydrogenation of alkynes to cis-alkenes. Unlike with other catalyst systems, overhydrogenation to the fully hydrogenated product and isomerisation to the trans olefin do not occur with **NanoSelect** LF 100 and LF 200.

NanoSelect Platinum Catalysts for the Selective Hydrogenation of Functionalized Nitroarenes

NanoSelect Pt-100 and Pt-200 consist of colloidal platinum nanoparticles (0.8 wt%) highly dispersed on carbon powder supports. During the preparation of **NanoSelect** Pt-200, unreduced $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ is added as a promoter after deposition of the nanoparticles. Both catalysts are very effective at mediating the selective hydrogenation of nitroarenes to aniline, even in the presence of ketones, nitriles, halides, and other functional groups

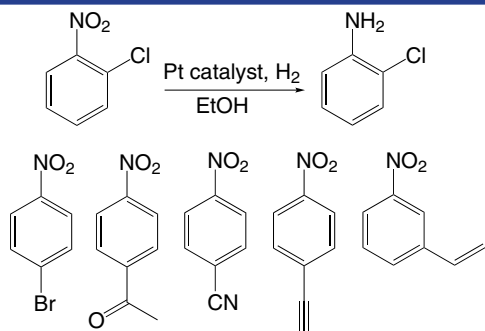


Figure 5: Substituted nitroarene substrates for selective hydrogenation to the corresponding anilines using Nanoselect pt-100 or Pt-200.

The **NanoSelect** platinum catalysts are attractive for nitroarene reduction to anilines. Use of these catalysts does not lead to accumulation of unstable hydroxylamine intermediates or the production of undesired azoxy and azo species due to unwanted side reactions. This is true even with functionalized nitroarenes, which are known to suffer from these issues when the hydrogenation is carried out with most conventional precious metal powder catalysts.

Compared to a widely used commercial nitrobenzene reduction catalyst ((1% Pt+2% V)/C), the **NanoSelect** catalysts provided a similar yield of aniline but with much higher activity. In addition, under optimized reactions conditions, **NanoSelect** catalysts provide high chemoselectivity for reduction of the nitro group, even in the presence of alkyne and alkene substituents.

References:

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2. "NanoSelect Pd Catalysts: What Causes the High Selectivity of These Supported Colloidal Catalysts in Alkyne Semi-Hydrogenation?", Witte, Peter T.; Boland, Susan; Kirby, Fiona; van Maanen, Ramon; Bleeker, Bas F.; de Winter, D. A. Matthijs; Post, Jan A.; Geus, John W.; Berben, Peter H., *ChemCatChem* **2013**, 5, 582 – 587.
3. "Highly active and selective precious metal catalysts by use of the reduction-deposition method", Witte, Peter T.; de Groen, Mariëtte; de Rooij, Ralph M.; Bakermans, Pablo; Donkervoort, Hans G.; Berben, Peter H.; Geus, John W., 10th International Symposium "Scientific Bases for the Preparation of Heterogeneous Catalysts"; Gaigneaux, E.M.; Devillers, M.; Hermans, S.; Jacobs, P.; Martens, J.; Ruiz, P. (Editors) **2010** Elsevier B.V.

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