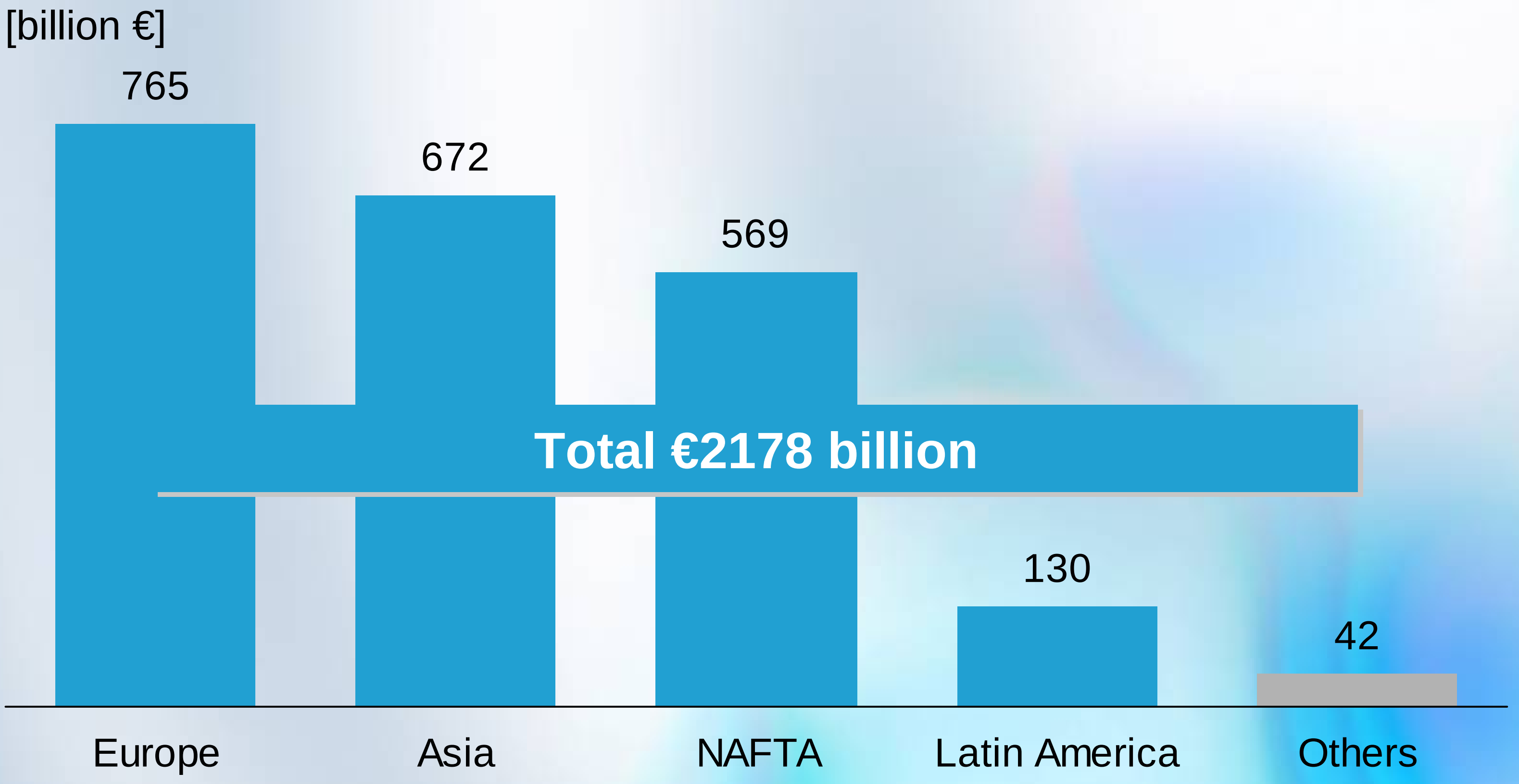
BASF NanoSelect™ Technology

Innovative Lead-Free Replacements for Lindlar Catalysts

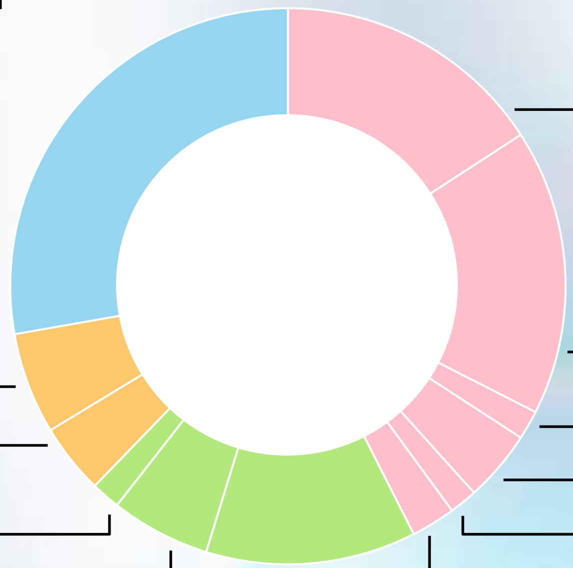
World chemicals sales
2006



Source: Cefic Chemdata International

Chemicals Industry Sales
2006

Sectoral breakdown
(Europe)

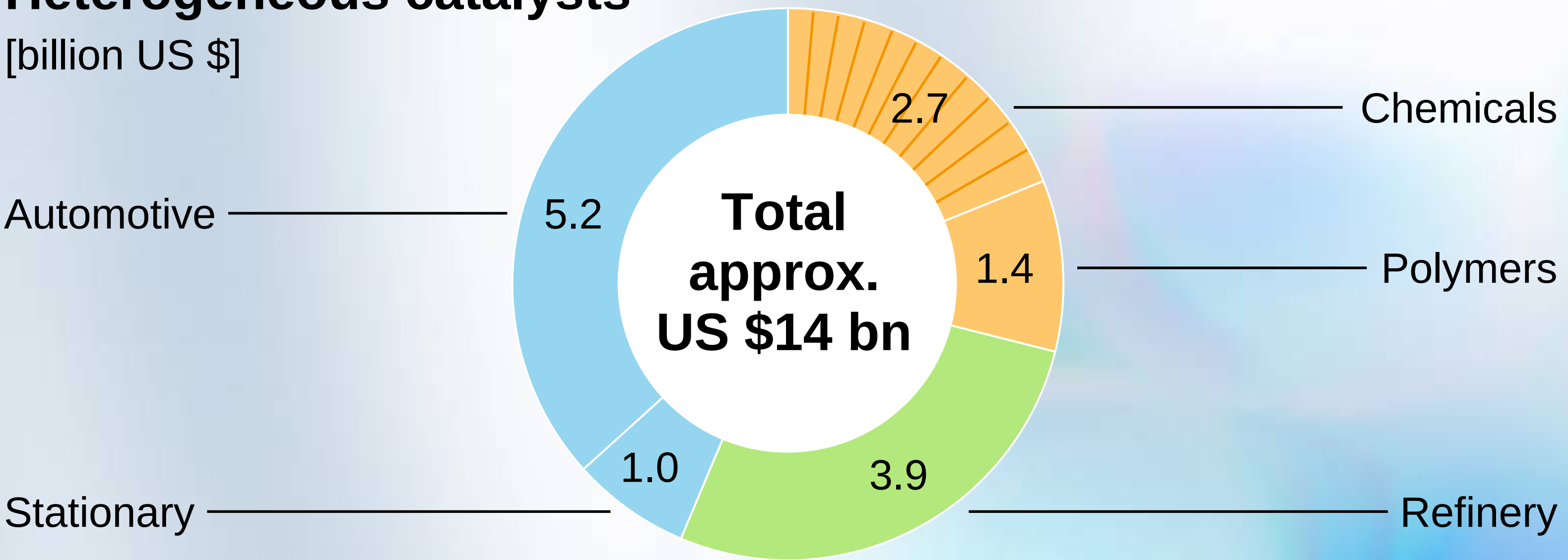


Base chemicals	42.7%
Pharmaceuticals	27.9%
Specialty chemicals	19.2%
Consumer chemicals	10.2%

Source: Cefic, Facts and Figures, 2007 (www.cefic.be)

Global catalyst market
2007

Heterogeneous catalysts
[billion US $]



Environment	US $6.2 bn	44.0%
Chemical industry	US $4.1 bn	29.0%
Refinery	US $3.9 bn	27.0%

Source: The Catalyst Group Resources, “Intelligence Report”, 2008
BASF estimates

Some things which would be different without catalysis

- Much less people since food for 6 billion people can not be produced without fertilizers

- Much higher pollution levels due to lack of catalytic flue gas treatment

- Much higher gasoline prices and lower remaining reserves due to lack of catalytic cracking

- Completely different slates of materials for most purposes at much higher prices

Economic Impact of Catalysis

- At BASF, we employ catalysts in more than 80% of our own production facilities
  Source: BASF

- >80% of all chemical and pharmaceutical production processes, worth ~ €1500 billion, depend on catalytic technologies
  Source: SusChem 2005

- Catalysis contributes directly 2 – 3% of the EU's GDP and 10 times this amount taking into account industries depending on chemical raw materials
  Source: SusChem 2005

- Catalysis is a decisive technology in tapping new feedstock, producing high performance materials and creating environment-friendly processes
  Source: SusChem, Vision 2025

Importance of heterogeneous catalysts to the chemical industry

- **Economy**
  - Capital expenditure
  - Manufacturing costs

- **Broad range of applications**
  (Feedstock purification, synthesis, product separation)

- **Ecology**

- **Technical advances**

Homogeneous vs. Heterogeneous Catalysis

Properties determine fields of application

Sugar

+

Water

=

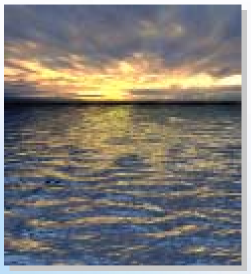
Sweetened water

"Homogeneous (catalysis)"

- (+) Each catalyst molecule (beyond nano!) easily accessible and highly active
- (−) Homogeneous catalysts are not easily separated from the products

Sand

+



Water

=

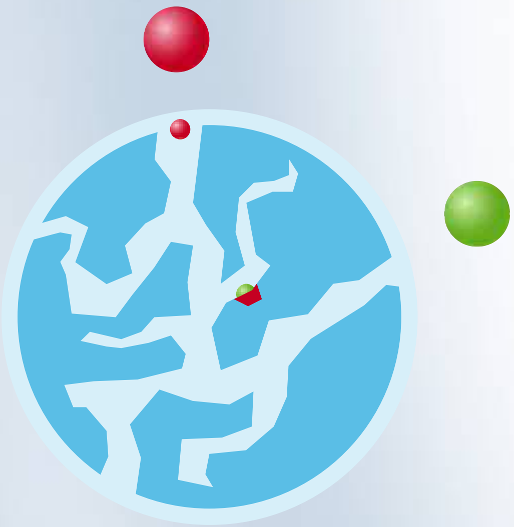
Beach

"Heterogeneous (catalysis)"

- (−) Only surface sites are active, activity differs for each site ("hot spots")
- (+) Easy separation, very lean process designs possible

Homogeneous vs. Heterogeneous Catalysis
Modes of action

Heterogeneous catalyst

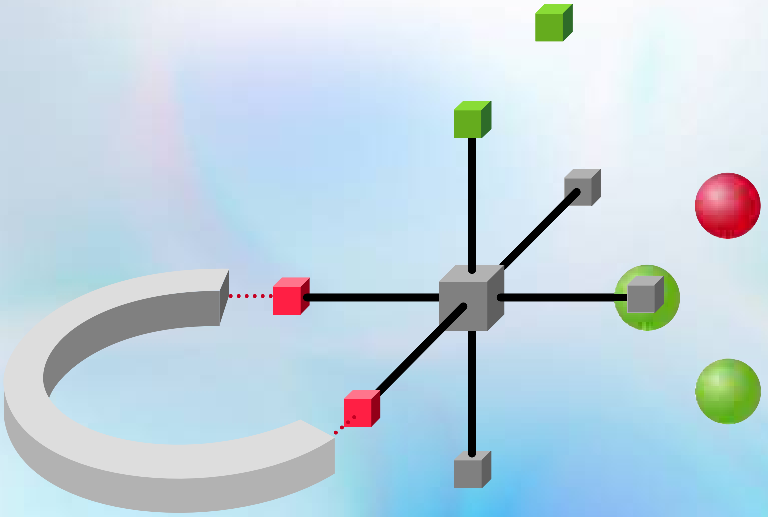


Reactivity controlled by:

- Particle and pore size, character of catalytic site, element composition, type of support material, external (process) parameters, ...

➔ **Very high complexity**

Homogeneous catalyst



Reactivity controlled by:

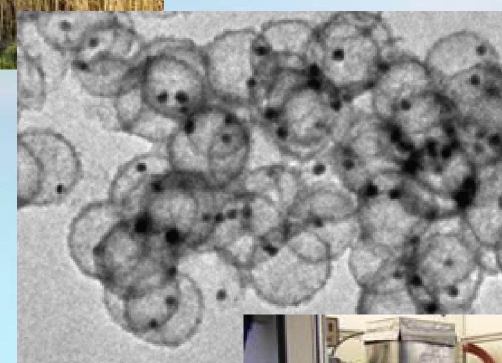
- Choice of metal
- Type of ancillary ligands

➔ **Improvements through geometric and electronic tuning of reactive coordination sites possible**

Challenges for catalysis

Novel Feedstocks

Novel Materials



Novel Methods

BASF's research sites
for heterogeneous catalysis

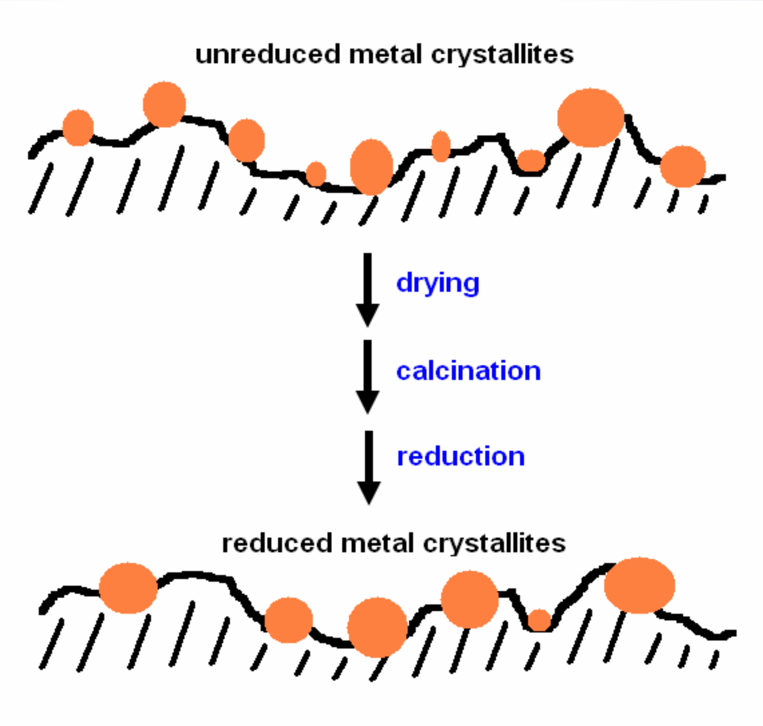
Heterogeneous catalyst preparation techniques

- Traditional techniques:
  - Impregnation
  - Precipitation-deposition
  - Co-precipitation

- Important catalyst parameter
  - Metal crystallite size / dispersion / metal surface area

Heterogeneous catalyst preparation techniques

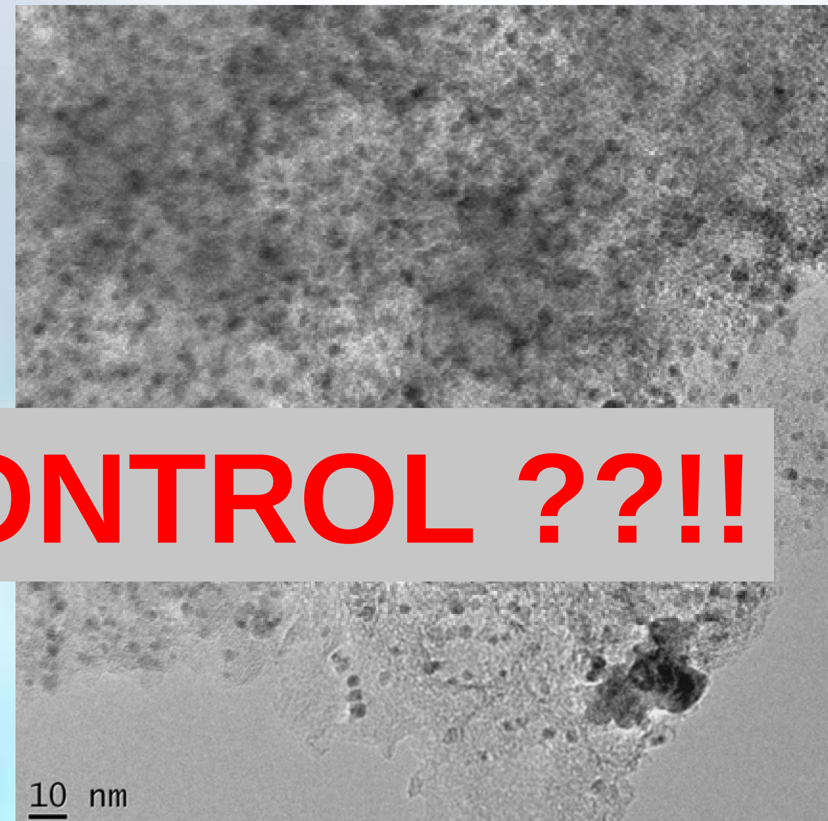
- First step yields supported unreduced metal crystallites
- Extra processing step used to prepare final catalyst
- Initial metal crystallite size alters after extra processing steps



Heterogeneous catalyst prepared by traditional methods

- Variable metal crystallites sizes
- Some very large metal crystallites also present

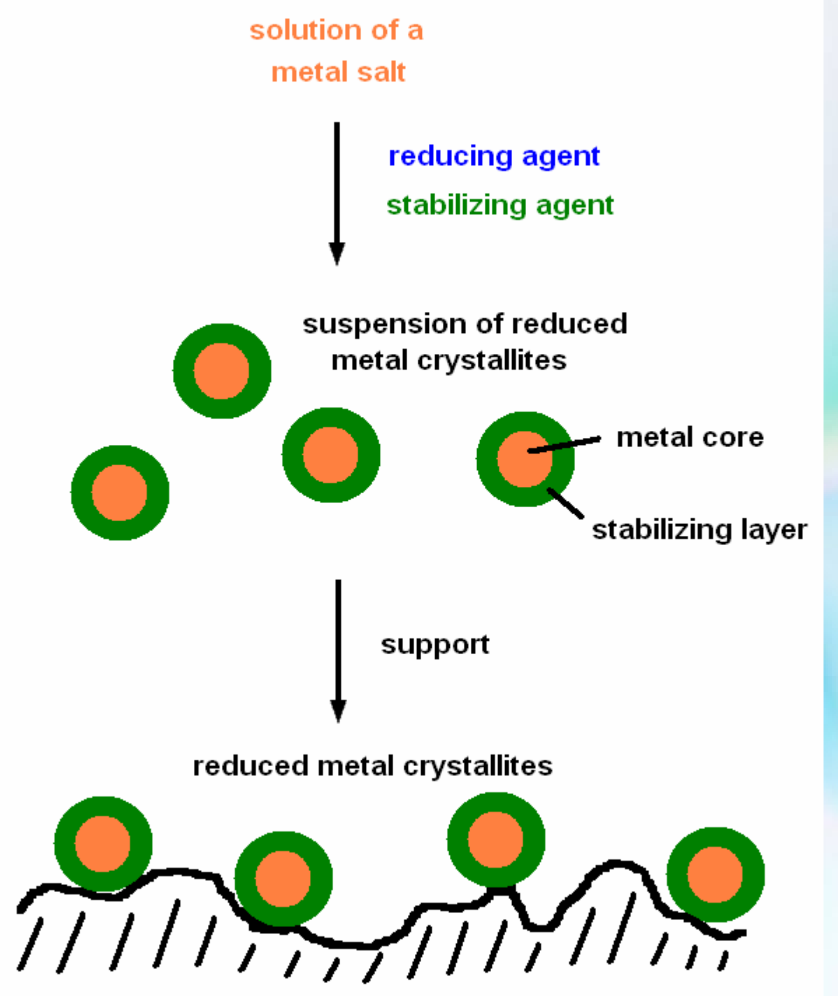
HOW TO CONTROL ??!!



TEM photograph of commercial 5%Pd/CP

Alternative method: Reduction-Deposition technology

- Metal crystallite size independent of support
- Metal crystallite size does not change after first formation



- Citrate as reducing and stabilizing reagent: Turkevich et. Al. *Science*, **1970**, *169*, 873
- Alcohol as reducing agent and PVP as stabilizer: Hirai et. Al. *Reactive Polymers*, **1985**, *3*, 127
- Ammonium Borohydride as reducing and stabilizing reagent: Bönnemann et. Al. *Appl. Organometall. Chem.*, **1994**, *8*, 361

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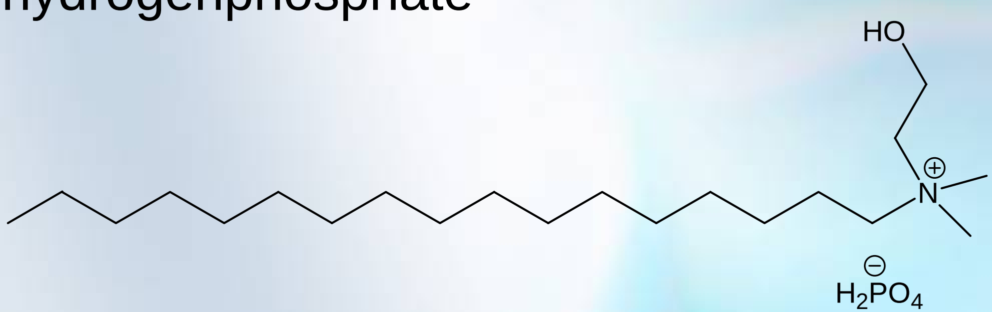
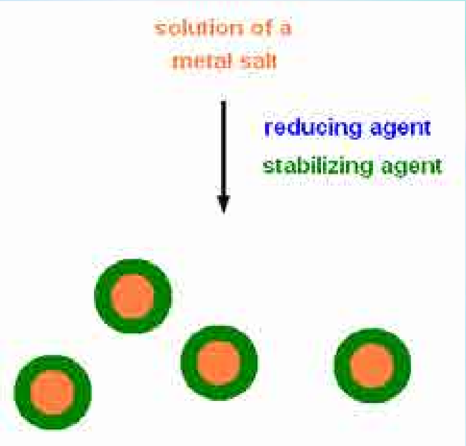
metal salt + HHDMA → metal colloid

- Reducing and stabilizing function combined in one reagent
- Hexadecyl(2-hydroxyethyl)-dimethylammonium dihydrogenphosphate

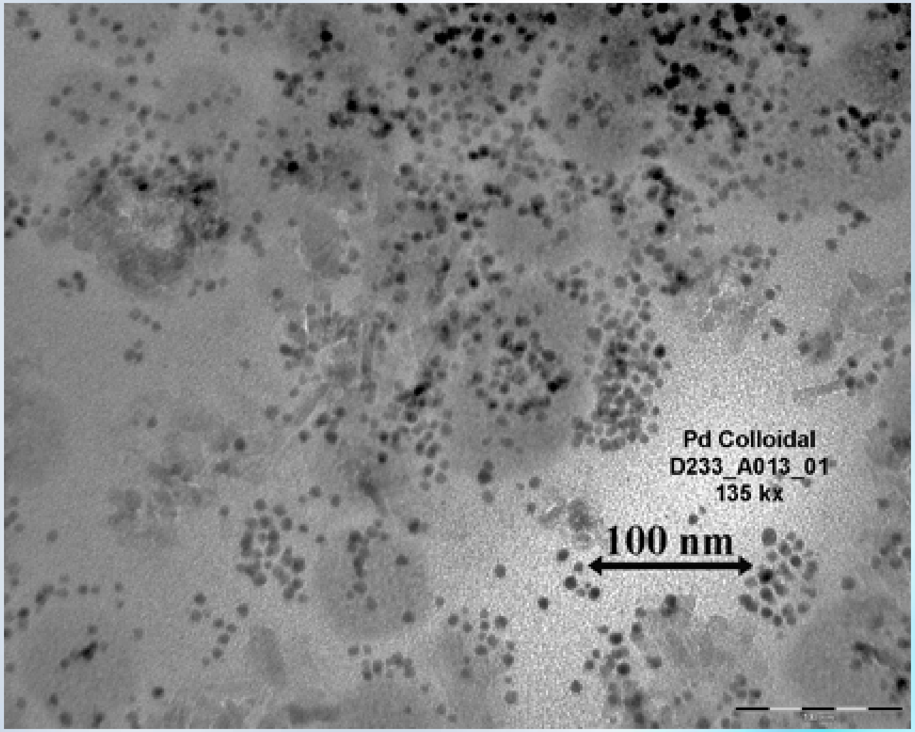




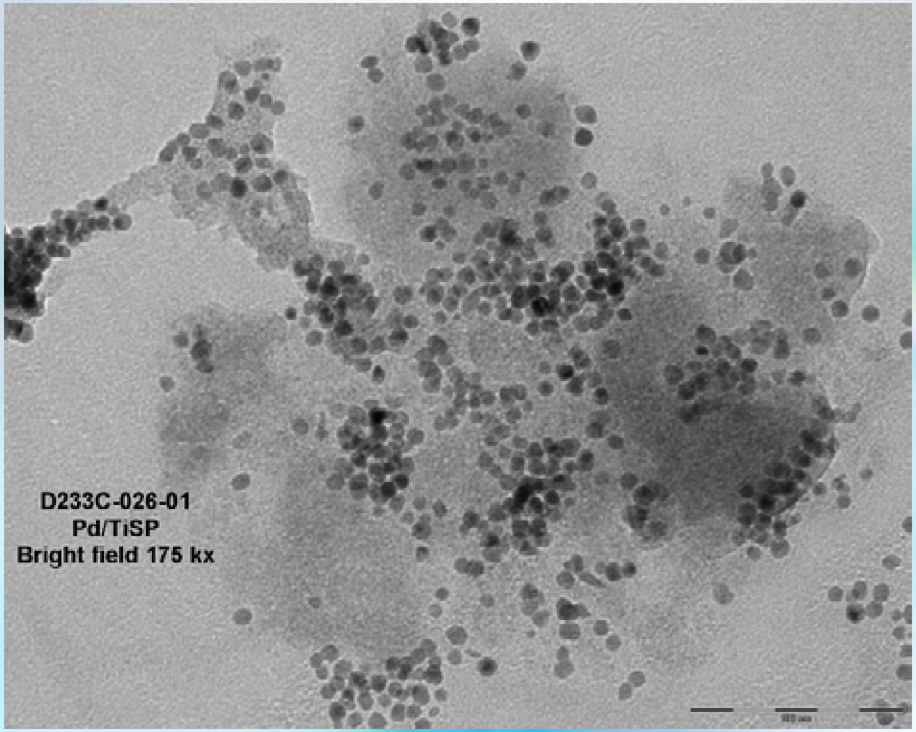
- Water-soluble, air-stable, BASF compound EP08150726.1-2104

NanoSelect Technology

Free colloids



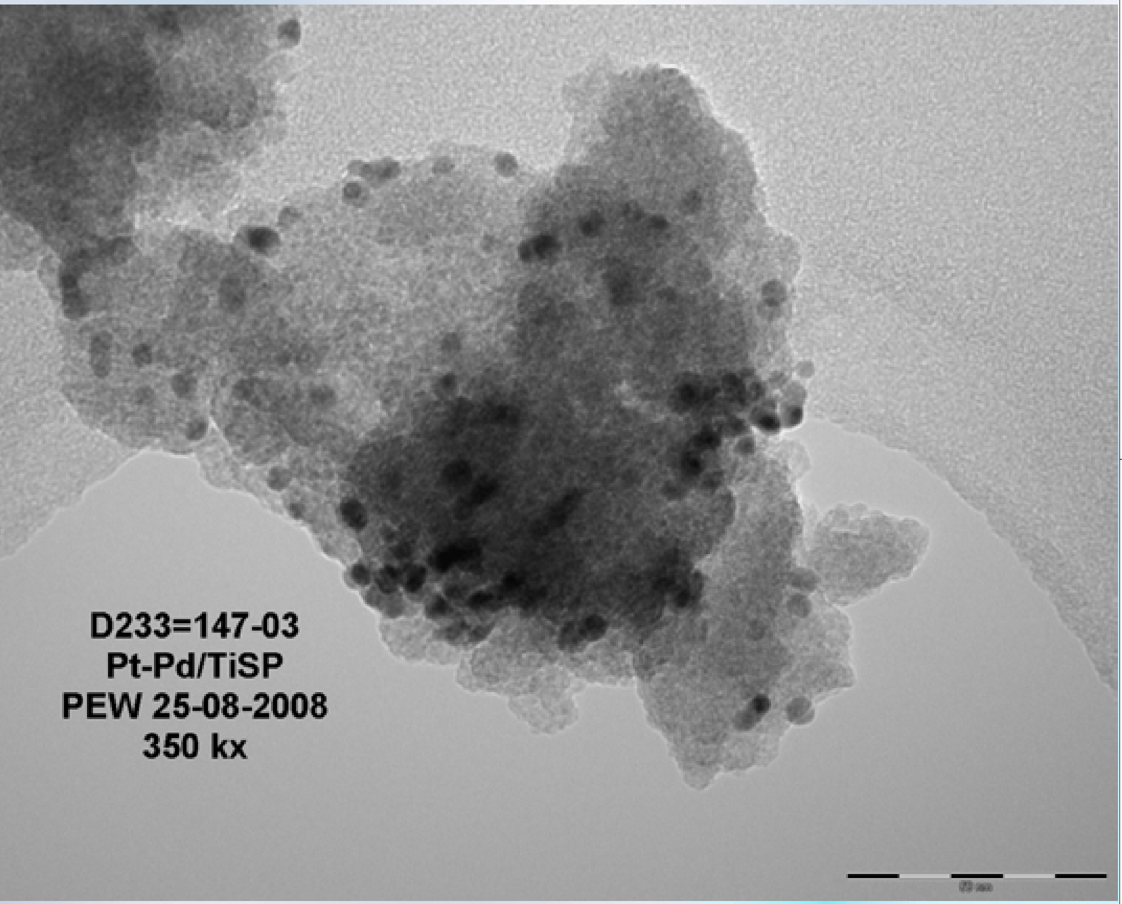
Heterogenized colloids

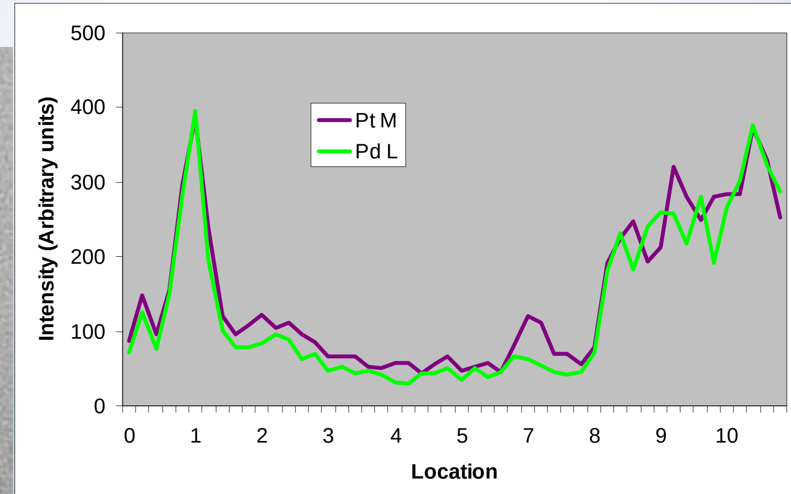


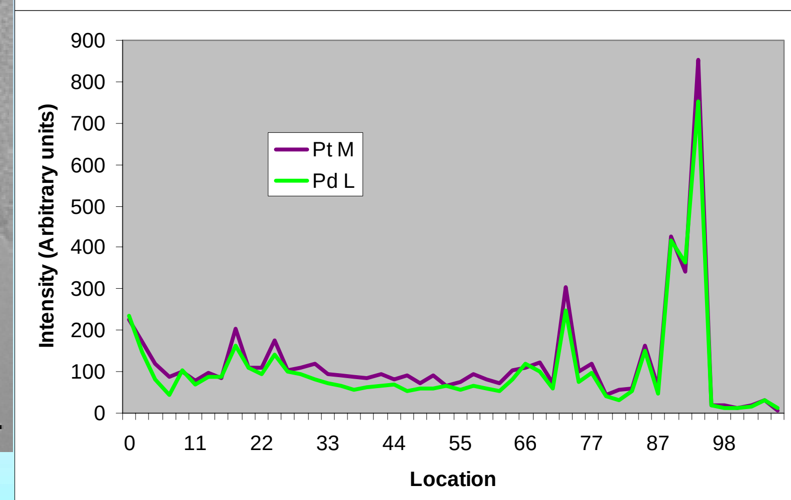
EP08150726.1-2104

NanoSelect Technology
Pd-Pt bimetallic catalyst

BASF
The Chemical Company







NanoSelect™ Technology

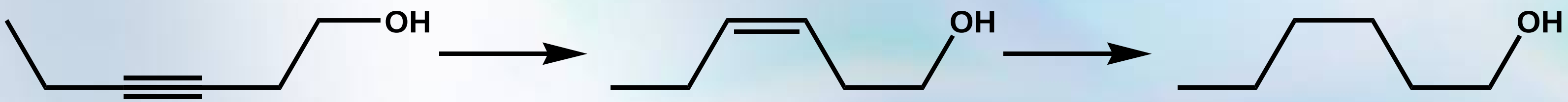
- Heterogeneous catalysts prepared by reduction-deposition
- Better control over metal crystallite size
  - Reaction temperature, ratio metal/stabilizer, stabilizer, pH, metal concentration
  - No effect of extra conditioning steps or of the support
- Commercial manufacturing method:
  - No organic solvents, no protective atmosphere, high metal concentration possible

NanoSelect Pd-catalysts
(partial hydrogenation of alkynes)

- NanoSelect LF 100
  - 0.6% Pd-colloid on C
- NanoSelect LF 200
  - 0.5% Pd-colloid on TiS
- For comparison
  - Commercial 5%Pd/C
  - Lindlar catalyst 5%Pd-2.7%Pb/$CaCO_3$

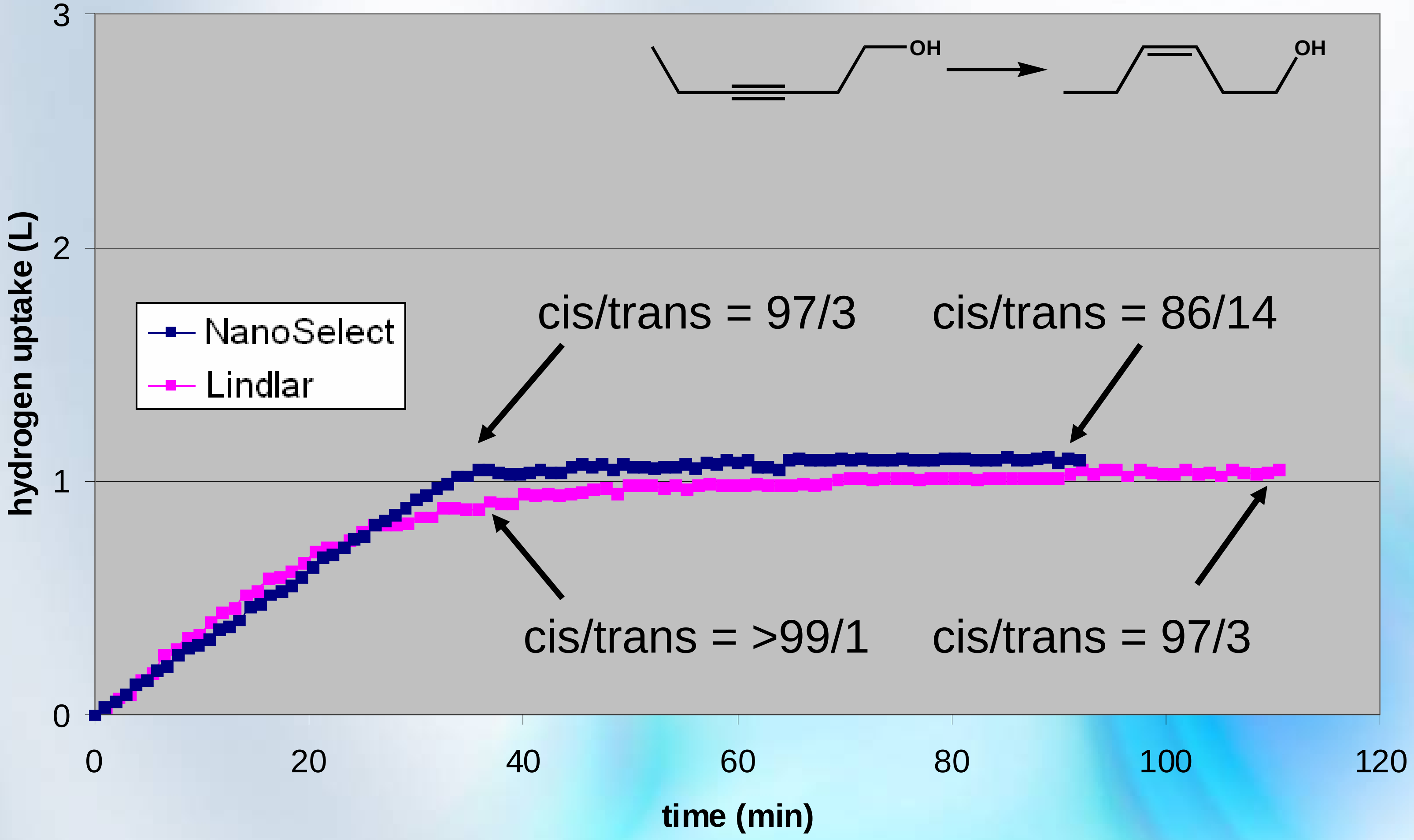
Hydrogenation of 3-hexyn-1-ol

- Catalyst, 100 mL 95% EtOH, 5 mL 3-hexyn-1-ol
- 30°C
- 3 bar H_2



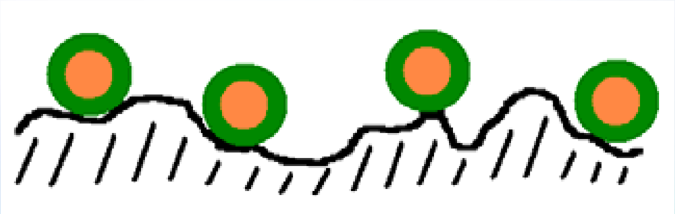
- H_2 consumption recorded
- 2 L H_2 is 100% hexanol formation

NanoSelect LF 200 vs. Lindlar

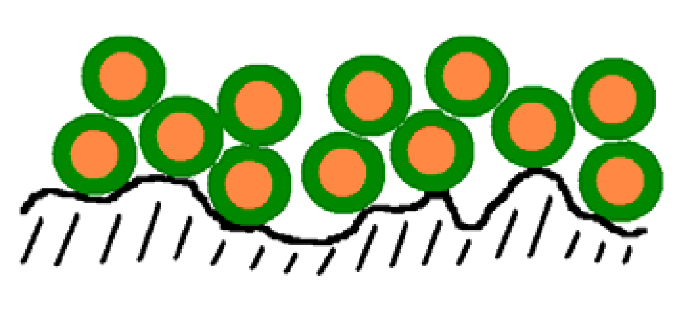


Heterogeneous or homogeneous?

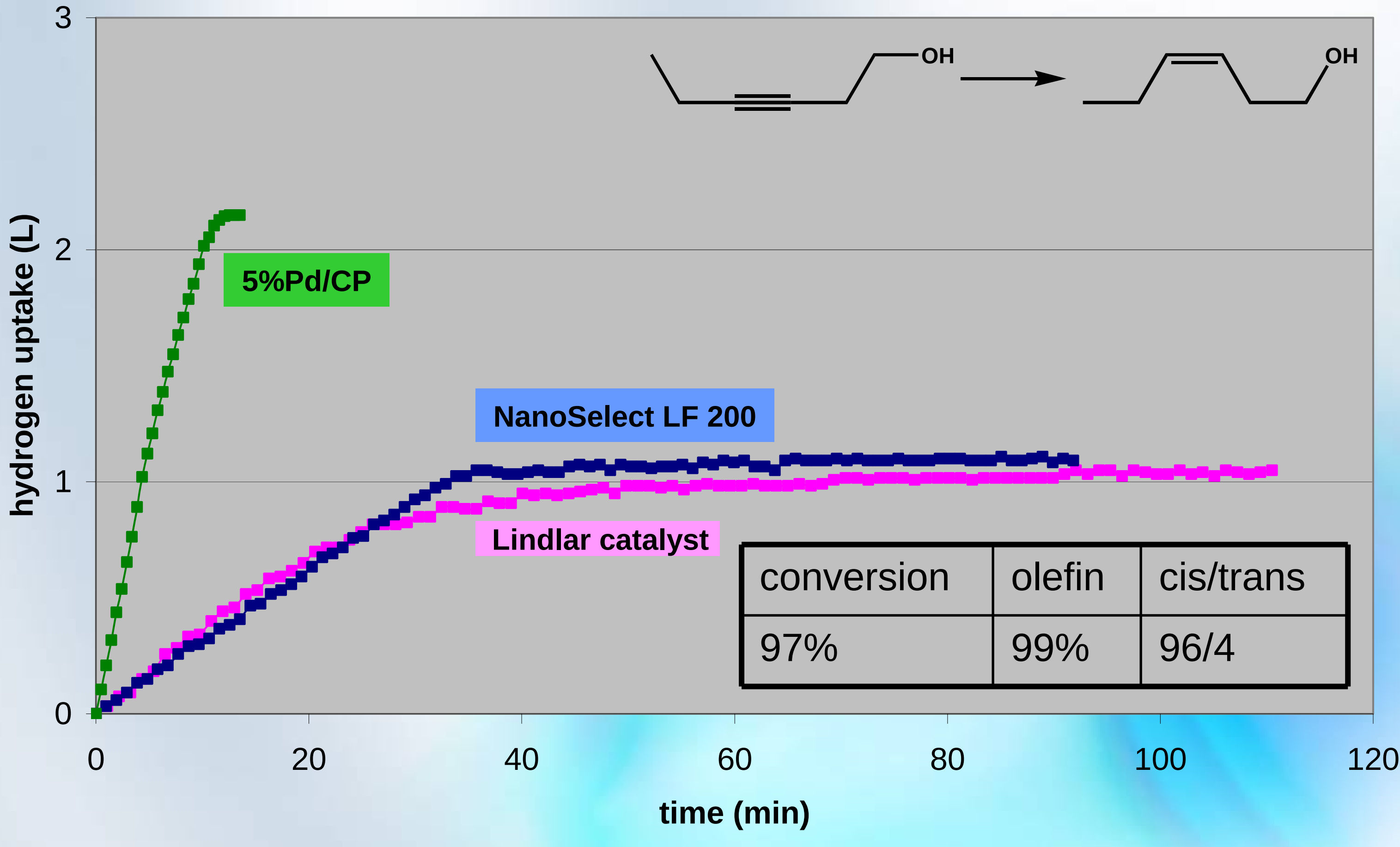
- Filtration experiments indicate that no metal leaching takes place at low Pd-loadings
  - 0.6%Pd/C or 0.5%Pd/TiS



- At higher Pd-loading leaching occurs



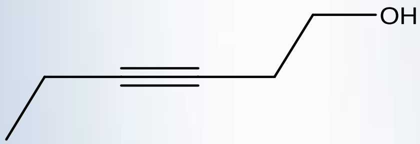
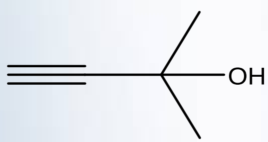
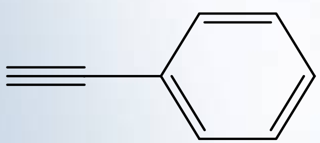
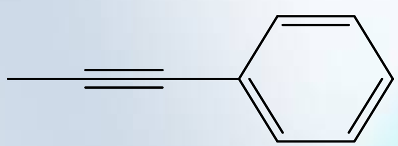
NanoSelect LF 200 vs. Lindlar catalyst
(50 mg catalyst)



conversion	olefin	cis/trans
97%	99%	96/4

Substrates scope

NanoSelect LF 100, LF 200 vs. Lindlar

substrate	catalyst	conversion (%)	olefin (%)	cis product (%)
	LF-100	96	>99	98
	LF-200	97	99	97
	Lindlar	95	>99	>99
	LF-100	98	95	n.a.
	LF-200	97	95	n.a.
	Lindlar	>99	96	n.a.
	LF-100	96	95	n.a.
	LF-200	93	94	n.a.
	Lindlar *	95	97	n.a.
	LF-100 *	85	92	97
	LF-200 *	90	89	97
	Lindlar *	48 **	96	98

n.a. = not applicable
* = 5 times more catalyst is used
** = reaction stops before full conversion is reached

Conclusions

CONTROLLED FLEXIBILITY

- NanoSelect technology for commercial manufacturing of heterogeneous catalysts:
  - Better control over metal crystallite size and size distribution
  - Various mono- and bimetallic catalysts possible
  - Different supports possible

- NanoSelect LF 100 and LF 200: are new lead-free Pd-catalysts that can be used as alternatives for Lindlar catalysts:
  - Lead-free replacements for Lindlar catalysts
  - Same activity and selectivity as Lindlar catalysts
  - Tenfold decrease in Pd amount

NanoSelect LF 100 and LF 200
Lead-free Lindlar catalyst replacement

- Innovative nano-colloid technology
- Unimodal Pd colloids formed
- Highly active for alkyne-to-alkene hydrogenation
- High selectivity towards cis-product
- 10-fold lower palladium content

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