Nanoporous Gold Catalyst for the Selective Semihydrogenation of Alkynes

**Significance:** A nanoporous gold catalyst (AuNPore), which was prepared by dealloying a homogeneous Au_{30}Ag_{70} alloy in nitric acid (70 wt%), catalyzed the semihydrogenation of alkynes with organosilanes and water as the hydrogen source to afford the corresponding alkenes. The reaction of phenylacetylene with PhMe_{2}SiH and water in DMF proceeded in the presence of 2 mol% of AuNPore to give styrene as the sole product (method A: 35 °C, 3 h, 96% yield). 1-Dodecyne underwent the semihydrogenation efficiently in acetonitrile with 50 mol% of pyridine (method B: 80 °C, 8 h, 98% yield).

**Comment:** The catalytic ability of various catalysts was examined for the semihydrogenation of phenylacetylene: AuNPore (96%), AuCl (18%), Au_{20}Ag_{70} alloy (0%), PdNPore (54%), and Pd/C (20%). The authors proposed the reaction pathway including the generation of the H^+ on the AuNPore surface ([AuNPore-H]^+) and pyridinium cation ([H^+Py]^+) which subsequently react with the alkynes to form the corresponding Z-alkenes.
Asymmetric Hydrogenation Using Polymer-Supported BINAP

Preparation of chiral Ru/PCP–BINAP 5:

Selected results:

Significance: A polymeric BINAP–ruthenium complex (Ru/PCP–BINAP) was prepared by treatment of [RuCl₂(PhH)]₂ with the mesoporous cross-linked polymeric (R)-BINAP ligand 4. Ru/PCP–BINAP catalyzed the asymmetric hydrogenation of β-keto esters under hydrogen (2 MPa) to give the corresponding β-hydroxy esters 7a–h in >99.5% conversion with 94.3–99.0% ee.

Comment: Ru/PCP–BINAP was readily recovered and reused six times without significant loss of its catalytic ability (1st reuse: >99.5% conversion, 94.3% ee, 6th reuse: >99.5% conversion, 95.3% ee).
Asymmetric 1,4-Addition with a Chiral Calcium–Pybox Catalyst

**Significance:** A polymer-supported homochiral Pybox–calcium chloride complex catalyzed the asymmetric 1,4-addition of 1,3-dicarbonyl compounds 1 to nitroalkenes 2, to afford the corresponding adducts 3 in up to 98% yield and 95% ee under batch or flow conditions.

**Comment:** The flow system worked for 204 hours without significant loss of catalytic activity to give 3a in 95.5% yield with 92.0% ee on average. The total amount of product was 291.4 mmol and the turn-over number (TON) reached 228.

**Selected examples:**

- **3a** (12–216 h) 88–98% yield, 91–93% ee TON = 228
- **3b** (12–18 h) 90–92% yield, 91% ee
- **3c** (12–18 h) 81–88% yield, 95% ee
- **3d** (12–18 h) 86–87% yield, 91% ee
- **3e** (12–18 h) 94–95% yield, 90% ee
- **3f** (12–18 h) 76–82% yield, 91% ee
- **3g** (12–18 h) 31–82% yield, 75–90% ee
- **3h** (12–18 h) 95–95% yield, 87–88% ee
The Suzuki-Miyaura Coupling with Pd@Peptide

**Significance:** Palladium nanoparticles supported on peptide nanofiber (Pd@Peptide) were prepared by complexation of peptide nanofiber \(2\), prepared via self-assembling of peptide amphiphile \(1\), with \(\text{Na}_2\text{PdCl}_4\) in aqueous NaOH followed by reduction with ascorbic acid (eq. 1). Pd@Peptide catalyzed the Suzuki–Miyaura coupling of aryl halides with arylboronic acids in water to give the corresponding biaryls in up to 99% conversion (10 examples, eq. 2)

**Comment:** Pd@Peptide were characterized with TEM, SEM, XRD, and TGA. In the coupling reaction of bromobenzene and 4-methoxyphenylboronic acid, the catalyst was reused four times without significant loss of catalytic activity (1st reuse: 97% conversion, 2nd reuse: 97% conversion, 3rd reuse: 97% conversion, 4th reuse: 95% conversion).

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In Situ Generated Iron Oxide Nanocrystals as Efficient and Selective Catalysts for the Reduction of Nitroarenes Using a Continuous Flow Method


Reduction of Nitroarenes Using In Situ Generated Iron Oxide Nanocrystals

Reduction of nitroarenes using the batch system:

\[
\begin{align*}
\text{R-} & \quad \text{Fe(acac)}_3 (0.25 \text{ mol}%) \\
\text{NO}_2 & \quad \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} (1.2 \text{ equiv}) \\
\text{MeOH} & \quad \text{MW, 150 °C, 2–8 min} \\
\text{NH}_2 & \quad \text{20 examples} \\
\text{eq. 1) } & \quad \text{95–99% yield}
\end{align*}
\]

Selected examples:

- 2 min, 99% yield
- 2 min, 99% yield
- 2 min, 99% yield
- 8 min, 99% yield
- 4 min, 99% yield
- 6 min, 99% yield
- 6 min, 95% yield
- 4 min, 99% yield
- 2 min, 99% yield
- 4 min, 98% yield

Continuous-flow reduction of nitroarenes:

\[
\begin{align*}
\text{R-} & \quad \text{Fe(acac)}_3 (0.25 \text{ mol}%) \\
\text{NO}_2 & \quad \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} (1.2 \text{ equiv}) \\
\text{MeOH, 150–170 °C} & \quad 6–12 \text{ mL/min} \\
\text{residence time: 1.3–1.6 min} \\
\text{NH}_2 & \quad \text{eq. 2) } \\
\text{95–99% yield}
\end{align*}
\]

Selected examples:

- 96% yield
- 95% yield
- 97% yield
- 96% yield

Significance: Iron oxide nanocrystals, generated in situ from Fe(acac)_3 and hydrazine hydrate, catalyzed the reduction of nitroarenes with hydrazine hydrate under microwave conditions to give the corresponding anilines in 95–99% yield (20 examples, eq. 1). In the reduction of nitrobenzene to aniline using the batch system, the catalyst was magnetically separated from the reaction mixture and reused seven times.

Comment: The reduction of nitroarenes was also performed using a continuous-flow system to afford the anilines in 95–97% yield (eq. 2). The in situ generated iron oxide nanoparticles were characterized by XRD and HRTEM analyses. ICP-MS showed 7.9% iron leaching from the catalyst during the reduction using the batch system.
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Gold Nanoparticles-Catalyzed Activation of 1,2-Disilanes: Hydrolysis, Silyl Protection of Alcohols and Reduction of tert-Benzylic Alcohols


Silylation of Alcohol Derivatives with 1,2-Disilanes Catalyzed by Au/TiO₂

Significance: Gold nanoparticles supported on titanium dioxide (Au/TiO₂) catalyzed the silylation of water and primary, secondary, and tertiary aliphatic alcohols with 1,2-disilanes via Si–Si bond cleavage to give the corresponding silyl ethers in up to >99% yield (eq. 1). When tertiary benzylic alcohols were used for the reaction, the reduction proceeded to afford the corresponding alkanes as the major products (eq. 2).

Comment: The authors previously reported the oxidative cycloaddition of 1,1,3,3-tetramethyldisiloxane to alkynes catalyzed by Au/TiO₂ (J. Am. Chem. Soc. 2011, 133, 10426). The catalytic activity of Au/TiO₂ for the silylation of water was superior to that of gold nanoparticles supported on other supports such as aluminum oxide (Al₂O₃) and zinc oxide (ZnO).

Typical results:

\[
\begin{align*}
\text{R}^1\text{O} + \text{Si} & \xrightarrow{\text{Au/TiO}_2 (1 \text{ mol}\% \text{ Au})} \text{R}^1\text{OSiR}^2 \quad (1) \\
\text{R}^2\text{R}^3\text{Si} & \xrightarrow{\text{EtOAc, 25–55 °C}} \text{R}^2\text{R}^3\text{O} \\
\text{Me} & \xrightarrow{1 \text{ h}, 25 \text{ °C}} >99\% \text{ yield} \\
\text{Me} & \xrightarrow{0.5 \text{ h}, 25 \text{ °C}} 98\% \text{ yield} \\
\text{Ph} & \xrightarrow{1 \text{ h}, 25 \text{ °C}} 98\% \text{ yield} \\
\text{Et} & \xrightarrow{16 \text{ h}, 25 \text{ °C}} 87\% \text{ yield} \\
\text{Ph} & \xrightarrow{3 \text{ h}, 25 \text{ °C}} 96\% \text{ yield} \\
\text{MeO} & \xrightarrow{3 \text{ h}, 55 \text{ °C}} 67\% \text{ yield} \\
\text{O} & \xrightarrow{4 \text{ h}, 25 \text{ °C}} 98\% \text{ yield}
\end{align*}
\]

\[
\begin{align*}
\text{Ar}^1\text{O} + \text{Me} & \xrightarrow{\text{Au/TiO}_2 (1 \text{ mol}\% \text{ Au})} \text{Ar}^1\text{OSiMe} \\
\text{R}^2\text{R}^3\text{Si} & \xrightarrow{\text{EtOAc, 55 °C}} \\
\text{Me} & \xrightarrow{1.5 \text{ h}, 25 \text{ °C}} \text{75:25} \text{ yield} \\
\text{Me} & \xrightarrow{1 \text{ h}, 25 \text{ °C}} 92\% \text{ yield} \\
\text{Ph} & \xrightarrow{3 \text{ h}, 25 \text{ °C}} 98\% \text{ yield} \\
\text{Me} & \xrightarrow{4 \text{ h}, 25 \text{ °C}} 97\% \text{ yield} \\
\text{Br} & \xrightarrow{3 \text{ h}, 25 \text{ °C}} 98\% \text{ yield}
\end{align*}
\]
**Annulation Reactions Catalyzed by Amberlite-Bound Hexafluorophosphate**

**Significance:** Amberlite resin-bound hexafluorophosphate (Amberlite-PF$_6$) was prepared by treatment of Amberlite 900 with aqueous NaPF$_6$ (eq. 1). In the presence of Amberlite-PF$_6$, the annulation of phenylenediamines 1 with aldehydes 2 took place to give the corresponding benzimidazoles 3 (25 examples, 72–96% yield).

**Comment:** The binding of hexafluorophosphate on Amberlite resin was confirmed by IR spectra (557 and 832 cm$^{-1}$), though other characterizations were not given. Phenylenediamines 1 also reacted with α-bromoketones 4 in the presence of Amberlite-PF$_6$ to give the corresponding quinoxalines 5 via an aromatization step.

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Asymmetric Aldol Reaction with BINAM-Sulfonyl Polymeric Organocatalyst

**Significance:** The BINAM-sulfonyl polymeric organocatalyst 2 was prepared by the AIBN-promoted copolymerization of BINAM-derived sulfonamide 1, styrene, and divinylbenzene (eq. 1). Polymer 2 catalyzed the asymmetric aldol reaction of aliphatic ketones with aromatic aldehydes to give the corresponding aldol products 3 in up to 89% yield with up to 95% ee (9 examples, eq. 2).

**Comment:** In the aldol reaction of cyclohexanone with 4-nitrobenzaldehyde, the catalyst was recovered by filtration and reused six times with a slight decrease in its catalytic activity (1<sup>st</sup> reuse: 90% yield, 90% ee, anti/syn = 87:13, 6<sup>th</sup> reuse: 77% yield, 92% ee, anti/syn = 86:16).

**Selected examples:**

<table>
<thead>
<tr>
<th>Example</th>
<th>Yield</th>
<th>ee</th>
<th>[anti/syn]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>88%</td>
<td>93% ee</td>
<td>89:11</td>
</tr>
<tr>
<td>3b</td>
<td>82%</td>
<td>82% ee</td>
<td>73:27</td>
</tr>
<tr>
<td>3c</td>
<td>74%</td>
<td>85% ee</td>
<td>60:40</td>
</tr>
<tr>
<td>3d</td>
<td>69%</td>
<td>95% ee</td>
<td>85:15</td>
</tr>
<tr>
<td>3e</td>
<td>83%</td>
<td>56% ee</td>
<td>in the absence of H₂O</td>
</tr>
<tr>
<td>3f</td>
<td>48%</td>
<td>72% ee</td>
<td></td>
</tr>
<tr>
<td>3g</td>
<td>76%</td>
<td>87% ee</td>
<td>83:17</td>
</tr>
</tbody>
</table>
Asymmetric Miyaura–Michael Reaction with Polymeric Rh/Ag Catalysts

**Preparation of PI/CB Rh/Ag catalyst 2:**

1. carbon black (CB)
2. NaBH₄, diglyme
3. [Rh(OAc)₂]₂, AgSbF₆
4. co-polymer 1 x:y:z = 29:35:36
5. no solvent
6. 150 °C, 5 h
7. NaBH₄, diglyme, 6 h
8. 1) wash with H₂O-THF
9. 2) wash with CH₂Cl₂ and THF
10. 170 °C, 5 h
11. PI/CB Rh/Ag catalyst 2
12. Rh/Ag = 1:1
13. Rh/Ag = 1:3

**Asymmetric 1,4-addition with PI/CB Rh/Ag catalyst 2:**

R⁻⁻⁻⁻⁻⁻Ph
O
\[ + \text{Ar(B(OH))₂} \]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>98%</td>
<td>quant.</td>
</tr>
<tr>
<td>2b</td>
<td>89%</td>
<td>97%</td>
</tr>
<tr>
<td>2a</td>
<td>87%</td>
<td>95%</td>
</tr>
<tr>
<td>2a</td>
<td>86%</td>
<td>97%</td>
</tr>
<tr>
<td>2b</td>
<td>92%</td>
<td>72%</td>
</tr>
<tr>
<td>2b</td>
<td>70%</td>
<td>95%</td>
</tr>
</tbody>
</table>

**Significance:** Polystyrene-based polymer-incarcerated bimetallic rhodium nanoparticle catalysts PI/CB Rh/Ag 2a-b were prepared from co-polymer 1, carbon black (CB), [Rh(OAc)₂]₂, and AgSbF₆. Asymmetric 1,4-addition of arylboronic acids to enones was carried out with 2 and chiral ligand 3 to give the corresponding ketones in 70–99% yield with 74–98% ee without leaching of rhodium.

**Comment:** Catalyst 2a was reused 13 times for the reaction of phenylboronic acid with 2-cyclohexenone. After the 10th use, the recovered catalyst was heated at 170 °C to regain its catalytic activity (1st–8th use: >94% yield, 9th use: 67% yield, 10th use: 60% yield, 11th–14th use: >90% yield, with 98% ee in all cycles).
Polymer-Supported Iron(III) Catalyst for the Selective Oxidation of Toluene

Significance: Poly(4-vinylpyridine-co-divinylbenzene)-supported iron(III) catalysts bearing different amounts (2–50%) of DVB cross-linker [Fe(III)-PVPDVB2–50%] were prepared and applied to the oxidation of toluene with hydrogen peroxide (73.0–89.7% conversion, 88.3–91.2% selectivity to benzoic acid). The polymer-supported catalyst containing 10% DVB [Fe(III)-PVPDVB10%] led to the selective oxidation of toluene to benzoic acid in 90% conversion with up to 96% selectivity under optimized conditions.

Comment: The catalytic activity of reused Fe(III)-PVPDVB10% decreased due to leaching of iron ions from the polymer support. No oxidation of toluene occurred in the absence of the polymer-supported iron catalysts or in the presence of iron-free PVPDVB. The toluene oxidation with the homogeneous counterpart, FeCl₃·H₂O, resulted in lower substrate conversion (<58%), while the reaction selectivity was as high as with the polymer catalyst (92%).
Aerobic Oxidation of Alcohols with Ru@PMO-IL

**Significance:** Perruthenate was supported on ionic-liquid-based periodic mesoporous organosilica (Ru@PMO-IL) via the reaction of 1,3-bis-(3-trimethoxysilylpropyl)imidazolium chloride with tetramethoxysilane, followed by treatment with KRuO₄ (eq. 1). Ru@PMO-IL catalyzed the oxidation of alcohols in trifluorotoluene at 70–85 °C under 1 atm of oxygen to give the corresponding carbonyl compounds in up to >99% yield (24 examples, eq. 2).

**Comment:** The catalyst was recovered by centrifugation and subjected to recycling runs. ICP-AES analysis showed no significant ruthenium leaching (<1 ppm) under the reaction conditions. Nitrogen adsorption and TEM analyses of the recovered catalyst revealed no morphology change of the mesoporous structure. However, a slight loss of catalytic activity was observed during the recycling runs (for the oxidation of benzyl alcohol; 2nd reuse: 99%, 4th reuse: 89%, 5th reuse: 75%).
Ullmann Homocoupling in Water or Molten TBAOAc with Gold Nanoparticles

Significance: Gold nanoparticles, generated in situ from Au(OAc)₃ and glucose, catalyzed the Ullmann homocoupling of aryl iodides or β-bromostyrene in aqueous tetrabutylammonium hydroxide (TBAOH) or in molten tetrabutylammonium acetate (TBAOAc) at 90 °C to afford the corresponding coupling products in up to 98% yield (10 examples) or in up to 96% yield (10 examples), respectively.

Comment: The gold nanoparticles were characterized with TEM, UV/Vis, DLS, and XPS. The particle size of the nanoparticles was about 1 nm in aqueous TBAOH and 20 nm in TBAOAc, respectively. The smaller nanoparticles showed higher catalytic activity because of their larger surfaces.