Nanoporous Gold Catalyst for Highly Selective Semihydrogenation of Alkynes: Remarkable Effect of Amine Additives

Significance: A nanoporous gold catalyst (AuNPore), which was prepared by dealloying a homogeneous Au30Ag70 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 PhMe2SiH 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%), Au30Ag70 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 ([HPy⁺]) 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-dicarboxyl 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.
The Suzuki-Miyaura Coupling with Pd@Peptide

**Results:**

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Reaction Conditions</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>K₃PO₄, 4 h</td>
<td>H₂O, pH 7</td>
<td>99%</td>
</tr>
<tr>
<td>Br</td>
<td>NaOH, 4 h</td>
<td>H₂O</td>
<td>99%</td>
</tr>
<tr>
<td>I</td>
<td>K₃PO₄, 1 h</td>
<td>H₂O</td>
<td>99%</td>
</tr>
<tr>
<td>Br</td>
<td>NaOH, 24 h</td>
<td>H₂O</td>
<td>99%</td>
</tr>
<tr>
<td>I</td>
<td>K₃PO₄, 1.5 h</td>
<td>H₂O–EtOH (1:1), 80 °C</td>
<td>99%</td>
</tr>
<tr>
<td>MeO</td>
<td>K₃PO₄, 1 h</td>
<td>H₂O–EtOH (9:1)</td>
<td>99%</td>
</tr>
<tr>
<td>F</td>
<td>K₃PO₄, 1 h</td>
<td>H₂O</td>
<td>99%</td>
</tr>
<tr>
<td>MeO</td>
<td>K₃PO₄, 1 h</td>
<td>H₂O</td>
<td>99%</td>
</tr>
</tbody>
</table>

**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 Na₂PdCl₄ 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:

\[
\text{Fe(acac)}_3 (0.25 \text{ mol\%}) + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} (1.2 \text{ equiv}) \rightarrow \text{R-} \text{NH}_2 \quad (\text{eq. 1})
\]

MeOH
MW, 150 °C, 2–8 min

Selected examples:

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

2 min, 99% yield
2 min, 99% yield
2 min, 99% yield
8 min, 99% yield
4 min, 99% yield

Continuous-flow reduction of nitroarenes:

\[
\text{Fe(acac)}_3 (0.25 \text{ mol\%}) + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} (1.2 \text{ equiv}) \rightarrow \text{R-} \text{NH}_2 \quad (\text{eq. 2})
\]

MeOH, 150–170 °C
6–12 mL/min
residence time: 1.3–1.6 min

Selected examples:

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl}
\end{align*}
\]

6 mL/min, 150 °C
residence time: 1.6 min
96% yield

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.

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.

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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:**

1. **H-O-H**
   or
   R₁-O-H

   + Au/TiO₂ (1 mol% Au)
   EtoAc, 25–55 °C
   1–16 h

   \[ \text{Si-Si} \quad R₂ \quad R₃ \quad \text{Me-Me-Me-Me} \]

   - Me Me Me Me >99% yield 1.5 h, 25 °C
   - n-C₆H₁₃ Me Me Me Me 97% yield 1.5 h, 25 °C
   - Ph Me Me Me Me 98% yield 0.5 h, 25 °C
   - Ph Me Me Me Me 92% yield 1 h, 25 °C
   - Ph Me Me Me Me 93% yield 1.5 h, 25 °C
   - Me Me Me Me 96% yield 4 h, 55 °C

2. **R₁-O-H**

   + Au/TiO₂ (1 mol% Au)
   EtoAc, 55 °C

   \[ \text{Si-Si} \quad R₂ \quad R₃ \quad \text{Me-Me-Me-Me} \]

   - Me Me Me Me 93% yield 3 h, 25 °C
   - Ph Me Me Me Me 98% yield 3 h, 25 °C
   - Ph Me Me Me Me 96% yield 4 h, 25 °C
   - Br Me Me Me Me 76% yield 3 h, 25 °C

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**Category:** Polymer-Supported Synthesis

**Key words:** gold nanoparticles, titanium dioxide, 1,2-disilanes, alcohols
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 $\alpha$-bromoketones 4 in the presence of Amberlite-PF$_6$ to give the corresponding quinoxalines 5 via an aromatization step.

Selected examples:

- 25 examples, 72–96% yield
- 96% yield (r.t., 1 h)
- 88% yield (r.t., 2 h)
- 79% yield (r.t., 8 h)
- 82% yield (90 °C, 14 h)
- 84% yield (r.t., 4 h)
- 78% yield (r.t., 5 h)
- 68% yield (r.t., 8 h)

Selected examples:

- 15 examples, 58–98% yield
- 94% yield (6 h)
- 86% yield (6 h)
- 84% yield (7 h)
- 98% yield (6.5 h)
- 58% yield (6 h)
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 (1st reuse: 90% yield, 90% ee, anti/syn = 87:13, 6th reuse: 77% yield, 92% ee, anti/syn = 86:15).
Asymmetric Miyaura–Michael Reaction with Polymeric Rh/Ag Catalysts

**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).
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.

**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 K\textsubscript{2}RuO\textsubscript{4} (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; 2\textsuperscript{nd} reuse: 99%, 4\textsuperscript{th} reuse: 89%, 5\textsuperscript{th} reuse: 75%).

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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.

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