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$_{30}$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 ([HPy]$^+$) which subsequently react with the alkynes to form the corresponding Z-alkenes.

**Selected examples:**

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>Yield (%)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>$n$-C$<em>6$H$</em>{11}$</td>
<td>96%</td>
<td>method A</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>98% yield</td>
<td>method B</td>
</tr>
<tr>
<td>Hex</td>
<td>CO$_2$Me</td>
<td>95% yield</td>
<td>method A</td>
</tr>
<tr>
<td>Ph</td>
<td>CO$_2$Et</td>
<td>90% yield</td>
<td>method B</td>
</tr>
<tr>
<td>MeO$_2$C</td>
<td>CO$_2$Me</td>
<td>80% yield</td>
<td>method B</td>
</tr>
<tr>
<td>$R_1$</td>
<td>$R_2$</td>
<td>Yield (%)</td>
<td>Method</td>
</tr>
<tr>
<td>Hex</td>
<td>CO$_2$Me</td>
<td>80% (4:1)</td>
<td>method A</td>
</tr>
</tbody>
</table>

**Synfacts contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Takuma Sato

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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.
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 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).

**Results:**

- X = I, K₃PO₄, 4 h, 99% conv.
- X = Br, NaOH, 4 h, 99% conv.
- X = I, K₃PO₄, 1 h, 99% conv.
- X = Br, NaOH, 24 h, 99% conv.
- X = I, K₃PO₄, 1.5 h, H₂O–EtOH (9:1), 80 °C, 99% conv.
- X = I, K₃PO₄, 1 h, 85% conv.
- X = I, K₃PO₄, 1 h, 99% conv.
- X = Br, NaOH, 12 h, H₂O–EtOH (9:1), 99% conv.

**Equations:**

1. \[ \text{Pd@Peptide} \]  
   \[ \text{Pd} + \text{Peptide nanofiber} \]  
   \[ \text{NaOH} \]  

2. \[ \text{R}^1X + (\text{HO})_2B\text{R}^2 \rightarrow \text{R}^1\text{R}^2 \]  
   \[ \text{Pd@Peptide} (1.5 \text{ mol\%}) \]  
   \[ \text{base (2.0 equiv), H}_2\text{O, r.t.} \]
Reduction of Nitroarenes Using In Situ Generated Iron Oxide Nanocrystals

Reduction of nitroarenes using the batch system:

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

Selected examples:

\[
\begin{align*}
\text{R} & \quad \text{NH}_2 \\
\text{Cl} & \quad \text{Cl} \\
\text{MeO} & \quad \\
\text{HO} & \\
\text{HN} & \\
\end{align*}
\]

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.

SYNFACTS Contributors: Yasuhito Uozumi, Fumie Sakurai

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Gold Nanoparticles-Catalyzed Activation of 1,2-Disilanes: Hydrolysis, Silyl Protection of Alcohols and Reduction of tert-Benzyllic Alcohols


Silylation of Alcohol Derivatives with 1,2-Disilanes Catalyzed by Au/TiO\textsubscript{2}

**Significance:** Gold nanoparticles supported on titanium dioxide (Au/TiO\textsubscript{2}) 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 benzyllic 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-tetramethylsiloxane to alkynes catalyzed by Au/TiO\textsubscript{2} (J. Am. Chem. Soc. 2011, 133, 10426). The catalytic activity of Au/TiO\textsubscript{2} for the silylation of water was superior to that of gold nanoparticles supported on other supports such as aluminum oxide (Al\textsubscript{2}O\textsubscript{3}) and zinc oxide (ZnO).

**Typical results:**

1. **Silylation of Water**
   - Me\textsubscript{3}Si-O-SiMe\textsubscript{3} + Au/TiO\textsubscript{2} (1 mol% Au) → Me\textsubscript{3}Si-O-SiMe\textsubscript{3}
   - 1 h, 25 °C
   - >99% yield

2. **Silylation of Primary Alcohols**
   - PhMe\textsubscript{2}Si-O-SiMe\textsubscript{3} + Au/TiO\textsubscript{2} (1 mol% Au) → PhMe\textsubscript{2}Si-O-SiMe\textsubscript{3}
   - 1 h, 25 °C
   - 96% yield

3. **Silylation of Secondary Alcohols**
   - PhMe\textsubscript{2}Si-O-SiMe\textsubscript{3} + Au/TiO\textsubscript{2} (1 mol% Au) → PhMe\textsubscript{2}Si-O-SiMe\textsubscript{3}
   - 3 h, 25 °C
   - 93% yield

4. **Silylation of Tertiary Alcohols**
   - PhMe\textsubscript{2}Si-O-SiMe\textsubscript{3} + Au/TiO\textsubscript{2} (1 mol% Au) → PhMe\textsubscript{2}Si-O-SiMe\textsubscript{3}
   - 4 h, 25 °C
   - 98% yield

5. **Reduction of tert-Benzyllic Alcohols**
   - PhMe\textsubscript{2}Si-O-SiMe\textsubscript{3} + Au/TiO\textsubscript{2} (1 mol% Au) → PhMe\textsubscript{2}Si-O-SiMe\textsubscript{3}
   - 1 h, 25 °C
   - 98% yield
Annulation Reactions Catalyzed by Amberlite-Bound Hexafluorophosphate

**Significance:** Amberlite resin-bound hexafluorophosphate (Amberlite-PF₆) was prepared by treatment of Amberlite 900 with aqueous NaPF₆ (eq. 1). In the presence of Amberlite-PF₆, 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-PF₆ to give the corresponding quinoxalines 5 via an aromatization step.

**SYNFACTS Contributors:** Yasuhiro Uozumi, Makoto Nagaosa

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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 (1st reuse: 90% yield, 90% ee, anti/syn = 87:13, 6th reuse: 77% yield, 92% ee, anti/syn = 86:15).

Selected examples:

3a 1 d, 88% yield 93% ee, anti/syn = 89:11
3b 3 d, 82% yield 82% ee, anti/syn = 73:27
3c 3 d, 74% yield 85% ee, anti/syn = 60:40
3d 3 d, 69% yield 95% ee, anti/syn = 85:15
3e* 2 d, 83% yield 56% ee (* in the absence of H2O)
3f 5 d, 48% yield 72% ee
3g* 3 d, 76% yield 87% ee, anti/syn = 83:17
## 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 copolymer 1, carbon black (CB), [Rh(OAc)\(_2\)], AgSbF\(_6\), and 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 10\(^{th}\) use, the recovered catalyst was heated at 170 °C to regain its catalytic activity (1\(^{st}\)–8\(^{th}\) use: >94% yield, 9\(^{th}\) use: 67% yield, 10\(^{th}\) use: 60% yield, 11\(^{th}\)–14\(^{th}\) use: >90% yield, with 98% ee in all cycles).

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

1. carbon black (CB)
2. NaBH\(_4\), diglyme
3. [Rh(OAc)\(_2\)], AgSbF\(_6\)
4. no solvent
5. 150 °C, 5 h

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

- **R**\(_1\): 0.3 mmol
- **ArB(OH)\(_2\)**: 0.45–0.6 mmol
- **ligand 3**: 1–2 mol% Rh
- **PhMe–H\(_2\)O (1:2)**
- **100 °C, 7–24 h, argon**

## Key words
- bimetallic nanoparticle catalysts
- rhodium
- silver
- asymmetric 1,4-addition
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)-PVPDV2–50%] 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)-PVPDV10%] 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)-PVPDV10% 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 PVPDV. The toluene oxidation with the homogeneous counterpart, FeCl3·6H2O, 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\text{RuO}_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%).
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.

SYNFACTS Contributors: Yasuhiro Uozumi, Noboru Kobayashi

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