Ammonoxidation of Alcohols with Aqueous Ammonia Using an Iron Single-Atom Catalyst

**Significance:** Iron atoms supported on nitrogen-doped porous carbon derived from a benzylamine-modified zeolitic imidazolate framework (Fe-N-C) were prepared according to equation 1. Fe₁-N-C catalyzed the selective ammonoxidation of alcohols with ammonium hydroxide under air to afford the corresponding nitriles in ≤99% yield (eq. 2; 20 examples).

**Comment:** The Fe₁-N-C catalyst was characterized by means of PXRD, SEM, STEM, EDX, XRD, BET, XANES, FTEXAFS, EXAFS, XPS, Raman, and ICP-OES analyses. In the reaction of benzyl alcohol with aqueous ammonia, the catalyst was recovered and reused five times without significant loss of its catalytic activity. ICP analysis showed that no iron leached into the solution during the reaction.
**Significance**: Sulfonated magnetic cellulose nanoparticles (MNP-cellulose-OSO₃H), prepared according to equation 1, catalyzed the three-component reaction of benzil or 9,10-phenanthrenequinone with aromatic aldehydes and ammonium acetate to give the corresponding imidazoles in ≤96% yield (eq. 2).

**Comment**: The MNP-cellulose-OSO₃H catalyst was characterized by means of FTIR, elemental analysis, ICP-OES, XRD, SEM, EDX, TEM, zeta potential analysis, VSM and TGA. In the reaction of benzil, benzaldehyde, and ammonium acetate, the catalyst was recovered and reused four times without significant loss of its catalytic activity.
Hydrothiolation of Alkenes and Alkynes on Carbon Nanotube-Supported Ru–Rh Nanoparticles

**Significance:** Bimetallic ruthenium–rhodium nanoparticles immobilized on multiwalled carbon nanotubes (RuRhCNT nanohybrid) catalyzed the hydrothiolation of alkenes and alkynes with thiols in ethanol at room temperature under air to give the corresponding thioethers in ≤98% and ≤97% yields, respectively (eq. 1).

**Comment:** The RuRhCNT nanohybrid was prepared according to previous reports (Y. Wang, J. Ren, K. Deng, L. Gui, Y. Tang *Chem. Mater.* 2000, 12, 1622; J. John et al. *Angew. Chem. Int. Ed.* 2011, 50, 7533). In the reaction of octadec-1-ene with 4-bromothiophenol, the catalyst was recovered and reused five times without significant loss of its catalytic activity.

Selected examples:

- **96% yield**
- **98% yield**
- **96% yield (3 h)**
- **93% yield (3 h)**
- **91% yield (3 h)**
- **97% yield (3 h)**
- **93% yield**
- **95% yield**
- **97% yield (3 h, E/Z >95:5)**
Willgerodt–Kindler Reaction on Supported Silver Nanoparticles

**Significance:** Silver nanoparticles supported on cellulose-reinforced poly(ethylene-co-vinyl acetate) (Ag/cellulose-PEVA), prepared according to equation 1, catalyzed the Willgerodt–Kindler reaction of benzaldehydes, morpholine, and S8 to give the corresponding thioamides (eq. 2).

**Comment:** In the Willgerodt–Kindler reaction of 4-hydroxybenzaldehyde, morpholine, and S8, the Ag/cellulose-PEVA catalyst was reused seven times without significant loss of its catalytic activity (first run: 98% yield, eighth run: 94%).
Asymmetric Aldol Reaction Catalyzed by a Chiral Proline-Substituted Porous Organic Cage

**Significance:** The chiral porous organic cage CPOC-Pro was prepared by self-assembly of the tetraformyl-functionalized calix[4]resorcinarene 1 with the proline-substituted diamine 2 (eq. 1). CPOC-Pro catalyzed the asymmetric aldol reaction of ketones with aromatic aldehydes to give the corresponding β-hydroxy ketones in up to 99% yield, 97:3 dr, and 92% ee (eq. 2).

**Comment:** In the model reaction of 4-nitrobenzaldehyde with cyclohexanone, the catalyst was recovered and reused four times without a significant loss of its catalytic performance. CPOC-Pro showed a higher catalytic activity and greater diastereoselectivity and enantioselectivity than L-proline (10 d; 80% yield, dr = 45:55, and 77% ee in the model reaction).
Hydrolytic Oxidation of Hydrosilanes on PtCu Nanowires Encapsulated in Ir(III) Porphyrinic MOFs

**Significance:** Platinum–copper nanowires encapsulated in an iridium(III) porphyrinic metal–organic framework (PtCu@Ir-PCN-222), prepared according to equation 1, catalyzed the hydrolytic oxidation of hydrosilanes to give the corresponding silanols in ≤96% yield (eq. 2).

**Comment:** In the hydrolytic oxidation of dimethyl(phenyl)silane, PtCu@Ir-PCN-222 was reused nine times without significant loss of its catalytic activity. TEM and PXRD analysis of the used catalyst revealed that its morphology remained intact during the reaction.
Hydrodeoxygenation of Lignin Derivatives Catalyzed by Kieselguhr-Supported Palladium Nanoparticles

**Significance:** Palladium nanoparticles supported on phosphoric acid-modified commercial Celite (Pd/PCE) were prepared according to equation 1. Pd/PCE catalyzed the hydrodeoxygenation of lignin derivatives to give the corresponding toluene derivatives (eq. 2).

**Comment:** Without phosphoric acid modification, the turnover frequency of the catalyst for the hydrodeoxygenation reaction to give vanillyl alcohol was significantly decreased.
Silk-Fibroin-Supported Palladium Catalyst for Suzuki–Miyaura and Ullmann Coupling Reactions of Aryl Chlorides


Suzuki–Miyaura and Ullmann Couplings of Aryl Chlorides Catalyzed by Silk-Fibroin-Supported Pd

**Significance:** A palladium catalyst supported on silk fibroin (Pd/SF) promoted the Suzuki–Miyaura coupling (eq. 1) and Ullmann coupling (eq. 2) reactions of aryl chlorides to give the corresponding bi-phenyls in ≥99% yield.

**Comment:** The authors have previously reported the preparation of Pd/SF (Eur. J. Org. Chem. 2020, 6992). WAXS investigations of Pd/SF suggested that monoatomic palladium species form stable complexes with the silk-fibroin.
Reductive N-Alkylation of Amines with Aldehydes and Ketones on a Zirconia-Supported Pd Catalyst

\[ \text{Pd(OAc)}_2 + \text{ZrO}_2 \xrightarrow{\text{PIME}} 40 \degree \text{C}, 8 \text{ h} \quad \text{Pd(OAc)}_2/\text{ZrO}_2 \quad (1) \]

Significance: A zirconia-supported palladium catalyst \([\text{Pd(OAc)}_2/\text{ZrO}_2]\) was readily prepared by mixing palladium acetate and zirconium oxide (eq. 1). \([\text{Pd(OAc)}_2/\text{ZrO}_2]\) catalyzed the N-alkylation of amines with aldehydes and ketones under a \(\text{H}_2\) atmosphere to give the corresponding \(\text{N}\)-alkylamines in \(\leq 99\%\) yield (eqs. 2 and 3).

Comment: In the N-alkylation of octylamine with benzaldehyde, \([\text{Pd(OAc)}_2/\text{ZrO}_2]\) was reused five times with gradual loss of its catalytic activity [fresh: \(>99\%\) yield (4 h), sixth run: 49\% (4 h)].

Selected results:

\[ \text{R}^\prime\text{O} + \text{H}_2\text{N}^\text{Ar} \xrightarrow{\text{Pd(OAc)}_2/\text{ZrO}_2 (\text{Pd}: 0.26 \text{ mol} \%) \atop \text{MeOH, H}_2 \text{ (balloon), 23–25 \degree \text{C}, 1.5–48 \text{ h}}} \text{R}^\prime\text{N}^\text{Ar} \quad (2) \]

Results:

\[ \text{n-Hep}^\text{N} \quad 90\% \text{ yield} \\
\text{Ph}^\text{N} \quad 92\% \text{ yield} \\
\text{n-Oct}^\text{N} \quad 95\% \text{ yield}^a \\
\text{MeO}^\text{N} \quad 53\% \text{ yield}^a \]

(a: 20 mmol of acetone was used)
Selective Hydrodeoxygenation of Acetophenone Derivatives Using a Fe\textsubscript{25}Ru\textsubscript{75}@SILP Catalyst: A Practical Approach to the Synthesis of Alkyl Phenols and Anilines

**Green Chem.** 2022, 24, 2937–2945, DOI: 10.1039/d1gc04189d.

**Hydrodeoxygenation of Acetophenone Derivatives on an Iron–Ruthenium Bimetallic Catalyst**

**Significance:** Bimetallic iron–ruthenium nanoparticles immobilized on an imidazolium-based supported ionic liquid phase (Fe\textsubscript{25}Ru\textsubscript{75}@SILP) catalyzed the hydrodeoxygenation of hydroxy, amino, and nitro derivatives of acetophenone to give the corresponding alkyl products in up to 94% yield (eq. 1).

**Comment:** The authors have previously reported the preparation of Fe\textsubscript{25}Ru\textsubscript{75}@SILP (Chem. Commun. 2020, 56, 9509). The catalyst was characterized by means of STEM-HAADF and SEM-EDX analyses. The hydrodeoxygenation of 4-hydroxyacetophenone in flow [175 °C, 50 bar H\textsubscript{2}, 0.6 mL/min substrate flow (25 mmol anisole soln), 17 s residence time] gave a 90–95% yield of 4-ethylphenol during five hours.
Significance: A mesoporous graphitic carbon nitride (mpg-CN) and Ni(dtbbpy)Br2 (dtbbpy = 4,4-di-tert-butyl-2,2'-bipyridine) catalyzed the cross-coupling reaction of aryl or alkenyl bromides with potassium [18-Crown-6] bis(catecholato) alkylsilicates under irradiation by LEDs (451 nm) to afford the corresponding alkylated products in ≥98% yield (25 examples).

Comment: The authors have previously reported the the synthesis of mpg-CN and its application in such reactions as the C–H functionalization of arenes (Science 2019, 365, 360) and the cross-coupling of aryl bromides with alkyl borates (ACS Catal. 2020, 10, 3526). In the formation of 3-[4-(trifluoromethyl)phenyl]propyl acetate, the Ni/mpg-CN catalytic system was reused three times (second run: 76% yield, third run: 77%, fourth run: 43%).