Heterogeneous Catalytic Systems for Organic Chemical Transformations in Water

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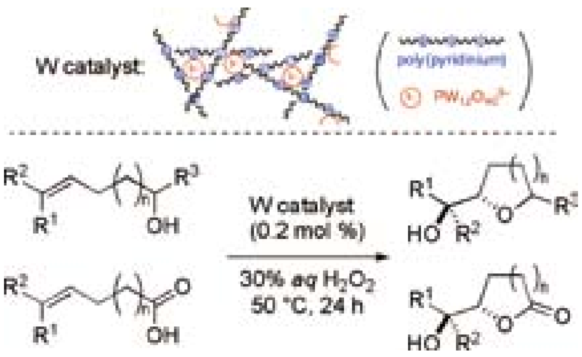
Various organic molecular transformations catalyzed by transition metals were achieved under heterogeneous aqueous conditions by use of amphiphilic resin-supported metal complexes or convoluted polymeric metal catalysts which were designed and prepared by this research group. In particular, highly stereoselective asymmetric π-allylic substitution and oxidative cyclization, both of which were performed in water under heterogeneous conditions with high recyclability of the polymeric catalysts, are highlights among the achievements of the 2007–2008 period to approach what may be considered ideal chemical processes of next generation. Representative results are summarized hereunder.

1. Development of Tightly Convoluted Polymeric Phosphotungstate Catalysts and Their Application to Oxidative Cyclization of Alkenols and Alkenoic Acids[1)]

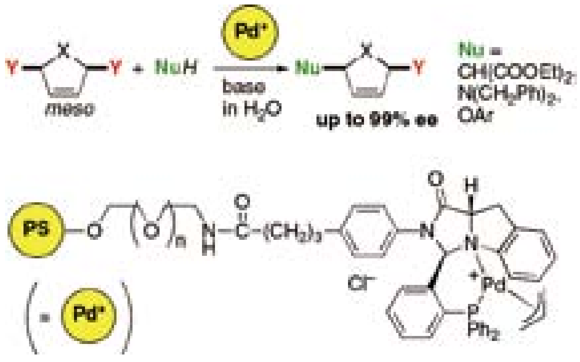
Tightly convoluted polymeric phosphotungstate catalysts were prepared via ionic-assembly of $H_3PW_{12}O_{40}$ and poly(alkylpyridinium)s. An oxidative cyclization of various alkenols and alkenoic acids was efficiently promoted by the polymeric phosphotungstate catalyst in *aq.* H_2O_2 in the absence of organic solvents to afford the corresponding cyclic ethers and lactones in high yield. The catalyst was reused four times without loss of catalytic activity. The polymeric phosphotungstate was unambiguously characterized by spectro- and microscopic studies (MAS $^{31}P\{^1H\}$ NMR, IR spectroscopy, elemental analysis, TEM, SEM, and EDS).



Scheme 1. Oxidative Cyclization of Alkenyl Alcohols and Alkenoic Acids with a Convoluted Polymeric Phosphotungstate.

2. Allylic Substitution of *meso*-1,4-Diacetoxycycloalkenes in Water with an Amphiphilic Resin-Supported Chiral Palladium Complex[3)]

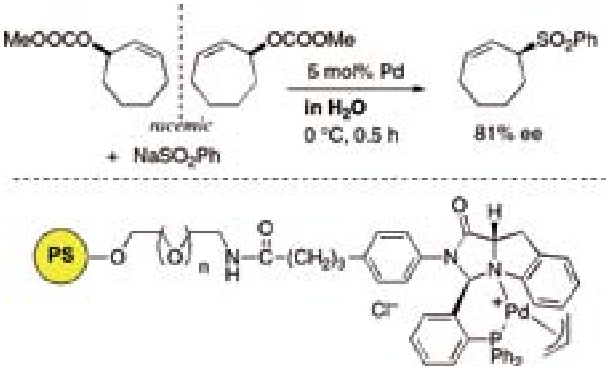
Asymmetric π-allylic substitution of *meso*-1,4-diacetoxycyclopentene and *meso*-1,4-diacetoxycyclohexene with various nucleophiles was performed with an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported chiral imidazoindole phosphine-palladium complex in water as a single reaction medium under heterogeneous conditions to give the corresponding 1-acetoxy-4-substituted cycloalkenes with up to 99% ee.



Scheme 2. Enantioselective Desymmetrization of *meso*-Cycloalkenyl Diacetate in Water with an Amphiphilic Resin-Supported Complex.

3. π-Allylic Sulfonylation in Water with Amphiphilic Resin-Supported Palladium-Phosphine Complexes[4)]

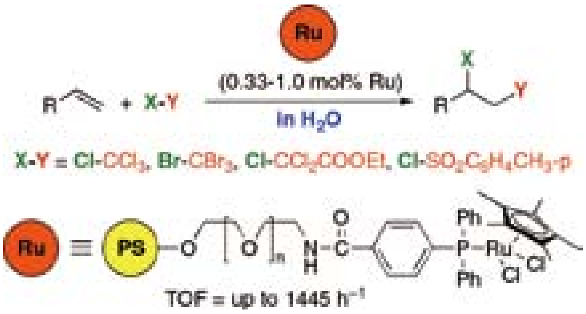
π-Allylic substitution of allyl esters with sodium arylsulfinate was performed with an amphiphilic polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported phosphine-palladium complex in water as a single reaction medium under heterogeneous conditions to give allyl sulfones in good to high yields. Catalytic asymmetric allylic substitution of cycloalkenyl esters also took place in water using a PS-PEG resin-supported chiral imidazoindolephosphine-palladium complex to give cycloalkenyl sulfones with up to 81% ee.



Scheme 3. Enantioselective Sulfonation of Cycloalkenyl Esters in Water with an Amphiphilic Resin-Supported Complex.

4. Highly Efficient Heterogeneous Aqueous Kharasch Reaction with an Amphiphilic Resin-Supported Ruthenium Catalyst[5)]

An amphiphilic polystyrene-polyethylene glycol (PS-PEG) resin-supported ruthenium complex was designed and prepared. The polymeric Ru complex was found to promote the transition metal-catalyzed atom transfer radical addition of halogenated compounds to olefins, the Kharasch reaction, in water under heterogeneous as well as AIBN-free conditions with a high level of atom-economy to meet green chemical requirements.



Scheme 4. Kharasch Reaction in Water with an Amphiphilic Resin-Supported Ruthenium Complex.

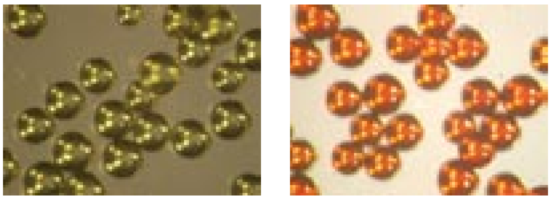


Figure 1. Microscopic Images of PS-PEG-NHCO-C_6H_4-PPh_2 (left) and PS-PEG-NHCO-C_6H_4-PPh_2-$RuCpCl_2$ (right).

References

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3) Y. Uozumi, H. Takenaka and T. Suzuka, *Synlett* 1557–1561 (2008).
4) Y. Uozumi and T. Suzuka, *Synthesis* 1960–1964 (2008).
5) Y. Oe and Y. Uozumi, *Adv. Synth. Catal.* **350**, 1771–1775 (2008).

Award

YAMADA, Yoichi M. A.; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology: The Young Scientists' Prize 2008.

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