

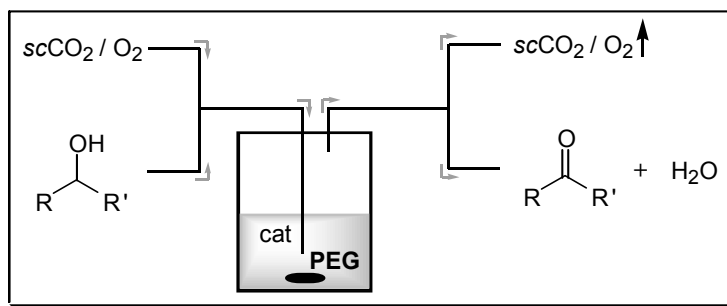
Continuous selective oxidation of alcohols with molecular oxygen in a two phase system consisting of scCO₂ and PEG

Zhenshan Hou^a, Nils Theyssen^a and Walter Leitner^{a,b*}

- a) Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm Platz 1, 45470 Mülheim an der Ruhr, Germany, e-mail: theyssen@mpi-muelheim.mpg.de
b) Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Worringer Weg 1, 52056 Aachen, Germany, e-mail: leitner@itmc.rwth-aachen.de, DGMK-No.: 102071

The selective oxidation of alcohols and olefins with molecular oxygen is of interest for both economics and environmental reasons. Thus, many active heterogeneous or homogeneous catalytic systems for aerobic alcohol oxidation have been reported. We try to make use of both intrinsic advantages by developing a two phase system able to work efficiently under continuous flow operation.

Supercritical carbon dioxide is a particularly attractive mobile phase for these approach for several reasons: i) it has a good solvent power for molecular oxygen and formed carbonyl compounds, ii) its fluid properties simplify mass transport and separation from the product (no residues) and, iii) its presence reduced the risk of explosions drastically which makes the system inherently safe. Like carbon dioxide, PEG is cheap, chemically stable and toxicological absolutely inoffensive but – choosing the right molecular weight – it is not extractable and especially in a compressed CO₂ atmosphere (which lowers the melting point and the viscosity) a good solvent for many metal catalysts and the organic substrates. All this characteristics make PEG a very appropriate stationary phase. Pioneering work in this immobilizing concept for a hydrogenation reaction of styrene was recently published by the group of *Jessop*.^[1]



Our study includes a screening (batch operation) of a broad variety of different alcohols (allylic, benzylic and cyclic) with Palladium nanoparticles or Palladium giant clusters. The performance of standard catalysts like Pd/Al₂O₃ or Pd/C were compared under identical reaction conditions. Most active systems were then tested in continuous flow operation to check long time stability, partially with excellent results.^[2]

[1] D. J. Heldebrant, P. G. Jessop, *J. Am. Chem. Soc.* **2003**, *125*, 5600-5601.

[2] Z. Hou, N. Theyssen, A. Brinkmann, W. Leitner, *Angew. Chem. Int. Ed.*, in press.