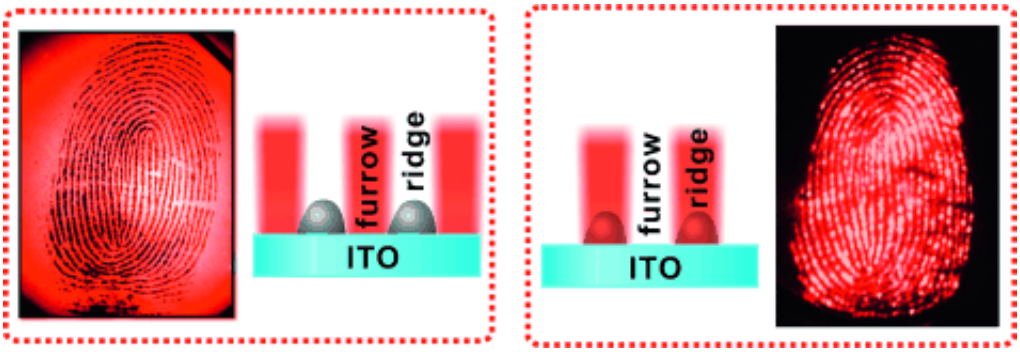
# Continuous hydrogenation of carbon dioxide to pure formic acid in supercritical CO2

August 6 2012




(Phys.org) -- To reduce fossil fuel consumption while simultaneously improving the carbon footprint of fuels and chemical products, the use of carbon dioxide as a carbon source could be an attractive option. In the journal *Angewandte Chemie*, German researchers have now introduced a method by which carbon dioxide can be catalytically hydrogenated to make formic acid. In this process, carbon dioxide is not only a starting material; it also acts—in a supercritical state—as the solvent for separation of the product. This integrated approach makes it possible to directly obtain free formic acid as the product in a single step for the first time.

The hydrogenation of $CO_2$ to formic acid ($HCO_2H$) is a subject of intensive research because it offers direct access to chemical products

based on waste products from the use of fossil fuels for energy. Formic acid is an important product in the chemical industry and has many applications, including agriculture, food technology, and the leather industry. It is also being contemplated as a potential hydrogen-storage material: vehicles powered by fuel cells could fill up with formic acid, from which the hydrogen could then be produced catalytically.

Homogeneous catalysts for the production of formic acid from $CO_2$ have been investigated since the mid 1970s. The trouble with this process is that it involves an equilibrium reaction for which the equilibrium heavily favors the reactants. In order to suppress the constantly occurring back-reaction, the formic acid must be removed—in the form of a salt, adduct, or derivative—to take it out of the equilibrium. To obtain the desired free formic acid in the end, additional separation steps are thus required to separate the adducts from the catalyst and finally to release and isolate the formic acid.

A team led by Walter Leitner at the RWTH Aachen University has now developed a new concept that can be used to produce pure formic acid in a continuous process. The reaction and separation steps are integrated in a single processing unit.

Their trick is to use a two-phase reaction system that employs supercritical $CO^2$ as the mobile phase and a liquid salt—an ionic liquid—as the stationary phase. The catalyst and the base used to stabilize the formic acid are both dissolved in the ionic liquid, which holds them both in the reactor. The $CO_2$ flows through the reactor at pressures and temperatures above the critical values (74 bar, 31 °C) and selectively removes the formic acid from the mixture. The dual role played by $CO_2$ as both reactant and extractive phase has significant advantages: The product is continuously extracted and flushed from the reactor, which causes the equilibrium to readjust constantly. Once out of the reactor, the free formic acid can be obtained with high purity by

decompression or washing. Ionic liquids do not dissolve in supercritical $CO_2$, nor do the catalyst and base, so these do not contaminate the product. The process can run continuously. In laboratory experiments, stable operation was demonstrated for over 200 hours.

“Our results with formic acid demonstrate that the systematic implementation of modern solvent techniques in continuous reactor equipment makes it possible to perform conversions that cannot be achieved under conventional conditions,” says Leitner. “Naturally we can’t ‘defeat’ thermodynamics in this way—but there are many possibilities for the integration of reactions and materials separation that may open new routes for more efficient and sustainable processes.”

**More information:** Walter Leitner, Continuous-Flow Hydrogenation of Carbon Dioxide to Pure Formic Acid using an Integrated scCO2 Process with Immobilized Catalyst and Base, *Angewandte Chemie International Edition*, dx.doi.org/10.1002/anie.201203185

Provided by Wiley

Citation: Continuous hydrogenation of carbon dioxide to pure formic acid in supercritical CO2 (2012, August 6) retrieved 26 April 2024 from https://phys.org/news/2012-08-hydrogenation-carbon-dioxide-pure-formic.html