A metal-free, sustainable approach to carbon dioxide reduction

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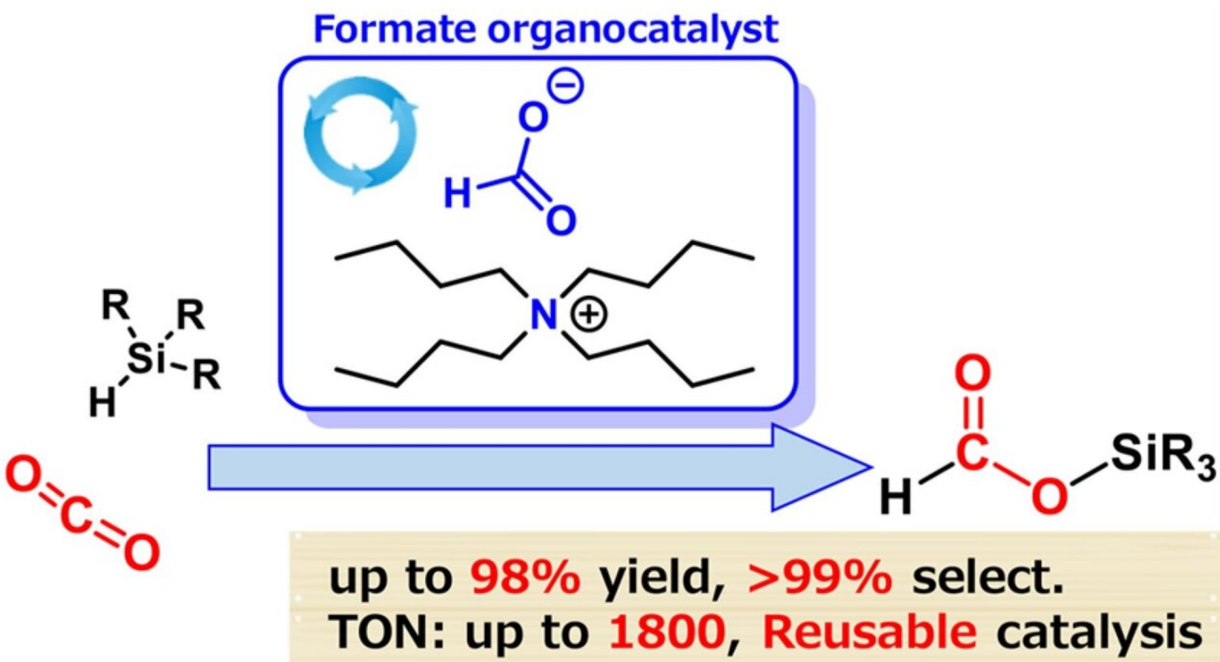

Representation of the process whereby formate salts serve as active and selective catalysts for the hydrosilylation of CO2. Credit: ACS Sustainable Chem. Eng.

Researchers in Japan have presented an organic catalyst for carbon dioxide (CO_2) reduction that is inexpensive, readily available and recyclable. As the level of catalytic activity can be tuned by the solvent conditions, their findings could open up many new directions for converting CO_2 to industrially useful organic compounds.

Sustainability is a key goal in the development of next-generation catalysts for CO_2 reduction. One promising approach is a reaction called the hydrosilylation of CO_2. However, most catalysts developed to date for this purpose have the disadvantage of containing metals that are expensive, not widely available and potentially detrimental to the environment.

Now, scientists at Tokyo Institute of Technology (Tokyo Tech) and the Renewable Energy Research Center at Japan's National Institute of Advanced Industrial Science and Technology (AIST) have demonstrated the possibility of using a fully recyclable, metal-free catalyst.

By comparing how well different organic catalysts could achieve hydrosilylation of CO_2, the team identified one that surpassed all others in terms of selectivity and yield. This catalyst, called tetrabutylammonium (TBA) formate, achieved 99 percent selectivity and produced the desired formate product with a 98 percent yield. The reaction occurred rapidly (within 24 hours) and under mild conditions, at a temperature of 60°C.

Remarkably, the catalyst has a turnover number of up to 1800, which is more than an order of magnitude higher than previous results.

In 2015, team leader Ken Motokura of Tokyo Tech's Department of Chemical Science and Engineering and his colleagues found that formate salts show promising catalytic activity. It was this hint that provided the basis for the current study. Motokura explains: "Although we did expect formate salts to exhibit good catalytic activity, TBA formate showed much higher selectivity, stability and activity that went beyond our expectations."

In the current study, the researchers found that the catalyst can be made reusable by using toluene as a solvent. They showed that Lewis basic solvents such as N-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO) can accelerate the reaction, meaning that the catalytic system is tunable.

Overall the findings—published in the online edition of the journal *ACS Sustainable Chemistry & Engineering*—offer a new, environmentally friendly path to reducing CO_2 at the same time as yielding industrially important formate products.

Silyl formate can be easily converted to formic acid, which can serve as an important hydrogen carrier, for example, in fuel cells. The high reactivity of silyl formate enables its conversion into intermediates for the preparation of organic compounds such as carboxylic acids, amides and alcohols.

"This efficient transformation technique of CO_2 to silyl formate will expand the possibilities for CO_2 utilization as a chemical feedstock," Motokura says.

More information: Ken Motokura et al, Formate-Catalyzed Selective Reduction of Carbon Dioxide to Formate Products using Hydrosilanes, *ACS Sustainable Chemistry & Engineering* (2019). DOI: 10.1021/acssuschemeng.9b02172

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