Electrocatalytic CO_2 Insertion into Unreactive Organic Molecules

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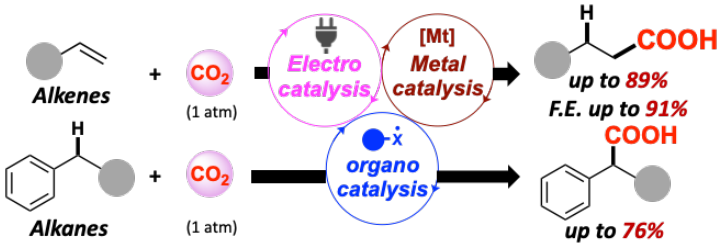
The utilization of CO_2 gas has attracted considerable attention as a solution to the current energy problems. Especially, the transformations to incorporate CO_2 into organic skeletons by C-C bond-forming reactions are highly attractive in terms of environmental-friendship and as a strategy to directly access various carboxylic acids. Whereas CO_2 insertion reactions into organic molecules with activated chemical bonds (e.g. carbon-halogen bonds) have been widely studied,[1] there have been only limited examples to accomplish direct CO_2 insertion reactions into unreactive organic molecules, such as alkenes and alkanes.

Herein, we achieved the electrochemical CO_2 insertion reactions into alkenes using a pentanuclear nickel complex composed of five nickel ions and six bpp^- ligands (**Ni5**, Hbpp = 3,5-bis(2-pyridyl)pyrazole) as a catalyst.[2] The CO_2 insertion reaction of styrene smoothly proceeded in high yields (up to 89%) and high Faradaic efficiencies (up to 91%) at a relatively low voltage (2–3 V), which is in sharp contrast to the previously reported relevant systems.[3] To the best of our knowledge, this is the first example to realize the electrochemical CO_2 insertion into unreactive organic molecules under mild conditions at an applied voltage of 2 V. Additionally, we successfully achieved the broad substrate generalities, including styrene derivatives, di- and tri-substituted alkenes, Michael acceptor alkenes and an aliphatic alkene. Moreover, we propose a plausible catalytic cycle involving the key **Ni5**-CO_2 adduct.

Furthermore, we achieved the first electrochemical CO_2 insertion reactions into alkanes bearing unactivated benzylic C(sp^3)-H bonds by developing a new electrochemical methodology comprising a Hydrogen Atom Transfer (HAT) catalyst, a metal catalyst and CO_2 gas.[4] Reaction development, substrate generalities and detailed mechanistic studies will be given in the presentation.



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