Endowed Research Section
– Water Chemistry Energy (AGC) –

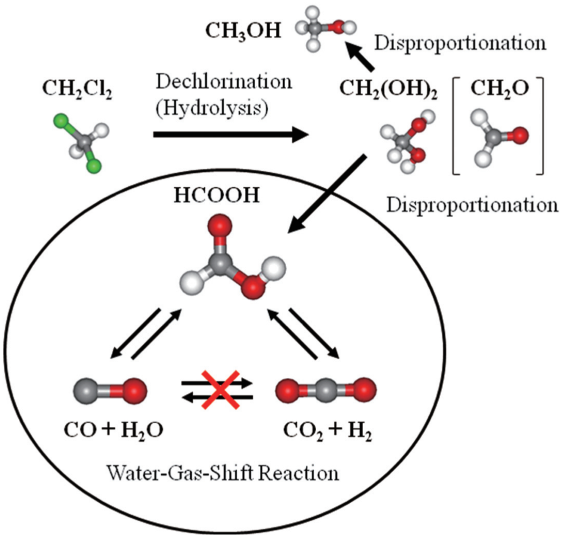
http://www.scl.kyoto-u.ac.jp/~nakahara/

Vis Prof
NAKAHARA, Masaru
(D Sc)

Program-Specific Assist Prof
TSUJINO, Yasuo

Scope of Research

A novel energy system using formic acid has been put forward as a method for developing low-carbon hydrogen society. Kinetic, thermodynamic, and statistical mechanical principles of physical chemistry have been successfully applied for synthesizing formic acid from CO_2 and H_2 in near-room-temperature water without catalyst. To make public the achievement of our endowed research section we organized Kyoto Symposium on Novel Energy Systems. New mechanisms have been found for ether pyrolysis leading to renewable fuel molecules.



KEYWORDS

Formic Acid
Hydrogen
Carbon Dioxide
Water-Gas Shift Reaction
Carbon Neutral

Selected Publications

Yasaka, Y.; Yoshida, K.; Wakai, C.; Matubayasi, N.; Nakahara, M., Kinetics and Equilibrium Study on the Formic Acid Decomposition in Relation to the Water-Gas-Shift Reaction, *J. Phys. Chem. A*, **110,** 11082-11090 (2006).

Yasaka, Y.; Wakai, C.; Matubayasi, N.; Nakahara, M., Controlling the Equilibrium of Formic Acid with Hydrogen and Carbon Dioxide Using Ionic Liquid, *J. Phys. Chem. A*, **114,** 3510-3515 (2010).

Yasaka, Y.; Klein, M. L.; Nakahara, M.; Matubayasi, N., Exploring the Reorientation of Benzene in an Ionic Liquid via Molecular Dynamics: Effect of Temperature and Solvent Effective Charge on the Slow Dynamics, *J. Chem. Phys.*, **134,** 191101-191104 (2011).

Kimura, H.; Nakahara, M.; Matubayasi, N., In Situ Kinetic Study on Hydrothermal Transformation of D-Glucose into 5-Hydroxymethylfurfural through D-Fructose with ^{13}C NMR, *J. Phys. Chem. A*, **115,** 14013-14021 (2011).

Tsujino, Y.; Yasaka, Y.; Matubayasi, N.; Nakahara, M., Pathways and Kinetics of Anisole Pyrolysis Studied by NMR and Selective ^{13}C Labeling. Heterolytic Carbon Monoxide Generation, *Bull. Chem. Soc. Jpn.*, **85,** 124-132 (2012).

Slow Reduction of Carbon Dioxide to Formic Acid Using Hydrogen in Ambient Water without Catalyst

Hydrogen comes from and returns to water of our environment when burned; $H_2+1/2O_2=1/2H_2O$. Hydrogen is thus renewable and clean. Hydrogen is obtainable from hot water via intermediate formic acid HCOOH as found in the new version of the Water-Gas-Shift reaction, $CO+H_2O \rightleftarrows HCOOH \rightleftarrows CO_2+H_2$. Hydrogen and oxygen in air are used for fuel cells to generate power without carbon dioxide emission. The burden on hydrogen society is the difficulty of hydrogen storage and transportation. Hydrogen gas has a low energy density, and it is often compressed into a bomb or liquefied at extremely low temperatures (<–253°C) consuming energy. Hydrogen society needs a condensed matter, liquid that serves as a chemical tank for the reversible storage and release of hydrogen. Formic acid (liquid between 8.4 and 100.8°C) is such a candidate. A challenge is made here to develop a robust cycle reaction for hydrogen through formic acid. Carbon dioxide is slowly fixed as $CO_2+H_2 \rightleftarrows HCOOH$. Principles of physical chemistry, kinetics and thermodynamics, are utilized here instead of metal catalysts employed in previous works. We are motivated to go back to the natural product water.

Water drives the fixation of carbon dioxide as formic acid when the reversibility is thermodynamically tuned. Water has a driving force due to the strong hydrogen-bonding hydration of formic acid on the product (HCOOH) side and the hydrophobic hydration of hydrogen on the reactant (CO_2+H_2) side. Carbon dioxide is rather neutral between hydrophilicity and hydrophobicity; the equilibrium partition in the gas (hydrophobic) and water (hydrophilic) is neutral with the densities (concentrations) are almost the same in both phases. The yield reached in water at 70°C exceeds the previous one where catalyst and base are employed in supercritical carbon dioxide.

A high yield of formic acid has been realized as shown in Figure 1. The reaction temperature is lowered down to 80°C. The yield reaches >200 mM, which is the champion record compared to that obtained so far using rare metal catalysts. The water-driven synthesis of formic acid without catalyst is controlled not by the kinetics but by the thermodynamics. The lower the reaction temperature becomes, the higher the yield is. The yield enhancement by temperature lowering can be understood in view of the reaction exothemicity.

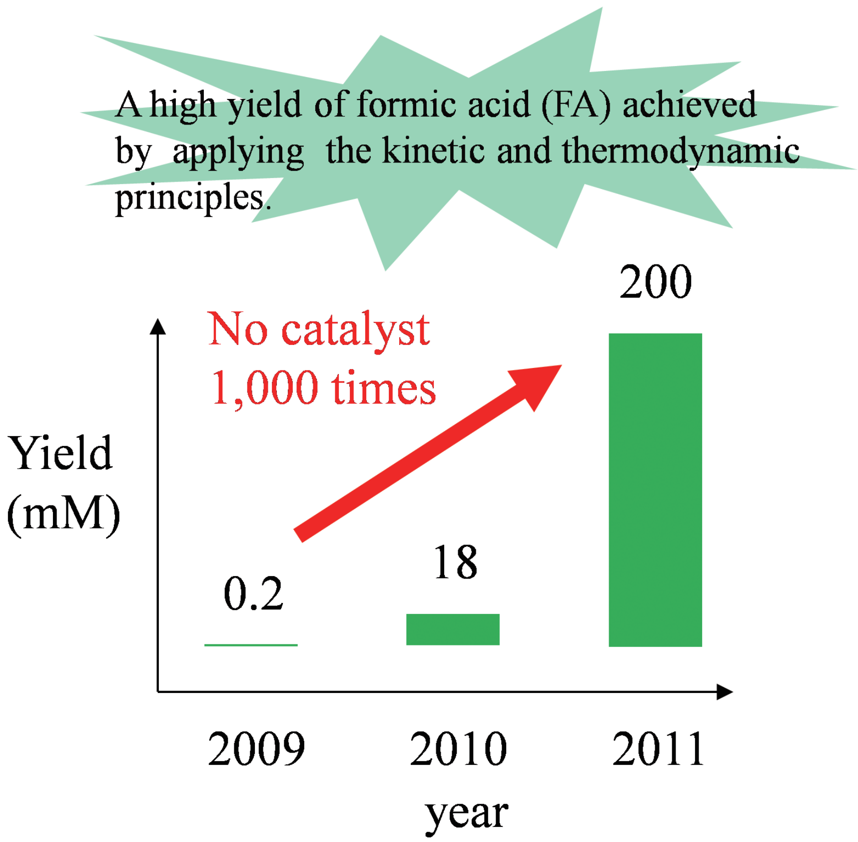


Figure 1. The hydrogen-water-energy-cycle via formic acid (FA) intermediate in the new version of the water-gas-shift reaction.