Endowed Research Section
– Water Chemistry Energy (AGC) –

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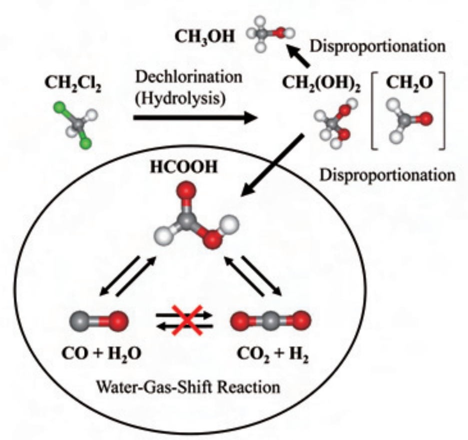
Scope of Research

Application of fundamental studies on decomposition and formation of formic acid to the hydrogen energy technology is under investigation using NMR, Raman, and IR spectroscopy. This hydrogen-water energy cycle does make a contribution to the CO_2 reduction and to a progress in energy-saving society. We are taking advantage of the solvation effect on the equilibrium of formic acid formation or decomposition from formic acid to capture and deposit CO_2 on a large scale. Fundamental aspects of pyrolysis of ethers (unimolecular reaction of ethers) are also investigated by NMR.

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



Selected Publications

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).
Nakahara M, Tsujino Y, Yoshida K, Yasaka Y, Uosaki Y, Wakai C, Matubayasi N: Recent Advances in Studies on Organic Reactions in Water at High Temperatures and High Pressures, *Rev. High Pressure Sci. Technol*, **20,** 40-49 (2010) (in Japanese).
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).
Matubayasi N, Nakahara M: Hydrothermal Reactions of Small Compounds: Free-energy Analysis of Equilibrium, *J. Chem. Phys.*, **122,** 074509-074520 (2005).
Yoshida K, Matubayasi N, Uosaki Y, Nakahara M: Scaled Polynomial Expression for Self-Diffusion Coefficients for Water, Benzene, and Cyclohexane over a Wide Range of Temperatures and Densities, *J. Chem. Eng. Data*, **55,** 2815-2823 (2010).

Topics

Green Chemical Approach to Energy and Environmental Problems Using Hot Water and Carbon Dioxide

Millions of natural and artificial organic and inorganic compounds have been found and synthesized by scientists and made useful directly in a KYOUSEI or earth-friendly style or after the industrial mass production. The materials processing and commercialization have helped us improve our way of life, welfare, and democracy for the past 300 years. Nevertheless molecular and/or ionic systems of tens of atoms, nanometer-sized, are not yet fully understood and utilized in harmony or coexistence with our environment (KYOUSEI). More advances in green science and technology are required for achieving the dream of society sustainability by solving environment and energy resource issues under the conditions of KYOUSEI. We should develop the green chemistry of rather small and simple molecules in hot water in order to reduce CO_2 emission. Thus we need to invent renewable synthetic fuels.

Energy is continuously necessary for keeping or developing our welfare for billions of people on Earth. The world-wide motorization can liberate us from severe labor work for men and women, e.g., coal and gold mining and house-keeping work. However civilization, a departure from the genuinely green primitive life, requires energy. Energy is generated by the oxidation of such fossil fuels as coal, petroleum, and natural gases where solar energy is chemically accumulated through photosynthesis by chlorophylls after the transformation and integration. Chemical energy is used directly in mechanical engines or indirectly through electricity. Also human beings and wild animals eat naturally produced or processed foods for the internal burning to generate energy. Anyway we consume energy and plants or greens on land and in sea storing energy from Sun into the chemical bonds, C-C, C-H, OH, etc. that lead to the exothermic oxidation reactions. Is our civilization merely destined to be like this? Are there no detours? Answers to these questions can create green chemistry. Can chemistry find them? Yes we can. A detour must be green. Such a green chemical way can be constructed by preventing or delaying the fossil burning as much as we can. The burning of hydrogen results only at the production of H_2O that is essentially our Earth environment because our planet is covered with water in the hydrosphere. Change the burning from carbon to hydrogen as much as we can. How to get hydrogen at a *low* cost? Cheap hydrogen is generated in iron works where hydrogen is generated as a by-product from the reaction of supercritical water and carbon, the water-gas-shift reaction. Such by-product hydrogen is also produced on a large scale by electrolysis of aqueous NaCl solution in soda industries.

Toward a new-generation hydrogen-fuel technology, we propose formic acid, which is hydrothermally connected with H_2, CO, and CO_2, as a chemical tank for hydrogen storage and transportation. This is a new version of the industrially famous water-gas-shift reaction.

In sub- and supercritical water, formic acid decomposes without catalysts in the following two pathways:

$$HCOOH \rightleftarrows CO + H_2O \text{ (decarbonylation)} \quad (1)$$

$$HCOOH \rightleftarrows CO_2 + H_2 \text{ (decarboxylation)} \quad (2)$$

The reversibility of the decarbonylation has been discovered by the direct NMR observation of the conversion of CO to HCOOH in hot water and furthermore by the stability analysis based on the free energies for the simple molecules (HCOOH, CO, CO_2, H_2, and H_2O) involved. The reversibility and the coupling of the reactions given by reactions (1) and (2) clearly indicate that formic acid exists as an intermediate in the water-gas-shift (WGS) reaction, which has long been known to generate hydrogen from water as a clean fuel. Now the new expression of the WGS reaction is:

$$CO + H_2O \rightleftarrows HCOOH \rightleftarrows CO_2 + H_2 \quad (3)$$

The kinetics and equilibrium of the new WGS reaction can be comprehensively established by determining the rate and equilibrium constants for the decarbonylation and the decarboxylation of formic acid by means of NMR. The kinetic and equilibrium investigations are carried out on the hydrothermal decomposition processes (1) and (2) of formic acid, the intermediate of the water-gas-shift (WGS) reaction, in hot water at temperatures of 170-330 °C. On the basis of the kinetics and equilibrium of the formic acid decomposition, the WGS reaction (3) can be controlled in a desirable direction by tuning temperature and pH of hot water. To develop the concept of the chemical-tank HCOOH for H_2 the optimization of the reaction parameters, such as temperature, pressure, and solvent (room temperature ionic liquids) is intensively surveyed. It has been found that when the temperature lowered to 150 °C the yield of HCOOH increases by a factor of 500 despite the slowdown of the reaction rate. The formation of HCOOH is exothermic as predicted.

[Adapted from the key-note lecture by M. Nakahara in the International, 10th KYOUSEI Science Center Symposium, Nara Women's University, 4 December 2010.]

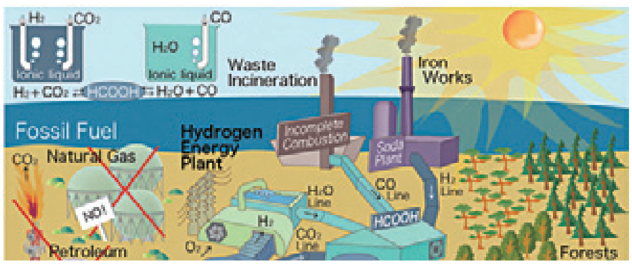


Figure 1. The hydrogen-water-energy-cycle via formic acid intermediate by using the water-gas-shift reaction.