Endowed Research Section - Water Chemistry Energy (AGC) -

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Prof ROSSKY, Peter J. University of Texas at Austin, USA, 25–29 June 2009

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 with formic acid 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.

Research Activities (Year 2009)

Publications

Yoshida K, Matubayasi N, Nakahara M: Self-diffusion Coefficients for Water and Organic Solvents in Extremely Low-density Supercritical States, *J. Mol. Liq.*, **147**, 96-101, 2009.

Yasaka Y, Wakai C, Matubayasi N, Nakahara M: Water as an In-situ NMR Indicator for Acid Impurities in Ionic Liquids, *Anal. Chem.*, **81**, 400-407, 2009.

Presentations

Supercritical Water from the Viewpoint of Nanoscience, Nakahara M, The 1st Symposium on Center for Nanoscience Research, Kyoto, 7 March 2009.

Solution Chemistry Today and Future Perspectives, Nakahara M, The 76th Conference on the Electrochemical Society of Japan, Kyoto, 31 March 2009.

The Old Man and the Chemistry, Nakahara M, Workshop on the Future of Solution Chemistry, Kyoto, 27 June 2009. Hydrothermal Chemistry of Formic Acid and New Scheme of Hydrogen Technology, Nakahara M, Yoshida K, Yasaka Y, Tsujino Y, Wakai C, Matubayasi N, International Conference on High Pressure Science and Technology (Joint AIRAPT-22 & HPCJ-50), Tokyo, 31 July 2009.

Formic Acid as a Chemical Tank for Hydrogen, Nakahara M, The International Association for the Properties of Water and Steam, Netherlands, 8 September 2009.

Grant

Nakahara M, Development of Formic Acid Production Highly Controlled by the Water-Gas Shift Reaction, Aiming at the Hydrogen Storage and the Hydrogen Transportation, to Promote Basic Research by Research Personnel in Private-Sector Business, Japan Science and Technology Agency, 1 December 2009–30 November 2010.

The Hydrogen-Water Energy Cycle with Formic Acid as a Chemical Tank for Hydrogen

Water is potentially a useful medium for organic chemical reactions. At room temperature, however, the utility of water as a reaction medium is restricted by the low solubility of organic compounds. Super- and subcritical water is a promising medium to overcome this restriction. When the temperature is elevated, water mixes well with organic compounds, including such nonpolar gases as H₂, CO, and CO₂. The hydrogen bonding persists in hot water, and the modified water-gas-shift (WGS) reaction,

 $CO + H_2O \leftrightarrows HCOOH \leftrightarrows CO_2 + H_2$,

can be controlled in hot water to develop the hydrogenwater-energy cycle technology. Our mission is to develop the earth-friendly technology using the new WGS reaction mentioned above. The new WGS reaction has the potential to store and transport hydrogen safely and to reduce the green-house gas CO_2 emission that may induce some climate changes. Hydrogen is an ultimately clean fuel compared with fossil fuels; CO₂ emission per energy from hydrogen is the lowest and is recyclable energy from H₂O and CO. However, the drawback of the hydrogen fuel arises from the low liquefaction temperature. This results in a high cost and delays the realization of the clean hydrogen age. Fuel compactness and fluidity, as attained in the liquid state, are necessary for the low-cost transportation and storage. This can be overcome by taking advantage of formic acid that is found as an intermediate in the water-gas shift reaction. CO₂ can be fixed to formic acid by utilizing surplus hydrogen which is discharged by a plant such as the soda plant and the iron work. The hydrogen-water-energy-cycle technology with the formic acid intermediate can realize both the new clean energy cycle and the low CO₂ emission, as shown in Figure 1.

On the basis of the kinetics and equilibrium of the formic acid decomposition, the new WGS reaction can be controlled in a desirable direction by tuning temperature and pressure of hot water or ionic liquids. The application of the new WGS reaction for hydrogen energy production and storage is thus hopeful in the future.



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