

## Chemical reactions in supercritical water and their applications

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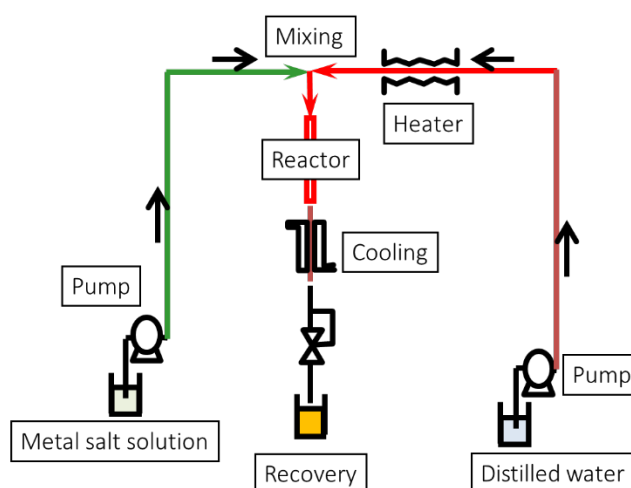
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### Abstract

This lecture will explain the supercritical water reactions and its related technologies that our group in Tohoku university has explored for more than 30 years. The research has focused on the fundamentals and applications of a flow reaction process that has enabled detailed kinetic studies of unusual reactions in supercritical fluids. The use of supercritical water in diverse applications has been studied such as heavy oil reforming, waste polymer decomposition and chemical raw materials recovery, cellulose hydrolysis and sugar recovery, lignin decomposition and chemical raw materials recovery, relevant organic reactions, and nanoparticle synthesis, all without using any catalysts. The research and developments have been done based on the understanding of the unique feature of supercritical water to dissolve organic molecules, and the ability of water molecules to function as an acid or base catalyst in promoting hydrolysis. That fundamental research led to the commercial process for the first supercritical chemical recycling process in Japan, in which the distillation bottom residue of the toluene diisocyanate (TDI) production process (raw material for polyurethane) was hydrolyzed in supercritical water without any catalyst to recover toluene diamine, which can be re-used in the TDI production process.

Regarding inorganic materials synthesis, the author invented “supercritical hydrothermal synthesis” for the continuous preparation of metal oxide nanoparticles, that have found worldwide industrial applications. In supercritical water, especially near the critical point, both the dielectric constant and density change significantly. Under constant pressure, the dielectric constant greatly decreases from near the critical point with increasing temperature. This change in the dielectric constant greatly affects the reaction. For example, in hydrothermal synthesis, which is the formation of a metal oxide by hydrolysis of the corresponding metal salt, a decrease in the dielectric constant greatly increases the rate of hydrolysis while substantially decreasing the solubility of the metal oxide product. The two-fluids mixing type flow system, where an aqueous metal salt solution was mixed with supercritical water shown in Figure 1 enables to heat the solution to the supercritical state with a very short mixing time constant, that could never be achieved by conventional reactor systems. Detailed kinetic combined with DFT simulation studies around the critical point have elucidated that the intrinsic reaction kinetics in SCW can be predicted by the Kirkwood theory, namely by the dielectric constant effect.



**Fig. 1** Two-fluids mixing flow system for particle synthesis in supercritical water

In the application of nanomaterials, one of the big challenges is the difficulty in the dispersion of nanomaterials in polymers and solvents. The affinity between nanoparticles and their carrier media (either polymer or solvent) can be improved by binding organic molecules to the surfaces of nanoparticles. However, while nanoparticles are hydrophilic and disperse well in water, organic molecules targeted for binding with

nanoparticles can only dissolve in organic solvents. Such organic modification with commercial productivity, namely at high concentration of organic molecules is therefore not possible.

Based on the understanding of both inorganic nanoparticle synthesis and organic reactions in supercritical water, the simultaneous reactions of these two reactions under supercritical conditions was studied. As a result, organic-inorganic hybrid nanoparticles could be synthesized in a supercritical state. Because organic molecules at high concentrations can form a homogeneous phase with water only under the supercritical condition, this material represents a new class of nanomaterials that can only be prepared in the supercritical phase. Figure 2 shows the images of dispersion of metal oxide nanoparticles synthesized in supercritical water.

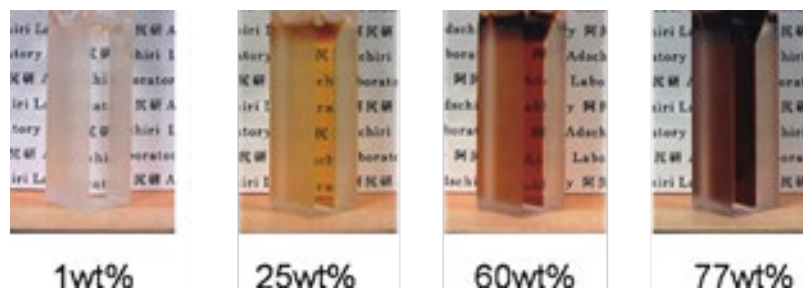


Fig. 2 Metal oxide nanoparticle completely disperse in organic solvent

Using this method of modification with organic compounds has led to the fabrication of nanoparticles with high affinity for organic solvents and polymers, and has thus allowed high concentration dispersions of these nanoparticles into those media (solvent or polymer) to be achieved. This achievement led to the successful synthesis of nano inks (highly concentrated nanofluids) for 3D inkjet printing and printed electronics. New hybrid polymers with nanoparticles demanded by the industry have also been developed, including transparent high-refractive-index flexible film materials, and materials with high thermal conductivity, high insulation, high adhesion, and modality.

Recent research in catalysis revealed that high catalytic activity can be achieved by controlling exposure of the active face of the catalyst. However, since the most active face is also typically the least stable face, the synthesis of crystals with the active face exposed is considered impossible in principle; This is the case especially for nanoparticles with high surface energy. However, in the case of organic-modified nanoparticle synthesis, an unstable face exhibits higher reactivity with the organic molecules, and thereby the most reactive face will be selectively modified and protected during nanoparticle formation and growth. Using this organic-modified nanoparticle synthetic method, nanoparticles bearing an exposed reactive face were successfully synthesized. In the evaluation of the catalytic activity, extremely high oxygen mobility and oxidative catalytic activity were obtained, even at low temperatures. In general, high oxygen mobility in such materials as ceramics is only observed at high temperatures of 400 °C or higher. In contrast, for the nanoparticles with the most active face exposed, high oxygen mobility was observed even at 150 °C, suggesting its use for low temperature solid electrolytes (oxygen carriers) or its high catalytic activity for oxidation. Indeed, it is demonstrated that steam reforming of heavy oils or biomass wastes (black liquor) in water can occur even at low temperatures. It is anticipated that this technology could also be applied to hydrogen synthesis using low-temperature waste heat, a process that until now has been considered impossible.