Continuous Flow Synthesis of Nanoparticles Using Supercritical Water: Process Design, Surface Control, and Nanohybrid Materials

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Abstract
A continuous flow reaction process in which a metal salt solution is rapidly mixed with high-temperature water was employed to achieve rapid heating up to supercritical conditions. A quarter of a century has passed since the supercritical hydrothermal method was first proposed. This paper introduces recent advances in science and technology related to the supercritical process. Process design, kinetics, reaction atmosphere (redox) control, morphology control, organic modification of nanoparticles, nanocatalysts, and organic-inorganic hybrid materials are reviewed for promising applications of the supercritical process.

Keywords: supercritical hydrothermal synthesis, nanoparticle, surface organic modification, organic-inorganic hybrid, nanocatalysts, nanofluids

1. Introduction
Understanding structural formation phenomena is essential for the fabrication and control of nanomaterials. The classification of these phenomena is possible with the degree of non-equilibrium achieved during processes such as supercooling and supersaturation (Adschiri T. and Yoko A., 2018). The process of homogeneous nucleation, which occurs when the degree of non-equilibrium is sufficiently high, is suitable for the fabrication of nanoparticles with small particle size and narrow size distribution. However, it is difficult to achieve a high degree of non-equilibrium.

In the supercritical hydrothermal method (Adschiri T. et al., 1992), high supersaturation can be achieved by rapid heating of a metal salt solution at room temperature up to supercritical conditions due to the low solubilities of ions in supercritical water. The solubilities of polar materials are low because of the low dielectric constant of supercritical water. In other words, in supercritical water, ionic materials are unstable while non-polar materials are stable. Rapid heating can be achieved by rapid mixing of fluids using continuous flow reactors, and the low kinetic viscosity of supercritical water accelerates mixing during fluid flow. Thus, a low dielectric constant and low kinetic viscosity are the key factors for supercritical hydrothermal synthesis, which cannot be obtained by conventional low-temperature batch-type hydrothermal reactions.

The properties of water change continuously with change in temperature because first-order phase transitions do not occur beyond the critical point (374 °C, 22.1 MPa). Fig. 1 shows the temperature dependence of water properties, such as density, viscosity, and dielectric constant. As can be seen in Fig. 1(a), the density of supercritical water is lower than that of liquid water but is much higher than that of steam (Wagner W. and Pruß A., 2002). On the other hand, the viscosity of supercritical water is as low as that of steam (Kestin J. et al., 1984). These physical properties of supercritical water are the origin of the characteristic transport properties, such as low kinetic viscosity. Fig. 1(b) shows the temperature dependence of the dielectric constant, which determines the character of solvents, and a significant change is observed in the supercritical region (Uematsu M. and Frank E.U., 1980). Fig. 1(c) shows the dielectric term in solvation energy from the Onsager model (Onsager L., 1936), which ranges between 0 and 0.5. The change in the dielectric constant around the critical point, shown in Fig. 1(c), is an important factor affecting the solubility and reaction rate of ionic reactions. The solvent effects are significantly tunable by changing the pressure around the critical temperature region, even
under isothermal conditions.

In some cases of nucleation and growth (e.g., solidification of liquid), just aggregation of monomer atoms or molecules occurs during nucleation and growth without any chemical reaction. However, in the case of hydrothermal synthesis, hydrothermal reactions occur through the nucleation and growth stages. Hydrothermal reactions, which include hydrolysis and dehydration of metal ions, are represented by the following equations:

\[
M(NO_3)_x + xH_2O = M(OH)_x + xHNO_3 \quad (\text{Eq. 1})
\]

\[
M(OH)_x = MO_x + \frac{x}{2}H_2O \quad (\text{Eq. 2})
\]

The reaction equilibria of these reactions shift to form hydroxides and oxides as the temperature increases. Particularly under supercritical conditions, a lower dielectric constant and solubility of ionic species lead to hydrothermal reactions with high reaction rates. One should note that water acts as a reactant and a solvent.

The phase behavior in supercritical water is another important aspect. As already explained, ionic materials are destabilized in supercritical water and the solubilities of inorganic materials are extremely low. Methods for estimating the solubility of ionic materials have been presented in previous studies (Helgeson H.C. et al., 1981; Tanger J.C. and Helgeson H.C., 1988; Oelkers E.H. and Helgeson H.C., 1993; Sue K. et al., 2002; Lencka M.M. and Riman R.E., 1993). In contrast to ionic materials, nonpolar organic materials, which lead to phase separation in low-temperature water, are miscible with supercritical water. This phase behavior is important for in situ organic surface modification.

Various studies on the supercritical hydrothermal synthesis method have been conducted in recent decades following the first proposal of the methodology (Adschiri T. et al., 1992). Recent scientific and technological advances of the supercritical process are reviewed in this paper.
2. Process design and kinetics

One of the characteristic aspects of supercritical hydrothermal synthesis is the rapid reaction realized by the use of a continuous flow reactor, as shown in Fig. 4. In essence, the low kinetic viscosity of supercritical water is a positive factor to accelerate fluid mixing. Mixing of supercritical water and low-temperature water has long been an important topic in supercritical hydrothermal synthesis because the mixing states affect the quality of the synthesized nanoparticles (e.g., particle size and its distribution). The rate of mixing should be high compared to the reaction rate. Various studies regarding the mixing state have been conducted, revealing that sufficient mixing can be determined using the Reynolds number \((Re)\) as an index for the mixing state (Kawasaki S. et al., 2010a, 2010b, 2015; Sue K. et al., 2010, 2011). For example, Kawasaki et al. reported that \(Re > 4 \times 10^4\) was required based on results from experiments on various materials (Kawasaki S. et al., 2010a, 2010b). The required mixing state differs depending on the materials because of the difference in the reaction rate for each material. The Damköhler number \((Da)\), defined as the ratio of reaction rate to mass transfer rate, was applied to determine the required mixing conditions for each target material (Aoki N. et al., 2016). \(Da\) can be expressed as the following equation for first-order reactions, where \(k\) denotes the reaction rate constant, \(d\) denotes the diameter of the mixer, and \(u\) denotes the flow velocity:

\[
Da = \frac{kd}{u}. \tag{Eq. 3}
\]

The practical design of supercritical hydrothermal synthesis process systems necessitates the evaluation of the reaction rate. The reaction rate and particle size of the products vary with different mixing conditions. Based on fluid mixing studies, it is possible to conduct kinetics studies for supercritical hydrothermal reactions under reaction control conditions without retardation of apparent reaction rates caused by insufficient mixing (Aoki N. et al., 2016). Fig. 5 shows the particle sizes of the obtained CeO_2 nanoparticles at different temperatures and \(Re\) during mixing. The particle size converged as \(Re\) increased, and similar convergence was observed for conversion of cerium ions. The reaction rate of cerium nitrate under sufficient mixing conditions, i.e., reaction control conditions, was studied through changing the residence time by changing the reactor volume. It was reported that the reaction can be considered as a first order reaction for cerium ion consumption. Acceleration of the reaction rate was observed near the critical point (Aoki N. et al., 2016), as shown in Fig. 6. The solvent effects of the dielectric constant can be analyzed with various models. The following equation shows the Onsager-Kirkwood model. Here, \(k\) is the reaction rate constant, \(k_g\) is the reference reaction rate constant, \(\mu^d\) and \(\mu_i\) represent the dipole moment in the
transition state and the initial state, respectively, \( r^\ddagger \) and \( r_i \) represent the molecular radius in the transition state and the initial state, respectively, \( R \) is the universal gas constant, \( T \) is the temperature, and \( \varepsilon \) is the dielectric constant.

\[
\ln k = \ln k_g + \left( \frac{\frac{\mu^{12}}{r^{13}} - \sum \frac{\mu_i^2}{r_i^3}}{RT} \left( \frac{\varepsilon - 1}{2(\varepsilon + 1)} \right) \right) \quad \text{(Eq. 4)}
\]

When the polarity difference between the initial state and transition state is large, the second term has a significant effect on the reaction rate. The destabilization effects of ionic compounds emerge under low dielectric constant conditions, as shown in Fig. 1(c), and the reaction rate constant becomes closer to that of gas-phase reactions \( k_g \) in Eq. 4.

3. Atmosphere control (redox control)

Supercritical water can be an oxidative medium because water can act as an oxidant. However, as explained in the introduction, supercritical water can form a homogeneous phase with gaseous materials, which enables control over the redox atmosphere. When hydrogen is used as a reductant, the following two reaction equilibria should be considered:

\[
M(NO_3)_x + \frac{x}{2}H_2 = M + xHNO_3 \quad \text{(Eq. 5)}
\]

\[
M + xH_2O = xH_2 + MO_x \quad \text{(Eq. 6)}
\]

Considering the redox potentials, noble metals such as Au and Pt can easily form. However, comparatively large amounts of hydrogen are required to obtain base metals such as Fe, Co, and Ni. Low-temperature conditions are favored for equilibrium because the reduction of metal oxides is an exothermic reaction. However, in terms of the phase behavior of hydrogen and water, higher temperature conditions are favored because of the homogeneous phase formation of hydrogen and water, as shown in Fig. 3. The chemical potential of dissolved hydrogen in water is higher than that of gaseous hydrogen. Thus, the reduction reactivity of metal oxides is higher in water, compared to the gas phase. Thus, near-critical conditions are appropriate for obtaining the metal state based on reaction equilibrium, phase behavior, and reactivity.

Metal and metal oxide nanoparticles can be synthesized in a reductive atmosphere. Various metal nanoparticles have been synthesized by loading formic acid, which produces hydrogen during decomposition under high-temperature conditions (Clercq M. le et al., 2001; Sue K. et al., 2004; Ohara et al., 2007a; Arita T. et al., 2011a). Thermodynamics (Arita T. et al., 2011a; Seong G. et al., 2011) and kinetics (Seong G. et al., 2014; Seong G., 2012) studies found that synthesis with a batch reactor required larger amounts of hydrogen than the theoretical amount, suggesting that reduction was retarded following the formation of large metal oxide particles. The use of a flow reactor suppressed the growth of metal oxide particles before the reduction reaction, and metal nanoparticles were formed when the theoretically predicted amount of hydrogen was used. Moreover, stability issues, such as surface oxidation, were investigated with and without organic modifiers. Iron-platinum metal alloy nanoparticles were also successfully synthesized in this reaction system (Arita T. et al., 2011b).

Valence control during nanoparticle synthesis is an important technique not only for metal particles but also for some types of metal oxides. Metal ions must be reduced to the appropriate valence state in order to form target materials. For example, copper oxide nanoparticles were synthesized using organic chelates as starting materials and the ligands of those chelates as reducing agents. Mono-phase Cu2O nanoparticles were obtained using [Cu(Gly)2]2 with the shortest ligand chain length (Togashi T. et al., 2010). Mono-phase CuAl2O4 was also successfully synthesized with control over the copper valence, using formic acid as a reducing agent (Sato T. et al., 2008). Co-doping of tin and zinc in indium oxide was also studied with the valence control of tin to produce the target phase using formic acid (Lu J. et al., 2016).

4. Composite oxides

Composite oxides are valuable for various applications. Not only mono-component particles but also various composite oxides have been synthesized by the supercritical
hydrothermal method. For example, LiCoO$_2$ and LiMn$_2$O$_4$ cathode materials have been synthesized for use in lithium-ion batteries by the supercritical hydrothermal method, and highly stable charge and discharge properties were recorded after several charge-discharge cycles (Adschiri T. et al., 2001). The high crystallinity of particles synthesized by supercritical hydrothermal synthesis possibly leads to better stability for the mobility of lithium ions, compared to materials with the same composition obtained from conventional processes.

Tuning of reaction conditions such as temperature, pH, heating rate, reaction time, and feeding ratio of starting materials are essential to obtain a single-phase composite oxide. Copper manganese oxide nanoparticles were synthesized using a batch reactor and a continuous flow reactor. Formation of byproducts was found to be suppressed with a continuous flow reactor (Rangappa D. et al., 2008). The results suggest that heating rates affect the structural formation of the composite oxide phase. Yttrium aluminum garnet (YAG) nanoparticles were synthesized with a continuous flow reactor, and it was shown that slow heating led to the formation of byproducts (Hakuta Y. et al., 1999).

The rapid reaction owing to high supersaturation causes a metastable or non-equilibrium state in supercritical water. The formation of unique structures such as metastable, highly doped, and deficient structures has been reported (Hakuta Y. et al., 1998; Yamamoto K. et al., 2014, 2015; Zhu Y. et al., 2015; Yoko A. et al., 2014, 2016a, 2016b, 2017). Barium hexaferrite could be synthesized in approximately 1 s in a continuous flow reactor with excessive barium (Hakuta Y. et al., 1998). The synthesized barium hexaferrite was transformed to barium di-ferrite and barium mono-ferrite after it was treated in batch reactors under the same temperature and pressure as the synthesis conditions, suggesting that the synthesized barium hexaferrite phase was a non-equilibrium state. Recently, Gd-doped ceria nanocubes (Yamamoto K. et al., 2014, 2015) and Cr-doped ceria (Zhu Y. et al., 2015) were synthesized by the supercritical hydrothermal method. High doping concentration, including non-equilibrium composition, can be achieved through rapid reactions in a flow reactor. Moreover, highly deficient structure formation was reported for several types of perovskite oxides due to the difference in the precipitation driving force (Yoko A. et al., 2014, 2016a, 2016b, 2017).

5. Organic modification

In addition to the synthesis of metal and metal oxide nanoparticles, surface modification of those nanoparticles in the reaction field during particle formation is also possible with supercritical hydrothermal synthesis. Table 1 shows the various types of surface modified nanoparticles reported by Adschiri group. Using in situ surface modification, particle size and shape control were achieved because the surfactant molecules can affect nucleation and growth, i.e., the interface energy can be tuned with organic molecules. Fuji et al. (2016) reported that the modification density varies depending on the length of modifiers, resulting in particle size variation.

Control over nanoparticle morphology as a result of crystal facet control was realized by the coexistence of organic molecules during nanoparticle formation, e.g., synthesis of CeO$_2$ nanocubes (Zhang J. et al., 2007), Co$_3$O$_4$ (Mousavand T., 2009), and CoAlO$_2$ (Rangappa D. et al., 2007a, 2007b), as shown in Fig. 7. Particle morphology was controlled by selecting the appropriate modifier species and the amount of them. Coexistence of modifiers can affect particle formation by decreasing the surface energy of the nanocrystals. The surface stability order of a CeO$_2$ crystal, determined by the surface energy of each CeO$_2$ crystal surface, is {100} > {110} > {111}, and the equilibrium shape of a CeO$_2$ crystal without organic modification is octahedral with exposed {111} surfaces. Particularly in the case of CeO$_2$, it is meaningful to expose the {100} surfaces because of their high catalytic activity, although it is difficult to expose such unstable surfaces. On the other hand, organic modifiers can attach to an unstable surface and stabilize the surface during nanoparticle formation. As such, it is possible to fabricate nanocubes by exposing the {100} surfaces. These controls are effective for fine-tuning the properties of ceramic nanocrystals. The applications of CeO$_2$ nanocubes are discussed in Section 8.

One of the significant factors enabling surface modification is the phase behavior of high-temperature water and organic compounds, as explained in the Introduction section. An experiment was conducted to confirm the phase behavior of the modifiers and water. Fig. 8 shows the visualized reaction field of octanoic acid and Ce(OH)$_4$ aqueous solution at different temperatures. At lower temperatures, phase separation of the organics and water was observed, and a homogeneous phase was formed at 330 °C (Adschiri T. et al., 2015).

Another important characteristic of surface modified nanoparticles is dispersibility. Surface-modified nanoparticles disperse well in solvents, which cannot be realized with ex situ surface treatments. The dispersibility and stability of surface-modified nanoparticle dispersions due to covalent surface modification are introduced in Section 7.

The important points of surface modification by supercritical hydrothermal synthesis are high modification density and covalent bonding on the metal oxide surface. As modifiers, carboxylic acids, amines, phosphonic acids, aldehydes, alcohols, and catechols have been applied as shown in Table 1. The degree of modification can be analyzed by
thermogravimeter differential analysis (TG-DTA). The modified state is analyzed using a Fourier transform infrared spectrometer (FT-IR) and nuclear magnetic resonance (NMR). The modification density is typically as high as 4–7 molecules per square nanometer, which is consistent with the number of metal atoms exposed at the particle surface. Fig. 9 shows an example of $^1$H NMR spectra comparing decanoic acid and decanoic acid-modified CeO$_2$ nanoparticles in CDCl$_3$ (Arita T. et al., 2011c). Obviously, the motion of the surfactants is restricted due to binding on the nanoparticles. Chemical bond formation by in situ modification of the supercritical method has been confirmed.

Very recently, surface-modification of CeO$_2$ nanoparticles synthesized in supercritical water was observed at the atomic scale using state of the art aberration-corrected scanning transmission electron microscopy (STEM) imaging and electron energy loss spectra (EELS) techniques (Hao X.D. et al., 2018). It was observed that the surface of the CeO$_2$ nanoparticles was covered by carbon, based on the composition distribution mapping of cerium, oxygen, and carbon, as shown in Fig. 10. Moreover, a single surfactant molecule can be detected using STEM analysis. The modification state can be confirmed at the atomic

| Core particles | Modifiers | Ref. |
|---------------|-----------|-----|
| AlOOH         | n-Hexyaldehyde, n-Hexylamine | Mousavand et al., 2007a |
| ZnO           | Hexanol, Hexanal, Hexylamine  | Ohara et al., 2007b |
| Fe$_3$O$_4$    | n-Decanoic acid                 | Takami et al., 2007 |
| Fe$_3$O$_4$    | n-Decylamine                     | Takami et al., 2007 |
| Heptanol       | 3,4-Dihydroxyhydrocinnamic      | Togashi et al., 2012 |
| Ions oxides    | Hexanoic acid                    | Arita et al., 2011a |
| CeO$_2$       | n-Decanoic acid, n-Decylamine    | Mousavand et al., 2009 |
| CeO$_2$       | Hexanedioic acid                 | Takami et al., 2008 |
| CeO$_2$       | Hexanoic acid, Decanoic acid, Stearic acid | Arita et al., 2010a |
| CeO$_2$       | Adipic acid, Pimelic acid, Sebacic acid, Dodecanedioic acid | Taguchi et al., 2009 |
| CeO$_2$       | Polyvinyl alcohol, Polyacryl acid | Taguchi et al., 2011 |
| CeO$_2$       | L-Glutamic acid, L-Aspartic acid, L-Arginine | Litwinowicz et al., 2014 |
| CeO$_2$       | Hexanoic, Octanoic, Decanoic, Dodecanedioic, Tetradecanoic, Hexadecanoic, Octadecanoic, Oleic acids | Taguchi et al., 2014 |
| Cr-doped CeO$_2$ | Decanoic acid                     | Zhu et al., 2015 |
| TiO$_2$       | Hexaldehyde                      | Mousavand et al., 2007b |
| TiO$_2$       | Ethyl 11-diethoxyphos-phoryldecanoate | Arita et al., 2010b, 2010c |
| ZrO$_2$       | 6-phenylhexanoic acid, 3-phenylpropionic acid | Takigawa et al., 2017 |
| HfO$_2$       | 3-phenylpropionic acid           | Hiyama et al., 2018 |
| HfO$_2$       | Decylamine, Decanal, Decanoic acid | Saharaneshin et al., 2012b |
| Bi$_2$O$_3$   | 3-phenylpropionic acid           | Hiyama et al., 2018 |
| Gd(OH)$_2$    | 3,4-Dihydroxyhydrocinnamic      | Singh et al., 2013 |
| FePt          | Oleic acid                      | Arita et al., 2011b |
| BaO·6Fe$_2$O$_3$ | Oleic acid                   | Rangappa et al., 2010 |
| CoAl$_2$O$_4$ | Oleic acid, Decanoic acid       | Rangappa et al., 2007a |
| CoAl$_2$O$_4$ | Hexanoic acid, 1-Hexylamine      | Rangappa et al., 2007b |
| CuMn$_2$O$_4$ | Hexanoic acid, 1-Hexylamine      | Rangappa et al., 2008 |
| ITO (Indium Tin Oxide) | Hexanoic acid | Lu et al., 2012 |
| IZTO (Zn dope ITO) | Hexanoic acid | Lu et al., 2016 |
level by direct observation.

The effects of modifiers on nanoparticle structure are also an interesting and significant topic. Stabilization of oxygen vacancies due to the existence of organic modifiers was reported for CeO$_2$ (Zhang J. et al., 2011a). The valence state of cations can also be affected by surface modifiers. This result suggests that the effects of modifiers on nanoparticle structure cannot be neglected in some cases.

6. Cluster formation

Arranging individual nanocrystals into superlattices is a challenging topic for applications of nanoparticles. Cluster synthesis has been achieved using the supercritical method. Modifiers with functional groups on both ends of a molecular chain, i.e., bifunctional compounds

![Fig. 7 TEM images of CeO$_2$ nanocubes with and without modifiers (Zhang J. et al., 2007), Co$_3$O$_4$ nanocubes (Mousavand T. et al., 2009), BaFe$_{12}$O$_{19}$ nanocubes (Rangappa D. et al., 2010), and CuAlO$_2$ nanocubes (Rangappa D. et al., 2007a, 2007b).](image)

![Fig. 8 Visualized phase behavior of modifiers and aqueous Ce(OH)$_4$ with increasing temperature (Adschiri T. et al., 2015).](image)

![Fig. 9 $^1$H NMR (400 MHz) spectra of decanoic acid-modified CeO$_2$ nanoparticles (5 mg) and free decanoic acid (1 mg) in 500 μL of CDCl$_3$. The numbering of carbon is indicated in the upper left corner. Reprinted with permission from Ref. (Arita T. et al., 2011c). Copyright: (2011) American Chemical Society.](image)
such as dicarboxylic acid, were used to bridge between nanoparticles (Takami S. et al., 2008), and it was found that the orientation of each nanoparticle was ordered. Surface-modified nanoparticles might behave as building blocks during superstructure formation. So far, the assembly of surface-modified CeO$_2$ (Takami S. et al., 2008; Litwinowicz A.A. et al., 2014) and Gd(OH)$_3$ (Singh V. et al., 2013) nanoparticles has been reported. Fig. 11 shows SEM and TEM images and selected area electron diffraction (SAED) patterns from the obtained Gd(OH)$_3$ cluster (Singh V. et al., 2013). In this case, 3,4-dihydroxy hydrocinnamic acid (DHCA) was used as a bridge molecule in an alkaline medium. Dissociation of the functional group and surface charge determined the interaction between nanoparticles, and surface modifiers resulted in distinct morphology changes. Nanocrystal ordering with specific orientation was observed from SAED patterns, suggesting that inorganic meso-crystals can be formed with organic molecules by applying this method. In addition, the formation of the characteristic secondary structure, composed of primary nanoparticles with preferential attachment of organic molecules through aggregation of primary particles, was investigated (Sahraneshin A. et al., 2012a).

The design of nanoclusters can be developed using opti-
mized organic modifiers during supercritical hydrothermal synthesis. Newly designed nanoclusters are expected to broaden further the application of nanoparticles.

7. Nanoparticle dispersion

The dispersibility of nanoparticles is a key factor for industry to make full use of nanoparticle characteristics. As explained in Section 5, nanoparticles synthesized in supercritical water can be dispersed in solvents owing to surface organic modification. Dispersed nanoparticle colloid systems or suspensions have been studied recently as nanofluids (Ogi T. et al., 2017). Nanoparticles covalently modified by organic molecules and synthesized by supercritical hydrothermal synthesis have also gained attention due to their high dispersibility and stability.

By using appropriate solvents and modifiers, highly concentrated nanoparticle dispersions up to 77 wt% can be fabricated (Arita T. et al., 2012). Fig. 12 shows a picture of decanoic acid modified CeO₂ nanoparticles in cyclohexane. The mono-dispersed colloids exhibit low viscosity, even at high concentrations (Arita T. et al., 2012).

A new heat transfer film was developed by applying the organic surface modification technique. High heat conductive materials such as silicon nitride and alumina were reacted with organic compounds, resulting in high affinity to polymer materials and high fluidity, even at loading rates as high as 80 vol%. The fabricated heat transfer film has thermal conductivity as high as 40 W/(mK). The implementation of a heat transfer film made of surface-modified nanoparticles in semiconductor packages was demonstrated, with the package maintaining high insulation and thermal conductivity. Fig. 13 shows a schematic diagram of the thermally conductive hybrid materials (Adschiri T. et al., 2012).

8. Catalytic reaction

Metal and metal oxide nanoparticles synthesized by the supercritical hydrothermal method can be used in several catalytic applications. As explained in Section 5, morphology controls are possible by using surface organic modification. In the case of CeO₂, {100}-exposed CeO₂ nanocubes were obtained in the presence of organic modifiers. The role of organic molecules here is to expose certain crystal surfaces. However, these molecules can hinder catalytic reactions at the surface. Thus, surfactants need to be removed for the modified structures to be used as catalysts, and as-synthesized particles are calcined to remove organic modifiers before the nanoparticles were used as catalysts. It should be noted that the cubic shape was maintained, even after being calcined at 300 °C.

The oxygen storage capacity (OSC) of synthesized CeO₂ nanoparticles has also been measured. It was found that OSC was significant at temperatures as low as 150 °C, whereas oxygen mobility was observed for ordinary, non-facet-controlled CeO₂ at approximately 400 °C (Zhang J. et al., 2011a). In addition, 5 mol% Cr-doped CeO₂ nanocubes were synthesized, exhibiting higher OSC than undoped CeO₂ nanocubes (Zhu Y. et al., 2015). As explained in Section 4, the supercritical hydrothermal method can be applied for high-concentration doping of metal oxide nanoparticles to further improve these nano-
catalysts.

Catalytic conversion of lignin was studied under hydrothermal conditions with facet-controlled CeO$_2$ nanocubes (Seong G. et al., 2017, 2018). As for the chemical recovery of phenolic compounds from lignin, polymerization of those phenolic compounds as lignin decomposition products is a key issue to be solved. Degradation of lignin with CeO$_2$ nanocubes was achieved alongside polymerization suppression. This occurs because aldehydes were oxidized rapidly, which can act as a bridge molecule during polymerization with phenolic compounds. Fig. 14 shows photographs and UV-vis spectra for a lignin aqueous solution before and after the reactions. The UV spectra at 280 nm are attributed to the phenolic compounds, suggesting that larger amounts of phenolic compounds can be recovered with CeO$_2$ nanocubes. Similar reactions were conducted for biomass waste from the paper industry (black liquor) and heavy oil. Black liquor and bitumen decomposition with CeO$_2$ nanocubes was observed, and hydrogen formation by water reforming with the partially reduced ceria was detected in both cases.

These reforming reactions are endothermic. Significant decrease in reaction temperatures can be achieved by using new catalysts, which enables the efficient use of low-temperature waste heat for the endothermic reforming reactions. Exposing specific active crystal faces, doping metals at high concentrations, and forming nanoclusters are expected to maximize catalytic activity. Further development of catalyst design is promising for use in a variety of catalytic reactions.

9. Conclusion

In this paper, recent advances in supercritical hydrothermal synthesis have been presented. Process kinetics and design are significant factors controlling the properties of the reaction products. Surface modification is a key technique that can be used to fabricate nanoparticle dispersion and control crystal facet exposure. Results on particle structure characteristics, such as non-equilibrium states, deficient structures, and strong bonding through modification, have broadened new technological fields and facilitated the development of new catalysts and hybrid materials. Further studies are necessary to implement the technology in particle and powder engineering applications.

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