



# A kinetic study of catalytic hydrothermal reactions of acetaldehyde with cubic CeO<sub>2</sub> nanoparticles



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## ABSTRACT

The hydrothermal reactions of acetaldehyde using cubic CeO<sub>2</sub> nanoparticles were performed on the assumption that repolymerisation of monolignin by aldehydes can be suppressed by catalytic oxidation in the presence of CeO<sub>2</sub> during depolymerisation of lignin. The catalytic potential of cubic CeO<sub>2</sub> nanoparticles was evaluated by comparing them with octahedral CeO<sub>2</sub> via their structural, morphological, catalytic characterisation and in terms of catalytic reactivity. In the cubic CeO<sub>2</sub> system, the conversion of acetaldehyde and the selectivity of acetic acid (oxidation of acetaldehyde) were higher than those in octahedral CeO<sub>2</sub>, while the selectivity of crotonaldehyde produced by aldol condensation was lower than that in octahedral CeO<sub>2</sub>. The overall reaction mechanism was also developed based on a kinetic study on the primary products of acetaldehyde using the first-rank Delplot method. According to its catalytic oxidation rate constant, cubic CeO<sub>2</sub> has 3–5 times higher oxidative catalytic potential than octahedral CeO<sub>2</sub>, suggesting that the repolymerisation of monolignin by aldehydes can be effectively suppressed by cubic CeO<sub>2</sub> nanocatalysts.

## 1. Introduction

Global warming caused by the increase in CO<sub>2</sub> emissions is one of the major challenges that the world is facing. Efforts for developing renewable energy sources to reduce CO<sub>2</sub> emissions while reducing the use of fossil fuels have continued for decades [1,2]. In particular, biomass energy received much attention as a carbon-neutral energy source given that plants, as the ingredient of biomass, are photosynthesized by H<sub>2</sub>O and CO<sub>2</sub>. That is, even if biomass energy is simply burned and used as thermal energy, the net CO<sub>2</sub> emissions in principle are zero [3].

Plant cell walls are composed of cellulose, hemicellulose, and lignin. Cellulose (glucose) and hemicellulose (glucose and xylose) are used to produce ethanol by hydrolysis followed by bio-fermentation [4]. In addition, owing to the recent advances in nanotechnology, several studies on nanofibers and nanocomposites have been conducted using both cellulose and hemicellulose in terms of energy and chemical valorisation [5–7].

Lignin, which accounts for most of the biomass waste, is a highly stable natural polymer with a complex three-dimensional structure; thus, it is difficult to recover its chemical components. This feature limits lignin to be used as a source of heat energy by combustion rather than chemical conversion [8]. However, if we could recover the

chemical components of lignin, we would not only reduce CO<sub>2</sub> emissions but also benefit from the acquisition of high value-added chemicals.

Depolymerisation and repolymerisation of lignin are important issues for lignin valorisation. Since lignin has a repetitive structure of phenolic compounds and their linkages, it is possible to recover the phenolic compounds by depolymerisation process such as pyrolysis, cracking, hydrolysis, solvent fractionation (including supercritical fluids), and enzymatic depolymerisation [9]. In these processes, however, there remains a critical problem of repolymerisation of the product by aldehydes (mostly glyceraldehyde) through the Friedel-Crafts reaction, generated from the degradation of the linkages. Thus, phenolic compounds (monolignin) such as guaiacol and vanillin are difficult to recover without preventing repolymerisation. Therefore, the treatment of aldehydes, the linking agents, is important [3].

When excessive *p*-cresol, a trapping agent, was introduced to the hydrothermal treatment of lignin, the aldehydes were trapped by *p*-cresol through the Friedel-Craft reaction so that the phenolic compound was successfully recovered in the form of 2-(4-hydroxy-benzyl)-4-methyl-phenol [10–15]. However, the use of *p*-cresol in industrial applications should be further investigated to determine the cost of *p*-cresol feedstock, separation, and purification processes.

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Alternatively, aldehydes can be directly and selectively decomposed through catalytic oxidation using  $\text{CeO}_2$ , known as a redox catalyst [16,17].  $\text{CeO}_2$  offers superior oxygen adsorption/desorption capability through the redox cycle between  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  [18–21], called the oxygen storage capacity (OSC). A unique synthesis method using supercritical water has been developed for obtaining  $\text{CeO}_2$  nanoparticles with a large specific surface area and a high OSC. This method enables the control of the exposed crystal planes of  $\text{CeO}_2$  using organic modifier. The resulting cubic  $\text{CeO}_2$  exhibited an OSC that is 2.6 times greater than that of irregular octahedral shaped  $\text{CeO}_2$  (400 °C). The cubic  $\text{CeO}_2$  exhibited OSC even at 150 °C [22,23]. In addition, it is possible to continuously synthesise  $\text{CeO}_2$  nanoparticles of small size and narrow size distribution using a flow-type reactor system [23,24].

Recently, both light [25–30] and heavy hydrocarbon systems such as bitumen upgrading [31] and black liquor treatment (waste from the pulp industry) [32] have been attempted using cubic  $\text{CeO}_2$  nanoparticles with higher OSC than the octahedral or a random type of  $\text{CeO}_2$ . In addition, under hydrothermal conditions, the introduction of  $\text{CeO}_2$  into the reaction system can facilitate the chemical reaction cycle that involves the release of lattice oxygen from  $\text{CeO}_2$  and reoxidation of reduced ceria ( $\text{CeO}_{2-x}$ ) by water with concomitant production of hydrogen [33–35]. Thus, the water reforming reaction is promoted by  $\text{CeO}_2$ ; however, to design the reactor for this catalytic reaction, the mechanism based on the kinetic analysis has not yet been elucidated.

In this study, hydrothermal reactions of acetaldehyde were carried out using cubic  $\text{CeO}_2$  nanoparticles to understand the oxidative decomposition of aldehydes, which represents the suppression mechanism of repolymerisation of monolignin. Here, the use of acetaldehyde with a relatively simple structure compared to glyceraldehyde allows for an easier understanding of the complicated aldehyde reactions, accompanied by the Cannizzaro reaction [36], aldol condensation [37], retro-aldol reaction [38], and water-gas-shift reaction [39]. First, structural, morphological, and catalytic characterisations of cubic  $\text{CeO}_2$  nanoparticles were performed and compared with those of octahedral  $\text{CeO}_2$ . Next, the hydrothermal reactions of acetaldehyde were performed in the presence of cubic or octahedral  $\text{CeO}_2$  nanoparticles and the entire reaction mechanism was elucidated through kinetic analysis of chemical reactions. Finally, catalytic potentials of both cubic and octahedral  $\text{CeO}_2$  nanoparticles were evaluated based on their catalytic properties and catalytic oxidation rates in the hydrothermal reaction.

## 2. Experimental section

### 2.1. Materials

Cerium(IV) hydroxide was purchased from Aldrich Chemical and cerium(III) nitrate hexahydrate was purchased from Wako Chemicals; these compounds were used as precursors for cubic and octahedral  $\text{CeO}_2$ , respectively. Hexanoic acid (99.0%) and toluene (99.5%) were purchased from Wako Chemicals and used as an organic modifier and a carrier solvent for hexanoic acid, respectively. Ethanol (99.5%) and cyclohexane (99.5%) were purchased from Wako Chemicals and used as washing and dispersion agents, respectively. Deionised water was

produced through an auto-still (Yamato Scientific Co., Ltd., WG250) and used in all syntheses. Purified water (resistivity: 8 M $\Omega$  cm) was purchased from Daiwa Pharmaceutical Co., Ltd. and used for catalytic reactions after filtration using a bottle-top filter (Nalgene, pore size: 0.2  $\mu\text{m}$ ). Acetaldehyde (anhydrous, 99.5%) and acetic acid (99.7%) were purchased from Fluka Analytical and Sigma-Aldrich, respectively, and used without further purification. Standard gases for calibration of the gas chromatograph were purchased from GL Sciences (can-type).

### 2.2. Synthesis of cubic $\text{CeO}_2$

Cubic  $\text{CeO}_2$  nanoparticles were synthesised using the flow-type reactor described in a previous work [31]. A precursor solution was prepared by dissolving cerium(IV) hydroxide (0.05 M) and hexanoic acid (0.30 M) in toluene. The precursor solution was mixed under continuous stirring for 40 min before being fed to the reactor. The precursor solution was fed using a high-pressure pump (Nihon Seimitsu Kagaku, NP-KX-540) at a flow rate of 7.0 mL/min. Simultaneously, deionised water was fed using another pump at a rate of 3.0 mL/min. The precursor solution was mixed with deionised water in a mixer and rapidly heated up to 380 °C using electric heaters. The pressure of the system was maintained at 30 MPa using a back-pressure regulator (TESCOM, 26-1700 series). The residence time in the reaction zone was 95 s. At the exit of the reactor, the product solution was rapidly cooled to room temperature using a water jacket.

The obtained product was kept at room temperature for several hours to separate the water and toluene phases. Cubic  $\text{CeO}_2$  nanoparticles in the toluene phase were then precipitated by adding ethanol as the anti-solvent. Three cycles of centrifugation (Prolabmas, Tomy MX-301) and decantation were conducted to remove any unreacted precursor and modifier. Finally, the particles were dispersed in cyclohexane and the dispersed particles were freeze-dried under vacuum for 8 h (EYELA, FDU-1200) to prevent further aggregation or agglomeration. To remove any organic ligands, cubic  $\text{CeO}_2$  nanoparticles were calcined at 300 °C for 2 h under air using a temperature-programmed muffle furnace (heating rate: 2 °C/min, Yamato, FO-100) and used in the catalytic reaction.

### 2.3. Synthesis of octahedral $\text{CeO}_2$

Octahedral  $\text{CeO}_2$  was synthesised using the same flow-type reactor without a modifier [31]. The precursor solution was prepared by dissolving cerium(III) nitrate hexahydrate (0.05 M) in deionised water. This precursor solution was then introduced into the reactor at a flow rate of 2.5 mL/min and mixed with pre-heated water (360 °C, 30 MPa, 10 mL/min). The residence time in the reaction zone was 1 s. After the reaction, the products were rapidly cooled to room temperature using a water jacket. The obtained products were purified by ethanol through three cycles of centrifugation and decantation. The octahedral  $\text{CeO}_2$  nanoparticles were dispersed in purified water and freeze-dried under vacuum for 24 h. The particles were used in the catalytic reaction without further calcination, since the influence of calcination was negligible (see Table 1).

**Table 1**

Crystal size, lattice parameter, specific surface area and OSC of different types of  $\text{CeO}_2$  nanoparticles.

Type of $\text{CeO}_2$	Particle size (nm)	Lattice parameter (Å)	<sup>a</sup> Rietveld refinement ( $R_{wp}$ (%), S)	Specific surface area (m <sup>2</sup> /g)	<sup>b</sup> OSC ( $\mu\text{mol-O/g-cat}$ )
Octahedral	23.2	5.4113	9.27, 1.244	46.8	110
Octahedral (calcined)	23.3	5.4099	9.8, 1.155	46.4	112
Cubic	6.60	5.4156	2.22, 1.413	–	–
Cubic (calcined)	6.73	5.4143	1.57, 1.191	84 <sup>c</sup> (1.79)	337 <sup>c</sup> (3.06)

<sup>a</sup> Space group Fm–3m, #225.

<sup>b</sup> The OSC value was obtained at 500 °C.

<sup>c</sup> The property ratio of cubic  $\text{CeO}_2$  (calcined) over octahedral  $\text{CeO}_2$ .

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