

# Chemical valorisation using CeO<sub>2</sub> nanocatalyst under nearcritical hydrothermal conditions

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## ABSTRACT

Chemical valorisation such as lignin fractionation and bitumen upgrading has been challenged by many researchers in an effort to prepare the depletion of crude oil, the source of energy and chemicals, over the last few decades. These reaction systems can be further improved by supporting with suitable catalysts. CeO<sub>2</sub> is one of excellent heterogeneous catalyst for those chemical reaction systems since it has high acidic, basic and redox reactivity. Recently, CeO<sub>2</sub> nanocubes synthesised by morphology control under supercritical water condition are found to be advantageous for oxidative reactions due to their large specific surface area and large oxygen storage capacity (OSC). Even at low temperature, CeO<sub>2</sub> nanocubes shows much higher OSC values than random type of CeO<sub>2</sub> nanoparticles. In addition, the catalytic potential of CeO<sub>2</sub> was further improved by metal doping with Cr<sup>3+</sup> using supercritical hydrothermal method. In this study, first, the improvement of catalytic potential of CeO<sub>2</sub> was investigated by controlling active crystal planes or metal ion doping. Then, the lignin fractionation and bitumen upgrading using CeO<sub>2</sub> nanocatalysts were evaluated. The chemical valorisation systems loaded with CeO<sub>2</sub> having high catalytic activity showed a high conversion and selectivity even at a relatively low temperature region.

## INTRODUCTION

Chemical valorisation such as lignin fractionation and bitumen upgrading has been challenged by many researchers in an effort to prepare the depletion of crude oil, the source of energy and chemicals, over the last few decades. These reaction systems are predicated on the supply of high heat energy sources since they are mostly large endothermic reactions. Therefore, it is still challengeable to commercialise it due to the problem of thermal

efficiency, which is directly related to the economical feasibility.

If a highly reactive and stable catalyst is used, the activation energy barrier of the reaction systems can be lowered, so that the operating temperature can be lowered, which not only increases the thermal efficiency but also increases the feasibility of the entire system. CeO<sub>2</sub> is one of excellent heterogeneous catalysts for those chemical reaction systems since it has high acidic, basic and redox reactivity [1]. In addition, CeO<sub>2</sub> nanocubes synthesised by morphology control under supercritical water condition are found to be advantageous for oxidative reactions due to their large specific surface area and large oxygen storage capacity (OSC). Even at low temperature, CeO<sub>2</sub> nanocubes shows much higher OSC values than random type of CeO<sub>2</sub> nanoparticles [2]. Moreover, the catalytic potential of CeO<sub>2</sub> can be further improved by metal doping such as Cr<sup>3+</sup> using supercritical hydrothermal method [3].

In this study, first, the improvement of catalytic potential of CeO<sub>2</sub> was investigated by controlling active crystal planes or metal ion doping. Then, the lignin fractionation and bitumen upgrading using CeO<sub>2</sub> nanocatalysts were evaluated [4, 5]. Finally, the catalytic activity of CeO<sub>2</sub> and the possibility of low temperature catalytic reaction system were investigated.

## **MATERIALS AND METHODS**

### *- Synthesis of Cr-doped CeO<sub>2</sub>*

Octahedral Cr-doped CeO<sub>2</sub> nanoparticles were synthesized using a laboratory-scale plug-flow reactor [3]. Aqueous solutions of Ce(NO<sub>3</sub>)<sub>3</sub>/Cr(NO<sub>3</sub>)<sub>3</sub> (0.01 M) (molar ratio of Ce:Cr = 9:1) were pumped using a high-pressure pump (Nihon Seimitsu Kagaku, NP-KX-540) at a flow rate of 2.0 ml/min through an SUS 316 tube with an inner diameter of 1.8mm. At the same time, deionized water was pumped by another pump at a flow rate of 8.0 ml/min and heated using a furnace. The precursor solution and heated water were mixed at a junction to raise the temperature up to 300 °C. The residence time in the heated zone was 1.6 s. A back-pressure regulator (TESCOM, 26-1700 series) controlled the pressure of the system at 30 MPa. The mixture was then cooled using a water jacket. The products were purified using deionised water, and then centrifugation and decantation were performed several times.

Cubic Cr-doped CeO<sub>2</sub> nanoparticles were synthesized using batch-type reactors with an internal volume of 5 ml [3]. In a typical synthesis, 0.25 mmol of Ce(OH)<sub>4</sub>/Cr(OH)<sub>3</sub> (molar ratio of Ce:Cr = 9:1) and 2.5 ml of distilled water were placed in a pressure-resistant SUS 316 vessel. To modify the surface of the nanoparticles and induce their anisotropic growth, 0.13 g of decanoic acid was also loaded into the reactor vessel. The hydrothermal reaction was performed using an electric furnace at 150 °C for 20 min as a pretreatment and then 400 °C for 10 min. After the reaction, the vessel was cooled in a water bath at room temperature. The decanoic acid-modified nanoparticles were extracted from the product mixtures with 5 ml of hexane. The final products were precipitated from the resulting hexane phase by the addition of 10 ml of ethanol as an anti-solvent reagent, and then separated using centrifugation.

- *Oxygen storage capacity*

The oxygen storage capacity (OSC) was measured using gas adsorption/desorption apparatus (Microtrac BEL, BELSORP CAT-II) [4]. About 50 mg of the samples were loaded into the glass tube, and then the glass tube was installed to the apparatus. Each sample was reduced for 2 h using hydrogen gas (99.999%) at the temperature to measure and then, O<sub>2</sub> pulse (99.999%) was introduced at the same temperature. The unreacted O<sub>2</sub> gas was detected with TCD (carrier gas: He, 99.999%) and the total amount of consumed O<sub>2</sub> was evaluated by integrating the consumed amount of O<sub>2</sub> at each pulse peak (the difference between unconsumed O<sub>2</sub> and loaded O<sub>2</sub> gas).

- *Lignin fractionation*

Hydrothermal treatment of dealkaline lignin was conducted at 350 °C for 10 min [4]. For the formation of homogeneous phase of water and organic materials, higher than 300 °C is required while the higher temperature accelerate the coke formation. Thus, 350 °C was chosen for the reaction temperature. First, 40 mg of dealkaline lignin (mostly water insoluble), 2.5 mL of water, and 0.2 g of cubic CeO<sub>2</sub> nanoparticles were loaded into a needle-valve-equipped batch-type reactor (Hastelloy, inner volume: head 0.44 mL, body 5.25 mL, AKICO). As a control experiment, the hydrothermal treatment of dealkaline lignin was also conducted in the absence of cubic CeO<sub>2</sub> nanoparticles. The reactor was loaded into an electric furnace and shaken back and forth at 120 times/min for 10 min (shaking angle: 45°). To halt the reaction, the reactor was quenched by submerging it in a water bath at room temperature. Then, a gas-sampling pack (aluminum, GL Sciences, inner volume: 0.1 L) was connected to the valve and the gas products were collected. The reactor was completely opened using a torque wrench, and the solid and liquid products were collected.

For all the experiment, the products were analysed by the same procedures as follows. The solid products (char and catalyst) were separated from the product solution using a filter (25 nm, Millipore) and then dried at 60 °C in the oven overnight. The dried samples were weighed. The unreacted lignin in the solid phase was recovered after being dissolved by adding sodium hydroxide aqueous solution (pH 13) and filtered. The alkali insoluble residue was regarded as the polymerised matter or char formed during the treatment. The liquid products were recovered with additional 12.5 mL of water and analysed by GC-FID (GC-2010, Rtx-Wax: 15 m, id = 0.32 mm). Identification of the products was performed with GC-MS (Shimadzu GC-2010Q, Rtx-Wax: 15 m, id=0.32 mm). The gas products were analysed using GC-TCD (Shimadzu, GC-2014, Shincarbon ST50-80: 2 m, id = 3.0 mm). Molecular weight distribution of the product solution was evaluated with GPC (JASCO Corp., GPC-900, OH-pack SB-03 and SB-04, Shodex) after two times dilution. The phosphate buffer solution (25 mM) and LiBr (25 mM) were used as stabilizers for the GPC eluent. The UV absorbance of the product solution was measured using an ultraviolet-visible spectroscopy (UV-VIS, JASCO Corp., V-570 with Quartz cuvettes) after 100 times dilution.

- *Bitumen upgrading*

Canadian oil sand bitumen obtained from the Athabasca area was used [5]. The bitumen, which consists of maltene and asphaltene, is a sticky liquid at room temperature and is completely soluble in 1-methylnaphthalene. Maltene is defined as the component soluble in *n*-pentane, while asphaltene is insoluble. The maltene and asphaltene were found to be 82 wt% and 18 wt% of the bitumen, respectively. The bitumen was diluted with 1-methylnaphthalene to reduce its viscosity, and a 10 wt% bitumen solution was used as the feedstock. Experiments were conducted in a pressure-resistant tube reactor (SUS 316) with an inner volume of 6.3 mL. The reactor was loaded with bitumen solution (1.00 g), water (1.00 mL), and CeO<sub>2</sub> nanoparticles (10–20 mg) as the catalysts, and then capped tightly and placed in an electric furnace adjusted at 723 K. After 1 h, the reactor was removed from the furnace and rapidly cooled in a cold-water bath to terminate the reaction. Liquid and solid products were recovered by rinsing the reactor with toluene.

The toluene-insoluble fraction (coke and catalysts) was separated by filtration using a membrane filter (pore size: 25 nm), and the toluene-soluble fraction was recovered using a rotary evaporator. The coke on the catalyst surface was calculated by weight loss with calcination of the recovered catalysts at 650 °C. The toluene-soluble components were then separated into *n*-pentane soluble and insoluble components (maltene and asphaltene, respectively). The asphaltene and coke yields were evaluated on the basis of the weight of the loaded sample and the products. Here, the maltene yield was determined on the basis of the calculated asphaltene and coke yields as follows:

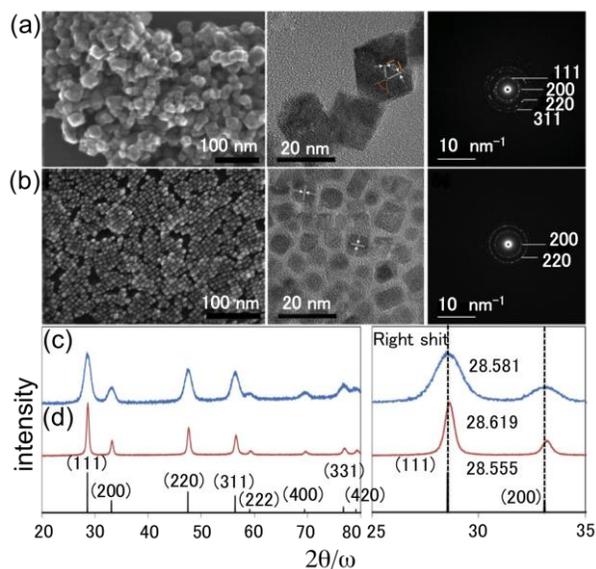
$$\text{maltene yield (wt\%)} = 100 - \text{asphaltene yield} - \text{coke yield} \quad (1)$$

The conversion of asphaltene was defined as the yield of asphaltene converted to maltene, gas and coke after bitumen upgrading.

## RESULTS

### - Cr-doped CeO<sub>2</sub> nanocatalysts

The nano-sized CeO<sub>2</sub> has a very low elimination energy barrier of lattice oxygen, so its lattice oxygen is easily absorbed and released from CeO<sub>2</sub>. Since this property leads the highly active lattice oxygen, a catalytic reaction can be expected in a relatively lower temperature range than generally used operating temperature for organic substances. Such CeO<sub>2</sub> can be more active by exposing its certain active crystal planes. The stability of the CeO<sub>2</sub> crystal plane was found to be {111}>{110}>{001} in the computational science [6], and the order of activity was in reverse order. Therefore, the CeO<sub>2</sub> nanocubes exposed to the {001} crystal planes can be considered to be a highly active catalyst.



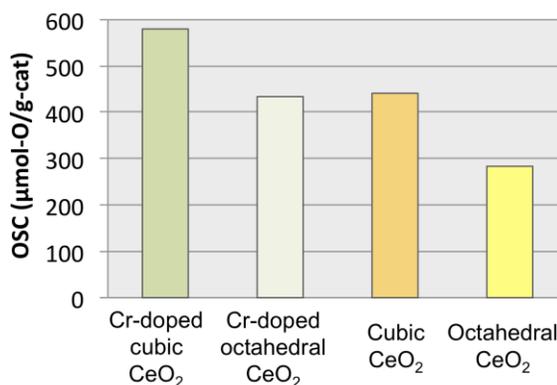
In addition to the surface control of nano-sized CeO<sub>2</sub>, it is possible to have highly active catalytic potential by doping metal ions into CeO<sub>2</sub> lattice. The Cr<sup>3+</sup> ion has much smaller ionic radius (Cr<sup>3+</sup> = 0.615 Å << Ce<sup>4+</sup> = 0.97 Å) and less oxidation number than the Ce<sup>4+</sup>, so that when the Cr<sup>3+</sup> is doped, it forms an oxygen deficiency of CeO<sub>2</sub>. In this study, Cr<sup>3+</sup> was doped into an octahedron type of CeO<sub>2</sub> using a flow type reactor, and was doped into CeO<sub>2</sub> nanocubes using an organic modifier in a batch type reactor.

Figure 1 shows the morphology and crystallographic phase of the synthesized Cr-doped CeO<sub>2</sub> nanoparticles. Fig. 1(a) is Cr-doped octahedral CeO<sub>2</sub> nanoparticles and Fig. 1(b) is Cr-doped CeO<sub>2</sub> nanocubes. From the left images, SEM, TEM and SAED images (selected area electron diffraction) are shown for each type of CeO<sub>2</sub>, respectively. As can be seen from the TEM images, Fig. 1(a) octahedron shape particles and Fig. 1(b) cube particles are both clearly observed, and their morphology and size are similar to the non-doped CeO<sub>2</sub> nanoparticles [2, 5].

Fig. 1(c) and (d) show their XRD patterns, Fig. 1(c) is the CeO<sub>2</sub> nanocubes, and Fig. 1 (d) is the octahedral CeO<sub>2</sub>. Both cases coincided with the reference peak pattern (PDF 00-034-0394), and byproducts peak were not observed. The cubic CeO<sub>2</sub> observed in the TEM has small particles sized of a few nanometers, so that relatively broad peaks are observed in this XRD pattern, while octahedron CeO<sub>2</sub> in the vicinity of 20 nm has a relatively sharp peak. The crystal size of each CeO<sub>2</sub> is 5.4 nm for the nanocubes and 14.7 nm for the nano-octahedrons based on the Scherrer equation. In addition, both XRD peak patterns are shifted to the higher angle side than the reference; because the lattice constant of CeO<sub>2</sub> becomes smaller when a smaller ion (Cr<sup>3+</sup>) doped into the CeO<sub>2</sub>. The XRD pattern of octahedron CeO<sub>2</sub> is shifted further to the higher angle side than that of nanocubes, i.e. more Cr<sup>3+</sup> doping, which is consistency with the result of EDS of those particles (5% for cubic CeO<sub>2</sub> and 9% for octahedral CeO<sub>2</sub>).

One of methods for directly or indirectly measuring the performance of nanocatalysts synthesised by the above methods is to measure their oxygen storage capacity (OSC). Figure 2 shows the measured OSCs (at 400 °C) of the synthesised nanoparticles. The two data on the right hand side are absence of Cr<sup>3+</sup> doping with and without the control of the exposure crystal planes (CeO<sub>2</sub> nanocubes and octahedral CeO<sub>2</sub>). The two data on the left hand side show the OSC of the Cr-doped CeO<sub>2</sub>, both Cr-doped octahedral CeO<sub>2</sub> and Cr-doped CeO<sub>2</sub> nanocubes. From the Figure 2, it can be seen that the OSC increases in the order of cubic > octahedron and Cr<sup>3+</sup> doping > non-doping, and the highest OSC value is obtained when both Cr<sup>3+</sup> doping and crystal plane controlling are performed at the same time. Although octahedral Cr-CeO<sub>2</sub> has higher

**Figure 1** Characterisation of the Cr-doped CeO<sub>2</sub> nanoparticles: (a) morphology and size of octahedral Cr-CeO<sub>2</sub> (b) morphology and size of Cr-CeO<sub>2</sub> nanocubes (c) XRD pattern of Cr-CeO<sub>2</sub> nanocubes (d) XRD pattern of octahedral Cr-CeO<sub>2</sub> [3].



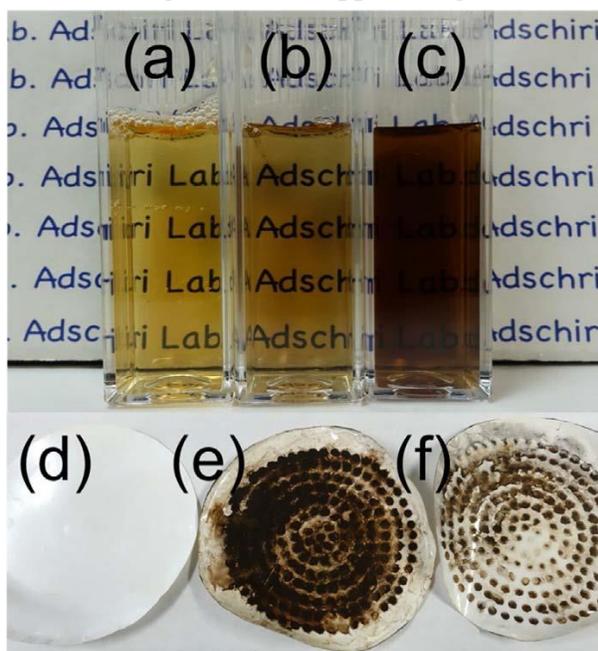
**Figure 2** Oxygen storage capacity (OSC) of the several types of CeO<sub>2</sub> nanocatalysts [3].

amount of Cr doping, its OSC value is similar to the non-doped CeO<sub>2</sub> nanocubes. That is, the increase in the OSC value is much higher in the case of exposing the active crystal plane.

#### - Lignin fractionation

Lignin is a natural polymer with a complex structure composed of phenol structures and several kinds of linkers between them [7]. It is chemically very stable and therefore its utilization is very difficult compared to cellulose and hemicellulose. In order to decompose the linkers of lignin, a high operation temperature is required, however, high temperature condition not only lowers the economical feasibility of the lignin fractionation but also causes the high ratio of recombination between linkers and the phenols (Friedel-Craft reaction). Here, if the linkers are decomposed or oxidized at a relatively low temperature using CeO<sub>2</sub> nanocatalysts having high activity, the yield and selectivity of phenols can be increased while the repolymerisation can be suppressed [4].

The possibility of lignin fractionation was evaluated at nearcritical conditions (350 °C, 10 min) using 0.1 g of CeO<sub>2</sub> nanocubes and is shown in Figure 3. The upper images (a–c) in Figure 3 are the water-soluble products of lignin solution, and the lower part is the filter images (d–f) after filtering the alkali solution of the solid component after the lignin fractionation. The lignin before the reaction is partially soluble in water (a) and completely soluble in the alkali (d). After the reaction in the nearcritical water condition, the water-soluble component slightly increased (b), but the repolymerisation actively proceeded to produce a lot of char that did not dissolve in the alkali (e). However, in the case of CeO<sub>2</sub> nanocubes loaded system, it can be seen that the water-soluble component of was significantly increased (c), and the repolymerisation is also suppressed compared to the other systems that CeO<sub>2</sub> was not loaded (f). Therefore, it can be said that the lignin fractionation can be enhanced only when the linkers are selectively decomposed and the recombination by the linkers is effectively suppressed simultaneously.



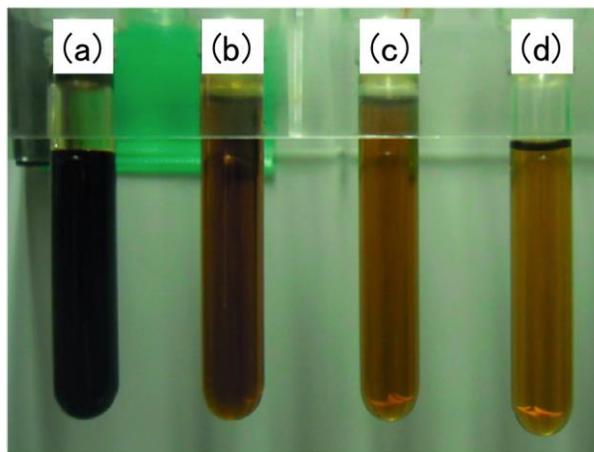
**Figure 3** Water-soluble components after lignin fractionations (a–c) and char produced by repolymerisation of phenols and aldehydes (d–f): (a)&(d) lignin; (b)&(e) after reaction (350 °C, 10 min); (c)&(f) after reaction in the presence of CeO<sub>2</sub> nanocubes [4].

#### - Bitumen oil upgrading

Bitumen is a non-traditional petroleum energy source, along with shale oil, and is attracting attention as a future energy source in the 21<sup>st</sup> century [8]. Since the beginning of

the 2000s, the extraction of bitumen has been advanced by the improvement of the extraction technology of bitumen from oil sands, but much research is still needed to improve the bitumen composition. Bitumen can be simply divided into light component (maltene, *n*-pentane soluble) and heavy component (asphaltene, *n*-pentane insoluble). The upgrading technology of the bitumen has been mainly developed using steam used in its extraction process (steam cracking) or pressurized water (supercritical hydrothermal cracking). Upgrading process of bitumen is a very large endothermic reaction. Asphaltene is decomposed at high temperature region, but formation of alkene radical from the decomposition leads to coke generation. If the lattice oxygen from the CeO<sub>2</sub> is used to inhibit (capture) the alkene radical reaction or to improve hydrogenation reaction of the alkene, the yield and selectivity of the maltene can be increased while those of coke can be suppressed [5].

Figure 4 shows the results of bitumen upgrading in a supercritical water condition (at 450 ° C for 1 h) using 0.02 g of two different types of CeO<sub>2</sub> nanoparticles. Fig. 4(a) shows the image of completely dissolved unreacted bitumen in 1-methyl naphthalene. Fig. 4(b) shows that the colour of the solution became bright after the reaction without any catalyst. Fig.4(c) shows the case of octahedral CeO<sub>2</sub>, and (d) shows the result of the upgrading reaction using CeO<sub>2</sub> nanocubes. In both cases, they are much lighter than (b). The conversion of each asphaltene is as follows: 48.9% for non-catalytic reaction; 71.7% for octahedral CeO<sub>2</sub>; 84.4% for CeO<sub>2</sub> nanocubes. The formation of coke was reversed order compare to the asphaltene conversion: 5.4 wt% for CeO<sub>2</sub> nanocubes, 8.9 wt% for octahedral CeO<sub>2</sub>, and 12.9 wt% for non-catalytic reaction.



**Figure 4** Photo images of upgraded bitumen from the supercritical hydrothermal cracking: (a) unreacted bitumen; (b) after sc-hydrothermal cracking; (c) in the presence of octahedral CeO<sub>2</sub> nanoparticles; (d) in the presence of CeO<sub>2</sub> nanocubes [5].

## CONCLUSION

The nano-sized CeO<sub>2</sub> was able to further increase its oxygen storage capacity (OSC), related to the catalytic potential, by either controlling active crystal plane or metal doping. In particular, Cr-doped CeO<sub>2</sub> nanocubes exposed to {001} crystal planes were found to be the highest catalytic activity among them. In addition, the catalytic reactions such as lignin fractionation and bitumen upgrading were conducted at a relatively lower temperature. In lignin fractionation, selective decomposition of linkages constituting lignin structure and inhibition of repolymerisation resulted in suppression of char formation and increasing yields of organic matter. In the bitumen upgrading, introducing CeO<sub>2</sub> nanocubes resulted in higher conversion of asphaltene and higher yield of maltene in the supercritical hydrothermal cracking. Therefore, the development of highly active CeO<sub>2</sub> nanocatalysts

and the related reaction systems are expected to accelerate the realisation of chemical valorisation systems in the non-pioneering energy fields.

## ACKNOWLEDGEMENTS

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