Process intensification for regeneration of facet-controlled nanocatalyst in supercritical water

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1. Introduction

Nanocatalysts, such as nanocubes, nanorods, nanowires, nanoplates, and nanopolyhedrons, have been developed for various chemical reaction processes. Nanosizing and exposed facet control can be cost-effective and resource-saving strategies without the additional use of expensive noble-metal for enhancing catalytic activity. However, the change of exposed surface from active facet to unreactive one by migration of surface atoms during their use as catalysts degrades its performance. Regeneration method that can recover the desired facets is of great importance to industrial applications of nanocatalysts.

To reorient the surface crystalline structure of degraded facet-controlled metal oxide nanocatalyst, recently, we developed supercritical hydrothermal treatment with organic modifier [1]. By this process, we can recover the active facet (Figure 1) and catalytic performance of nanocatalysts without additional metal precursors. To confirm the scalablility of this process, in this study, we investigate the mechanism of facet-reorientation process and the dependency on the treated particle concentration in the reactor.

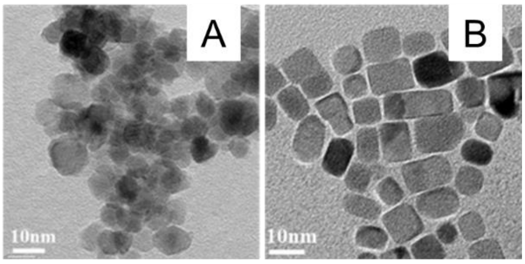

Figure 1. HRTEM images of (A) degraded CeO_2 nanocatalyst and (B) CeO_2 nanocatalyst regenerated by supercritical hydrothermal treatment [1].

2. Materials and Methods

In this study, CeO_2 nanoparticles are chosen as model nanocatalyst, because of their well-known facet-dependent catalytic activity. CeO_2 nanoparticles, 2.5 mL of H_2O, and decanoic acid as facet modifier were injected to 5 mL batch-type reactor. The reactor was heated to 400 °C by a custom-designed electric heater. In this system, the temperature reaches 400 °C within 5 min. After the heat treatment, the reactor was quenched in a room-temperature water bath. The treated sample was collected by using hexane and washed with cyclohexane and acetone to remove the unreacted modifier.

3. Results and discussion

As shown in Figure 1, by use of the supercritical hydrothermal treatment with organic modifier for 10 min, the morphology of degraded spherical CeO_2 nanocatalyst is changed to cubic nanoparticles with mainly exposing (100) facet. The organic modifier, decanoic acid, has stabilization effect for (100) facet, and also enhance the solubility of CeO_2 by the formation of organo-metallic complex [2]. Due to these effects, during the supercritical hydrothermal treatment, smaller spherical CeO_2 particles dissolves in water to be redeposited onto larger particles to form (100) facet. The facet-dependent dissolution and precipitation through the organo-metallic complex formation is the fundamental mechanism driving the facet transformation.

For process intensification, the increase in treated nanoparticle concentration contributes to the improvement of productivity, and the reduction in process cost. Thus, in this study, the morphological changes of CeO_2 nanoparticles with different concentration are used to investigate the scalability of the regeneration process for nanocatalyst using supercritical hydrothermal treatment.

Figure 2 shows HRTEM images of CeO_2 nanocatalysts treated at the concentration of (A) 5 mg/ml, (B) 10 mg/ml, and (C) 20 mg/ml. The initial CeO_2 nanoparticle has relatively spherical shape, and after the treatment, the morphology changed to cubic.

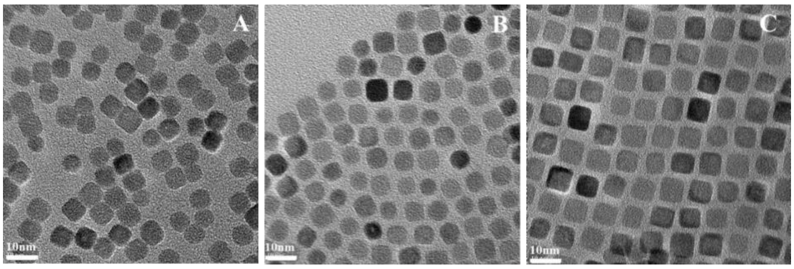

Figure 2. HRTEM images of CeO_2 nanocatalysts treated at the concentration of (A) 5 mg/ml, (B) 10 mg/ml, and (C) 20 mg/ml. (400 °C, Decanoic acid concentration: 0.24M, treatment time: 10min).

Interestingly, as increasing the particle concentration, the treated particles became more cubic-like. This mophological change in appearance is also confirmed by the computational image analysis.

This result support the above-mentioned mechanism of reorientation process for nanocatalyst. The dissolution of CeO_2 occurs at the particle surface, and after reaching the organo-metallic complex concentration to its solubility in treatment condition, the precipitation starts. At lower particle concentration, the time to reach complex concentration to its solubility becomes longer. Thus, at the particle concentration of 5 mg/ml, the morphological change into cubic shape had not completed. On the other hand, at higher particle concentration of > 10 mg/ml, the modification has completed, and the dependence on particle concentration was hardly observed. It is indicated that in the nanocatalyst regeneration process, the increase in treated nanoparticle concentration accelerates the orientation of surface crystalline structure, and contributes to the process intensification, such as improvement of productivity, and the reduction in process time, effectively.

4. Conclusions

In this study, we investigate the mechanism of facet-reorientation process using supercritical hydrothermal treatment and the dependency on the treated particle concentration. It is revealed that the increase in treated nanoparticle concentration accelerates the orientation of surface crystalline structure, and contributes to the process intensification. This facile facet reorientation strategy using supercritical fluid should be applicable to not only for the regeneration of other facet-controlled nanocatalyst but also for the improvement of catalytic performance of nanoparticles by post treatment.

References

1. T. Tomai, L. Tang, A. Yoko, Y. Omura, G. Seong, T. Adschiri, *Chemistry of Materials* **2021**, 33, 7780–7784.
2. Y. Omura, A. Yoko, G. Seong, T. Tomai, T. Adschiri, *CrystEngComm* **2021**, 23, 5353–5361.