

PREPARATION OF CERIA-ZIRCONIA MIXED OXIDE BY CONTINUOUS HYDROTHERMAL SYNTHESIS IN SUPERCRITICAL WATER AS CATALYST SUPPORT

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Summary

Ceria-zirconia mixed oxides were prepared by new continuous hydrothermal synthesis in supercritical water (supercritical synthesis) and also by the conventional co-precipitation method. Rh-loaded ceria-zirconia catalysts were prepared using the mixed oxides as support for Rh catalyst. Rh-loaded ceria-zirconia catalyst by supercritical synthesis showed superior performances for the catalytic reduction of NO by CO as well as better reducibility and higher thermal stability due to the sparsely-agglomerated morphology. Ceria-zirconia mixed oxide prepared by supercritical synthesis had more potential applications as catalyst support mainly due to its sparsely-agglomerated morphology and higher thermal stability, compared with co-precipitation method.

Keywords

Rational design of catalysts, Nanotechnology applications

Introduction

Ceria-zirconia mixed oxide is widely used as oxygen storage material, for example, in the three-way catalysts for the clean up of automotive gases. Recently, near-zero emissions and high durability are of urgent requirement and accordingly, the oxygen storage material with advanced thermal stability has been of great interest for catalyst preparation.

A number of different synthetic methods have been applied to prepare ceria-zirconia and related mixed oxides. Continuous hydrothermal synthesis in supercritical water (supercritical synthesis) is a method to prepare metal oxide nanoparticles rapidly and continuously using supercritical water as anti-solvent¹⁻². Highly crystallized nanoparticles of homogeneous complex metal oxides as well as single metal oxides could be produced easily by the supercritical synthesis. It would be valuable to compare the physicochemical properties of ceria-zirconia mixed oxides prepared by the supercritical synthesis and the other conventional methods.

Experiment

Ceria-zirconia mixed oxides were prepared by the new supercritical synthesis method and also by the conventional co-precipitation method. The schematic diagram of the apparatus for supercritical synthesis is shown in Figure 1. Rh-loaded ceria-zirconia catalysts were

prepared by incipient wetness impregnation method using the mixed oxides as support for Rh catalyst. The activities of Rh-loaded ceria-zirconia catalysts were investigated for catalytic reduction of NO by CO and their physicochemical properties were characterized with TPR, N₂ adsorption, O₂-uptake, XRD, SEM, AES, and H₂/CO chemisorption. The thermal stability of prepared ceria-zirconia mixed oxides and Rh-loaded ceria-zirconia catalysts could be evaluated by comparing the properties of the sample redox-aged at high temperature with those of the fresh sample.

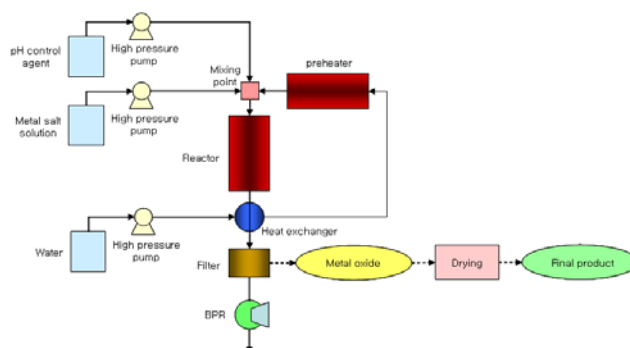


Figure 1. The schematic diagram of the apparatus for supercritical synthesis.

Results and discussion

The supercritical synthesis could lead to ceria-zirconia mixed oxides with higher thermal stability and better oxygen storage capacity (OSC) due to its sparsely-agglomerated morphology.

In case of the supercritical synthesis, a lot of metal oxide nanoparticles might be precipitated very fast and the precipitated nanoparticles could be agglomerated rather coarsely due to the weak interaction between the oxide nanoparticles. The sparsely-agglomerated morphology could be expected in supercritical synthesis. In case of the co-precipitation method, precipitation and agglomeration of metal hydroxide nanoparticles could occur simultaneously and the precipitated nanoparticles could interact with each other. On dehydrating the metal hydroxide to metal oxide by calcination, the nanoparticles would interact more strongly with each other, and accordingly the densely-agglomerated morphology could be obtained in co-precipitation method.

The pores with a diameter larger than 10 nm observed in the fresh mixed oxide prepared by the supercritical synthesis rather increased to near 30 nm after redox-aging, while the sparsely-agglomerated morphology was almost retained. On the other hand, the small pores of 3 nm and the densely-agglomerated morphology observed in the fresh mixed oxide prepared by the co-precipitation method were easily collapsed almost to complete sintering by redox-aging. It could be suggested that the densely-agglomerated morphology in the ceria-zirconia mixed oxide prepared by the co-precipitation method could prevent the lattice oxygen from migrating from the bulk to the atmosphere, leading to poor reduction and thermal property compared to those by the supercritical synthesis.

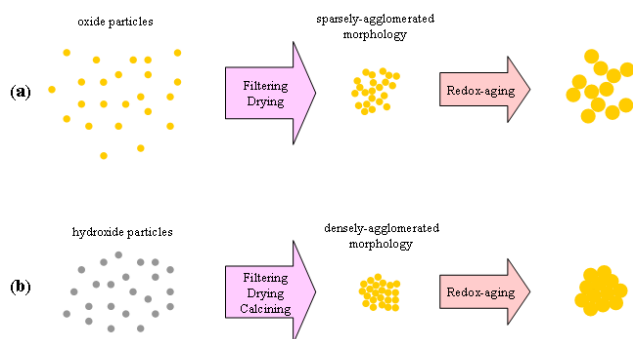


Figure 2. The morphologies of ceria-zirconia mixed oxides prepared by (a) supercritical synthesis and (b) co-precipitation method.

Rh-loaded ceria-zirconia catalyst by supercritical synthesis showed superior performances for the catalytic reduction of NO by CO as well as better reducibility and higher thermal stability, compared with co-precipitation method.

Rh-loaded ceria-zirconia catalyst by supercritical synthesis maintained relatively high Rh dispersion even after redox-aging. But in case of co-precipitation method, its Rh dispersion decreased significantly after redox-aging in spite of very high Rh dispersion of the fresh sample.

Rh-loaded ceria-zirconia catalyst by co-precipitation method encountered the collapse of pores during redox-aging and Rh particles in the pores must remain mostly in the bulk phase of ceria-zirconia mixed oxide and not on the surface accessible to the atmosphere (Figure 3).

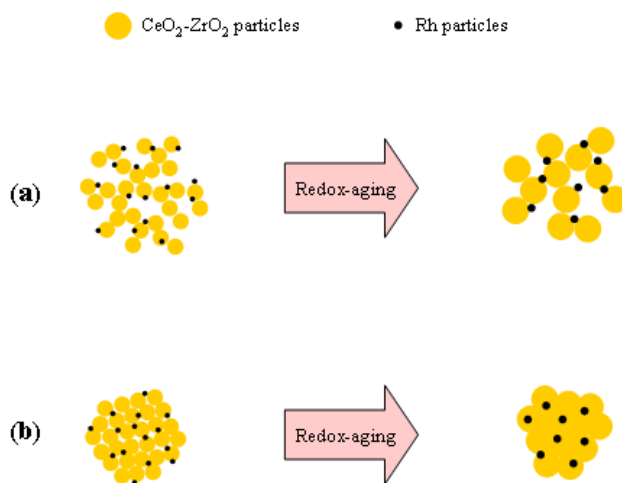


Figure 3. Rh particles in Rh-loaded ceria-zirconia catalysts by (a) supercritical synthesis and (b) co-precipitation method.

Ceria-zirconia mixed oxide prepared by supercritical synthesis had more potential applications as catalyst support mainly due to its sparsely-agglomerated morphology and higher thermal stability.

Conclusions

The supercritical synthesis could lead to ceria-zirconia mixed oxides with higher thermal stability and better oxygen storage capacity (OSC) due to its sparsely-agglomerated morphology. Rh-loaded ceria-zirconia catalyst by supercritical synthesis showed superior performances for the catalytic reduction of NO by CO as well as better reducibility and higher thermal stability, compared with co-precipitation method. Ceria-zirconia mixed oxide prepared by supercritical synthesis had more potential applications as catalyst support mainly due to its sparsely-agglomerated morphology and higher thermal stability.

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