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Design of Nanocluster Based Material with Catalytic Properties

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Abstract Modified inert gas condensation method was used to produce the nanocluster composites of CuO/ CeO_2. High-resolution TEM, SEM and catalytic measurements have been used to characterize the samples and study the synergistic effect between the CuO phase and CeO_2 (ceria) support. By varying the He pressure, the heating temperature and configuration of the heating boats inside the modified gas condensation chamber, nanoclusters of varying sizes, shapes and composition can be produced. The composition and nanostructured morphology were shown to influence the catalytic properties of the system. A copper content around 10 at% with a morphology that favors high-energy surfaces of ceria is shown to be beneficial for a high catalytic activity.

Keywords : Nanocluster, CuO-CeO_2 system, Active gas condensation, Catalytic properties

1. Introduction

Materials with grain sizes less than 10 nm defined as "nanocluster" have attracted much attention due to the physical and chemical properties which are significantly different from those of bulk materials, and the production of nanoclusters becomes one of the most important subjects of the new technologies.[1-3] The reduction in size of the materials and components plays an important role in the development of the miniaturization technology and causes new applications such as catalysts due to the great value of the surface to volume ratio.[4,5] Therefore, it is very important to have general methods for obtaining nanoclusters by simple and reproducible processing.

Cerium dioxide (ceria) is known to have excellent oxygen storage capacity (OSC) and redox properties[6,7] and widely used as an additive or support material in many industrial catalysts.[8] The presence of expensive noble metals like platinum is known to dramatically improve the reducibility of ceria and hence its catalytic effect.[9] Likewise, an addition of the transition metal oxide CuO improves the low-temperature oxidation activity of ceria by a synergistic mechanism.[10-13]

To investigate morphology and composition effects, which are closer to an industrial catalyst, we have produced nanocluster composites (NCC) in the CuO/ CeO_2 system with different composition, size and nanostructured morphology utilizing the active gas condensation (AGC) method combined with a co-evaporation process and uneven bar system.

2. Experimental Procedure

Ceria based NCCs were synthesized by the AGC method[4,14-16] combined with a co-evaporation process and uneven bar system.[4,14] Fig. 1 shows the schematic drawing of AGC method to synthesize the NCC. The configuration of the boats, which is the lateral and vertical distance between the boats, and helium-pressure in the chamber are parameters that control the size and shape of particles in the nanometer range.[4,14-16] The composition is controlled by individually regulating the temperature of the tungsten boats amperometrically.[16] To take a large amount of samples, metallic cerium and copper were used as source materials. These starting metals were co-evaporated in a chamber filled with helium (1.0 torr) and oxygen (1.0 torr) by resistance heated boats to have a homogeneous dispersion of ceria and copper oxide. The collector was cylindrical and rotated during the evaporation process to obtain a homogeneous mixture of the two phases.

After evaporation, particles were fully stabilized by oxygen gas exposure up to 10.0 torr. Subsequently, the powder mixture of ceria and copper oxides (mostly CuO) was scraped off the collector surface and

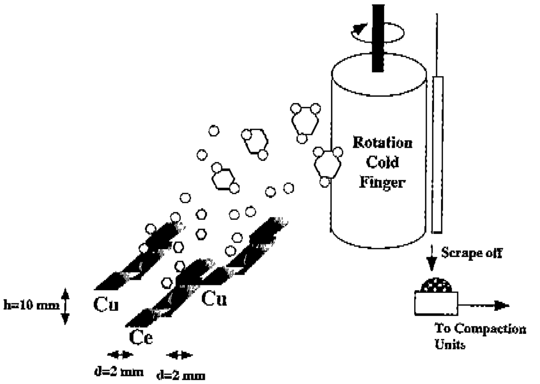

Fig. 1. Schematic illustration of the active gas condensation (AGC) method combined with a co-evaporation process and uneven bar system. The boat temperature is amperometrically regulated for each boat to give the desired nanocluster composite composition.

transported *in situ* to a chamber for compaction. The compaction condition was 10 MPa at room temperature. The microstructures of the NCC were studied by high resolution TEM. The content of the cerium and copper was measured by EPMA.

The catalytic measurements were performed using primarily a heated all-glass reactor working in batch mode. A temperature probe was placed just above the catalyst sample, and the temperature was kept at 423 ± 1 K. The reaction gas mixture consisted of 0.991 ± 0.02 vol% CO in synthetic air. A Varian 3400 gas chromatograph equipped with a Ni-catalyst methanator and a flame ionization detector (FID) was used to analyze the gas composition. This made it possible to monitor both the CO and CO_2 concentration simultaneously.

3. Results and Discussion

Figure 2(a-c) shows SEM micrographs of the as-received ceria and copper oxides NCCs, obtained at helium gas pressures of 10.0 torr. The compositions of the nanocomposites were analyzed by EDX. The primary particle size of the NCCs was estimated to be 6, 20 and 24 nm, respectively, from the micrographs. This result suggests that the particle size of ceria is smaller than that of copper oxide. The specific surface area (BET) for these samples varied between 30 to 120 m^2/g.

Figure 3 shows the TEM micrograph of the NCC with Cu content of 10.1 at%. It indicated that the ceria particles of 3~10 nm were partly coated with CuO amorphous or nanocrystalline layer of a few nm in size.

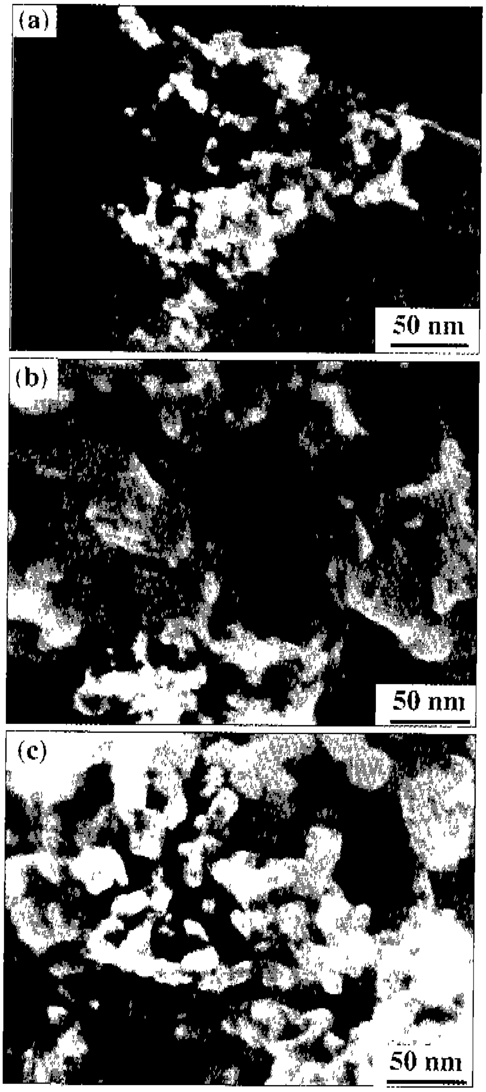

Fig. 2. SEM micrographs of the nanocluster composites with various Cu contents; (a) 100% Ce, (b) 37.2 at% Cu and (c) 100% Cu.

Since the oxides were nucleated from the atomic and/or cluster gas level that had been evaporated in the well-arranged heating boat position, the nanoclusters were characterized by very uniform and homogeneous microstructure. With uneven bars system, cerium nanoparticle acts as an embryo of copper oxides layer. Grain size of NCC (10.1 at% Cu; $d_{av.}$ = 4 nm) was smaller than that of NCC (1.0 at% Cu; $d_{av.}$ = 10 nm). Therefore, in this system, copper oxides layer acts both as catalyst and as grain growth inhibitor of ceria.

As the copper content is increased (25~60 at%), the

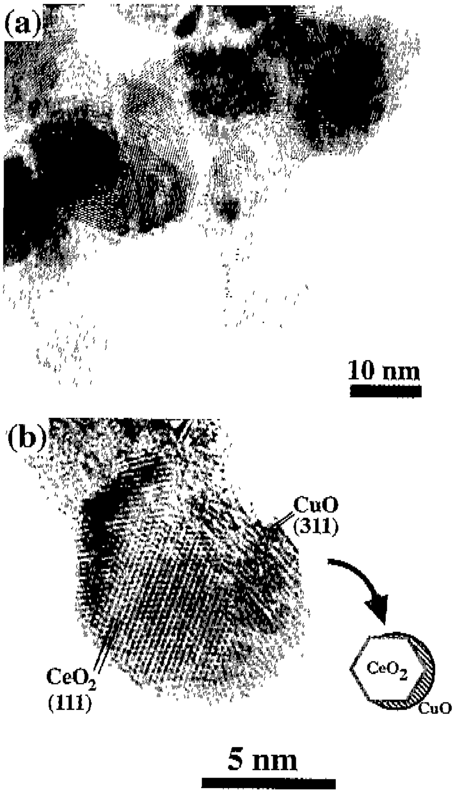

Fig. 3. HREM micrographs of the nanocluster CuO/CeO_2 composite with Cu content of 10.1 at%; (a) row magnification and (b) high magnification and its schematic drawing.

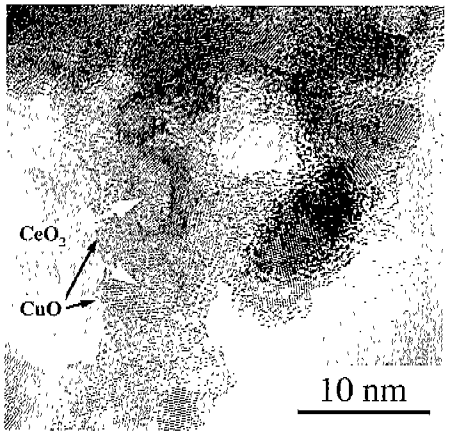

Fig. 4. HREM micrograph of the nanocluster CuO/CeO_2 composite with core-shell structure.

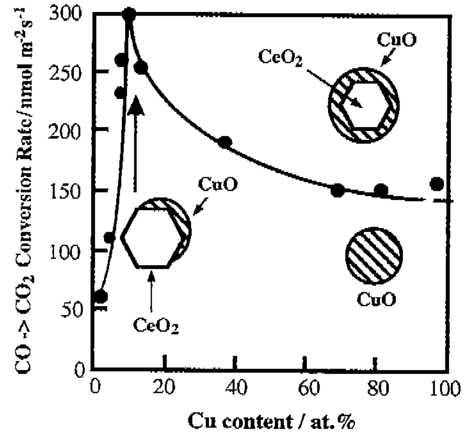

Fig. 5. Conversion rate of carbon monoxide to carbon dioxide versus copper content of the nanocluster Ce-Cu-O composite catalysts at 423 K. The dark curve illustrates an average value (Batch reactor). Inset figures are schematic drawings of each sample.

composite shows a tendency to form core-shell structures (Fig. 4). In special, TEM observation of the NCC containing more than 35 at% Cu (Fig. 4) revealed that the ceria nanocluster was almost completely surrounded with copper oxides and/or its amorphous layer. It has been suggested that the shell layer (CuO) inhibited an effective transfer of oxygen to core (CeO_2), thus it showed a low activity.[11]

At very low copper concentrations (< 4 at%), there is a tendency for an encapsulation of the copper oxide by CeO_2 and thereby making it inaccessible for the CO adsorption, as shown in Fig. 5. For very high copper contents (> 35 at%) the activity approaches that for pure CuO, which do exhibit rather high catalytic activity. For copper concentrations in the range of 10 to 20 at%. the composite consists mainly of well-dispersed copper oxide clusters (Fig. 3). Thus, the catalytic measurements indicate that such a composition is desirable to achieve the highest conversion rate of CO (Fig. 5). The interaction of ceria with CuO is a strong function of the type of crystallographic surface of ceria. Small crystals usually exhibit a higher degree of edges, steps, kinks etc., where crystallographic surfaces with higher surface energy also are present.[17] Hence, a small crystal size favors the formation of a higher proportion of reducible ceria surfaces. This will facilitate the transfer of oxygen from the ceria to the CuO phase and efficiently enhance the catalytic activity for CO oxidation.[18,19]

4. Conclusion

The nanocluster composites composed of ceria and copper oxides were successfully fabricated by the AGC method combined with a co-evaporation process and uneven bar system. With the AGC method, we can promote a composition and morphology of the nanocluster CuO/CeO_2 composites, in such a way that the formation of highly active CeO_2 surfaces. The presence of such highly reducible ceria surfaces, which easily can donate oxygen, can assist and even enhance the ability of the copper oxide phase to maintain a high catalytic activity at low temperatures, where oxygen bulk migration is slow.

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