Developing High-area Silica Supported High-entropy Oxide Nanoclusters for Heterogeneous Catalysis: Characterization Challenges

Jingyue (Jimmy) Liu, Yiwei Yu, Bailey Holmes

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Meeting-report

Developing High-area Silica Supported High-entropy Oxide Nanoclusters for Heterogeneous Catalysis: Characterization Challenges

Jingyue (Jimmy) Liu[1,*], Yiwei Yu[2], and Bailey Holmes[3]

[1]*Department of Physics, Arizona State University, Tempe, AZ, United States*
[2]*School for Engineering of Matter, Transport and Energy, Arizona State University, Tempe, AZ, United States*
[3]*School of Molecular Sciences, Arizona State University, Tempe, AZ, United States*

*Corresponding author: jingyue.liu@asu.edu

It has long been recognized that configurational entropy can induce phase transformation in spinel systems—cations transition between ordered and disordered site occupancy [1]. Similar to the development of high entropy alloys (HEAs) [2], entropy-stabilized oxide was accomplished by incorporating five different cations into a single-phase oxide system to demonstrate the entropy-driven structural stabilization effect [3]. Both HEAs and HEOs (high-entropy oxides) have been explored for applications in heterogeneous catalysis and distinct catalytic properties have been reported [4]. For practical applications in heterogeneous catalysis, however, HEAs/HEOs need to possess high specific surface area, which poses a significant challenge since high-temperature processing is usually required and sintering of HEO particles can drastically reduce their specific surface area.

We recently developed a robust synthesis protocol to fabricate ultra-small, functional nanoglues to localize single metal atoms or clusters [5]. This nanoscale architectural design strategy can be extended to synthesize HEO nanoclusters as active entities for catalytic reactions or as functional nanoglues to stabilize metal atoms, clusters or HEAs. Such a design strategy is based on grafting metal oxide nanoclusters onto robust, commercially available, and high-area fumed silica powders [5]. In this work, we modified our previous synthesis approach in order to produce ultra-small, multi-element metal oxide nanoclusters: mixing various types of precursor salts and then using an electrostatic-adsorption-assisted precipitation approach to deposit the metal species uniformly onto the silica support. Subsequent processing at high temperatures enables formation of crystalline nanoclusters with the appropriate amounts of each cation species. The advantages of this approach include the flexibility of varying the relative amounts of a specific cation component and the potential of combining many different types of cations. Full characterization of such ultra-small HEO nanoclusters, however, proves extremely challenging, especially when the high-area support is non-conductive.

Figure 1a shows a representative backscattered electron (BSE) image of the as-synthesized catalyst, revealing the general shapes and sizes of the fumed silica as well as the macropores. The sample composed of catalyst powders which had been embedded in resin, finely polished, and coated with a layer of carbon. The catalyst powders consist of ultra-small CeO_x nanoislands with the addition of five other elements: Mn, Fe, Co, Cu and La. The relative amount of each cation could be changed. Screening of large amount of catalyst powders by BSE imaging and EDS analyses unambiguously showed that the metal precursor species uniformly distributed throughout the silica support without the formation of large particles/agglomerations (e.g., >100 nm in size) of metals/metal oxides. Figure 1b shows a low magnification high-angle-annular dark-field (HAADF) image of the silica powders/agglomerates, clearly revealing the mesopores of the fumed silica and absence of large metal/metal oxide particles (e.g., > 10 nm in size). Figure 1c shows a representative atomic resolution image of the ultra-small metal oxide nanoislands, with sizes ranging from about 1 nm to 3 nm. The very small clusters were not stable under the electron beam even though the powders were coated with a layer of carbon (5-7 nm) and low-current electron probes were used to form these images. The appearance of some single metal atoms in the image was probably a manifestation of electron-beam induced effects. Carbon monoxide oxidation was used as a reaction probe to evaluate the catalytic properties of the ultra-small, multi-element nanoclusters and similarly sized CeO_x was used as a control sample. The CO conversion rates and the cycling study (Fig. 1d) clearly show that the newly synthesized multi-element, mixed oxide nanocrystallites are significantly more active than the CeO_x/SiO_2 control sample and were stable after cycling to 500 °C.

The characterization challenge is clearly demonstrated in Fig. 1c: How to correlate the observed structure to the catalytic performance. We do not know which specific cation or combinations of cations are the active sites for the enhanced CO oxidation activity. It is strongly desirable to develop techniques to identify surface atomic species in HEOs to develop structure-property relationships [6].

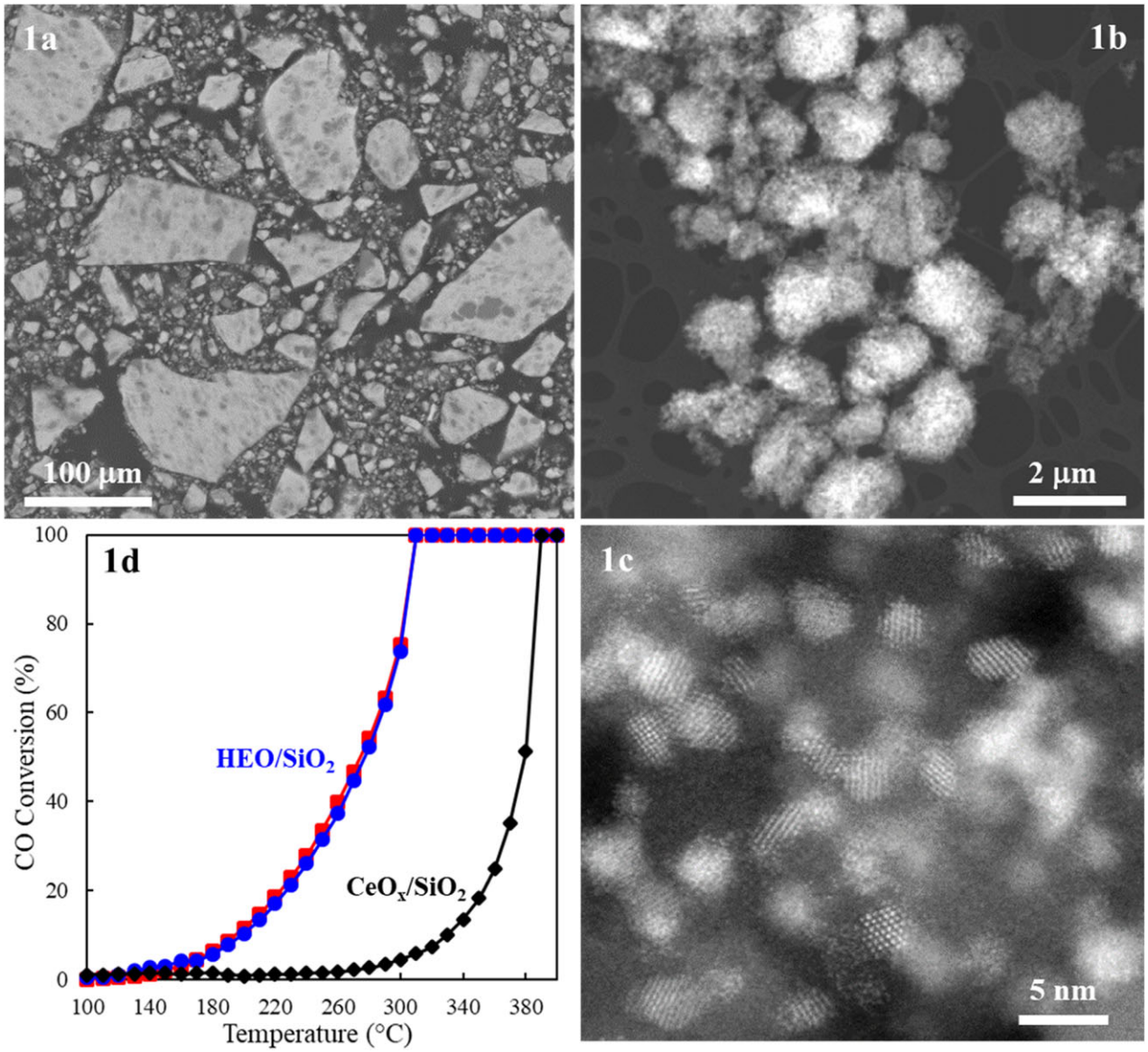

Fig. 1. Backscattered electron image (**1a**) of embedded/polished powders shows absence of large metal agglomerates. Low magnification HAADF STEM image (**1b**) shows mesopores of fumed silica support and absence of large metal/metal oxide particles within the mesoporous silica. Atomic resolution HAADF-STEM image (**1c**) reveals faceted metal oxide particles (1-3 nm in size). Low-dose electron probes were used to reduce electron-beam-induced damages of the ultra-small metal oxide particles. The CO conversion rates (**1d**) clearly demonstrate the significantly enhanced CO oxidation activity and cycling stability by mixing the five metal cations with the CeO_x nanoislands.

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