

Metal-Ceramic Nanocomposites for Utilization in Sulfur-Contaminated Fuel Streams

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Introduction

Due to increasing energy cost and decreasing fossil fuel reserves, the chemical and energy industries are starting to use increasingly low-quality fossil fuel feedstocks. This trend is leading to ever more stringent demands for efficient and robust materials and catalysts for processing of these fuels. Particularly the resistance against H₂S, a main constituent of typical fossil fuel contaminants, is of concern in catalytic fuel processing applications. Traditionally, this problem has been addressed through the use of desulfurization units that result in ultra-low sulfur streams. However, due to cost constraints and increasing sulfur ballast, interest in sulfur-tolerant catalysts and materials has increased strongly over recent years. In the present contribution, we are reporting on the development and testing of metal-oxide nanocomposite materials with the aim to combine of the high catalytic activity of well-controlled, nanosized metal particles (M = Cu, Ni, Fe) with the sulfur-capturing capability and high-temperature stability of an oxide matrix (BHA = Barium-Hexaaluminate, CeO₂, La₂O₃, and mixed La-Ce oxides) in order to obtain highly active and robust catalysts for fuel processing environments. The materials are tested in water-gas shift and in chemical looping combustion (CLC) of high-sulfur containing syngas streams, i.e. in two fundamentally different fuel processing applications as broad and stringent tests for the stability and applicability of the concept.

Materials and Methods

The synthesis procedure for the nanocomposites is based on a simple, one-pot reverse-microemulsion templated route, in which an aqueous solution of the respective metal salt (Ni, Cu, Fe) is mixed with isooctane and a surfactant (poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide)), followed by addition of the alkoxides of the respective matrix metals (Ce, La, Ba, Al). After aging for 36-72 hours, the aqueous and the organic phase are separated via temperature-induced phase separation, the product phase is washed several times with acetone, freeze dried, and calcined in air. A typical synthesis results in gram-amounts of metal-oxide nanocomposite powders. Samples with metal weight-loading between 1wt% and 37wt% were synthesized and characterized by BET, XRD, EDX, and TEM. The materials show an irregular, highly porous structure with pure textural porosity, and a highly homogeneous distribution of well-defined metal nanoparticles (d ~ 8-10nm) embedded in the ceramic matrix.

Results and Discussion

The materials were tested in TGA during exposure to syngas streams with and without 1vol% H₂S. La-, Ce-, and mixed La/Ce-oxides were used as matrix for typical WGS conditions, while BHA was used for chemical looping test. For the latter, the tests involved periodic cycling between exposure to syngas streams and regeneration in pure air streams.

We observe remarkably robust performance of the nanocomposites in both application environments. During exposure to sulfur-containing syngas streams at WGS reaction conditions, the La- and Ce-oxide matrix shows the intended efficient sulfur-capturing functionality (see figure 1). A clear break in the TGA curve (at t ~ 5 min.) allows identification of a transition from surface to bulk sulfidation. Due to the high surface area of the nanostructured oxides, which can be further tailored via the synthesis conditions, the surface capacity is sufficient to completely capture the S from the feed over several minutes at flow rates of 2 L/min syngas (1vol% H₂S) per gram catalyst.

Similarly, stable operation was observed in CLC for BHA-based nanocomposites at temperatures as high as 900°C in S-free and S-laden syngas streams. Interestingly, in this case the sulfidation of the BaO in the ceramic matrix results in significant increase in oxygen carrying capacity, i.e. exposure to H₂S did not deteriorate the carrier, but actually improved its efficiency. XRD studies (not shown) explain this effect due to the participation of BaS ↔ BaSO₄ in the oxygen storage process. Finally, again a strong shielding effect of the oxide matrix against S-exposure of the metal nanoparticle, as well as complete reversibility of the sulfidation of the nanocomposites is observed.

Figure 1. Sulfidation test of a nanostructured La₂O₃ sample at 450°C. TGA indicates a fast surface sulfidation during the first ~5 min. of exposure, followed by much slower bulk sulfidation. The H₂S signal (measured by QMS) shows essentially complete H₂S capturing up to t~26 min.

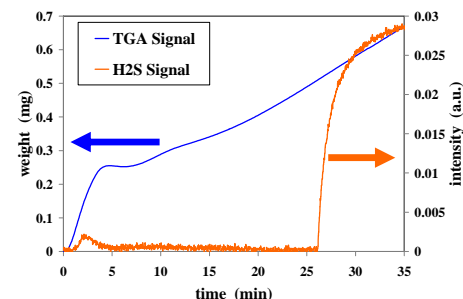
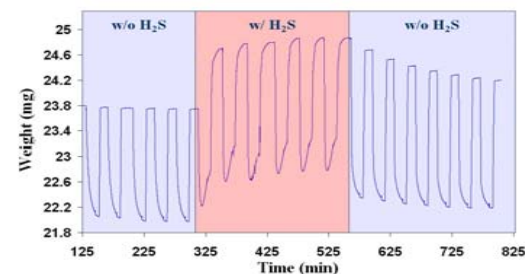


Figure 2. Performance of a Ni-BHA nanocomposite in CLC of syngas (multiple redox cycles in TGA at 900°C). Blue box: S-free syngas, red box: syngas with 1vol% H₂S. The sample weight increases due to sulfidation, but operation is stable and reversible.



Significance

The results demonstrate great potential for the proposed concept of metal-oxide nanocomposites as robust and efficient catalysts for processing of S-laden fuel streams at near-technical conditions.