Probing Structure-Property Relationship of Active Metal Nanoparticles on Mesoporous Silica Sorbent

Prashant Kumar,[1] Jong Seok Jeong,[1] Bahman Elyassi,[1] Nafiseh Rajabbeigi,[1] Michael Tsapatsis,[1] K. Andre Mkhoyan[1]

[1]Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN

Zinc-based adsorbents currently in use for H_2S removal from tail gas in the oil and gas industry have limited regenerability and reduced performance over multiple cycles [1,2]. Spatially well-distributed metal nanoparticles in mesoporous substrates can be effective in achieving better performance over multiple adsorption and regeneration cycles [3,4]. One of the critical aspects of understanding the functionality of these metal nanoparticles incorporated into mesoporous substrates is determination of the nanoparticle distribution throughout the substrate.

Using analytical scanning transmission electron microscopy (STEM), we studied spatial distribution of these nanoparticles. We examined freshly prepared amorphous mesoporous SiO_x framework (known as SBA-15), Cu- and Zn- incorporated SBA-15 (Cu-Zn-SBA-15), and sulfidated Cu-Zn-SBA-15. TEM samples were prepared by microtoming 60-100 nm sections containing the powder sample embedded in epoxy resin. Elemental mapping was performed by collecting spatially resolved STEM-EDS spectrum images in FEI Tecnai F30 STEM equipped with EDAX™ EDX spectrometer to identify the presence and distribution of Cu and Zn in the framework (Figure 1). Additionally, high-resolution HAADF-STEM images were obtained, using FEI Titan G2 60-300 S/TEM operated at 300 kV, to determine location of the Cu and Zn particles relative to mesopores of SBA-15 (Figure 2).

Presence of Cu and Zn observed in EDS elemental maps supports a previous Ar adsorption-desorption isotherm study, which indicated a median pore size reduction from 7.9 nm to 7.6 nm due to the incorporation of mixed metal nanoparticles. HAADF-STEM images of samples in two perpendicular orientations revealed that: (i) Cu and Zn nanoparticles are < 3 nm in diameter and (ii) they are uniformly distributed throughout the SBA-15 mesopores. Additionally, we did not observe aggregation of Cu and Zn nanoparticles after sulfidation in our HAADF-STEM images, which was further corroborated by the high adsorption capacity of H_2S after several cycles of adsorption-regeneration. Through focal HAADF-STEM image series also revealed that the Cu and Zn particles are located on the walls of mesopores [5].

References:

[1] P. Kumar *et al,* Microporous Mesoporous Materials **146** (2011) 127-133.
[2] M. Behl *et al,* Nature Nanotechnology **7** (2012) 810-815.
[3] G. Prieto *et al,* Nature Materials **12** (2013) 34-39.
[4] B. Elyassi *et al,* Microporous Mesoporous Materials (accepted).
[5] The authors acknowledge funding by the MRSEC Program of the National Science Foundation under Award Number DMR-0819885.
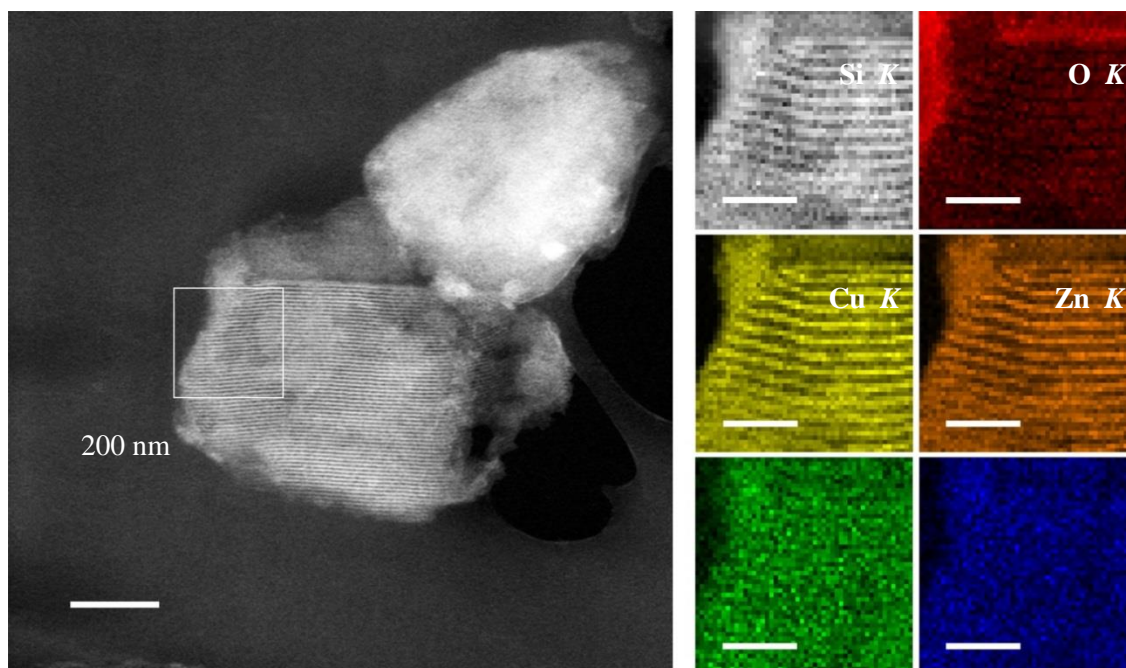
Figure 1. (a) HAADF-STEM image of Cu and Zn incorporated SBA-15 particle. (b) STEM-EDS elemental map of carbon, silicon, oxygen, copper and zinc (scale bar 100 nm) from section of the particle shown as a box in (a). Silicon and oxygen form the mesoporous SBA-15 substrate and Cu/Zn metal particles are distributed within the SBA-15 substrate.
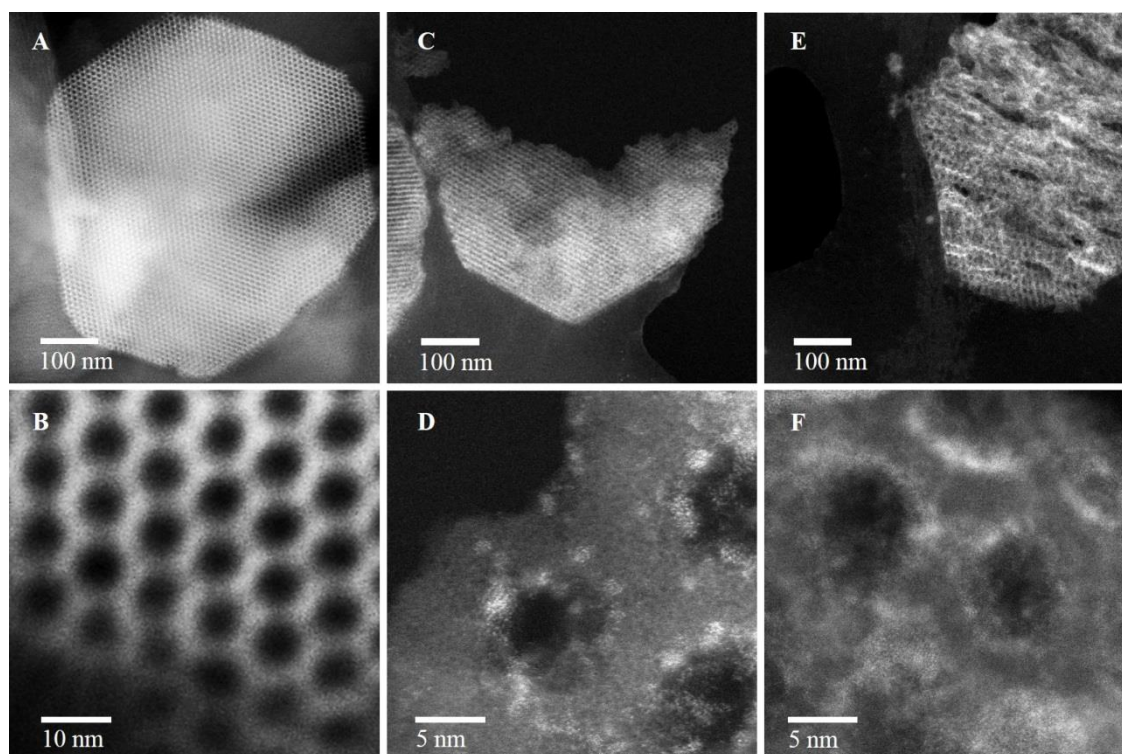
Figure 2. HAADF-STEM images of SBA-15 particles (a,b) without metal treatment; (c,d) after Cu/Zn incorporation; (e,f) after sulfidation of Cu/Zn incorporated samples.