Combustion-Generated Nanoparticles: The Role of Transition Metals in Nanoparticle and Pollutant Formation

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The human health and environmental effects of airborne nano- (ultrafine) particles are among the most important environmental issues facing our nation and the world. Combustion is the primary sources of these particles. Understanding the conditions under which they are formed and reactions that they undergo or catalyze can be used to control their emissions and reduce their environmental impacts. The goals of this program are:

1. Determination of the role of metal oxide nanoclusters in the formation and growth of primarily carbonaceous nanoparticles.
2. Determination of the role of metal oxides condensed on growing nanoparticles in the formation of organic pollutants.

In the first year of this program, we have focused our efforts on the synthesis of metal oxide nanoparticles that can be used as laboratory surrogates for combustion-generated particles. Copper oxide is typically the highest concentration redox active metal in combustion systems and silica is the most common non-volatile inorganic component. Thus copper oxide/silica nanoparticles are the most likely form of seed nuclei for particle growth and pollutant formation. We have succeeded in developing a robust method for preparing bulk quantities of size –controlled, non-agglomerating metal oxide nanoparticles with low size dispersity.

The particles were prepared using a dendrimer template-based synthetic approach. Tailoring of CuO nanoparticle size was readily achieved over the range of 1.6–3.2 nm by thermally treating Cu(II)-poly(propylene imine) dendrimer complexes of various stoichiometries supported on microscopic silica. Thermal decomposition and oxidation[30] of the silica-supported, $Cu(II)_x$–DAB-Am_{32} (where x = 4, 8, and 16) at 450 ºC under ambient atmosphere for 5 h resulted in formation of nanometer-sized particles on the silica support (cf. Figure 1). The size dispersity of the CuO nanoparticles is extremely small (~10%) (cf. Figure 2).

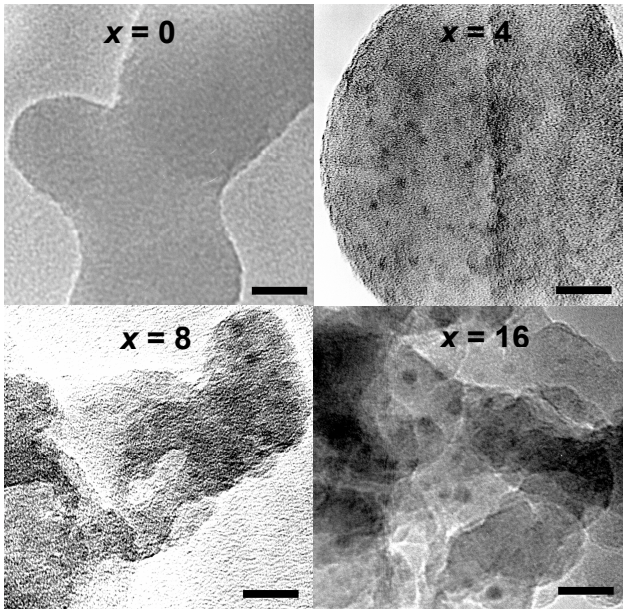

Figure 1. High-resolution electron micrographs of thermally treated (450 ºC) $Cu(II)_x$–DAB-Am_{32} on Cabosil silica. Scale bar is 10 nm in each image. The dark spots in the images are the copper oxide nanoparticles, and the gray background results from the silica support.

XANES spectra as well as XPS data, strongly suggested Cu(II)O was the dominant constituent of the nanoparticles present on the silica support. The shape of the pre-edge and edge absorption spectra for the template-

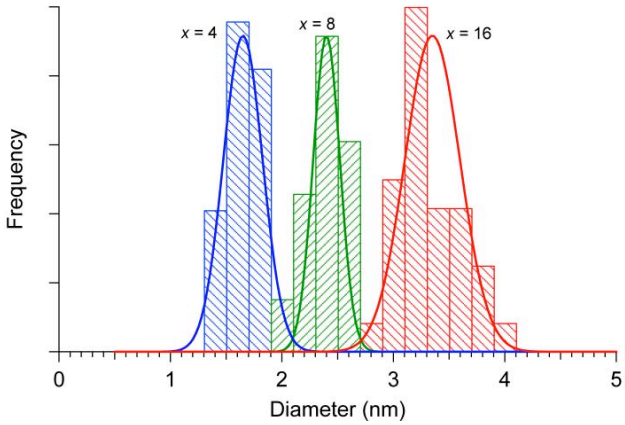

Figure 2. Size distributions for nanoparticles resulting from thermolysis of DAB-Am_{32}–$Cu(II)_x$ complexes supported on silica as a function of Cu(II):DAB-Am_{32} ratio, x. The mean nanoparticle diameters are 1.57± 0.19 nm (x = 4), 2.31±0.18 nm (x = 8), and 3.14±0.26 nm (x = 16).

synthesized copper oxide nanoparticles supported on silica were consistent with those of Cu(II)O standards. However small differences were noted in the "post-edge" region (> 9 keV), which may indicate the existence of structural differences between the nanoclusters and bulk Cu(II)O, possibly due to interactions between the silica support and the Cu(II)O nanoparticles or size effects of the Cu(II)O.

The diversity of the synthetic approach for fine-tuning the size of the CuO nanoparticles was demonstrated by use of the generation-5 dendrimer complexed to 32 copper ions, DAB-Am_{64}–$Cu(II)_{32}$**.** Thermal oxidation of this complex on Cabosil resulted in formation of CuO nanoparticles with a diameter of 2.20±0.14 nm. Furthermore, by lengthening the annealing time, the size of the CuO nanoparticles was increased to 195+/-10 nm. Thus, the method described here will allow for production of a series of supported CuO nanoparticles spanning a large size range with exquisite control over size and size dispersity. In addition, the method bodes well for other metals, such as Ag, Ni and Fe, for the complexes of these metals with DAB-Am_n are well known. In addition, the method should be easily extended to other oxide substrates, like TiO_2, Al_2O_3, and SnO_2, as the result of the known propensity of amine-terminated dendrimers to adsorb to oxide surfaces.

As a result of the characteristic, novel properties of this class of nanomaterials, the ability to make well-defined nanoscale metal oxides is of particular interest to the catalysis, sensor, semiconductor, and environmental fields,. While there has been good progress in the preparation of a variety of metal-oxide nanoparticles in recent years, a major obstacle to their widespread use in potential applications is precise regulation of nanoparticle size (selectivity) and size dispersity (control). These issues are of particular concern for supported metal oxide nanoparticles, whose reactivity is closely related to particle agglomeration, size, and size dispersity. Significant progress has been made in the synthesis of metal nanoparticles, by application of template-based methods that utilize precursors composed of metal ion-containers, such as dendrimers, micelles, and organometallic complexes. Application of this template-based direction, as well as others, to the synthesis of metal oxide nanoparticles has resulted in a group of studies that targets the fabrication of metal oxide nanoparticles of controlled size. The outcomes from these studies indicate that the made-to-order synthesis of metal oxide nanoparticles of controlled size and size distribution still has significant limitations for the most part. Thus, the development of routes for fabricating a wide variety of such well-defined nanoparticles is of great importance.

References.

"Size-controlled Copper Oxide Nanoparticles Supported on Silica", Slawomir Lomnicki*, Hongyi Wu, Scott N. Osborne, Jeff M. Pruett, Erwin D. Poliakoff, Robin L. McCarley, and Barry Dellinger (Submitted JACS communication)