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Combustion Synthesis of Ni-SiO_2 Nanoscale Materials

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Fabrication of metallic nanoparticles is of high interest for many industrial applications [1-2] including energy conversion and storage, electronics, and heterogeneous catalysts. However, it seems to be a challenging task because the metallic nanoparticles tend to agglomerate and grow into larger crystallites. The successful fabrication methods involves special strategies, for example, adding an organic ligand or inorganic capping agent, and creating of core-shell nanoparticles, in order to prevent the coalescence and growth of the metallic nanoparticles into larger aggregates [3]. The other approach employs the deposition of metal nanoparticles onto a porous solid to inhibit their aggregation and growth. Here we report the use of porous supports in conjunction with metal nanoparticles allows tailoring the textural properties of resulting materials.

The Ni-SiO_2 composite nanoscale materials were prepared by combustion synthesis method. The method involves preparation of stable silica gels mixed with metal nitrate and citric acid through the controlled hydrolysis of tetraethyl orthosilicate. As-prepared gels were dried and mixed with ammonium nitrate, and an exothermic self-propagating reaction was initiated in the mixtures by local preheating. Reaction in inert gas allowed to prepare of highly porous Ni-SiO_2 nanomaterials with metal content ranging from 5 to 30 wt.%. FEI Titan 80-300 transmission electron microscope (TEM) has been employed for atomic resolution imaging of the nano-materials, electron diffraction and chemical analysis by EDS.

The method allows changing the size of metal nanoparticles from 2 to 50 nm. Detailed TEM analysis suggested that a significant portion of nickel nanoparticles appeared inside the silica matrix. Figure 1a shows a high-resolution image of a typical Ni-SiO_2 nanoscale material with 5% Ni content. It is interesting that the average diameter of metal nanoparticles ~ 3 nm and most of the particles are smaller than 5 nm. Higher concentration metal nitrate in initial gels results in a product with two characteristic dimensions of metal nanoparticles. The diameter of small nanoparticles in materials containing 30% Ni is changing in the 2 – 10 nm range, while significant amounts of large particles (35 - 50 nm) can also be observed. TEM images also suggest that that the smaller nanoparticle appeared predominantly inside the silica matrix, whereas larger crystals mostly appear on the surface of porous aggregates.

Reaction in air atmosphere led to oxidation of metal nanoparticles resulting in NiO-SiO_2 composites. A high-resolution TEM image indicates the presence of NiO nanoparticles distributed on the silica for the product prepared in air. Statistical analysis shows that the particle size of NiO phase ranges from 3 to 10 nm with an average diameter of ~7 nm (Figure 1c). The differences of nanoparticle sizes for Ni and NiO phases for the same initial gels may be explained by higher oxidation temperature (~1000^oC) of nickel nanoparticles in a secondary combustion front that results in the significant growth of NiO phase.

The materials tested as catalysts in ethanol decomposition reaction. The catalysts exhibit high activity toward hydrogen generation for ~100 h. The materials were also sintered by spark plasma sintering

(SPS) to fabricate porous (70-80%) compact samples. As-sintered products exhibited significantly low thermal diffusivity, which makes them attractive for thermal management applications.

Our experiments show that the nickel nanoparticles formed by combustion synthesis predominantly located inside the porous silica. As a result, the nanoparticles remain stable during high-temperature reduction stage and catalytic run. However, the formation of carbonous residues was detected along with the main decomposition products of ethanol (hydrogen, carbon monoxide, and methane). Our results are in agreement with previous observations [4] about ethanol decomposition over the Ni-containing catalysts. It proceeds through ethoxy intermediate formation by O–H bond cleavage, followed by break the C-H and C-C bonds of adsorbed ethoxy to form hydrogen, methane, CO and carbon [5].

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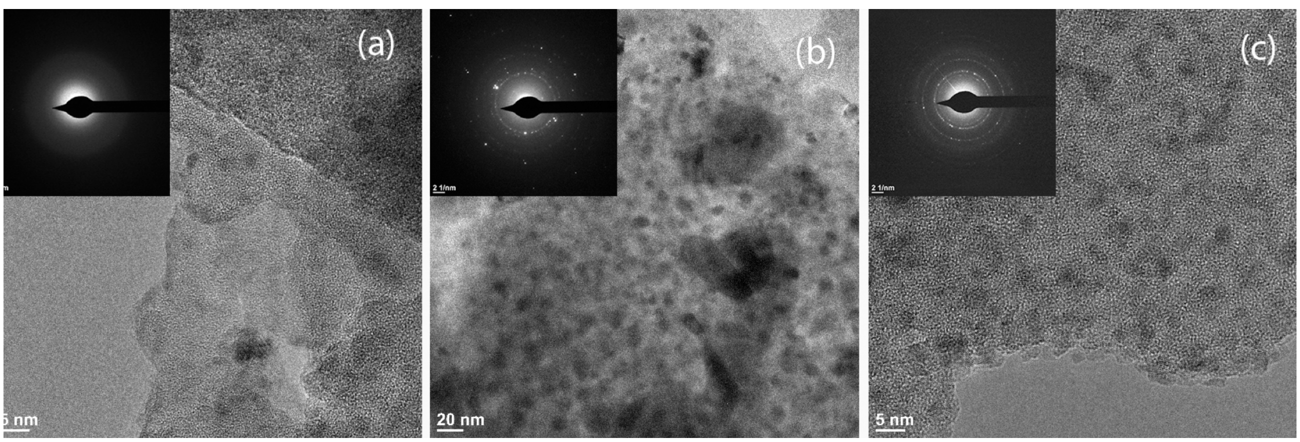

Figure 1. TEM images and corresponding diffraction patterns for different composites: 5%Ni-SiO_2 (a), 30%Ni-SiO_2 (b) and 5%NiO-SiO_2 (c)

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