ND*nano* Undergraduate Research Fellowship (NURF)
2011 Project Summary

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Project title: Design of nanocatalysts for efficient energy conversion

My research work over the summer session consists of two parts:

1. Development of earth-abundant metal catalysts for the conversion of 2-methyl furan (2-MF) into C_{10} alkanes.

This method includes three steps: (1) the ring opening of 2-MF which forms pentanal and pentan-2-one or alcohols, (2) the aldol self-condensation to form large molecules from pentanal and pentan-2-one, and (3) the hydrogenation of the products of aldol condensation to from hydrocarbons with ten carbon atoms (C_{10}). We used colloidal chemistry to synthesize near-monodisperse $Ni_{1-x}Cu_x$ and $Ni_{1-x}Co_x$ (x = 0.2–0.8) nanocrystals (NCs) by a one-pot thermolysis approach in hot surfactant solutions. These two kinds of NCs will be applied to the selective conversion of 2-MF to pentanal and pentan-2-one for the production of liquid fuels.

For a typical synthesis, 0.1 mmol $Ni(acac)_2$ and 0.1 mmol of $Cu(acac)_2$ (or $Co(acac)_2$ in $Ni_{1-x}Co_x$ case) were pre-dissolved in 1 mL of dry oleylamine at 358 K in an oil bath. Dry oleylamine and 1-octadecene in a given volume were put into a 50 mL round-bottom flask at room temperature. The solvent was heated to 413 K in an electro-mantle and evacuated at this temperature for 20 min to remove water and oxygen under magnetic stirring. The solvent was then heated to 503 K at the rate of 10 $K \cdot min^{-1}$. The pre-dissolved metal precursors were injected into the heated solvent inside the flask with a plastic syringe within 20 s, and were allowed to further react for 10 min at this temperature under Ar atmosphere. When the reaction was complete, 20 mL anhydrous ethanol was added at room temperature to form a cloudy black suspension. This suspension was separated by centrifugation (5000 rpm for 10 min), and the NCs were collected.

Figure 1 and 2 show the TEM images of the as-prepared $Ni_{0.5}Cu_{0.5}$ and $Ni_{0.5}Co_{0.5}$ samples, respectively. $Ni_{0.5}Cu_{0.5}$ NCs formed ordered two-dimensional (2D) hexagonal-close-packed (hcp) nanoarrays over large areas, demonstrating their low polydispersity and good surface capping by

oleylamine. However, the $Ni_{0.5}Co_{0.5}$ NCs were found to consist of well-dispersed dendritic shaped nanoparticles, demonstrating the high-yield formation of nanodendrites (~100%). The size of the nanodendrites narrowly ranged from 15 to 25 nm with an average diameter of 20 nm. A systematic test of catalytic activities of these NCs for 2-MF conversion to C_{10} alkanes will be conducted in the same laboratory soon.

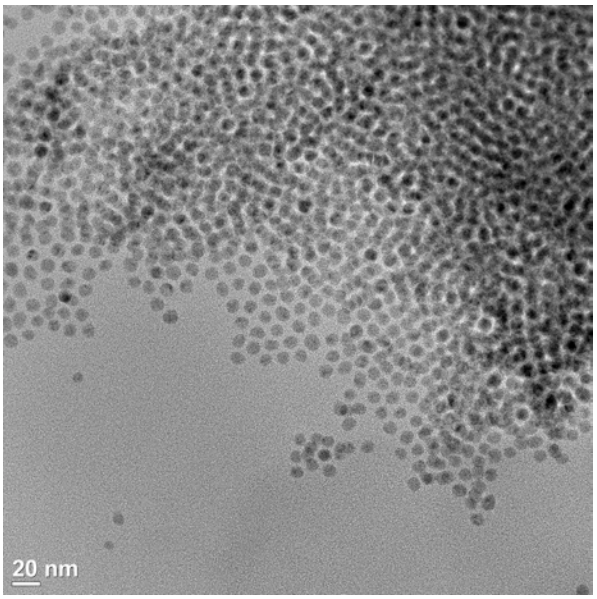

Figure 1. TEM image of $Ni_{0.5}Cu_{0.5}$ nanocrystals.

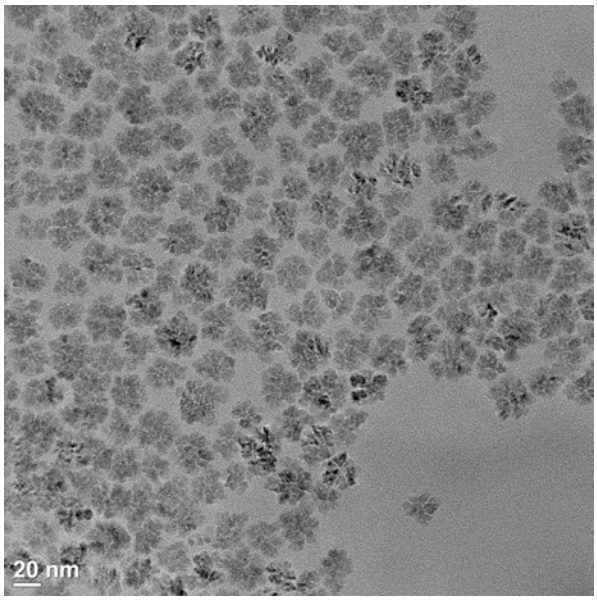

Figure 2. TEM image of $Ni_{0.5}Co_{0.5}$ nanocrystals.

2. Synthesis of carbon nanotube (CNT) encapsulated cobalt oxide for the study of the confinement effect of carbon nanotube on the activities and selectivities of Fischer–Tropsch Synthesis (FTS).

FTS is a heterogeneous catalytic process for the transformation of synthesis gas (syngas, $CO+H_2$) into hydrocarbons. The hydrocarbon products of FTS can be sulfur- and nitrogen-free high-quality fuels such as diesel fuels, which have been proven to be more environmentally benign than the petroleum-based fuels, and thus may easily meet the increasingly stringent environmental regulations. Moreover, chemicals such as a-alkenes or C_2–C_4 lower alkenes may also be directly produced from syngas if a highly selective FT catalyst can be developed. Therefore, FTS is a crucial step for the transformation of non-petroleum resources into super-clean fuels or valuable chemicals from syngas. In the present work, we intend to study the effects of confinement of catalyst within CNTs on the FTS activity and selectivity.

The synthesis of CNT encapsulated cobalt oxide catalyst was carried out by suspending 0.4 g capped CNTs in 20.0 g concentrated HNO_3 (~70%) containing 1.0 g $Co(NO_3)_2 \cdot 6H_2O$ and refluxing for 4.5 h in an oil bath at 413 K. After that, the suspension was cooled down to room temperature naturally and the supernatant solution was decanted. The resulting insoluble black product was obtained by quick vacuum filtration and dried in an oven at 393 K for 12 h. The obtained sample was denoted as Co-in-CNT. For comparison, the same amount of cobalt oxide was deposited on the outer surface of nanotubes by impregnating CNT with aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution. For this CNT with closed caps were used, which were obtained by refluxing CNTs in 35% HNO_3 solution at 383 K for 5 h. After impregnation, the same drying procedure was applied and Co-out-CNT was obtained.

TEM images reveal that the Co_3O_4 particles of Co-out-CNT are dispersed on the outer surface of the nanotubes (Figure 3). The particle size has a bi-model distribution with over 80% particles in the range of 3–8 nm while the remaining from 12–20 nm. In the samples of Co-in-CNT, we found that there are 80 ± 5% particles located inside the tubes (Figure 4). In addition, the particle size is obviously smaller (~3 nm on average) and the distribution is much more narrower than its counterparts. The activity test of FTS is being conducted on a self-made high-pressure, high-temperature stainless steel fixed-bed reactor.

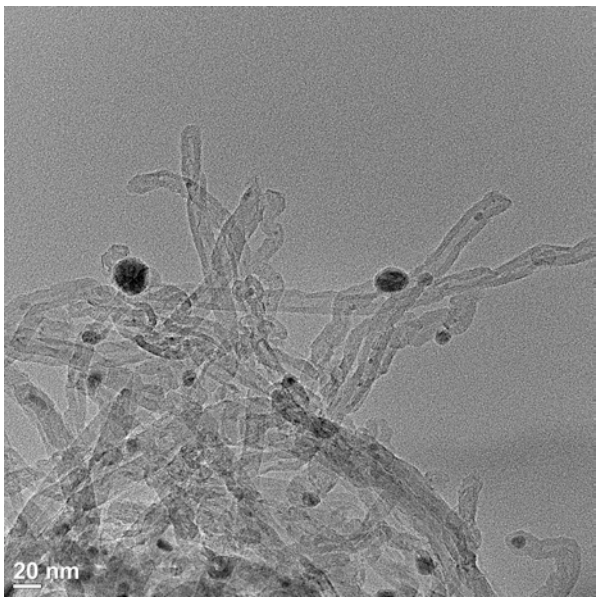

Figure 3. TEM image of Co-out-CNT

Figure 4. TEM image of Co-in-CNT