

Towards Biomimetic Catalysts by Epitaxial Growth of Microporous Polymer Layers Around Uniform Metal Nanocrystals

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Introduction

Nearly all of the chemistry upon which humanity relies involves catalysis. Enzymes govern precise, biological chemistry while homogeneous and heterogeneous catalysts facilitate the massive scale chemical processes of modern civilization. What enzymes lack in stability, they make up for in selectivity; conversely, high-throughput heterogeneous catalysts often lack appropriate selectivity for many reactions. Combining the advantages of these two types of catalysts has been a long-standing goal in the field^{1,2}. Constructing such a thermally stable, biomimetic 3D active site would enable stabilization of reactive intermediates, thereby enabling major improvements in challenging catalyzed chemical reactions.

Porous Organic Frameworks (POFs) are a medium for constructing such 3D active site. POFs are organic polymers formed through Schiff base linkages that are thermally stable to 350°C,³ have micropores that resemble enzyme pockets, and have tunable chemical functionality. We introduce a modular catalyst synthesis approach for systematic design of 3D controlled active sites from POFs and colloidal nanocrystals. Well-defined metal nanocrystals are deposited and activated on thermally treated POFs, upon which additional layers of POFs are grown in an epitaxial fashion to encapsulate the particles with pendant functional groups stemming from the POF material. This approach has a broad scope of possible catalyst designs due to the combination of independent control of both POF layer chemistry as well as nanocrystal composition and shape. These hybrid materials with tailorable chemical and electronic environments can be used to engineer selectivity of transition metal catalysts.

Materials and Methods

An initial POF support was synthesized following literature conditions by condensation of terephthalaldehyde and melamine.³ Novel POFs were synthesized by introducing other functional groups in the starting building blocks (e.g. 5-(tert-butyl)-2-hydroxyisophthalaldehyde, 2-bromoisophthalaldehyde) in place of terephthalaldehyde. Products showed the expected FT-IR signature, high surface areas (600-900 m² g⁻¹), and thermogravimetric analysis and differential scanning calorimetry in line with high thermal stability in air up to at least 300 °C, showing minimal signs of degradation.

Mono- and bimetallic nanocrystals were synthesized according to procedures developed in our group. Transmission electron microscopy and energy dispersive x-ray spectroscopy demonstrated the uniform in size and composition. The nanocrystals were deposited onto a POF support from hexanes and sonicated for 15 minutes. Ligands were removed by thermal treatments in air at varying temperatures. The accessibility of the metallic surfaces was measured with CO chemical adsorption.

Epitaxial overgrowth of POF layers was performed under conditions similar to the synthesis of initial POF. POF-supported nanocrystals were dispersed in a solution containing POF monomers and heated under nitrogen for 24 hours. Similar characterization was performed.

Catalytic characterization for CO oxidation was performed in a fixed bed reactor with plug-flow dynamics using 0.25% CO, 4.75% O₂ and balance Argon. Thermal ramps were run from 50 °C to 250 °C at 3 °C min⁻¹. Reactants and products were quantified by gas-phase FT-IR spectroscopy and gas-chromatography.

Results and Discussion

Various colloiddally synthesized metal nanocrystals (Pd, Pt, Au, Ru, Ni) as well as bimetallic (Pd/Au, Ru/Pd) nanocrystals were successfully encapsulated in POFs with this method. TEM images of encapsulated Pd nanocrystals are shown in Figure 1. Image analysis indicates that particles retain size and shape throughout the synthesis process and indicate encapsulation based on domains of high and low concentration of nanocrystals.

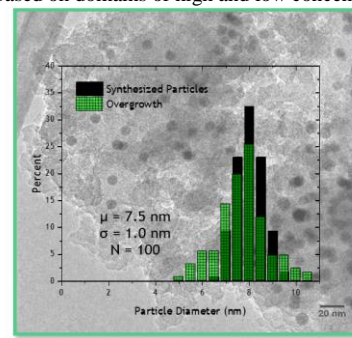


Figure 1. TEM of encapsulated Pd nanocrystals

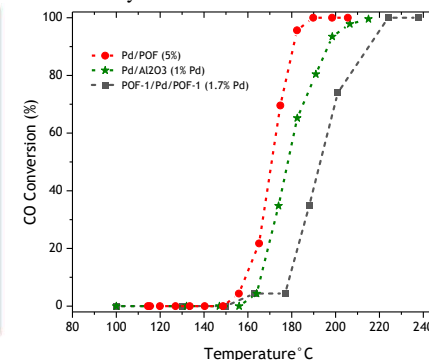


Figure 2. FTIR catalytic data

Gas adsorption measurements indicate micropores in the 5-6 Å range, which allow confinement of reaction intermediates in strained geometries at metal sites, along with mesopores, which give reasonable mass transport of gaseous species through the bulk of the POF layers. CO oxidation thermal ramps in Figure 2 indicate that both supported and encapsulated metal nanocrystals with POFs are active on the same order as metals supported on metal oxides. Turn-over-frequencies calculated based on CO adsorption measurements indicate that activity is increased when particles are encapsulated. Kinetic analysis and in-depth characterization with synchrotron techniques indicate that improved activity in catalysts containing epitaxial overgrowth is attributable to stabilization of reaction intermediates by means of the amino groups in the POF structure. Greater catalytic stability for POF-supported materials is also demonstrated, opening novel pathways for the exploration of this largely unknown catalytic supports to mimic enzymes on the way to selective chemical conversions.

Significance

This novel, general, modular approach to biomimetic catalysis can be applied with many iterations stemming from the easily tailorable metal coordination environment and colloidal particles to generate structure-activity relationships. The potential increases in selectivity with this design are applicable to gas phase reactions where selectivity is limiting, like with methane selective oxidation to methanol or CO₂ selective reduction to liquid products.

References

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