Characterizing the Active Sites of Ligand-Capped Transition Metal and Metal Phosphide Nanoparticle Catalysts: Ligand Removal and Surface Acidity

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Introduction

Ligand-capped metal nanoparticles have emerged as the preeminent method to control active metal shape, phase, and particle size [1]. This degree of control is owed to the thermodynamic stabilizing effect of the ligands which prevents particle agglomeration. These nanoparticles can be deposited on a support for catalytic applications, but the ligands covering the particles must be removed to access the active sites. Ligand removal methods have been investigated in the literature, including thermal treatment [2], oxidative treatment [3], and solvent washing [4]. None of these methods are universally effective, and they can lead to particle sintering [5], which limits the nanoparticles’ catalytic utility. The present work aims to elucidate the effect of thermal pretreatment temperature and gaseous environment on ligand-nanoparticle interactions, nanoparticle phase, and accessible active site densities for a series of ligand-capped metal and metal phosphide nanoparticle catalysts supported on silica. These catalyst properties were probed using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray diffraction (XRD).

Materials and Methods

Nanoparticles were synthesized by the solution-phase decomposition of a single-source molecular precursor with oleylamine as a capping agent and dispersed on silica to yield the following catalysts: Ni/SiO₂, NiₓP/SiO₂, Pt/SiO₂, RhₓP/SiO₂. DRIFTS spectra under flowing nitrogen and air were collected at 35 °C after successively higher pretreatment temperatures ranging from 150 – 500 °C by increments of 50 °C. The C-H stretch for oleylamine at 2855 cm⁻¹ was monitored. Pyridine-DRIFTS experiments were also conducted to measure the concentration of acid sites following pretreatment. XRD patterns of pretreated catalysts were collected over the range of 2θ from 20° to 80° at 10°/min to detect phase changes.

Results and Discussion

DRIFTS revealed that the ligands are removed under inert atmosphere in the range of 250 – 450 °C; this range varied based on metal and phosphide type (Figure 1). Incorporation of phosphorous into the nickel structure increased the ligand removal temperature by ~100 °C, which could be attributed to stronger ligand adsorption to the electronically-altered Ni metal sites, or stronger binding to P sites. A similar electronic structure argument can be employed to explain the comparatively facile ligand removal from noble metals.

Pretreatment under air removed ligands more easily in all cases; however, XRD showed complete oxidation of both nickel and nickel phosphide phases to nickel oxide. The less pronounced difference in removal between nickel and nickel phosphide could be explained by the progressive oxidation of nickel phosphide sites. Ligands likely decompose, rather than desorb, under air. This decomposition pathway is supported by pyridine-DRIFTS (Figure 2), which shows a complete loss of acid sites after ligand removal in air. This loss of sites can be explained by blocking of the acid sites.

Figure 1. Fraction of ligand remaining on all catalysts under inert (left) and air (right) as a function of temperature. Lines are included to guide the eye.

Under inert atmosphere, pyridine-DRIFTS confirmed effective ligand removal from Ni/SiO₂ as evidenced by the linear increase in acid site numbers with ligand removal. Acid sites decreased for NiₓP/SiO₂, however, suggesting a ligand decomposition pathway is favored for this material. These results highlight the importance of both nanoparticle phase and pretreatment atmosphere on the fate of the ligands (desorption vs. decomposition).

Significance

Understanding ligand chemistry will allow for effective pretreatments to be tailored to catalyst type and application. Efficiently using the available metal on a catalyst in this way is an avenue for cutting costs, and further studies of a nanoparticle’s intrinsic activity will be possible with pretreatments that can preserve a well-defined active surface.

References