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Synthesis of stable monodisperse AuPd, AuPt, and PdPt bimetallic clusters encapsulated within LTA-zeolites

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ABSTRACT

AuPd, AuPt, and PdPt bimetallic clusters uniform in size and composition were prepared using hydrothermal assembly of LTA crystals around cationic precursors stabilized by protecting mercaptosilane ligands. The sulfur moiety in these bifunctional ligands forms adducts that prevent premature reduction or precipitation of metal precursors during crystallization. The silane groups can form bridges with silicate oligomers as they form, thus enforcing homogeneous distributions of precursors throughout crystals and ensuring that subsequent reductive treatments lead to the two elements residing within small and nearly monodisperse clusters. Their confinement within LTA crystals, evident from microscopy and titrations with large poisons, renders them stable against sintering during thermal treatments at high temperatures (820–870 K). Infrared spectra of chemisorbed CO show that bimetallic surfaces are free of synthetic debris after thermal treatments; these spectra also indicate that intracluster segregation occurs upon CO chemisorption, a demonstration of the presence of the two elements within the same clusters. The number and type of atoms coordinated to a given absorber atom, determined from the fine structure in X-ray absorption spectra, are consistent with bimetallic structures of uniform composition. The rates of ethanol oxidative dehydrogenation on these bimetallic clusters were essentially unaffected by exposure to dibenzothiophene, a large poison that suppresses rates on unconfined clusters, indicating that bimetallic clusters are protected within the confines of LTA crystals. These synthetic protocols seem generally applicable to other bimetallic compositions and zeolites, for which the monometallic counterparts have been successfully encapsulated within several microporous frameworks using ligand-stabilized precursors and hydrothermal crystallization methods.

1. Introduction

Bimetallic nanoparticles are useful as catalysts because of the unique electronic and structural features conferred by atomic mixing of two or more elements at the nanoscale. Such features, in turn, are consequential for turnover rates and selectivities in reactions as diverse as CO oxidation [1], alkane dehydrogenation [2], and NO_x reduction [3]. These bimetallic synergies also bring ancillary benefits [4]; a second metal can assist the reduction of another one [5], inhibit sintering during thermal treatments [6], or weaken the effects of site blocking by S-atoms or other titrants [7]. These consequences may reflect ligand effects that cause one element to influence the electronic properties of another one [8] or ensemble effects caused by the dilution of monometallic domains [9]. The dissection of such effects into their causative components requires the synthesis of particles uniform in composition and size [9], an elusive objective because of the dearth of effective and general synthetic strategies.

Sequential adsorption and precipitation or co-impregnation of two metal salts onto mesoporous scaffolds [10] does not consistently place the component metals in atomic proximity [10], a challenge that can be addressed by sequential grafting of organometallic precursors onto supports [10]. Such grafting enforces metal-metal binding through covalent attachments between the first and second precursors deposited. The availability of precursors that prefer mutual interactions over those with the

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support limits the scope of such protocols, which often lead to the concurrent formation of monometallic clusters of the second precursor used in the sequence [10]. Galvanic displacement and electroless deposition, in contrast, selectively place a second metal into existing clusters of another metal via redox reactions [11]. Compositional uniformity in these methods requires seed clusters uniform in size and strategies to minimize homogeneous nucleation of the second component using solvents as reductants [9]. Colloidal synthesis methods involving the reduction of precursors in the presence of protecting polymers [11] can also form small clusters uniform in size and composition [9,12]; such uniformity, however, is frequently compromised by thermal treatments essential to deprotect the metal surfaces, as required for their catalytic function [9,11].

The nanometer-sized voids provided by crystalline zeolite frameworks can be used as containers for bimetallic clusters [11]. Their confinement within such voids allows the selection of certain reactants and transition states over others based on molecular size and the protection of active surfaces from large titrants and poisons by exploiting zeolite shape selectivity [13,14]. Confinement is often achieved by the exchange of solvated cationic precursors into the anionic zeolite frameworks [4]. Reductive treatments then form monometallic clusters, and the subsequent exchange and reduction of a second metal can form, in some instances, confined bimetallic clusters that are less prone to sintering than their monometallic counterparts [4]. Inhomogeneous cluster compositions, however, are often observed and such exchange methods require zeolite channels that allow the diffusion of the solvated cationic precursors and their charge-balancing double layer [11,15].

Here, we report an alternate route for the synthesis of small bimetallic clusters, uniform in size and composition, within LTA zeolite crystals, a framework with apertures too small to allow precursor exchange. We illustrate this general synthetic strategy for a range of AuPd, AuPt, and PdPt compositions. In doing so, we extend techniques that use protecting ligands to stabilize metal cation precursors against premature precipitation as colloidal metals of oxyhydroxides at the hydrothermal conditions required to crystallize zeolite frameworks [13,14]. Hydrothermal LTA crystallization in the presence of ligated precursors of two different elements leads to the formation of nearly monodisperse bimetallic clusters (1–2 nm); these clusters expose surfaces free of synthetic debris after sequential thermal treatments in O_2 and H_2, without compromising LTA crystallinity. The bimetallic nature of the clusters was shown by X-ray absorption spectroscopy and confirmed by the infrared spectra of chemisorbed CO. The protecting 3-mercaptopropyl-trimethoxysilane ligands prevent precipitation, reduction, and coalescence of the metals before the formation of LTA frameworks. These ligands also form siloxane bridges with silicate oligomers to enforce confinement and uniform placement of precursors throughout zeolite crystals, thus ensuring bimetallic mixing and the nucleation of small confined clusters, even after thermal treatments that remove the ligands and their S-atoms. The retention of these clusters within zeolite crystals was demonstrated from ethanol oxidation rates on samples exposed to dibenzothiophene, which would irreversibly poison any unconfined clusters [13].

2. Experimental methods

2.1. Reagents

$HAuCl_4{\cdot}3H_2O$ (99.999%, Sigma-Aldrich), $Pd(NH_3)_4(NO_3)_2$ (99.99%, Sigma-Aldrich), $Pd(NH_3)_4Cl_2$ (99.99%, Sigma-Aldrich), H_2PtCl_6 (8% wt. in H_2O, Sigma-Aldrich), 3-mercaptopropyl-trimethoxysilane (95%, Sigma-Aldrich), NaOH (99.99%, Sigma-Aldrich), Ludox AS-30 colloidal silica (30% wt. suspension in H_2O, Sigma-Aldrich), $NaAlO_2$ (53% Al_2O_3, 42.5% Na_2O, Riedel-de Haën), mesoporous SiO_2 (Davisil, grade 646, surface area: 294 $m^2\,g^{-1}$), fumed SiO_2 (Cab-O-Sil, HS-5, 310 $m^2\,g^{-1}$), $CaCl_2{\cdot}2H_2O$ (EMD Millipore), acetone (99.9%, Sigma-Aldrich), ethanol (99.9%, Sigma-Aldrich), ethylenediamine (98%, Sigma-Aldrich), dibenzothiophene (98%, Sigma-Aldrich), air (extra dry; 99.999%, Praxair), H_2 (99.999%, Praxair), He (99.999%, Praxair), Ar (99.999%, Praxair), 25% O_2/He (99.999%, Praxair), and 1.0% CO/He (99.999%, Praxair) were used as received.

2.2. Materials synthesis

2.2.1. Synthesis of Au, Pd, Pt and AuPd, AuPt, and PdPt clusters within LTA crystals

Preparation procedures for bimetallic metal-encapsulated Na-LTA zeolites (M_1M_2NaLTA, where M_1 and M_2 are Au, Pd, or Pt) were adapted from hydrothermal synthesis protocols for monometallic systems [13,14]. Similar synthetic protocols were used for monometallic (AuNaLTA, PdNaLTA, PtNaLTA) and bimetallic (Au_nPd_{100-n}NaLTA, Au_nPt_{100-n}NaLTA, Pd_nPt_{100-n}NaLTA; n is the atomic percentage of the first element) samples. For example, $Au_{50}Pd_{50}$NaLTA was prepared by dissolving 3-mercaptopropyl-trimethoxysilane (0.96 g) and NaOH (4.8 g) in deionized H_2O (17.9 MΩ resistance; 18 cm^3) in an open polypropylene bottle (125 cm^3) using magnetic stirring (6.7 Hz; 8 h). Then, aqueous $HAuCl_4{\cdot}3H_2O$ (0.156 g in 9 cm^3 deionized H_2O) and $Pd(NH_3)_4(NO_3)_2$ (0.118 g in 9 cm^3 deionized H_2O) solutions were concurrently added dropwise to the ligand-NaOH solution over 0.5 h while stirring (6.7 Hz). Colloidal silica (10.67 g, Ludox AS-30) was then added, and the polypropylene bottle was capped and heated to 353 K for 0.5 h with continuous agitation (6.7 Hz). The bottle and its contents were then cooled to ambient temperature, and an aqueous solution of $NaAlO_2$ (6.0 g dissolved in 18 cm^3 deionized H_2O at ambient temperature) was added dropwise while stirring (6.7 Hz, 2 h). This procedure formed a homogeneous synthesis gel with a molar composition of 1.7 SiO_2/1 Al_2O_3/3.2 Na_2O/110 H_2O/0.013 Au/0.013 Pd/0.156 ligand, which was heated to 373 K while stirring (6.7 Hz, 12 h) to form $Au_{50}Pd_{50}$NaLTA.

The solids formed were filtered (Pyrex 3606 fritted funnel, 4–5.5 μm), washed with deionized H_2O until the rinse liquids reached a pH of 7–8, and treated in ambient air within a convection oven at 373 K for 8 h. They were then heated in flowing dry air (1.67 $cm^3\,g^{-1}\,s^{-1}$) from ambient temperature to 623 K (at 0.033 K s^{-1}) and held for 2 h, cooled to ambient temperature, and then heated to 623 K (at 0.033 K s^{-1}) in flowing H_2 (1.67 $cm^3\,g^{-1}\,s^{-1}$) and held for 2 h. A final heating procedure in air (1.67 $cm^3\,g^{-1}\,s^{-1}$) at 723 K (0.033 K s^{-1}) was then conducted for 2 h.

Bimetallic compositions were adjusted by varying the ratio of cationic precursors ($HAuCl_4{\cdot}3H_2O$, $Pd(NH_3)_4(NO_3)_2$, H_2PtCl_6) in the gel, while maintaining the same nominal 1% wt. metal loading as in the monometallic samples. Six moles of 3-mercaptopropyl-trimethoxysilane were used per mole of metal for all compositions. The metal contents in all samples were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer 5300 DV optical emission ICP analyzer.

Metal-NaLTA samples (0.42 nm apertures, [13]) were exchanged with Ca^{2+} ions after O_2 and H_2 treatments to convert them to CaLTA (0.50 nm apertures, [14]) before CO chemisorption and infrared studies (Section 2.3.3). Na^+ was exchanged for Ca^{2+} to widen the LTA apertures and allow more rapid diffusion of CO into the interior of the crystallites [14]. The exchange was performed by adding metal-NaLTA samples (1–5 g) to an aqueous solution of $CaCl_2{\cdot}2H_2O$ (1 M; 100 cm^3/g zeolite) and stirring (6.7 Hz. 8 h) at ambient temperature. This procedure was repeated ten times to ensure full Ca^{2+} exchange [14]. The solids were finally filtered