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Challenges and strategies in the encapsulation and stabilization of monodisperse Au clusters within zeolites

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ABSTRACT

This study describes successful strategies and guiding principles for the synthesis of small and monodisperse Au clusters protected against coalescence and poisoning by their uniform dispersion throughout the void space of LTA and MFI zeolites. These protocols involve hydrothermal zeolite crystallization around Au^{3+} precursors stabilized by mercaptosilane ligands, which prevent their premature reduction and enforce connectivity with incipient crystalline frameworks. The confining nanometer scale voids restrict cluster mobility during thermal treatment and allow the selection of reactants, products, and transition states and the exclusion of organosulfur poisons in catalytic applications based on molecular size. UV–visible spectra show that Au^{3+} forms Au^0 clusters in O_2 or H_2 in a narrow temperature range that sets the dynamics of nucleation and growth and thus cluster size. Reduction protocols that maintain stable temperatures at the lower end of this range lead to small clusters uniform in size (LTA: 1.3 nm, MFI: 2.0 nm; 1.06–1.09 dispersity indices) with clean and accessible surfaces, as shown by their infrared spectra upon chemisorption of CO. Their unprecedented size and monodispersity are retained during oxidative treatments (773–823 K) that sinter Au clusters on mesoporous supports. Oxidative dehydrogenation rates of small (ethanol) and large (isobutanol) alkanols and the poisoning of unprotected clusters by organosulfur titrants show that >90% of the Au surfaces reside within intracrystalline LTA and MFI voids. Their very different structures, compositions, and synthesis protocols suggest that these encapsulation strategies can be adapted readily to other zeolite frameworks with apertures too small for post-synthesis exchange of Au precursors. This study illustrates how confinement favors small, uniquely stable, and monodisperse clusters, even for Au, a metal prone to cluster growth at conditions often required for its catalytic use.

1. Introduction

The synthesis and the mechanistic interpretation of the reactivity of Au nanoparticles have attracted significant attention because of their unique catalytic properties and adsorbate binding characteristics, which resemble those of less noble Pt group metals in reactions as diverse as alkene epoxidation, CO oxidation, hydrogenation, and alcohol oxidation [1–3]. Preserving their monodisperse and small sizes (<5 nm) during thermal treatments and catalysis remains essential, because their unique properties are often conferred by coordinatively unsaturated surface atoms that prevail in small clusters [4,5]. These requirements present formidable challenges because of the low Tammann temperature of Au (620 K) [6] and also because cluster melting points decrease markedly with decreasing particle size [7].

The encapsulation of nanoparticles within microporous solids may improve the inherent instability of Au nanoclusters by sequestering them within voids that prevent their coalescence with other clusters, while also restricting the size to which they can grow through spatial constraints. Confinement within such voids can also preclude access by reactants or poisons to Au surfaces, retain undesired products until they can convert and then diffuse as smaller species, or stabilize specific transition states, in all cases dictated by the size of the voids or channels in a specific microporous framework [8,9]. Strategies to confine Au within zeolites, however, often face synthetic challenges that prevent selective and efficient encapsulation.

Encapsulation within large-pore zeolites (12-member ring (12-MR) or larger) is relatively straightforward, because solvated metal cations can enter via exchange, impregnation, or adsorption

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methods after the framework has formed [10]. Au clusters within such zeolites, however, often do not show greater stability than those prepared by colloidal precipitation methods and subsequent dispersion of clusters onto mesoporous scaffolds. For example, Au nanoparticles with ~3 nm mean diameter are present in FAU after exchange with Au(III)-ethylenediamine, but treatment in O_2 or H_2 at 473 K causes their growth to ~10 nm clusters [11]. Similar strategies in LTL zeolites initially form ~2 nm clusters that coalesce and grow to ~5 nm after treatment in air at 498 K [12]. The sputtering of Au metal onto SiO_2, in contrast, forms clusters with 3.2 nm mean diameter after treatment in O_2 at 773 K [6], while deposition-precipitation methods on γ-Al_2O_3 lead to 4 nm Au clusters after treatment at 873 K in O_2 [13]. Au can be simply encapsulated into large-pore zeolites, but these previous studies show that the clusters in these zeolites are often less stable than those on mesoporous scaffolds, in spite of the posited benefits of encapsulation.

Medium-pore (10-MR) zeolites with more constrained apertures, such as MFI, confer greater stability than large-pore materials, but reported synthetic procedures typically lead to bimodal size distributions, with a significant fraction of the clusters (>10 nm in size) at external MFI crystal surfaces [14,15]. The introduction of ligand-stabilized colloidal Au into an MFI synthesis gel led to the intact encapsulation of only a subset of these particles; the encapsulated clusters are stable at 823 K in air, but those excluded from the intracrystalline voids sinter to very large Au crystals (>20 nm) [15]. The impregnation of aqueous cationic Pt or Au precursors onto alkali-treated MFI (to form mesopores that enhance imbibition by these solutions) gave metal clusters with ~3 nm mean diameter after O_2 (823 K) or H_2 (623 K) treatments [5,16], but the significant fraction of the clusters present at external zeolite surfaces again formed large (>10 nm) clusters [16]. These diverse techniques have led to improved encapsulation and greater size stability of Au clusters, but they do not form encapsulated clusters of unimodal size or allow extensions to zeolites with even smaller apertures, for which impregnation or exchange is impossible because solvated precursors are much larger than the intracrystalline passages [8].

Here, we report the selective encapsulation of Au clusters into LTA (small-pore) and MFI (medium-pore) zeolites by incorporating ligand-stabilized monomeric Au^{3+} precursors into hydrothermal synthesis gels and decomposing such precursors after zeolite crystallization using protocols that lead to small and nearly monodisperse clusters (1–2 nm) with clean surfaces; these clusters remain stable against growth at 773 K in both H_2 and O_2 environments. Transmission electron microscopy (TEM), X-ray diffraction (XRD), and infrared (IR) spectroscopy of chemisorbed CO are used to determine the size and dispersity of Au clusters, the zeolite crystallinity, and the Au surface cleanliness, respectively. The bifunctional 3-mercaptopropyl-trimethoxysilane ligands provide chemical protection from reduction or precipitation of Au^{3+} precursors in strongly alkaline synthesis gels, while also promoting the nucleation of silicate oligomers around ligated metal precursors. The thiol group binds to Au^{3+} cations to form stable Au–S adducts [17,18] and the alkoxysilane moiety forms siloxane bridges with the silica precursors in alkaline conditions [19], thus encouraging the uniform dispersion of Au precursors throughout the zeolite crystals formed. Treatment in O_2 and then H_2 leads to 1–2 nm particles that are narrowly distributed in size (as determined by their dispersity index [8,9] (DI) values) and expose surfaces free of synthetic debris. Their mean diameter can be systematically varied without loss in monodispersity by varying the temperature of the post-synthetic H_2 treatment, which is shown by UV–vis spectroscopy to represent the most consequential synthesis stage for the formation of Au^0 and its nucleation and growth into clusters. These reduced clusters, once formed, do not coalesce during later treatments in O_2 or H_2 environments up to 773 K, consistent with their encapsulation and protection by the intervening windows and cages within zeolite crystals.

The oxidative dehydrogenation (ODH) of large and small alkanols confirmed the extent and consequences of confinement. Ethanol (0.40 nm kinetic diameter) [9] ODH turnover rates are much higher than for isobutanol (0.55 nm) [9] on Au/CaLTA (0.50 nm apertures) [20], consistent with the exclusion of isobutanol from Au clusters within intracrystalline regions. Ethanol ODH rates after exposing AuNaLTA (0.42 nm apertures) [20] to thiophene (0.46 nm) [9] and AuNaMFI (0.55 nm apertures) [21] to dibenzothiophene (DBT, 0.9 nm kinetic diameter) [22] confirmed that active Au surfaces are protected from large titrants and predominantly confined within LTA and MFI voids.

2. Methods

2.1. Reagents

Ludox AS-30 colloidal silica (30 wt.% suspension in H_2O, Sigma–Aldrich), tetraethyl orthosilicate (TEOS; 98%, Sigma–Aldrich), fumed SiO_2 (Cab-O-Sil, HS-5, 310 $m^2\ g^{-1}$), 3-mercaptopropyl-trimethoxysilane (95%, Sigma–Aldrich), $NaAlO_2$ (53% Al_2O_3, 42.5% Na_2O, Riedel-de Haën), NaOH (99.99%, Sigma–Aldrich), 1 M tetrapropylammonium hydroxide (TPAOH; 98%, Sigma–Aldrich), $HAuCl_4 \cdot 3H_2O$ (99.999%, Sigma–Aldrich), calcium chloride dihydrate (EMD Millipore), ethanol (99.9%, Sigma–Aldrich), isobutanol (99.9%, Sigma–Aldrich), thiophene (99%, Alfa Aesar), dibenzothiophene (98%, Sigma–Aldrich), ethylenediamine (98%, Sigma–Aldrich), acetone (99.9%, Sigma–Aldrich), He (99.999%, Praxair), 25% O_2/He (99.999%, Praxair), air (extra dry; 99.999%, Praxair), H_2 (99.999%, Praxair), and 1.0% CO/He (99.999%, Praxair) were used as received.

2.2. Synthesis of Au cluster catalysts in LTA, MFI, and mesoporous SiO_2

2.2.1. Au cluster encapsulation within LTA

Au-encapsulated Na-LTA zeolite (AuNaLTA) was prepared by adding 3-mercaptopropyl-trimethoxysilane to a synthesis gel using hydrothermal synthesis techniques [8] that were modified to allow the incorporation and persistence of Au^{3+} cations in the gel at the conditions of synthesis. In a typical synthesis, NaOH (4.8 g) and 3-mercaptopropyl-trimethoxysilane (0.82 g) were added to deionized H_2O (17.9 MΩ resistance; 18 cm^3) in an open 125 cm^3 polypropylene container and stirred by a magnetic bar (6.7 Hz; 8 h); during this process the methanol formed by hydrolysis of the ligands (Section 3.1) evaporates, thus preventing methanol from reducing the Au^{3+} precursors when they are added later. An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.26 g) in deionized H_2O (18 cm^3) was added dropwise to the basic methanol-free ligand solution under agitation by a magnetic bar (6.7 Hz) over a period of 0.5 h. Colloidal silica (10.67 g, Ludox AS-30) was added to the polypropylene container, which was capped, sealed, and heated to 353 K under agitation by a magnetic bar (6.7 Hz) for 0.5 h. Finally, $NaAlO_2$ (6.0 g) dissolved in deionized H_2O (18 cm^3) was added dropwise to the Au^{3+}, ligand, and silica solution and mixed by magnetic stirring (6.7 Hz) for 2 h at ambient temperature; this led to a homogeneous synthesis gel with molar ratios of 1.7 SiO_2/1 Al_2O_3/3.2 Na_2O/110 H_2O/0.02 Au/0.12 ligand. The gel was heated at 373 K while magnetically stirring (6.7 Hz) for 12 h under its autogenous pressure to form AuNaLTA. The Au content in the final solids (as measured by optical emission spectroscopy, discussed in Section 2.3) was adjusted by increasing or decreasing the amount of added Au to achieve 0.5–1.0 wt.% theoretical loadings, while keeping a constant 3-mercaptopropyl-trimethoxysilane to Au molar ratio of 6. The solids formed were filtered (Pyrex 3606