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Synthesis of highly dispersed cobalt oxide clusters encapsulated within LTA zeolites

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ABSTRACT

Small Co_3O_4 nanoparticles uniformly distributed in size were encapsulated within LTA zeolite crystals in a one-step process through hydrothermal self-assembly of crystalline frameworks around ligated Co^{2+} precursors. The use of bifunctional ligands containing a chelating bidentate amine functionality and an alkoxysilane moiety prevented the precipitation of Co^{2+} species as colloidal hydroxides in the highly alkaline synthesis gels, while also allowing the formation of linkages between precursors and the framework during the nucleation and growth of LTA crystals. Oxidative treatments of ligated compounds occluded within zeolite crystals removed ligand residues and formed small Co_3O_4 nanoparticles visible in transmission electron micrographs. These nanoparticles retained their small size (average diameter 1.5 nm) after oxidative treatment at 620–870 K, a reflection of their stabilization by confinement within zeolite voids. The infrared spectra of adsorbed CO on Co-LTA samples confirmed the absence of Co^{2+} as exchanged cations or aluminosilicates, indicating the presence of Co oxide clusters, with dynamics and stoichiometry of reduction in H_2 corresponding to small Co_3O_4 clusters. Ethanol oxidation rates on Co-LTA samples, exchanged with K^+ or Ca^{2+} cations to vary the diffusive properties of LTA crystals, indicated that more than 97% of the active surfaces on these Co_3O_4 clusters resided within zeolite crystals, where ethanol and O_2 concentrations depend on the diffusive properties of the LTA framework. The Co_3O_4 clusters prepared by these methods, in contrast with Co^{2+} in exchanged or aluminosilicate forms, exhibit reactivity in CO and NO oxidation. Their turnover rates (per exposed Co atom), however, were lower than on bulk Co_3O_4 powders, because of the combined effects of diffusional constraints imposed by the confining framework and the small size of these clusters, which leads to lower intrinsic reactivities as a result of their more difficult reduction during catalytic redox cycles. These clusters would be attractive in catalytic applications requiring stability against sintering during reaction or regeneration, reactant or product shape selectivity, or protection from contact with large molecules that block active surfaces. Such oxide clusters cannot be formed by sequential ion exchange, detachment by reduction to Co^0, and re-oxidation because the extremely high temperatures required for reduction destroy the aluminosilicate frameworks. The synthesis protocols and their mechanistic interpretations described herein represent a conceptual and practical platform for the encapsulation of nanoparticles of base elements within a broad range of confining crystalline environments through one-step hydrothermal self-assembly.

1. Introduction

The synthesis of Co oxide nanoparticles and their applications in heterogeneous catalysis are of interest because they are among the most active catalysts in CO oxidation [1], oxidative dehydrogenation [2], oxidative abatement of volatile organic compounds [3], and alcohol oxidation [4]. Co oxides are also precursors to Co metal particles active in Fischer-Tropsch synthesis catalysis [5]. The structure and size of such clusters influence turnover rates and selectivities for many of these reactions [4,5], and rigorous assessments of their effects on reactivity require the synthesis of clusters that are thermally stable and narrowly distributed in size. Several strategies have been proposed for the synthesis of CoO_x particles; these include incipient wetness impregnation onto mesoporous supports [6,7], sol-gel methods [8], electrochemical deposition of Co^{2+} precursors onto solid substrates [9], and thermal

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decomposition of organometallic precursors in air [10] or under solvothermal conditions [11]. These methods, with some exceptions [7], typically lead to particles >10 nm and broadly distributed in size [6,10]. Cobalt oxide clusters as small as 4 nm have been prepared through incipient wetness impregnation of cobalt precursors into mesoporous MFI zeolite nanosheets [7]. Such clusters reside within the mesoporous regions of the zeolite sheets and take on the size of the mesopores, which confer improved thermal stability to the cobalt oxide clusters relative to particles dispersed on γ-Al_2O_3. Clusters prepared through this technique, however, cannot retain sizes smaller than the mesopores produced natively by the zeolite synthesis ($\sim$4 nm) and do not benefit from the molecular sieving or size-selective effects of the zeolite during catalysis, which reflects their location within fully accessible mesoporous regions [7]. The full extent to which the cobalt particles are stabilized by the mesopores against sintering is also unclear. Highly dispersed CoO_x species make efficient use of Co atoms, but tend to sinter at the temperatures and reactive environments required for their use as catalysts [12].

Synthesis techniques that form metal (Au, Pd, Pt) and alloy (AuPd, AuPt, PdPt) nanoparticles within zeolitic voids of molecular dimensions have been shown previously to circumvent the stability and dispersity hurdles inherent to small metal particles [13–15]. Encapsulation within such voids inhibits the mobility and restricts the size of metal clusters [13], while also providing sieving and shape selective effects that allow preferential access to active sites by certain molecules [16], while stabilizing transition states with preferences that sense their fit within the confining voids [13,14]. When so required for catalytic use, such metal clusters can be converted to their corresponding oxides by thermal treatments in O_2. Most aqueous cations of base metals (e.g. Co^{2+}, Mn^{2+}, Ni^{2+}) [17,18], but not the cationic forms of noble metals (e.g. Pd^{2+}, Pt^{2+}, Au^{3+}) [19], can enter small-pore (8 member-ring (MR) apertures), as well as medium-pore (10 MR) and large-pore (12 MR) zeolites. Encapsulation is viable through post-synthesis aqueous ion exchange when solvated precursors can enter the apertures that connect the voids, but exchanged cations of base metals require reductive treatments at temperatures that often lead to significant sintering of the particles formed and to extracrystalline metal agglomerates [17,18]. Co^{2+} cations attached to LTA framework exchange sites, in particular, require treatments in H_2 above 1000 K to form Co^0 metal particles [17].

Here, we describe an alternate strategy to form Co_3O_4 nanoparticles within LTA zeolite crystals; such clusters are small (1.4–1.6 nm) and nearly monodisperse (dispersity index (DI) [20] 1.03–1.07). These protocols prevent the direct attachment of Co^{2+} cations to framework ion exchange sites through the use of ligands that preclude Co^{2+} species from exchange while promoting the self-assembly of the zeolite around Co precursors during hydrothermal crystallization. Bidentate amine ligands (N-[3-(trimethoxysilyl)propyl]ethylenediamine; TPE) chelate Co^{2+} cations to prevent premature $Co(OH)_2$ precipitation in highly alkaline synthesis gels and form siloxane linkages with LTA nuclei to induce their incorporation as crystallization occurs, without interfering with framework crystallinity at Co contents up to 4 wt.%. These Co^{2+}-TPE complexes do not form cation-framework linkages that render Co^{2+} species inert towards the formation of CoO_x clusters during subsequent thermal treatments. Ligands are removed by treatment in O_2 at 623 K, leading to the formation of small and nearly monodisperse Co_3O_4 clusters, resistant to sintering even after O_2 treatment at 870 K.

The temperature and H_2 consumption stoichiometry during reduction confirmed their small size and their Co_3O_4 composition; they reduce at temperatures between those required for the reduction of bulk Co_3O_4 and Co^{2+} exchanged onto LTA. Infrared (IR) spectra did not detect bands for CO bound to exchanged Co^{2+} cations, cobalt silicates, or cobalt aluminates. Ethanol oxidation rates varied as different cations (Na^+, Ca^{2+}, K^+) were exchanged onto LTA crystals to change their intracrystalline diffusivities, consistent with the presence of Co_3O_4 clusters within such crystals. These LTA-encapsulated Co_3O_4 nanoparticles, but not exchanged Co^{2+} cations, were active for CO and NO oxidation, demonstrating their ability to undergo reduction-oxidation cycles and to dissociate molecular oxygen.

These encapsulation strategies, described here for Co-based LTA systems seem generally applicable to other base metals (Cu, Fe, Ni), which form similar stable amine complexes [21] that are essential for stabilization and encapsulation, and to other zeolites (e.g. FAU, EDI, GIS, SOD) that crystallize under hydrothermal conditions similar to those required to form LTA [22].

2. Experimental methods

2.1. Source and purity of reagents used

$CoCl_2\cdot6H_2O$ (99.99%, Sigma-Aldrich), $[Co(NH_3)_6]Cl_3$ (99.99%, Sigma-Aldrich), $Co(NO_3)_2\cdot6H_2O$ (>98%, Sigma Aldrich), ethylenediamine (98%, Sigma-Aldrich), N-[3-(trimethoxysilyl)propyl]ethylenediamine (TPE; 98%, Sigma-Aldrich), Ludox AS-30 colloidal silica (30 wt.% suspension in H_2O, Sigma-Aldrich), NaOH (99.99%, Sigma-Aldrich), $NaAlO_2$ (53% Al_2O_3, 42.5% Na_2O, Riedel-de Haën), $CaCl_2\cdot2H_2O$ (EMD Millipore), KCl (>99.0%, Sigma-Aldrich), Co_3O_4 (99.9%, Sigma-Aldrich), fumed SiO_2 (Davisil Grade 62, Sigma-Aldrich, 300 m^2 g^{-1}), acetone (99.9%, Sigma-Aldrich), ethanol (99.9%, Sigma-Aldrich), air (extra dry; 99.999%, Praxair), H_2 (99.999%, Praxair), He (99.999%, Praxair), Ar (99.999%, Praxair), CO_2 (99.999%, Praxair), N_2 (99.999%, Praxair), 4% H_2/Ar (99.999%, Praxair), 1% CO/He (99.999%, Praxair), CO (99.999%, Praxair), 3% NO/He (99.999%, Praxair), and 1% NO_2/He (99.999%, Praxair) were used as received.

2.2. Materials synthesis

2.2.1. Synthesis of CoO_x clusters within LTA zeolites and cobalt oxide clusters dispersed on SiO_2

LTA was prepared in its Na form (NaLTA) with encapsulated CoO_x species (CoNaLTA) by adding Co cations protected by amine ligands (ammonia, ethylenediamine, or TPE) to zeolite synthesis gels and subsequent hydrothermal crystallization (373 K, 12 h). Syntheses with ethylenediamine or TPE ligands involved the initial dropwise addition of aqueous $CoCl_2\cdot6H_2O$ (0.18–0.91 g in 9 cm^3 deionized H_2O, 17.9 Ω cm resistivity) at a rate of 0.2 cm^3 s^{-1} to aqueous ligand solutions (0.09–1.39 cm^3 ethylenediamine or 0.16–1.65 cm^3 TPE dissolved in 9 cm^3 deionized H_2O) while mixing with a magnetic stir bar (6.7 Hz). The amount of ligand used was adjusted for different batches to give ligand/metal molar ratios between 1 and 3. For the case of NH_3 ligands, $[Co(NH_3)_6]Cl_3$ (0.20–1.00 g) was initially dissolved in 18 cm^3 of deionized H_2O. The aqueous solutions of ligands and metal cations were then transferred into 125 cm^3 polypropylene bottles, and colloidal silica (5.3 g, Ludox AS-30) and NaOH (2.4 g) were sequentially added; the containers were sealed and kept at 353 K for 0.5 h with stirring by a magnetic bar (6.7 Hz) and then cooled to ambient temperature. Aqueous $NaAlO_2$ (3.0 g in 9 cm^3 deionized H_2O) was then added, and the mixtures were magnetically stirred (6.7 Hz) for 2 h at ambient temperature. The resulting homogeneous synthesis gels contained molar ratios of 1.7 SiO_2/1 Al_2O_3/3.2 Na_2O/110 H_2O/0.066–0.33 Co/0.066–0.99 ligand. The bottles containing the gels were sealed and the contents heated to 373 K for 12 h while stirring (6.7 Hz) to form as-synthesized CoNaLTA samples.