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Anchoring of cobalt hydroxide catalysts on nanozeolite crystals for photocatalytic water oxidation

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ABSTRACT

Synthesis of cobalt hydroxide on ~40 nm zeolite crystallites by treatment of Co^{2+}-exchanged zeolite (Co-NZ) with either sodium hydroxide (Co-NZ-OH) or tetramethyl ammonium hydroxide (TMA–NZ) is being reported. With the NaOH-treated sample, an additional hydrothermal treatment was carried out (HT-Co-NZ-OH). X-ray photoelectron spectroscopy in the Co2p satellite region indicate the presence of Co (II). Transmission electron microscopy of HT-Co-NZ-OH showed nanometer thick film-like deposits of cobalt compound on the surface of the nanocrystal, whereas for TMA-NZ, the deposits were spherical ~3 nm particles on the surface of the nanozeolite. Using the $Ru(bpy)_3^{2+}$ – persulfate system, the photocatalytic activity of these materials for water oxidation was tested by measuring dissolved oxygen. The initial rate for TMA-NZ was 3.1×10^{-2} mol O_2/mmol Co.s, whereas for HT-Co-NZ-OH, it was 1.4×10^{-2} mol O_2/mmol Co.s. However, with the TMA-NZ sample, the photocatalytic rate dropped by an order of magnitude with the recovered catalyst, while the rate was unchanged for HT-Co-NZ-OH. With TMA-NZ, the ~3 nm cobalt species on the zeolite are mechanically unstable and fall off during the photocatalytic reaction, whereas the cobalt deposits on the HT-Co-NZ-OH are stable. The catalytic performance of HT-Co-NZ-OH is an order of magnitude higher than comparably prepared micron sized zeolites, due to the better utilization of the cobalt on the surface of the nanozeolite. Internal porosity of the zeolite is still accessible with HT-Co-NZ-OH for photochemical reaction with access to the catalyst on the surface.

1. Introduction

Zeolites are extensively used as supports for anchoring catalysts, successfully promoting a range of chemical reactions [1]. With the advancements in zeolite synthesis, nanozeolites (<100 nm) are now readily accessible [2]. Nanozeolites not only offer an increased surface area, but another unique feature is that they form clear dispersions in solvents, making photochemical applications with uniform light penetration over the entire sample possible [3]. Several studies have explored this light penetration feature for intrazeolitic organic photochemistry [4]. There are however, only a few studies regarding anchoring heterogeneous catalysts on nanozeolite supports, particularly with silver clusters [5,6].

Water oxidation to oxygen is a multielectron (hole) process, and catalysis of this reaction by both homogenous and heterogeneous catalysts is an active area of research [7–13]. Solar energy based systems typically use molecular chromophores or quantum dots [14] that participate in one-electron oxidations. These photo-oxidized species need to be coupled to catalysts for the multielectron (hole) water oxidation. There are numerous heterogeneous catalysts that have been examined for water oxidation, and some of the best catalysts are oxides of ruthenium and iridium [15,16]. Development of catalysts using earth abundant metal ions such as iron, nickel [17], manganese [18] and cobalt [19] are attractive from a practical perspective.

Cobalt oxides and hydroxides have been examined as catalysts for many decades [20]. Since performance is dependent on catalyst morphology, studies have focused on nanoscale dispersions of oxides/hydroxides on a variety of supports. Synthetic strategies for such supported catalysts typically involve impregnation and oxidation. Supports examined include silica [20], alumina [21], titania [22], as well as microporous and mesoporous supports [23]. Mechanistic studies of the CoO_x heterogeneous clusters for water oxidation has been reported [23,24].

Zeolites are well studied as supports, but most of these studies site the catalysts within the microporous volume of the zeolite [25]. Our emphasis has been to move the catalysts on to the zeolite surface to allow for photochemistry to occur within the zeolite

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cages, with access to the surface catalysts [26–28]. Towards that goal, we have investigated RuO_2 as a H_2 evolving catalyst on a zeolite membrane [29]. In a recent study, we investigated the synthesis of brucite-like layered $Co(OH)_2$ on micron-sized zeolite surfaces, and examined their water oxidation catalytic activity using the photochemical $Ru(bpy)_3^{2+} - S_2O_8^{2-}$ system [30].

In this paper, we investigate nanozeolites as supports, with the goal of obtaining a better dispersion of the $Co(OH)_x$, which should be reflected in enhanced catalytic activity. There have been no studies to date on nanozeolite supported water oxidation catalysts. Methods of anchoring of cobalt hydroxide on nanozeolites, as well as the structural, morphological and catalytic properties of the $Co(OH)_x$ and comparison to micron-sized zeolites as support is presented.

2. Experimental section

2.1. Hydrothermal synthesis of zeolite Y nanocrystals

Colloidal zeolite Y was synthesized following a previously reported method [31]. In a typical synthesis, 12.5 g aluminum isopropoxide, 41.84 g tetramethylammonium hydroxide (TMAOH) and 76.5 g water were stirred vigorously in a water bath at 70 °C until the solution became clear. After cooling to room temperature, 11.3 g of tetramethylammonium bromide (TMABr) was added and the solution was stirred until the solid dissolved. For the silica source, 26.2 g of Ludox HS-30 and 10.46 g of TMAOH were mixed and stirred for 30 min. Both sources were combined and aged for 3 days under constant stirring at room temperature and the reaction mixture transferred to an oil bath and kept at 100 °C for 4 days. Nanocrystals were then purified by dialysis and centrifugation.

2.2. Anchoring of cobalt hydroxide on nano-sized zeolite Y

A dispersion of zeolite Y nanocrystals was ion-exchanged with 20 mL of 0.01 M $CoCl_2$ for 2 h at room temperature. The crystals were recovered via rigorous centrifugation for 1.5 h and redispersed in 3 mL of deionized water. These cobalt-exchanged nanocrystals were treated with 10 mL of 0.1 M NaOH at 90 °C for 2 h. Hydrothermal treatment involved heating the NaOH-treated zeolite dispersed in water at 90 °C in an oil bath, and stored as a dispersion to prevent any irreversible aggregation.

2.3. Characterization

Powder diffraction patterns were acquired using the Rigaku X-Ray Diffractometer with Cu Kα radiation. Raman spectra were acquired using a 785 nm laser line at 0.5% power, using a Renishaw Raman microprobe. The use of a spinning cell was necessary to preserve sample integrity. Axis Kratos X-Ray Photoelectron Spectrometer was used with monochromatized Al K_{∞} source (12 kV, 10 mA) as the X-ray source. Transmission micrographs were acquired using Titan3 80-300 Probe-Corrected Monochromated (S) at low voltages (~140 kV). Dynamic light scattering (DLS) was performed in a water suspension using the Malvern Zetasizer. BET measurements were done with a Quantachrome 2200e.

2.4. Elemental analysis

Digestion of zeolite-supported catalysts was performed following a method reported in the literature [32]. Briefly, 10 mL of solution containing HNO_3: HCl: HF (equal parts) was added to a pre-weighed Teflon bottle containing 50 mg of catalyst. After dissolution, 75 mL of ~0.86 M boric acid was added to the clear solution to neutralize HF. The solution was diluted with deionized water. Cobalt loading was determined by atomic absorption spectroscopy (AAS). We estimated the amount of sodium nanozeolite in the aqueous dispersion by weighing the residue, and used this number for calculating the Co weight percent. There is definitely some error in such measurements.

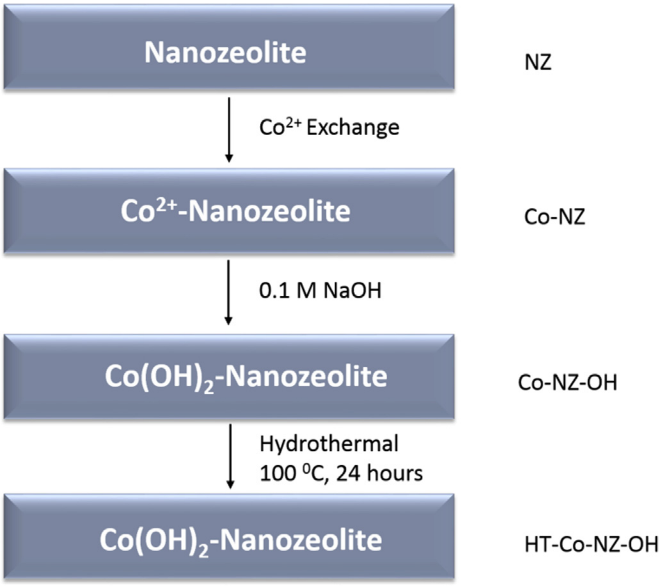
2.5. Photocatalytic water oxidation

Dissolved oxygen measurements were recorded using YSI Instruments ProODO oxygen sensor. The sensor was calibrated using 100% air saturated DI water at 25 °C (8.26 ppm) and 0.13 M Na_2SO_3 solution (0 ppm). A Pyrex® photolysis reactor containing 0.333 mg of sodium persulfate (0.02 M, 70 mL), 0.994 g sodium sulfate (0.1 M, 70 mL), 0.0059 mg of tris(2,2′-bipyridyl) ruthenium chloride, 0.050 g of nanozeolite catalyst in a Na_2HPO_4—$NaHCO_3$ (pH 7.0) buffer was purged with nitrogen gas for 15 min while stirring or until baseline oxygen reading was 0.0—0.10 ppm. The reactor was illuminated with visible light using an Hg lamp equipped with a 420 nm cutoff filter and with an incident power of 360 mW/cm^2. Gas phase oxygen experiments were performed in a glass photolysis vessel containing 0.2 g sodium persulfate, 0.6 g sodium sulfate, the catalyst to be screened and 0.1 M Na_2HPO_4—$NaHCO_3$ (pH 7.0) buffer solution. The sealed vessel was purged with N_2 gas for 15 min while stirring. After purging, the vessel was illuminated by visible light using a Hg lamp equipped with a 420-nm cutoff filter and 360 mW/cm^2 intensity. This aqueous suspension was maintained under stirring and illumination for 150 min. Headspace gas analysis of oxygen was carried out using a SRI 310 gas chromatograph equipped with a thermal conductivity detector and 13X packed molecular sieve column at intervals of 15 min. The gas chromatograph was calibrated using room air to establish a correlation between peak area and moles of oxygen.

3. Results

3.1. Anchoring of $Co(OH)_x$ on nanozeolite crystals

A schematic description of the synthesis process and the various materials examined is shown in Scheme 1. In contrast with



Scheme 1. Description of the various materials used in this study and the synthetic approach.