



Effect of gold oxidation state on the epoxidation and hydrogenation of propylene on Au/TS-1

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ABSTRACT

Gold nanoparticles on titanium oxide and titania-silica supports are active for the formation of propylene oxide by the oxidation of propylene with hydrogen and oxygen mixtures. Cyanide treatment of gold supported on titanosilicate zeolite supports (Au/TS-1) yielded unexpected results. Catalysts treated with weak solutions of sodium cyanide resulted in preferential removal of small gold particles, while catalysts treated with strong solutions resulted in dissolution of the gold and re-precipitation as gold (+1) cyanide. X-ray absorption spectroscopy demonstrated that catalysts that produce propylene oxide in the presence of hydrogen and oxygen mixtures had supported gold (+3) oxide nanoparticles of 3 nm size after synthesis, which were reduced to gold metal at reaction conditions. Samples treated with strong solutions of sodium cyanide resulted in supported gold (+1) cyanide particles of large size, 9–11 nm. These particles did not produce propylene oxide but, surprisingly, showed high selectivity toward propylene hydrogenation. Increasing gold (+1) cyanide particle size resulted in a decrease in hydrogenation activity.

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1. Introduction

Supported gold has been a subject of great interest in heterogeneous catalysis since the discovery that nanosized gold particles oxidize carbon monoxide [1]. Heterogeneous gold catalysts show high activity, mostly for oxidation reactions [2–4], among which the oxidation of propylene to propylene oxide has received considerable attention [5–10]. Reviews are available on this subject [11] and on epoxidation mechanisms in general [12].

Catalysts consisting of gold nanoparticles supported on titanosilicates have demonstrated high selectivity in the oxidation of propylene to propylene oxide (PO) with hydrogen and oxygen [13–15]. Supports such as mesoporous Ti-TUD and nanoporous TS-1

are by themselves mild oxidation catalysts which can epoxidize propylene with hydrogen peroxide [16–18]. It is generally accepted that hydrogen and oxygen first react on the gold to form hydrogen peroxide, which then migrates to Ti centers to form hydroperoxide species that react with propylene to form PO and water [19–21].

The original objective of this study was to study finely dispersed gold in the propylene epoxidation reaction with hydrogen and oxygen to investigate a suggestion in the literature that 3-atom gold clusters might be active for the reaction [22,23]. Such small particle sizes had not been directly observed before. In order to obtain such clusters, a procedure described in the literature was adopted which consisted of treating supported gold catalysts with sodium cyanide solutions [24]. This procedure was reported to produce atomically dispersed ionic gold species [25]. Instead, it was unexpectedly found that the cyanide treatment resulted in the dissolution of the gold and re-precipitation of larger Au (+1) cyanide particles. It was found that Au (+1) nanoparticles generated in this treatment were no longer active for propylene oxidation but instead were active for propylene hydrogenation. This study demon-

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strates that oxidizing supported gold nanoparticles to a +1 state can fundamentally alter their catalytic behavior such that the gold takes on Pt-like behavior.

2. Experimental

2.1. Synthesis of samples

The TS-1 zeolite was synthesized using a sol–gel method as described in the literature [21]. In a typical synthesis, HCl (0.05 M, 30 g) (1.5 mmol) was stirred in an ice bath, while 39.2 g (188 mmol) tetraethylorthosilicate (TEOS, Aldrich, 98%, batch 06526BC) was added dropwise, followed by 0.642 g (1.88 mmol) of titanium (+4) butoxide (Aldrich, lot 11131JE) in isopropyl alcohol. The solution was stirred for 10 min and 5.65 g (27.8 mmol) tetrapropylammonium hydroxide (TPAOH, 1.0 M in water, Aldrich, batch 09026ME) added, forming a gel. The gel was allowed to age for 2 h and then was placed in a 373 K drying oven for 24 h. This material was subsequently autoclaved with 12.45 g (61.2 mmol) TPAOH at 448 K for 24 h, washed with 1 l distilled water, and vacuum filtered. The material was dried at 393 K for 24 h, ground to a fine powder, and finally calcined in air at 773 K for 5 h. The yield based on TEOS was 93%.

Gold nanoparticles were deposited on the TS-1 support using a deposition–precipitation (DP) method [26]. Gold (+3) chloride hydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, Fluka, batch 456,301/1) (30 mg, 0.0728 mmol, 14 mg Au) was dissolved in 100 ml distilled water, and this solution was stirred and heated to 343 K. The solution had a pH of approximately 2.8 at this temperature (OAKTON Acorn pH-6), which was increased to 7.0 using NaOH before 1.00 g of TS-1 powder was added. The solution was stirred for 1 h and then removed from heat, and the solids were separated from the solution by centrifugation. The solids were re-suspended in water and centrifuged again. The remaining solids were removed and dried overnight under room temperature vacuum without calcination.

2.2. Cyanide treatment

Gold was selectively removed from the samples by cyanide leaching [24]. Sodium cyanide (NaCN, 95+%, Aldrich, lot 05629PE) was dissolved in water to 0.05 wt.% (0.010 M), 1.0 wt.% (0.20 M), and 2.0 wt.% (0.41 M), and NaOH was added to achieve a pH of 12.5. Au/TS-1 (2.0 g) was added to each 50 ml solution and stirred at room temperature for 1 h, and 100 ml water was added prior to vacuum filtration. The solids were again suspended in water and filtered, and this was repeated a total of 10 times to remove as much NaCN as possible, and the remaining solids were dried for 8 h in room temperature vacuum. A solution of NaOH at 12.5 pH with no NaCN was used to produce a control sample. The samples were denoted as Au-0.0 (no cyanide), Au-0.05 (0.05% cyanide), AuCN-1.0 (1.0% cyanide), and AuCN-2.0 (2.0% cyanide).

The gold content of the Au/TS-1 samples was determined using X-ray fluorescence spectroscopy (Institute of X-ray Technologies Co., Ltd., ED-05) as well as inductively coupled plasma atomic emission spectroscopy (Spectro CirOS VISION, using aqua regia). An Au/TS-1 sample that was not further treated was determined to have a gold content of 1.12 wt.%, indicating 80% of the gold in solution was deposited onto the catalyst. X-ray photoelectron spectroscopy (XPS) was obtained with a PHI-5500 spectrometer with Al K α radiation (1253.6 eV) and referenced to the Si 2p line at 103.4 eV.

2.3. Transmission electron microscopy

High-resolution transmission electron microscopy (TEM) images were obtained using a Philips CM200 FEG (200 kV) and a

spherical-aberration-corrected FEI Titan (300 kV). The Philips CM200 FEG has a point resolution of 0.2 nm, while the Titan utilizes a spherical-aberration corrector that can compensate for the delocalization of image details, which manifests itself as an extension of the perimeter of a sample beyond the actual surface in conventional TEM [27]. Particle size distributions were determined by selecting a representative image for each sample and measuring the diameter of all visible Au particles.

2.4. Reactivity testing

Catalytic activity was measured in a differential flow reactor consisting of a 5-mm-diameter quartz tube placed vertically in a furnace assembly. Temperature monitoring and control was through a RKC REX-P24 temperature controller, using a thermocouple centered within the catalyst bed. Feed gases used were propylene (Takachiho Chemical, >99.8%), oxygen (Taiyo-Nissan, >99.5%), argon (Taiyo-Nissan, >99.9997%), and hydrogen (Shimadzu OPGU-2100S hydrogen generator, >99.99%), regulated by mass flow controllers. All experiments used 0.30 g of catalyst, which was activated in reaction gases (10/10/10/70 $\text{H}_2/\text{O}_2/\text{C}_3\text{H}_6/\text{Ar}$, 35 $\text{cm}^3_{\text{NTP}} \text{min}^{-1}$, 7000 $\text{cm}^3 \text{h}^{-1} \text{cat}^{-1}$) and heated from room temperature to reaction temperature at 0.5 K min^{-1} . The catalysts were held at 443 K for 2 h and then heated at 0.5 K min^{-1} to 473 K and held for a further 2 h.

The effluent was sampled every 0.5 h using a pair of two-column gas chromatographs. A FPAP column and flame ionization detector (FID) were able to separate and quantify propylene oxide, propionaldehyde, acetone, and acrolein, while a Gaskuropak column and FID were used to measure propylene and propane. A Porapak Q column and thermal conductivity detector (TCD) measured carbon dioxide, carbon monoxide, and water, and a MS5A column and TCD were able to measure hydrogen and oxygen. Quantifiable amounts of propionaldehyde, acetone, acrolein, and carbon monoxide were not detected under any conditions.

2.5. X-ray absorption spectroscopy

In situ Au L_{III}-edge X-ray absorption spectroscopy (XAS) measurements were carried out at beamline NW10A of the Photon Factory Advanced Ring in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (PF-IMSS-KEK) in Tsukuba, Japan. A specially designed reactor cell and flow delivery system [28] were used to reproduce the pretreatment and reaction conditions used for catalyst screening. The 0.3 g of catalyst was used in a pellet form. Helium was used as a dilution gas instead of Ar to minimize attenuation of X-rays by the reaction gas mixture. In situ measurements were taken at 443 K at 10-min intervals using a step-scanning mode. Pretreatment and reaction conditions were monitored and controlled from outside the radiation-shielded hutch, and all spectra were obtained in fluorescence mode using a solid state detector (SSD). The monochromator was calibrated against the L_{III} edge of a gold foil sample at $E_0 = 11,919 \text{ eV}$.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were analyzed using IFEFFIT 1.2.8 [29]. For each spectrum, a pre-edge background was subtracted using a least-squares linear fit to $-150 < E_0 < -30 \text{ eV}$, and the data were normalized to an edge jump of 1 using a least-squares cubic fit to $150 < E_0 < 763 \text{ eV}$. The white line area was calculated by shifting these background-subtracted and normalized spectra to the same E_0 as the bulk gold standard and integrating the area between the white line feature and bulk gold [30–32].

For EXAFS analysis, a post-edge background $\mu_0(E)$ was subtracted from each normalized spectrum and the wavevector k was substituted for energy E , yielding the EXAFS function $\chi(k)$. A Fourier transform on this k^3 -weighted function in the range of $2 < k < 7 \text{ \AA}^{-1}$ using a Kaiser-Bessel window with $\Delta k = 2 \text{ \AA}^{-1}$ gener-

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