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Selective oxidation of ethanol over Ag, Cu and Au nanoparticles supported on $Li_2O/\gamma\text{-}Al_2O_3$

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ABSTRACT

In an effort to verify a previous striking report that ethanol could be oxidized selectively to ethylene oxide, ethanol oxidation on Ag, Cu, or Au nanoparticles supported on $Li_2O/\gamma\text{-}Al_2O_3$ or $\gamma\text{-}Al_2O_3$ was examined between 100 and 400 °C. Ag and Cu catalysts were found to be highly selective to acetaldehyde (>95% on Ag below 325 °C and on Cu below 250 °C). On Au, selectivities to acetaldehyde were lower, with higher selectivity to ethyl acetate and acetic acid. No ethylene oxide was observed under any conditions. Our results, including selectivity variations among these metals, are consistent with previous studies of ethanol oxidation over coinage metals supported on $\gamma\text{-}Al_2O_3$, with no changes in primary product identity and minor changes in selectivity upon addition of Li_2O. Unfortunately, these results are in direct contradiction to previous work reporting the desirable direct conversion of ethanol to ethylene oxide on Ag, Cu, and Au on $Li_2O/\gamma\text{-}Al_2O_3$.

1. Introduction

With the growing emphasis on fuels and chemicals from renewable resources, much attention has been devoted to catalytic conversion of biologically derived feedstocks. Of the possible chemical intermediates, ethanol is attractive because of its large-scale production for transportation fuel. While ethanol can be dehydrated to produce ethylene that can be utilized in the existing petrochemical production chain, direct conversion of ethanol to higher value chemical products, e.g., in integrated biorefineries [1,2], is highly desirable.

Gas-phase oxidation of alcohols over copper and silver catalysts for commercial production of aldehydes dates back to the 19th century. Studies in the scientific literature since that time have examined the performance of these catalysts and defined the mechanism of the reaction. Recent work has shown that ethanol can selectively produce acetaldehyde over nanoparticles of the coinage metals (Ag, Cu, Au) supported on $\gamma\text{-}Al_2O_3$ [3–5]. It was therefore quite surprising when Lippits and Nieuwenhuys reported in 2010 that Ag, Cu, and Au supported on $\gamma\text{-}Al_2O_3$ can produce ethylene oxide (EO) and, with the addition of Li_2O to the support, can do so with EO selectivities above 95% at complete conversion [6,7]. EO is an important industrial chemical and its direct production from ethanol at high conversion and selectivity would be a very attractive alternative to ethylene epoxidation.

In spite of the myriad potential benefits, including economic ones, of such a process, as far as we are aware there have been no published studies to date that have tried to reproduce the Lippits results. We therefore set out to do so. Unfortunately, we find no evidence for the direct oxidation of ethanol to ethylene oxide.

2. Experimental

Two sets of catalyst materials were prepared following the procedures described by Lippits and Nieuwenhuys [6,7]. The first set used commercially available pseudo-boehmite (BASF, surface area ~300 m^2/s) calcined to 550 °C for 1 h. The resulting gamma alumina phase, verified with XRD, had a BET surface area of 260 m^2/g. $LiNO_3$ (1.38 g) was dissolved in 6.25 ml of ultrapure water and added dropwise, at room temperature, to 5.0 g of $\gamma\text{-}Al_2O_3$ to obtain a Li/Al ratio of ~3/15. The support was then dried at 110 °C for 8 h followed by calcination at 350 °C (using a 10 °C/min. ramp rate) for 4 h. Following calcination at 350 °C, the Cu, Ag, or Au were deposited on the prepared $Li_2O/\gamma\text{-}Al_2O_3$ support using homogeneous deposition-precipitation with urea as precipitating agent. Cu

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$(NO_3)_2$, $AgNO_3$, or $HAuCl_4$ (all purchased from Alfa-Aesar) was added to a suspension of the $Li_2O/\gamma\text{-}Al_2O_3$ support material in a ratio of 50 ml of ultrapure water per 1 g support. Urea (3/2 g urea/g support) was then added to the rapidly stirred suspension, then heated to 80 °C and held for ~18 h until the solution reached a pH of 8–8.5. The material was then filtered, washed, and dried overnight at 80 °C. The intended metal to aluminum ratio was ~1/75 for all prepared materials (i.e., 2.7 wt% Ag, 1.6 wt% Cu and 4.8 wt% Au). The urea co-deposition step results in the leaching of lithium from the support, so a higher than intended loading (3/15 Li/Al) was used as the starting material. The intended Li/Al ratio following metal deposition is 1/15. Actual Li and metal loadings were determined using ICP-OES (Varian) with calibration standards prepared by diluting relevant standards (Inorganic Ventures). BET surface areas of all final catalysts prepared using the pseudo-boehmite support (i.e., $Me/Li_2O/\gamma\text{-}Al_2O_3$) were 218–231 m^2/g. A comparison of the physical properties of the lithium-promoted catalysts used in this study with those reported by Lippits and Nieuwenhuys [6,7] is contained in Table S1 of the Supplemental Information.

Materials were also synthesized with a lower surface area gamma alumina support (Inframat Advanced Materials 26R-0804UPG, surface area of 70–100 m^2/g). Following calcination at 350 °C, the Cu, Ag, or Au were deposited on the $\gamma\text{-}Al_2O_3$ support using homogeneous deposition precipitation with urea as the precipitating agent. $Cu(NO_3)_2$, $AgNO_3$, or $HAuCl_4$ (all purchased from Alfa-Aesar) was added to a suspension of the $\gamma\text{-}Al_2O_3$ support material (9.98 g) in approximately 50 ml ultrapure water. The urea precipitation and subsequent treatment steps were carried out as above. The intended metal to aluminum ratio was ~1/75 as above. Actual Li and metal loadings were verified by Galbraith Laboratories (ICP-OES).

Reactions were carried out in either a quartz tube reactor or a reactor cell (supplied by Harrick) using 40–100 mg (tube reactor) or 20–30 mg (Harrick cell) of catalyst. The material was loaded into the reactor and exposed to a pure helium gas stream at 298 K for 15 min. The catalyst was then reduced in hydrogen (4 vol%, balance helium) at 400 °C for 2 h followed by cooling to 100 °C. Upon reaching a steady temperature of 100 °C (~1 h), the reactant stream was switched from bypass to the reactor. The reactant stream was prepared by passing a stream of 3 vol% O_2 in He through a bubbler containing absolute ethanol held in a recirculating cooling bath. The temperature of the bath (~15 °C) was adjusted to give an ethanol to oxygen ratio of 1:1. For all experiments carried out in the tubular reactor, a GHSV of 2500 h^{-1} was used. These conditions we chosen to match those of the Lippits experiments [6,7]. For all experiments performed in the Harrick cell, a GHSV of 10,000 h^{-1} was used. All experiments were performed at atmospheric pressure at the catalyst bed outlet.

Following the preparation procedure above and the introduction of the reactant stream, the temperature was held for 1 h at 100 °C. Experiments were then carried out with two cycles of the following temperature program: Increase temperature by 25 °C at a rate of 5 °C/min, hold 55 min at a constant temperature, repeat up to 400 °C, lower temperature back to 100 °C. As noted below, the hold time at each temperature step was sufficient for the reaction to reach steady state, as determined by mass spectrometry. The bed temperature was monitored and controlled using a k-type thermocouple inserted into the inlet side of the reactor tube and placed in direct contact with quartz wool at the top of the catalyst bed.

The effluent stream was analyzed using an on-line gas chromatograph (Agilent) with a DB-1 column and a molecular sieve and Hayesep Q column. All measured peaks were identified by comparison to peak elution times determined using custom gas mixtures and liquid injections of mixtures containing relevant species and a reference (ethanol). GC calibration experiments using a gas stream containing both ethylene oxide and acetaldehyde provided retention time separation of ~1 min using the DB-1 column, allowing for unambiguous resolution of these product species. Species assignments were confirmed by gas chromatography with mass spectrometry (GC–MS (Agilent)) on a separate reactor system. The effluent stream was sampled every 30 min, yielding 1 data point during the initial transient observed after reaching a new stable temperature and 1 data point at steady state per temperature ramp step. Product signals reached steady state after 10–15 min at a new temperature as determined by continuous sampling with mass spectrometry for all catalysts investigated. No differences in steady state signals from one ramp cycle to the next were observed. Data in figures below represent an average of at least 3 ramp cycles.

Conversion was determined by comparing the measured ethanol signal to those measured at 100 °C through the reactor (negligible conversion) and through the bypass. This ethanol signal was collected both before and after running the temperature program. Using this conversion as a basis, a carbon balance indicated that a small fraction of ethanol (<10%) decomposed to deposit solid carbon or to produce unidentified secondary products at temperatures above 350 °C for all supported nanoparticle catalyst materials. Below 350 °C, total carbon was balanced within 5% or better. Selectivity was calculated on a per carbon basis by dividing by the ethanol conversion and the ratio of the number of carbon atoms in ethanol and the respective product species.

3. Results

3.1. Characterization of $\gamma\text{-}Al_2O_3$, $Li_2O/\gamma\text{-}Al_2O_3$, and Metal/$Li_2O/\gamma\text{-}Al_2O_3$ catalysts and ethanol selective oxidation over $\gamma\text{-}Al_2O_3$, $Li_2O/\gamma\text{-}Al_2O_3$

Fig. 1 shows the X-ray diffraction patterns of the pseudo-boehmite (PAL-M 300), calcined for 1 h at 550 °C, and lithium deposited on the calcined pseudo-boehmite support material. Both the calcined PAL-M 300 and lithium-deposited support (denoted hereon as $Li_2O/\gamma\text{-}Al_2O_3$) exhibited broad features consistent with the gamma alumina ($\gamma\text{-}Al_2O_3$) phase. Following the urea co-deposition of Ag and Cu and subsequent reduction of the final catalyst at 400 °C, as performed prior to reaction studies, this material exhibited an XRD pattern consistent with $\gamma\text{-}Al_2O_3$ with no additional diffraction peaks, indicating the majority of metal resides in particles with sizes below the instrument detection limit. Upon Au deposition, broad diffraction peaks consistent with small crystalline gold nanoparticles were observed (Fig. 1). Additional characterization of these $Au/Li_2O/\gamma\text{-}Al_2O_3$ materials with SEM provided an average particle size of 4.5 nm. SEM of the Cu and Ag containing materials found that, relative to the Au materials, a significantly smaller number of nanoparticles per unit area were visible with larger diameters of 5–25 nm (See supplemental information for representative SEM images). As the molar Metal/Al ratio is the same for all materials, this smaller number of visible particles is consistent with the XRD results indicating that the majority of Cu and Ag does not reside in crystalline nanoparticles >3 nm in diameter. Based on the XRD and SEM results for the Cu and Ag catalysts, it is clear that urea co-deposition is not an effective synthesis method for producing uniform nanoparticle catalysts using Cu or Ag Nitrates as precursors. Actual lithium, Au, Ag, and Cu loadings for each material used in reaction studies were determined using ICP-OES and are presented in Table 1.

Ethanol oxidation data is organized into fractional conversion, fractional yield and fractional selectivity plots for all materials as a function of reactor temperature ranging from 100 to 400 °C. The conversion of ethanol and oxygen, Fig. 2(a), over the calcined