



Enhancing the stability of copper chromite catalysts for the selective hydrogenation of furfural with ALD overcoating (II) – Comparison between TiO₂ and Al₂O₃ overcoatings



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ABSTRACT

TiO₂ atomic layer deposition (ALD) overcoatings were applied to copper chromite catalysts to increase the stability for 2-furfuraldehyde (“furfural”) hydrogenation. After overcoating, about 75% activity was preserved compared to neat copper chromite: much higher activity than an alumina-ALD-overcoated catalyst with a similar number of ALD cycles. The effects of ALD TiO₂ on the active Cu nanoparticles were studied extensively using both *in-situ* TPR/isothermal-oxidation and *in-situ* furfural hydrogenation via Cu XAFS. The redox properties of Cu were modified only slightly by the TiO₂ ALD overcoat. However, a subtle electronic interaction was observed between the TiO₂ ALD layers and the Cu nanoparticles. With calcination at 500 °C, the interaction between the TiO₂ overcoat and the underlying catalyst is strong enough to inhibit migration and site blocking by chromite, but is sufficiently weaker than the interaction between the Al₂O₃ overcoat and copper chromite that it does not strongly inhibit the catalytic activity of the copper nanoparticles.

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1. Introduction

The energy demand in the US can be divided into petroleum (39%), natural gas (24%), coal (23%), nuclear (8%), and renewable energies (6%) [1]. Due to growing demand, the global energy requirements are projected to double in the next 25 years. Fossil energy (natural gas, coal, and petroleum) is limited and therefore cannot be used exclusively and in perpetuity to supply the increased demand. For this reason, there is a strong interest in developing renewable energy sources. Currently, biomass accounts for about 53% of all renewable energy sources in the U.S. [1]. As such, biofuels will remain the primary source of sustainable alternative transport fuels for some time. As part of a biofuels market, the selective hydrogenation of 2-furfuraldehyde (“furfural”) to make furfuryl alcohol is an important step along the route for converting cellulosic and hemi-cellulosic materials into fuels [2].

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Copper chromite has been shown to be an effective catalyst for a variety of selective hydrogenation reactions, including the hydrogenation of furfural [3,4]. However, this catalyst suffers from significant deactivation under both gas-phase and trickle-bed reactions [4,5]. Our previous work focused on understanding the deactivation mechanism and attempting to improve the stability of this catalyst for gas-phase conversion [4,6]. We found that coke formation and migration of chromium over the copper are the two main causes for the deactivation of Cu-chromite. Recently, Lu and co-workers [7] discovered that coke formation and sintering can be reduced in the oxidative dehydrogenation of ethane by applying Al₂O₃ atomic layer deposition (ALD) “overcoatings” to palladium nanoparticles significantly improving the yield of ethylene. Dumesic and coworkers [5] also found that Al₂O₃ ALD overcoating can suppress the deactivation of Cu caused by sintering and leaching of the metal under trickle-bed conditions in biomass conversion.

Our recent work also found that a thin layer of ALD alumina can increase the stability of Cu-chromite for furfural hydrogenation in the gas phase [6]. Though initially fully covered by the thin film,

the overcoated Cu becomes accessible to reagent gases following high-temperature annealing that introduces microporosity in the overlayer. In addition, Lu et al. [7] speculated that the Al₂O₃ overcoat preferentially segregates onto step edges and surface defects that, if exposed, are believed to break C–C bonds leading to coke formation. Our recent work shows, furthermore, that alumina ALD overcoatings alter the selectivity for furfural hydrogenation due to the selective coverage of defect sites versus terrace sites of supported Pd nanoparticles [8].

The ALD modification of heterogeneous catalysts has proven beneficial in other applications, such as carbon nanotube growth [9], CO oxidation [10], and lithium–O₂ batteries [11]. However, alumina-ALD-overcoated Cu-chromite loses more than 80% of its original activity compared to uncoated Cu-chromite prior to deactivation [6]. We speculated that this was due to the formation during ALD treatment of an inactive copper aluminate interphase between the Al₂O₃ overlayer and Cu nanoparticles. Presumably, as a result of the interphase species, the interaction between Cu and ALD layer is so strong that more than 80% of the Cu active sites are densely covered. What is needed, therefore, is an overcoating method that can increase the stability of Cu-chromite without significant loss of activity. Huber and coworkers [12] found that TiO₂ ALD overcoated onto a cobalt catalyst can increase the stability in the aqueous-phase hydrogenation (APH) of furfuryl alcohol by reducing both leaching and sintering of the active Co. In this work, they speculated that alumina ALD led to formation of an irreducible cobalt aluminate phase that destroyed all catalytic activities. Additional work needs to be done to clarify the mechanism by which the TiO₂ ALD layers (compared to Al₂O₃ ALD) modify the metal nanoparticles and result in large differences in catalytic performance.

In the current work, we investigate the use of TiO₂ ALD overcoating to increase the stability of Cu-chromite catalysts during the gas-phase furfural hydrogenation reaction. Mechanistic information was developed using both *ex-situ* and *in-situ* XANES/EXAFS techniques to study the redox properties and the active Cu species during furfural hydrogenation.

2. Materials and methods

2.1. Materials

The commercial copper chromite catalyst (Cu-chromite) and 2-furfuraldehyde (named as furfural for short reagent, >99%) both were purchased from Sigma–Aldrich. Hydrogen and nitrogen gases were all UHP grade, obtained from Airgas [13].

2.2. Atomic layer deposition

ALD was performed using a viscous flow reactor previously described in detail elsewhere [14]. Approximately 0.5 g Cu-chromite powder was spread uniformly onto a stainless steel sample holder topped with a stainless steel mesh [15]. The sample holder was then loaded into the reactor and allowed to equilibrate for at least 30 min at 200 °C under a flow of UHP N₂ at 1 Torr. Titania ALD was done using alternating pulse–purge cycles of titanium isopropoxide (TTIP, Sigma–Aldrich, 97%) and deionized water at 200 °C. The TTIP bubbler was heated to 80 °C to increase its vapor pressure. A typical dose–purge timing sequence for a single TiO₂ ALD cycle includes the following: TTIP dose (90 s)–purge (150 s)–H₂O dose (90 s)–purge (150 s). The Cu-chromite catalyst was coated with 20, 30, and 40 ALD cycles of TiO₂. The Al₂O₃ ALD used alternating exposures to trimethyl aluminum (TMA, Sigma–Aldrich, 97%) and deionized water at 200 °C. Typical timing

sequences for a single Al₂O₃ ALD cycle are as follows: TMA dose (60 s)–purge (120 s)–H₂O dose (60 s)–purge (120 s).

Post-treatment in flowing air at 500 °C was performed to induce porosity in the TiO₂-ALD Cu-chromite catalysts. These post-treated samples are labeled as, for example, ALD Cu-chromite-TiO₂-20c-500 for material with 20 ALD titania cycles over the Cu-chromite catalyst followed by heat treatment at 500 °C (abbreviated as 20c TiO₂). Forty-five cycles of alumina-ALD-overcoated Cu-chromite catalyst followed by calcination at 700 °C is named as 45c Al₂O₃.

2.3. Vapor-phase hydrogenation of 2-furfuraldehyde

Vapor-phase conversion of furfural was conducted at atmospheric pressure in a 1/2" stainless steel tubular reactor placed in a clamshell furnace equipped with a temperature controller. For each reaction test, about 60–65 mg of ALD-treated Cu-chromite (or 30 mg Cu-chromite) was diluted with SiC (70 mesh, mass ratio of sample to diluent is 1:12) to mitigate hot spot formation in the catalyst bed due to the exothermic reaction. The sample was then loaded onto a quartz wool bed, sitting in a 1/4" stainless steel tubing located in the bottom half of the reactor to help fix the catalyst bed position.

Prior to reaction, the catalyst was reduced *in-situ* in 10% H₂/He for 1 h at 200 °C. After reduction, 50% H₂/He was purged into the unit for half an hour to allow stabilization. Furfural was introduced to the reactor by sweeping a carrier gas of 50% H₂/He through a bubbler containing pure furfural. The bubbler temperature was controlled by a circulating bath set to 65 °C. Reactor effluents were analyzed by an online gas chromatograph equipped with a flame ionization detector (FID) and a packed column (EC-Wax, 30 m * 0.32 mm * 1 μm, ECONO-CAP, Grace Davison). All the chemical transfer lines and valves, from the bubbler to the online GC injector, as well as the gas sampling valve in the GC were heat traced to prevent condensation of either the reactant or the products.

Selective hydrogenation of furfural was studied over Cu-chromite, 20c TiO₂, 30c TiO₂, and 40c TiO₂. Typical reaction conditions were 2% furfural and 50% H₂ (molecular ratio, balance helium) to make the ratio of H₂:furfural = 25:1 and a total gas flow rate between 50 and 100 cc/min. WHSV was defined as the total mass flow rate of furfural divided by the total mass of the catalyst (i.e., the mass including overcoat and chromite). Fresh catalyst was used for each test to ensure identical reaction conditions.

2.4. X-ray absorption fine-structure (XAFS) data collection and analysis

In-situ X-ray absorption measurements at Cu K-edge (8980.48 eV) were conducted at the Materials Research Collaborative Access Team (MRCAT) 10ID and 10BM beam lines at the Advanced Photon Source (APS) at Argonne National Laboratory. Cu K-edge X-ray absorption spectra were collected in transmission mode with minimum data point interval of 0.5 eV. Each spectrum required about 1.5 min at 10ID or about 3 min at 10BM. A Cu foil spectrum was acquired simultaneously with each measurement for energy calibration. Approximately 10 mg neat catalyst (per sample) was loaded as a self-supporting wafer into a stainless steel holder with six individual 4.0-mm-diameter holes. The holder was placed into a quartz sample tube (25.4 mm o.d.), centered in a clamshell furnace, described by Neylon et al. [16]. The sample temperature was measured by a thermocouple positioned near the sample holder inside the quartz tube.

Prior to temperature-programmed reduction (TPR), samples were initially heated to 150 °C for 30 min in flowing helium to eliminate moisture and other adsorbed molecules from the catalyst

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