Enhancing the stability of copper chromite catalysts for the selective hydrogenation of furfural using ALD overcoating

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ABSTRACT

The stability of a gas-phase furfural hydrogenation catalyst ($CuCr_2O_4 \cdot CuO$) was enhanced by depositing a thin Al_2O_3 layer using atomic layer deposition (ALD). Based on temperature-programed reduction (TPR) measurements, the reduction temperature of Cu was raised significantly, and the activation energy for furfural reduction was decreased following the ALD treatment. Thinner ALD layers yielded higher furfural hydrogenation activities. X-ray absorption fine structure (XAFS) spectroscopy studies indicated that Cu^{1+}/Cu^0 are the active species for furfural reduction.

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1. Introduction

Fossil fuels provide the majority of our current energy supply, especially in the transportation fuel sector [1]. These fossil fuel resources took millions of years to be formed and are currently being consumed at a rate that is orders of magnitude higher than their natural regeneration cycle, making them non-renewable sources of energy. Fuels generated from biologically-derived feedstocks are a good alternative to replace fossil sources [2]. Furfuryl alcohol, an important intermediate molecule in the conversion of biomass to the biofuels, can be synthesized via the selective hydrogenation of furfural, an important step along the route for converting hemi-cellulosic materials into biofuels [3].

Copper chromite ($CuCr_2O_4 \cdot CuO$), due to its mild catalytic reduction properties, has been used extensively for years in various industrial processes such as the partial hydrogenation of vegetable oils and fatty acids as well as the decomposition or dehydration of alcohols [4]. The utilization of these catalysts in hydrogenation reactions stems from their capability to selectively hydrogenate carbonyl bonds while leaving unsaturated C=C bonds virtually untouched. This same catalyst has also been used for the reduction of furfural due to its high activity and selectivity to furfuryl alcohol [5]. However, copper chromite catalysts suffer severe deactivation under the normal working conditions. For instance, the total activity for furfural reduction can decrease by 40% in 4 h at a 52 h^{-1} WHSV for a commercial copper chromite catalyst [6]. Previous work has shown that coke formation, metal sintering/leaching [7], and support migration over the active site [6] are all potential mechanisms for the deactivation of the Cu-based catalyst. Our recent results have shown that coke formation along with chromite migration over the active sites of Cu are the major causes

for deactivation of the Cu chromite catalyst in the gas-phase reduction of furfural [6].

Recently, Lu and co-workers [8] discovered that coke formation and sintering can be prevented in the oxidative dehydrogenation of ethane by applying Al_2O_3 ALD "overcoatings" to palladium nanoparticles, significantly improving the yield of ethylene. Though initially fully covered by Al_2O_3 thin films, the Al_2O_3-coated Pd NPs became accessible to reagent gases through annealing the catalyst to induce microporosity in the overcoating layer following. In addition, they speculated that the Al_2O_3 overcoat preferentially segregated onto step edges and surface defects that, if exposed, are believed to break C—C bonds leading to coke formation [9]. ALD modification of heterogeneous catalysts has proved beneficial in other applications, such as carbon nanotube growth [10], CO oxidation [11], lithium–O_2 batteries [12], and biomass conversion [13]. Recently, Dumesic and coworkers [7] found that ALD Al_2O_3 overcoating can suppress the deactivation of Cu caused by sintering and leaching of the metal under trickle bed conditions. These workers found that the deactivation of the ALD catalyst by the deposition of carbonaceous species (i.e., coke) is reversible upon calcination, whereas deactivation of the same catalyst without the ALD overcoating by Cu leaching or sintering is irreversible. However, this previous work did not examine the effects of catalyst overcoating for vapor-phase furfural hydrogenation, which is thought to be a much more promising process for furfural conversion. In addition, the mechanism by which the ALD layers modify the metal nanoparticles underneath is still unclear.

In the current work, *in situ* and operando X-ray absorption methods were used to elucidate the mechanism of alumina ALD overcoating of Cu nanoparticles and the effect of ALD overcoatings against vapor-phase furfural reduction reactions over Cu chromite. A factor analysis method was used to break down the XANES spectra into several components corresponding to different Cu states, and these were analyzed during the reductions. Different numbers of ALD Al_2O_3 cycles were performed on the Cu catalysts to vary the thickness of the protective overcoats and evaluate the effect of thickness on the Cu reduction and the furfural hydrogenation reaction. This report will provide insight into the reduction process of Cu chromite before and after ALD treatment and demonstrate that the ALD process can improve the stability of Cu chromite catalysts in vapor-phase furfural hydrogenation. Finally, we will show that Cu^{1+}/Cu^0 are the active species for this reaction.

2. Materials and methods

2.1. Materials

The commercial copper chromite catalyst (Cu chromite) and 2-furfuraldehyde (Reagent, >99%) both were purchased from Sigma–Aldrich. Hydrogen and nitrogen gases were all UHP level, obtained from Airgas.[2]

2.2. Atomic layer deposition

ALD was performed in a viscous flow reactor that has been described in detail elsewhere [14]. 0.5 g Cu chromite powder was spread uniformly onto a stainless steel sample plate with a mesh top to contain the powder while still allowing gaseous access to the precursor vapors [15]. The samples were loaded into the reactor and kept for at least 30 min at 200 °C in a 160 sccm flow of UHP N_2 at 1 Torr pressure to allow temperature stabilization and to dry the powder. Next, the Cu-chromite catalyst was coated with 10, 20,

30, and 45 ALD cycles of Al_2O_3. These samples are denoted as, e.g., ALD Cu-chromite-10c for the 10 ALD Al_2O_3 cycle-treated Cu-chromite. The Al_2O_3 ALD used alternating exposures to trimethyl aluminum (TMA, Sigma–Aldrich, 97%) and deionized water at 200 °C. Typical timing sequences for a single Al_2O_3 ALD cycle are as follows: TMA dose (60 s)–purge (120 s)–H_2O dose (60 s)–purge (120 s).

Post-treatment in flowing N_2 at 700 °C was performed to induce porosity in the ALD Cu-chromite catalysts. These post-treated samples are labeled as, e.g., ALD Cu-chromite-10c-700 for 10 ALD alumina cycles over Cu-chromite followed by heat-treatment at 700 °C.

2.3. Vapor-phase hydrogenation of 2-furfuraldehyde

Vapor-phase conversion of 2-furfuraldehyde (furfural) over ALD-treated copper chromite was conducted at atmospheric pressure in a 1/2″ stainless steel tubular reactor placed in a clam-shell furnace equipped with temperature controllers. 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 nature of this reaction. The sample was then loaded onto a quartz wool bed, sitting on a 1/4″ stainless steel tubing located at the bottom half of the reactor to help fix the bed position.

Prior to reaction, the catalyst was reduced *in situ* in 10% H_2/He for 1 h at 200 °C. After reduction, 50% H_2/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% H_2/He through a bubbler containing pure furfural. The bubbler temperature was controlled by a circulating bath. Reactor effluents were analyzed by an online gas chromatography 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. Cold spot avoidance is the key to obtaining high quality, stable and accurate data with proper mass balances.

Selective hydrogenation of furfural was studied over Cu-chromite, ALD Cu-chromite-10c-700, ALD Cu-chromite-20c-700, ALD Cu-chromite-30c-700, and ALD Cu-chromite-45c-700, respectively. Typical reaction conditions were 2% furfural and 50% of H_2 to make the ratio of H_2: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 copper chromite catalyst. Fresh catalyst was used each time 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 (insertion device) and 10BM (bending magnet) at the Advanced Photon Source (APS) at Argonne National Laboratory. Cu K edge XAS spectra were collected in transmission mode with minimum data point interval of 0.5 eV. Each spectrum took about 1.5 min of scanning. A Cu foil spectrum was acquired simultaneously with each measurement for energy calibration. Approximately 10 mg of up to three samples was loaded as self-supporting wafers into a multi-sample stainless steel holder with six individual 0.12 in. diameter holes. The holder was placed into a quartz sample tube (1 in. o.d.), centered in a clam-shell furnace, described by Neylon et al. [16]. The sample temperature was measured by a thermocouple positioned near the sample