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

Hongbo Zhang^a, Yu Lei^{b,c}, A. Jeremy Kropf^a, Guanghui Zhang^a, Jeffery W. Elam^{b,*}, Jeffery T. Miller^a, Fred Sollberger^d, Fabio Ribeiro^d, Cem M. Akatay^e, Eric A. Stach^f, James A. Dumesic^g and Christopher L. Marshall^{a,*}

^a Chemical Science and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA

^b Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439, USA

^c Current address: Department of Chemical and Materials Engineering, University of Alabama in Huntsville, Huntsville, AL 35899, USA

^d FRNY 2158 Purdue University School of Chemical Engineering Forney Hall of Chemical Engineering 480 Stadium Mall Drive West Lafayette, IN 47907-2100

^e Nanotechnology Center Purdue University 1205 West Lafayette, IN, 47907, USA

^f Center for Functional Nanomaterials Brookhaven National Laboratory Upton, NY, 11973, USA

^g Department of Chemical and Biological Engineering, University of Wisconsin, Madison, WI 53706, USA

*Authors to whom correspondence should be addressed: marshall@anl.gov

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Abstract

The stability of a gas phase furfural hydrogenation catalyst ($\text{CuCr}_2\text{O}_4\cdot\text{CuO}$) was enhanced by depositing a thin Al_2O_3 layer using atomic layer deposition (ALD). Based on temperature-programmed 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 $\text{Cu}^{1+}/\text{Cu}^0$ are the active species for furfural reduction.

Key Words: Selective hydrogenation, 2-Furfuraldehyde, Furfuryl alcohol, Stability, Copper chromite, TPR, XAFS, ALD, operando

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 ($\text{CuCr}_2\text{O}_4 \cdot \text{CuO}$), 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 $\text{C}=\text{C}$ 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 4h at a 52h^{-1} WHSV for a commercial copper chromite catalyst.⁶ Previous work has shown that coke formation, metal sintering/leaching⁷, and support migration over the active site⁶ 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, Lu⁸ and co-workers discovered that coke formation and sintering can be prevented in the oxidative dehydrogenation of ethane by applying Al₂O₃ ALD “overcoatings” to palladium nanoparticles, significantly improving the yield of ethylene. Though initially fully covered by Al₂O₃ thin films, the Al₂O₃-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 Al₂O₃ 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 growth¹⁰, CO oxidation¹¹, lithium-O₂ batteries,¹² and biomass conversion.¹³ Recently, Dumesic⁷ and coworkers found that ALD Al₂O₃ 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 Al₂O₃ 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 $\text{Cu}^{1+}/\text{Cu}^0$ are the active species for this reaction.

2. Materials and Methods

Materials

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

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 vapors¹⁵. The samples were loaded into the reactor and kept for at least 30 minutes at 200 °C in a 160 sccm flow of UHP N₂ 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 Al₂O₃. These samples are denoted as, e.g., ALD Cu-chromite-10c for the 10 ALD Al₂O₃ cycle -treated Cu-chromite. 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: TMA dose (60s) - purge (120s) - H₂O dose (60s) - purge (120s).

Post-treatment in flowing N₂ 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.

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 30mg 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% H₂/He for 1 hour 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. Reactor effluents were analyzed by an online gas chromatography equipped with a flame ionization detector (FID) and a packed column (EC-Wax, 30m * 0.32mm * 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 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 H₂ to make the ratio of H₂: furfural = 25:1 and a total gas flow rate between 50- 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.

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

In situ X-ray absorption measurements at Cu K-edge (8,980.48 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 minutes of scanning. A Cu foil spectrum was acquired simultaneously with each measurement for energy calibration. Approximately 10mg of up to three samples were 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 holder inside the quartz tube. Before starting the TPR process, all the samples were first heated to 150 °C for 30 min to eliminate moisture and other adsorbed molecules from the catalyst surface. Then the samples in the cell were heated up to 700 °C with a ramp rate of 2 °C/min under a 60sccm flow of H₂ (3.5%) in He. Scans of all samples were recorded every 1-2min during the TPR process with 70-80 spectra per sample collected during each run. Every second spectrum is plotted here.

Temperature programmed reduction (TPR)

TPR was performed on an Altamira AM-200 unit equipped with a thermal conductivity detector (TCD). The outlet gases were also analyzed by a Stanford Research System Residual Gas Analyzer (RGA, mass spectrometer). Approximately, 80-100 mg of sample were loaded into a 1/8 in. quartz U-tube and installed on the unit. Prior to the TPR runs, each sample was pretreated in 50 sccm He at 150 °C for 1h to eliminate water, and then cooled to room

temperature. The catalyst was then heated to 700 °C (ramp rate of 5 °C / min) under (4%) H₂/Ar at a flow rate of 50 sccm separately.

Operando reaction

Operando XAS measurements furfural reduction was also conducted at beamline MRCAT-10ID at the APS. The reactor was made of glassy carbon, and more details about the operando reactor can be found in the previous work did by Kispersky et. al.¹⁷ Cu-K edge XAS spectra were collected in transmission mode and each spectrum took about 1.5 minutes of scanning. About 4-5 spectra were merged to make one final spectrum. 17 mg of Cu-chromite was mixed with 500 mg SiC and put into the reactor for operando reaction testing, while 100 mg ALD Cu-chromite-45c-700 was added to the operando reactor for comparison based on the total activity for these two catalysts. The catalyst was first reduced at 200 °C for 30 min using 60 sccm 50% H₂/He (v/v), the operando XAFS spectrum was collected and named '200 °C H₂'. Furfural was then added through a bubbler preheated to 65 °C. This XAFS spectrum was named '200 °C Fur'. After GC analysis of the reaction performance, the furfural was switched off. The catalyst temperature was then increased to 300 °C and reduced in H₂ while holding at this temperature for 30 min. After lowering the temperature to 200 °C, furfural was introduced into the reactor for a second time. The reaction performance of this catalyst after 300 °C reduction was collected and the operando XAFS spectrum was named '300 °C Fur'. The reaction performance and the XAFS spectrum of this catalyst after 400 °C reduction ('400 °C Fur') were collected in the same way. Cu XAFS spectra were recorded continuously during the catalytic experiments. It should be noted that all the reaction performance data was collected at 200 °C.

Transmission electron microscopy (TEM)

The TEM measurements were performed on a FEI Titan 80-300 S/TEM spectroscopy.

3. Results

Figure 1. TEM images of (a) Cu-chromite, (b) ALD Cu-chromite-10c-700, (c) ALD Cu-chromite-20c-700 and (d) ALD Cu-chromite-45c-700; (scale bars are 5nm).

Figure 1 shows TEM images of (a) Cu-chromite, (b) ALD Cu-chromite-10c-700, (c) ALD Cu-chromite-20c-700 and (d) ALD Cu-chromite-45c-700. From the scans across the TEM images, it is clear that Cu-chromite is well crystallized both before and after the ALD overcoating treatment. No amorphous polymorph is visible on the surface of Cu-chromite before the Al_2O_3 ALD. Careful inspection of the TEM image recorded for the sample with 10 cycles of

ALD overcoating (ALD Cu-chromite-10c-700, Figure 1b) reveals a thin amorphous coating with an average thickness of 1.4 nm. This value matches well with the expected thickness after 10 ALD Al₂O₃ cycles: 1.3 nm. After 20 cycles of ALD overcoating, the average thickness of the ALD layer is ~2.3 nm, in good agreement with the expected thickness of ~0.1 nm/cycle increment shown on Table 1. The overcoating thickness appeared to vary for different locations on the nanoparticles. This apparent non-uniformity may result from different TEM focusing conditions across the sample. Alternatively, the ALD Al₂O₃ might nucleate differently on different crystalline planes of the Cu chromate. This phenomenon has been seen previously for SiO₂ ALD on BN nanoparticles where the SiO₂ deposited only on the edges but not on the basal plane of the BN¹⁸. The thickness of the amorphous alumina became even thicker when 45 cycles of ALD overcoating used (Figure 1d). The non-uniformity of the ALD Al₂O₃ is especially apparent in this image. The average thickness for the different overcoating cycles are shown in Table 1. Both the average thickness and the ranges of the thickness increase along with increasing number of cycles. The weight gain is not linear with increasing number of cycles probably due to blocking of surface sites with increasing number of ALD cycles. The N₂ adsorption/desorption isotherms of uncovered and ALD overcoated catalysts as well as their corresponding pore size distributions are included in supporting information. (Figure S1)

Table 1: Range of the thickness values, average thickness, and weight gain of ALD layers for different cycles of ALD overcoatings;

Catalyst	Thickness range (nm)	Average thickness (nm)	Weight gain (wt%)
Cu-chromite	0	0	0
ALD Cu-chromite-10c-700	0.7-1.8	1.4	12.5
ALD Cu-chromite-20c-700	1.5-3.5	2.3	23.5
ALD Cu-chromite-45c-700	1.9-6.6	3.6	42

Figure 2 (a) TCD signal trace during the H₂-TPR of Cu-chromite and ALD Cu-chromite-45c-700 in 4% H₂/Ar at 5°C/min; (b) XANES spectra of standard Cu²⁺, Cu¹⁺ and Cu⁰; stacked normalized Cu K-edge XANES spectra of (c) Cu-chromite and (d) ALD Cu-chromite-45c-700 collected during the *in situ* H₂-TPR experiment.

Figure 2a shows the H₂-TPR profile for the Cu-chromite and ALD Cu-chromite-45c-700 samples. The uncoated Cu-chromite can be fully reduced to Cu⁰ below 250 °C, much lower than the Cu catalyst modified by 45 cycles of alumina ALD layers. After ALD overcoating, the TPR reduction profile of Cu (ALD Cu-chromite-45c-700) is very broad. As shown in Figure 2a, Cu²⁺

is not fully reduced to Cu^0 until 550 °C, which is observed in the TPR profile of ALD Cu/ γ - Al_2O_3 -45c (45 cycles of alumina ALD overcoating against γ -alumina supported copper catalyst) and Cu aluminate (made from calcination of Cu/ γ - Al_2O_3 at 700 °C for 5h, Cu/ γ - Al_2O_3 was bought from Sigma-Aldrich) shown in the supporting information (Figure S2a). The formation of Cu aluminate by calcination of Cu/ γ - Al_2O_3 was determined by XRD detection shown in the supporting information, too (Figure S2b). Complete reduction of the ALD Cu/ γ - Al_2O_3 -45c sample occurs at a temperature above 500 °C. This demonstrates that ALD overcoatings dramatically affect the reduction temperature (chemistry) of the underlying nanoparticles. Dumesic and coworkers⁷ also found that Cu is partially oxidized in the presence of the alumina overcoating layers, but the mechanism is still unclear.

In situ XAFS measurements were undertaken next to determine the effect of ALD Al_2O_3 overcoatings on the underlying Cu nanoparticles. XAFS measurements at the Cu K-edge were collected on three reference samples as shown in Figure 2b: CuO (red, Cu^{2+}), cuprous oxide (Cu_2O) (black, Cu^{1+}) and Cu foil (blue, Cu^0). The Cu^{2+} spectrum has a small pre-edge peak at a higher energy compared to the Cu^{1+} , which shows the largest pre-edge feature. The edge energy for the Cu^0 is shifted to even lower energy from around 8.99 to 9.01keV. The differences between these reference spectra imply that the main oxidation state of the copper in the catalyst can be identified based on the overall features, the pre-edge positions and the height of the pre-edge peaks.^{16, 19}

Figure 2c-d shows a normalized stacked plot of the Cu K-edge XANES of (c) Cu-chromite and (d) ALD Cu-chromite-45c-700 collected during the *in situ* XAFS/ H_2 -TPR experiment. The XANES features for the ALD Cu-chromite-45c-700 (two peaks above the absorption edge and higher intensity for the second peak) are different from that of Cu-chromite (only a single peak

above the absorption edge), neither does Cu nor CuOx (Figure 3b). The overcoated sample is similar to copper aluminate.²⁰ Previous workers have found that copper aluminate can easily be synthesized from Cu/Al₂O₃ by heating to >700 °C, similar to our pre-treatment conditions (700 °C) for the ALD Cu-chromite-45c-700. Comparing the XANES spectra for Cu-chromite and ALD Cu-chromite-45c-700 prior to reduction shows that they are similar to the Cu²⁺ reference spectrum. We therefore propose that a thin layer forms at the interface between the ALD Al₂O₃ and the Cu nanoparticles. The existence of the pre-edge peak of ALD Cu-chromite-45c-700 prior to reduction further demonstrates that a new phase forms after the ALD overcoating. The XANES pre-edge features are highly sensitive to the local symmetry of the absorbing atom,²¹ there is no pre-edge peak for Cu-chromite sample before reduction. In addition, the reduction of ALD Cu-chromite-45c-700 occurs over a wider temperature range compared to the Cu-chromite. It is observed that Cu-chromite is reduced from Cu²⁺ to Cu⁰ in a narrow temperature range between 200-300°C (Figure 2c). In contrast, the ALD overcoated catalyst (ALD Cu-chromite-45c-700) was not completely reduced until about 650 °C, in agreement with the *ex situ* H₂-TPR measurement (Figure 2a). This provides further evidence for the formation of copper aluminate at the interface, with the copper aluminate increasing the reduction temperature of the underlying Cu.^{20b, 22} The characteristic spectral features of Cu²⁺, Cu⁺ and Cu⁰ were evident in the pre-edge region.^{16, 19} The small nano-pores⁸ formed within the ALD layers after heat-treatment may restrict the diffusion of feed and products to/from the Cu nanoparticles and may also influence the reduction temperature of Cu covered by ALD layers.

Figure 3. Percent of the different Cu species as a function of temperature during *in situ* H₂-TPR from XANES data by Factor Analysis over Cu-chromite and ALD Cu-chromite-45c-700;

XANES linear combination fitting of the *in situ* XAFS/H₂-TPR measurements (Figure 2c-d) reveals the evolution of the two components: Cu²⁺ and Cu⁰ as a function of temperature (Figure 3). No Cu¹⁺ species was observed, which suggests that the reduction of Cu¹⁺ to Cu⁰ is faster than the reduction of Cu²⁺ to Cu¹⁺.^{16, 19} The temperature for the 50% reduction was ~100°C higher for the ALD overcoated catalyst, and the temperature for complete reduction was more than 300 °C higher than the uncoated material. This quantitative analysis provides further evidence that the Cu reduction was modified by the ALD Al₂O₃ overcoating. FT-XAFS spectra (Figure S3a-b) also showed that the reduction temperature of ALD Cu-chromite-45c-700 was increased by about 300 °C. There also is a smaller amount of Cu agglomeration for the ALD overcoated catalyst based on a comparison of the FT-XAFS spectra than bare Cu-chromite.

Both the *ex-situ* and *in-situ* H₂ TPR experiments demonstrate that ALD overcoatings dramatically affect the reduction temperature (chemistry) of the underlying nanoparticles. The reduction temperature for 45c alumina ALD catalyst is about 300 °C higher than the non-coated catalyst. This could be because the small nano-pores⁸ formed within the ALD layers after heat-

treatment which may restrict the diffusion of feed and products to/from the Cu nanoparticles. Cu aluminate formation could also influence the reduction property of Cu. The reduction of Cu before or after ALD overcoatings was from Cu^{2+} to Cu^0 ; Cu^{1+} is barely seen during this reduction.

Table 2. *In situ* XAFS/ H_2 -TPR parameters comparison between different layers of ALD overcoating based on Cu-XANES spectra (shown in figure S4);

	T-onset($^{\circ}\text{C}$)	T-middle($^{\circ}\text{C}$)	T-completion($^{\circ}\text{C}$)	Cu^{1+} percentage at T-mid (%)
Cu-chromite	250	275	308	0
ALD Cu-chromite-10c-700	210	325	640	20
ALD Cu-chromite-20c-700	212	354	640	12
ALD Cu-chromite-30c-700	220	350	641	0.4
ALD Cu-chromite-45c-700	215	352	650	0

The modification of the metal particles created by the ALD overcoatings can be further understood by examining the changes in the XAFS spectra with different number of ALD overcoating cycles (Figure S4). Table 2 summarizes the reduction parameters obtained from the different ALD overcoated catalysts. The reduction onset temperatures are similar between the catalysts with and without ALD overcoatings. The temperature for complete reduction of the uncoated Cu-chromite is 308°C while all of the ALD modified catalysts are not completely reduced until $\sim 640^{\circ}\text{C}$. The temperature when 50% of the Cu is reduced (T-middle) are almost the same for all the ALD coated catalysts, about 75°C higher than uncoated Cu-chromite catalysts. However, the concentration of Cu^{1+} at T-mid is strongly dependent on the number of ALD overcoating cycles. From the XANES linear combination fittings it can be seen that the thinner overcoating layers exhibit a higher percentage of the Cu^{1+} species at T-mid. The difference in the Cu^{1+} concentrations may be because the different layers of ALD overcoatings create different pore distributions following heat treatment. Thinner layer may have smaller

pores within the layers which can limit the diffusion of H_2 and H_2O to and from the copper surface. The concentration of the reactant or the product changes the observed reduction temperature of Cu (Figure 2c-d and figure 3) Therefore reduction of Cu^{2+} to Cu^{1+} and Cu^{1+} to Cu^0 were both inhibited for the thinner coatings. A larger percentage of Cu^{1+} can be identified on ALD Cu-chromite-10c-700 after heat-treatment in figure S4a, suggesting that a larger percentage of $CuAlO_2$ is formed.

Figure 4. (a) Selective hydrogenation of furfural over copper chromite, ALD Cu-chromite-10c-700, ALD Cu-chromite-20c-700, ALD Cu-chromite-30c-700 and ALD Cu-chromite-45c-700; (b) Arrhenius plots for furfural hydrogenation over Cu-chromite, ALD Cu-chromite-10c-700, ALD Cu-chromite-20c-700 and ALD Cu-chromite-30c-700, all the reaction rates were normalized to the same initial value.

Since ALD overcoatings can change the reduction temperatures of the underlying Cu, the coating thickness should also influence the catalytic activity. To test this hypothesis, furfural hydrogenation reaction kinetic data were collected on Cu-chromite, ALD Cu-chromite-10c-700, ALD Cu-chromite-20c-700, ALD Cu-chromite-30c-700 and ALD Cu-chromite-45c-700 in the vapor phase. Figure 4a shows the furfural conversion as a function of time-on-stream over the

different catalysts. For these measurements, the catalysts were first reduced *in situ* using 10% H₂ for 1 hour at 200 °C. All catalytic reactions were run at the same temperature (200°C). The carbon balance stayed constant throughout the reaction process (about 98% ± 2%) indicating that almost all of the reaction products were accounted for. Two products were detected from the reactor effluent: furfuryl alcohol (the desired product) and 2-methyl furan (a known by-product). This result is consistent with literature reports indicating that dehydration of furfuryl alcohol forms 2-methyl furan. The selectivities to furfuryl alcohol were over 95% for all five catalysts. (Table S1) The lower the activity for furfural hydrogenation was the higher the selectivity to furfuryl alcohol would be, in good agreement with our previous studies.²³ Severe catalyst deactivation was observed for the commercial Cu-chromite.²⁴ Furfural conversion dropped from 100% initially to 30% within 3 hours. This differs from previous results⁶ because smaller WHSV (17 h⁻¹ rather than 52 h⁻¹ in the literature⁶) was used for a better comparison between Cu-chromite and ALD overcoating catalyst after stabilization. The most active ALD catalyst following ALD overcoating is the one with only 10 cycles of alumina.

Catalyst deactivation is a major problem limiting the application of copper chromite in furfural hydrogenation. Both coke formation and chromite migration lead to blocking of the active sites of Cu, and are the main causes for deactivation.⁶ This work showed that copper sintering (based on FT-XAFS shown in figure S3) is not a big problem for this catalyst most likely because the Cu loading of the Cu-chromite is high (about 38 wt%). Previous work has shown that the Cu particles are very large (103 nm based on XRD characterization), so any sintering that occurs is not a big problem for this system.⁶

Analogous to ALD Al₂O₃-coated Pd catalysts for oxidative dehydrogenation of ethylene⁸, different cycles of ALD-Al₂O₃ were coated over Cu-Chromite to minimize the deactivation of

this reaction. All of the ALD overcoated catalysts showed improved stability for furfural hydrogenation compared to the uncoated Cu-chromite. The catalytic activities decreased with increasing ALD Al_2O_3 coating thickness. However, the ALD coated catalysts also remained more active with time on stream. For instance, after 12 hr on stream, the activity for the 10c sample was almost the same as that of the Cu-chromite catalyst (if the WHSVs were the same). The stability of the ALD Cu-chromite-10c-700 is much higher than that of the Cu-chromite. More interestingly, when 45 cycles was applied, there is almost no deactivation within 5h's run. Furthermore, there is no deactivation at the beginning of the reaction. The selectivity for all of the ALD catalysts is higher than 97% after stabilization, which is better than that of the Cu-chromite catalyst (92%). Since there can be no leaching of Cu for the vapor phase reaction versus the liquid phase⁷ the ALD Cu-chromite catalysts shows potential for further application. The improved stability of the ALD catalysts may be due to the unique microporosity properties within the ALD Al_2O_3 layers, which has proven to be effective for minimizing coke formation, as proposed by Lu and co-workers.⁸ They found that after high temperature treatment, the alumina overcoats preferentially segregated onto step edges and surface defect sites on the Pd nanoparticle surfaces, which are believed to attack C-C bonds leading to coke formation. They also proposed that the micropores generated by heating the ALD Al_2O_3 film exposed the Pd(111) facet which selectively attacked C-H bonds producing ethylene.⁹ The copper aluminate formation may also influence the stability of our Cu catalyst. Because both the copper aluminate and the ALD Al_2O_3 may minimize chromite migration over the top of the copper, the active sites should remain accessible to the feed and remain active even after prolonged operation.⁶

Figure 4b shows Arrhenius plots for furfural hydrogenation over Cu-chromite, ALD Cu-chromite-10c-700, ALD Cu-chromite-20c-700 and ALD Cu-chromite-30c-700; all reaction rates

were normalized to the same initial value. These data show that the activation energy for furfural hydrogenation over Cu-chromite (55.4 KJ/ mol) was reduced with increasing Al_2O_3 overcoating thickness. This may be related to the different concentrations of Cu^{2+} , Cu^{1+} and Cu^0 between the ALD catalysts and the bare Cu-chromite catalyst after reduction at 200°C (based on H_2 -TPR results). Furfural conversion may have a different activation energy depending on the oxidation state of the Cu. The furfural activation energy on copper nanoparticles shown here is similar to that of Cu on activated carbon²⁵, while the activation energy is slightly lower than reported for a CuMgAl catalyst.²⁶ Our results are in good agreement with previous work on the activation energy of furfural hydrogenation over Cu-chromite at low temperature (413K) but high H_2 pressure (720Torr) by Rao et. al., which is about 50 KJ/mol.⁵

Figure 5(a), operando furfural reduction reaction performance under different reduction temperatures over Cu-chromite and ALD Cu-chromite-45c-700; (b) Cu EXAFS spectra of the working catalyst (ALD Cu-chromite-45c-700) before (RT He), after reduction at 200 °C (200 °C H_2) and during furfural reduction reactions (200 °C Fur), higher reduction temperatures were also applied here (300 °C Fur and 400 °C Fur). All the reactions were carried out at 200 °C.

Operando XAFS characterization was performed on the ALD Cu-chromite-45c-700 to elucidate the active species of the working catalyst. The performance of the Cu-chromite under identical conditions is shown in Figure 5a. The catalysts were reduced at different temperatures, while the catalytic performance shown here were collected at 200 °C. As shown in Figure 5(a), after 200 °C reduction, the ALD Cu-chromite-45c-700 shows 96% activity with about 80% furfuryl alcohol selectivity. (The activity was obtained from the yield of furfuryl alcohol plus 2-methyl furan at nearly 100% carbon balance of this reaction while the selectivity was determined from the yield of each product.) As the reduction temperature increased, the activity of the ALD Cu-chromite-45c-700 decreased. For example, the activity of the ALD Cu-chromite-45c-700 drops to 40% after reduction at 300°C, which means that the ALD Cu-chromite-45c-700 loses 50% activity by simply increasing the reduction temperature from 200°C to 300°C. This activity loss is further increased by pre-reduction of the catalyst at 400°C with the ALD catalyst having near zero activity. The same trend of lower activity at higher pre-reduction temperatures can be seen in the uncoated Cu-chromite catalyst (Figure 5a). From the selectivities of the ALD Cu-chromite-45c-700, it can also be found that the higher the activity the lower the selectivity to furfuryl alcohol in good agreement with previous work.⁶ In addition coke formation is not expected to be a major problem for the ALD coated catalyst. As seen by Lu and co-workers, the ALD overcoating helps minimize coke formation over Pd overcoated catalysts carried out at over 600°C with ethylene as one of the products.⁸ We also found that there is almost no deactivation for the ALD catalyst in furfural reduction even after 12 hr on stream. Chromite migration should be held back by 45 cycles of ALD overcoatings. Therefore we propose that loss of the active component may cause the reduction in activity with increasing reduction temperature.

Figure 5b shows the Cu EXAFS spectra of ALD Cu-chromite-45c-700 under reaction conditions at several temperatures. From the spectra, the Cu-O coordination peak and Cu-Cu coordination peak can be easily identified in agreement with previous work.²⁷ Comparing the as-prepared sample (RT He) with the reduced sample (200 °C H₂), obvious signs of reduction can be seen. The Cu-O peak is much smaller in the reduced sample as compared to the as-prepared sample. As furfural was introduced, the Cu-O peak increased while the Cu-Cu peak decreased, demonstrating that the Cu is being oxidized, and the EXAFS spectrum shows a mixture Cu¹⁺ and Cu⁰.²⁷ This finding is in good agreement with previous work by Rao and his co-workers, who showed that the furfural reduction activity correlates with the concentration of Cu¹⁺ sites, which appear to be involved in the catalytic process. They also showed the necessity of Cu⁰ sites for catalytic activity.⁵ Therefore, the active species of the working catalyst (200 °C Fur) is Cu¹⁺/Cu⁰; neither Cu¹⁺ nor Cu⁰ alone are sufficient for this ALD catalyst. Further increasing the reduction temperature decreased the Cu-O peak intensity and increased the intensity of the Cu-Cu peak (300 °C Fur/ 400 °C Fur). The ALD catalyst loses activity for furfural reduction at the same time: further evidence that the active catalyst has a combination of both Cu¹⁺ and Cu⁰, consistent with our previous work.⁶

Furthermore, based on the difference between the EXAFS spectra ('200 °C H₂' vs. '200 °C Fur'), it is clear that the addition of furfural to the ALD Cu-chromite-45c-700 after reduction results in the formation of some oxygenates on the Cu surface. Therefore, some oxygen containing components are generated during the reaction, even though the catalyst was fully reduced to Cu⁰ prior to reaction. Further increasing the reduction temperature reduces the concentration of Cu oxygenates (Fig. 5b) while simultaneously reducing the furfural reduction activity (Fig. 5a). The EXAFS spectrum '200 °C Fur' is similar to Cu¹⁺, while Cu²⁺ cannot exist

stably under such a reducing atmosphere (50% H₂ plus 2% furfural) at 200 °C. Therefore, we propose that both Cu¹⁺ (not Cu²⁺) and Cu⁰ are required for furfural hydrogenation in agreement with the previous work by Rao and co-workers.²⁵ Since thinner ALD overcoating layers increase the Cu¹⁺ concentration (Table 2), this may also explain why thinner ALD overcoating layers produce a higher furfural hydrogenation activity after stabilization (Figure 4a). In addition, a few cycles of alumina ALD coating block less active sites of ALD Cu-chromite-45c-700. The Cu¹⁺ sites discussed here can be Cu₂O or CuAlO₂.

4. Discussion

Hydrogenation is a fundamental reaction in biomass conversion.^{2b, c} Furfural possesses both C=C and C=O bonds, and is a special kind of α , β unsaturated compound, because the C=C stays within one 5 member ring and 6 electron stabilized system. This makes the C=C bond very stable. The adsorption mode of furfural also influences the selectivity of the furfural hydrogenation, and C=O is most likely adsorbed on the surface of Cu.²³ Therefore, the C=O bond can be reduced most easily on Cu nanoparticles. However, one problem is that the initial product from furfural hydrogenation, furfuryl alcohol, can be further dehydrated to form 2-methyl furan.²³ Consequently, a higher activity can result in a lower selectivity to furfuryl alcohol. ALD modification would seem to be a good way to block some of active sites on Cu-chromite to suppress the activity while increasing selectivity to furfuryl alcohol.

ALD is a variation on chemical vapor deposition in which metals, oxides, and other materials are deposited on surfaces by a sequence of self-limiting reactions. The self-limiting character of these reactions makes it possible to achieve uniform deposits on high-surface-area porous solids. Therefore, design and synthesis of advanced catalysts on the nanoscale becomes possible

through precise control over the structure and composition of the underlying support, the catalytic active sites, and the protective layer. Even if the catalytic nanoparticle surfaces are initially fully covered by the ALD thin films, these surfaces can become accessible to reagent gases through pores formed in the overcoat as a result of high-temperature treatment. In addition, the ALD overcoat can preferentially segregate onto step edges and surface defects. These mechanisms might be responsible for the enhancement of the stability of the ALD coated Cu-chromite catalysts in our study.

One might anticipate that the overcoating thickness would be critical to catalyst performance. If the coating is too thick, it might completely shut off the catalytic activity, but if it is too thin, then sintering and migration will not be inhibited. Here we found that fewer ALD layers (e.g. 10 cycles) showed higher furfural hydrogenation activity but lower catalyst stability. In contrast, the thicker ALD coatings (e.g. 45 cycles) exhibited lower activity but improved stability. This result differs from a previous study²⁸ of methanol decomposition on overcoated Pd nanoparticles. Their study showed that a single ALD Al_2O_3 cycle was sufficient to suppress sintering during methanol decomposition at 270 °C for 6 h. Dumesic⁷ and coworkers found that 45 cycles alumina ALD overcoating can eliminate the deactivation of Cu caused by sintering and leaching of the metal under trickle bed conditions.

Coke formation may be another cause of deactivation of Cu-chromite. A previous study⁶ showed coke formation on the surface of used Cu-chromite based on XPS measurements, while there is no coke on the surface of a fresh catalyst. Recently, Lu et.al.,⁸ found that the coke formation on Pd-NPs can be suppressed by 45 cycles alumina ALD overcoating. 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. CO chemisorption²⁸ was

further applied to study how the ALD overcoating influences the molecule adsorption. No clear shifts of CO adsorption were observed for different cycles of ALD Pd catalysts. Therefore, we believe that there should not be typical electronic effect between alumina ALD layers and the underlying nanoparticle. Notwithstanding, the reduction temperature of Cu was increased dramatically. This could be due to formation of copper aluminate and micropores inside the ALD layers after heat-treatment; that will influence the transport of gas to or from the surface of Cu. Changing the reduction temperature of Cu after ALD overcoating would change the composition of different copper species after reduction at 200 °C during the reaction. Perhaps this explains how ALD overcoating can lower the activation energy of furfural on Cu.

Rao²⁵ and coworkers found that the TOF of furfural hydrogenation over different Cu based catalysts decreased steadily as the fraction of surface Cu^{1+} sites decreased from 0.3 to zero (i.e., 100% Cu^0). Simple Langmuir–Hinshelwood models involving a bimolecular surface reaction as the rate-determining step described these data well and a two-site model, which could represent Cu^0 and Cu^{1+} sites, is shown to very satisfactorily fit the data for all the catalysts surveyed. They propose that both Cu^0 and Cu^{1+} are necessary species for the furfural reduction reaction. However, they did not identify the active species using any of characterization method. We use operando XAFS to study the active species of ALD Cu-chromite-45c-700 during furfural hydrogenation reaction. We found that Cu was first reduced nearly to Cu^0 after reducing at 200 °C. Then, furfural/ H_2 /He (v/v/v: 1/25/25) was introduced to the reactor. The Cu catalyst was partially oxidized to Cu^{1+} at the same time. The active species for this reaction indeed appears to be Cu^0 and Cu^{1+} . As the reduction temperature was increased, the activity of furfural reduction decreased commensurate with the lower concentration of Cu^{1+} , which is further evidence that Cu^{1+} and Cu^0 both required active species for furfural hydrogenation. Moreover, Cu^{1+} may

function as electrophilic or Lewis acid sites to polarize the C=O bond via the electron lone pair on oxygen²⁹, thus improving the reactivity of the carbonyl group in furfural. That is consistent with the behavior reported for crotonaldehyde hydrogenation on copper based catalysts.^{29b, 30} Dandekar et al.^{29b} have shown that significantly higher TOFs were observed on Cu dispersed on a nitric acid-treated activated carbon, and it is proposed that oxygen-containing acidic groups on the surface of this carbon enhance the activity by providing additional adsorption sites for crotonaldehyde that can react with hydrogen spilled over from Cu⁰ sites. Unusually low TOFs were exhibited by Cu deposited on the graphitized fibers by an ion exchange technique.^{29b} Fridman and Davydov have reported that the oxidation state of Cu can affect not only the dehydrogenation activity but also the selectivity, and in their study of cyclohexanol dehydrogenation over Cu-Mg and Cu-Zn-Al catalysts, they found that Cu¹⁺ was significantly more active than Cu⁰ for cyclohexanone formation, while Cu⁰ was active for the aromatization reaction of cyclohexanol to phenol.³¹

5. Conclusions

Highly stable furfural reduction reaction performance of CuCr₂O₄·CuO was achieved by applying ALD Al₂O₃ overcoatings, which appears to decrease coke formation, sintering of Cu and coverage of the active copper by chromite migration. Furthermore, the alumina ALD overcoating increases the reduction temperature of Cu nanoparticles and lowers the activation energy of the furfural hydrogenation process. Thinner ALD layers exhibit higher furfural reduction activity. Finally, based on the operando reaction studies, Cu¹⁺/ Cu⁰ are both necessary and active species for the furfural reduction reaction.

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(*Notes: Airgas USA, LLC North Central Region 1250 W. Washington Street, West Chicago, IL 60185.)

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Supporting Information:

Figure S1 (a) N₂ adsorption/desorption isotherms of Cu-chromite, ALD Cu-chromite-10c-700, ALD Cu-chromite-20c-700, ALD Cu-chromite-45c-700 and (b) their corresponding pore size distributions from desorption branch (equilibrium transition).

Figure S1(a) shows the adsorption and desorption isotherms of nitrogen at 77 K for Cu-chromite, ALD Cu-chromite-10c-700, ALD Cu-chromite-20c-700 and ALD Cu-chromite-45c-700 catalysts. From the shape of the isotherms, this is a typical type five isotherms. This type of isotherm is convex to P/P_0 axis at the low P/P_0 regin, then there is a pore condensation and hysteresis. There is no inflection point indicates the stage at which monolayer coverage is complete and multilayer adsorption begins to occur, indicates that the attractive adsorbate-adsorbent interactions are relatively weak. The hysteresis loop is associated with the occurrence of pore condensation. The hysteresis loop obtained for uncoated and ALD overcoated catalysts spreads over a P/P_0 range from 0.7 to 0.98, which may be due to the presence of a large pore volume and a small surface are. Aluminate ALD overcoating makes the Cu-chromite catalyst lose surface area from 34.5 m²/g(Cu-chromite) to 9.3m²/g (ALD Cu-chromite-45c-700) and also

lose the amount of N_2 adsorbed during BET characterization. Then the corresponding pore size distributions from desorption branch (equilibrium transition) were shown in figure S1(b). The pore diameters for uncoated and ALD overcoated catalysts ranges from 2nm to about 100nm. The most concentration of pore distributions located at 11nm. The distribution of pore diameters becomes smaller when alumina ALD applied, small pores with the diameter less than 3nm dismissed after 30cycles used. 10 cycles sample is a little different from the other samples on the pore diameter distributions. That may be because the thickness of ALD layers for ALD Cu-chromite-10c-700 is smaller than the other ones, and the pore distribution within the ALD layers was influenced by the thickness of the ALD layers.

Figure S2(a) Temperature-programmed reduction (H_2 -TPR) of ALD $Cu/\gamma-Al_2O_3-45c-700$ and $Cu/\gamma-Al_2O_3-700$; (b) XRD spectrum of $Cu/\gamma-Al_2O_3-700$. It is clear that the $Cu/\gamma-Al_2O_3-700$ contains big percentage of copper aluminate from $Cu/\gamma-Al_2O_3$ calcination at 700 °C for 5h.

Figure S3. Cu FT-XAFS spectra of *in situ* H₂-TPR on (a) Cu-chromite and (b) ALD Cu-chromite.

Figure S4. Percent of the different Cu species as a function of temperature during *in situ* XAFS/H₂-TPR from XANES data by linear combination fittings over different layers of ALD overcoatings, (a) ALD Cu-chromite-10c-700, (b) ALD Cu-chromite-20c-700 and (c) ALD Cu-chromite-30c-700; Cu foil (Aldrich, 99.999%), Cu₂O (Aldrich, 99.99%) and CuO (Aldrich, 99.999%) were used as the standards to generate these results.

Table S1. Reaction performance of Cu-chromite, ALD Cu-chromite-10c-700, ALD Cu-chromite-20c-700, ALD Cu-chromite-30c-700 and ALD Cu-chromite-45c-700.

	Conversion (%)	FA Selec. (%)	2-MF (%)	Reaction Rate (mMol/g _{Cu-surf} *S)
Cu-chromite	20.3	100	0	1.21
ALD Cu-chromite-10c-700	27.6	95.8	4.2	0.72
ALD Cu-chromite-20c-700	12.2	97.5	2.5	0.36
ALD Cu-chromite-30c-700	9.7	98.6	1.4	0.33
ALD Cu-chromite-45c-700	9.3	100	0	0.37

* Note: FA represents furfuryl alcohol and 2-MF represents 2-methyl furan, Cu-surf means copper on the surface. The conversion and selectivities were collected when the catalysts were stabilized.