Enhancing the Stability of Copper Chromite Catalysts for the Selective Hydrogenation of Furfural with ALD Overcoating (II) - Comparison Between TiO_2 and Al_2O_3 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.

Key Words: Selective hydrogenation, 2-Furfuraldehyde, Furfuryl alcohol, Stability, Copper chromite, TPR, XAFS, ALD, *in-situ* experiment

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 next the 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

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-workers⁷ 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 coworkers⁵ 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, Lu⁷ et. al. 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. Huber¹² and coworkers 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 activity. 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 TiO_2 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

Materials

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

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. The sample holder was then loaded into the reactor and allowed to equilibrate for at least 30 minutes 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 include: TTIP dose (90s) - purge (150s) - H₂O dose (90s) - purge (150s). 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, e.g., 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 (named as 20c TiO₂ for short). Forty five cycles alumina ALD

overcoated Cu-chromite catalyst followed by calcination at 700 °C was named as 45c Al₂O₃.

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 clam-shell 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 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 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, 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.

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 50-100 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.

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 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 minutes at 10ID or about 3 minutes 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 clam-shell furnace, described by Neylon et al. 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 surface. The samples in the cell were then heated up to 700 °C with a ramp rate of 2 °C/min under a 60 sccm flow of H₂ (3.5%) in He. A scan of each sample was recorded every 5 min during the TPR process with 70-80 spectra per sample collected during each run. Every second spectrum is plotted here.

Before starting the isothermal oxidation process (at 10BM), all the samples were pre-reduced at 400 °C for 60 min. The samples in the cell were then cooled down to 150 °C and held

at this temperature for 8 h under a 10 sccm flow of O₂ (20%) in He. A spectrum of each sample was recorded every ~17 min during the TPO process with 29 spectra per sample collected during the entire run.

In-situ XAFS measurements (at 10BM) were performed under furfural hydrogenation reaction conditions. Copper chromite was diluted with silica gel (Davisil 644, Sigma–Aldrich) with mass ratio of 1:5.6. The diluted sample was pressed into a cylindrical holder, with a thickness chosen to give a total absorption of approximately 2.0 (μ x), which resulted in a copper K-edge step ($\Delta\mu$ x) of ca 0.5. The same quartz tube reactor and furnace were used to measure these spectra. Diluted copper chromite catalyst was reduced in 3.5% H₂/He (100 ml/min) at 200 °C for 1 h. The sample at this point in the experiment is referred to as the fresh catalyst. About 0.33% of furfural was then flowed into the reactor by passing 3.5% H₂/He through a bubbler containing pure furfural at room temperature. A four-port two-position actuator (VICI Instrument) was used to switch the gas flow to ensure that the fresh catalysts remained in the reduced state without exposure to residual air in the tubing. The hydrogenation reaction remained at 200 °C for 4 h before shut down. XAFS spectra were collected continuously (about every 17 min) throughout both the reduction and reaction processes. Different reduction temperatures were applied here, such as 300 °C and 400 °C, but all the reactions were carried out at 200 °C.

Temperature programmed reduction (TPR)

Hydrogen TPR was performed on an Altamira AM-200 unit equipped with a thermal conductivity detector (TCD). The outlet gases were analyzed by a Stanford Research System Residual Gas Analyzer (RGA, mass spectrometer). Approximately, 80-100 mg of sample were loaded into a 3.2 mm 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 1 h to eliminate water, and then cooled to room temperature. Each catalyst was then heated to 700 °C (ramp rate of 2 °C / min) under (3.5%) H₂/Ar at a flow rate of 50 sccm.

3. Results & Discussions

Figure 1 (a) TCD signal trace the H₂-TPR study of Cu-chromite, 20c TiO₂ and 40c TiO₂ in 4% H₂/Ar at 2°C/min; (b) XANES spectra of standard samples Cu²⁺ (CuO powder), Cu¹⁺ (Cu₂O powder) and Cu⁰ (metal foil); stacked normalized Cu K-edge XANES spectra of (c) Cu-chromite and (d) 40c TiO₂ collected during the *in-situ* H₂-TPR experiment.

Figure 1a shows the H₂-TPR profile for the Cu-chromite, 20c TiO₂ and 40c TiO₂ in 3.5% H₂/Ar at 2°C/min. Both the uncoated Cu-chromite and TiO₂ ALD overcoated catalysts are fully

reduced to Cu^0 below 300 °C, much lower than the Cu catalyst modified by 45 cycles of alumina ALD layers.⁶ For comparison, after alumina ALD overcoating, the TPR reduction profile of Cu (45c Al_2O_3) is very broad. This was thought to be influenced by copper aluminate formation.⁶ For TiO_2 ALD overcoating, copper titanate is not formed, therefore the reduction profiles are similar to the uncoated catalyst.

XAFS measurements at the Cu K-edge were collected on three reference samples as shown in Figure 1b: CuO (Cu^{2+}), cuprous oxide (Cu_2O) (Cu^{1+}) and Cu foil (Cu^0). Cu^{1+} shows the largest and most distinct pre-edge feature, with a peak near 8982.5 eV. The Cu^{2+} spectrum has two pre-edge peaks; first, a very small peak near 8979 eV and second, a peak at about 8987 eV. Metallic copper has the lowest energy inflection point at 8980.48 eV, but with a broader peak with a maximum at just slightly lower energy than Cu^{1+} . The differences between these references spectra imply that the primary 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.¹⁶⁻¹⁷

Figures 1c and 1d show normalized stacked plots of the Cu K-edge XANES of (c) Cu-chromite and (d) 40c TiO_2 collected during an *in-situ* XAFS/ H_2 -TPR experiment. The XANES features for the 40c TiO_2 are similar to the uncoated Cu-chromite. When compared with the spectra in figure 1b, it indicates that initially the material is primarily Cu^{2+} ; the very small pre-edge peak derived from the 1s to 3d transition is observed at about 8979 eV: the fingerprint feature of Cu^{2+} .¹⁶⁻¹⁷ Therefore the chemical state of Cu-chromite and 40c TiO_2 catalysts prior to reduction are primarily Cu^{2+} . Based on the reduction profiles these catalysts are considered to have similar redox properties, although the reduction temperature of 40c TiO_2 is slightly higher than the uncoated Cu-chromite. This difference could be due to electronic modification of the

copper by the TiO_2 layers or influences on the diffusion of H_2 or H_2O by the micropore structure within the TiO_2 layers. We can clearly see the influence of the ALD layers restricting diffusion within the alumina ALD layer when comparing the reduction temperatures between the sample calcined at 300 °C (sample named as 45c Al_2O_3 -300, the calcination at 300 °C or 700 °C is to generate pores or cracks within the ALD layers⁶) and bare catalyst (Cu-chromite) in Figure S1. In Figure S1, the calcination temperature was done at 300 °C rather than 700 °C to make sure no copper aluminate was formed. Because 300 °C is far lower than the formation temperature of copper aluminate by calcination of a mixture of copper and alumina, the only influence over the reduction profile should come from the pore structure within alumina ALD layers and the influence of the overlayer on diffusion. Only a 150 °C increase of the reduction temperature was identified by comparing the reduction temperature between Cu-chromite and 45c Al_2O_3 -300. A similar influence on the diffusion of molecules to or from the copper surface would be expected for TiO_2 -overcoated catalysts.

Based on the ex-situ XRD study by Kalaivani et. al.,¹⁹ the formation of homogeneous single phase calcium copper titanate (CCTO) starts at 800 °C, while the initial formation temperature for the CCTO phase is 650 °C; 650 °C is significantly higher than our calcination temperature at 500 °C for TiO_2 ALD overcoated catalysts. By keeping the calcination temperature below that necessary for CCTO formation, the interphase is not formed, weakening the interaction between the Cu and TiO_2 layers compared to Al_2O_3 .⁶

Figure 2. Cu speciation from XANES spectra as a function of temperature during *in-situ* H₂-TPR .

XANES spectra were fit to a linear combination of the standard spectra (LC-XANES fit). A LC-XANES fit of the *in-situ* XAFS/H₂-TPR spectra (Figure 1c-d) reveals the evolution of the two components, Cu²⁺ and Cu⁰, as a function of temperature (Figure 2). Copper titanate is not formed in the TiO₂ overcoated samples contrary to copper aluminate formation in the Al₂O₃ overcoated Cu-chromite. This might be one reason why the TiO₂ overcoated catalysts and bare Cu-chromite exhibit nearly identical TPR behaviors. No Cu¹⁺ species was observed, similar to the alumina ALD overcoated Cu catalyst, suggesting that the reduction of Cu¹⁺ to Cu⁰ is significantly faster than the reduction of Cu²⁺ to Cu¹⁺.¹⁶⁻¹⁷ This reduction profile is in good agreement with previous work by Rodriguez et. al.^{17, 20} Although the temperature for the 50% reduction was ~25°C higher for the 40c TiO₂ ALD overcoated catalyst compared with the uncoated Cu-chromite, the temperature for complete reduction was nearly the same for both catalysts. The alumina ALD overcoated catalyst shows a much higher reduction temperature than either the uncoated or the TiO₂ ALD overcoated catalyst, further evidence that the modification effect of TiO₂ ALD overcoating on Cu reduction is different from alumina ALD overcoating.

Additional results from the *in situ* TPR/XAFS characterization is given in Table S1 in the supporting information.

Figure 3. (a) Conversion vs. time on stream for the selective hydrogenation of furfural and (b) activities and composition of the product stream at 500 minutes. WHSV was set to 6.9 h⁻¹.

Figure 3 shows (a) selective hydrogenation conversion of furfural over five catalysts; copper chromite, 20c TiO₂, 30c TiO₂, 40c TiO₂ and 45c Al₂O₃ as a function of time on stream; and (b) product selectivity in furfural hydrogenation (same samples) after 500 min on stream. It is clear that Cu-chromite catalyst is unstable under these reaction conditions, losing 80% of its initial activity in the 12 h run. Based on our previous work, this deactivation is due to the migration of chromite, blocking the active sites of copper as well as coke formation.⁴ Figure 3a shows that the stability of all the TiO₂ ALD overcoated catalysts is much higher than the uncoated catalysts.

The 20c TiO₂ catalyst exhibits only about a 15% loss in activity (from its maximum) after 10 h on stream. In addition, the activity remaining after the 12-h run (about 75% of the initial Cu-chromite activity) is much higher than the activity of Cu-chromite after a 10-h run (<20% of

initial activity). Therefore, a thin TiO_2 ALD overlayer dramatically increases the stability of the Cu nanoparticles. More importantly, high initial activity is preserved in the TiO_2 case in comparison to the Al_2O_3 ALD overcoated catalyst or uncoated catalyst. The 10 cycles alumina ALD catalyst (not shown) retains only 30% of Cu-chromite's initial activity under the same reaction conditions,⁶ while the 45c Al_2O_3 has only about 10% activity. More comparisons with alumina ALD can be found in Figure S2 in the supporting information.

For all the catalysts shown, furfuryl alcohol is the primary product (see Figure 3b). This is probably due to the adsorption mode of furfural on the copper surface. Previous work has shown that only the oxygen atom from carbonyl group of furfural adsorbs on the surface of copper precluding any decarbonylation activity over copper catalysts.²¹ In addition, since the copper catalyst is not as active as noble metal catalysts for ring hydrogenation,⁸ the selectivity to 2-methylfuran byproduct is always very low.^{21a, b}

Table 1. Cu loadings, weight gain, BET surface area and ALD coverages for Cu-chromite samples both before and after TiO₂ or Al₂O₃ ALD overcoating; also, turn over frequencies (TOF) at the beginning and at 500 min for furfural hydrogenation reaction.

Cat.	Cu-Loadings (wt%)	Weight gain (wt%)	BET (m²/g)	ALD coverage (%)	TOF (S⁻¹) 0min	TOF (S⁻¹) 500min
Cu-chromite	38.0	0	32.7	0	0.3	0.1
20c TiO ₂	35.7	6.0	21.0	57.0	0.9	0.9
30c TiO ₂	32.7	14.0	17.9	63.0	----	0.5
40c TiO ₂	31.5	17.0	34.9	89.0	0.7	0.3
45c Al ₂ O ₃	22.0	42.0	9.3	----	----	----

Table 1 shows the chemical and physical characteristics of both the TiO₂ ALD and Al₂O₃ ALD overcoated catalysts. From Table 1, it is clear that ALD overcoating decreases the apparent Cu loading from 38% to about 32% for TiO₂ ALD catalysts, while the Cu loading for 45c Al₂O₃ is only 22% due to the weight gain by ALD. The weight gain increases systematically along with increasing the number of cycles on TiO₂ ALD overcoatings from 6% for 20 cycles to 17% for 40 cycles of TiO₂ ALD. The much higher 42% weight gain for 45c Al₂O₃ is due to the alumina ALD overcoat being much denser on the Cu-chromite surface than the TiO₂ ALD, in good agreement with previous results in the literature.²²

At the same time the BET surface areas of the ALD catalysts are smaller than original Cu-chromite catalyst. As the number of cycles of TiO₂ ALD increase, we observe a decrease in the surface area of the material. Further increasing the ALD cycles (such as 40 cycles of TiO₂ ALD) increases the surface area, which may be due to new 3D structures in the TiO₂ ALD layers. Thus, for comparable loadings, alumina ALD yields smaller surface areas compared to TiO₂

ALD. It is already known that the TiO_2 ALD shows about half thickness of Al_2O_3 ALD when a similar number of ALD cycles are deposited.²²

We can use CO chemisorption at low temperature (-36°C) to estimate the percentage of surface Cu not covered by the ALD layers. Based on previous study since there is little agglomeration of Cu either before or after ALD overcoating,⁶ we propose that the dispersions of Cu for different catalysts shown here are similar. We found that the fraction of Cu coverage following ALD for 20c TiO_2 is about 57%, while 40c TiO_2 is about 89%. (i.e. Cu coverage by TiO_2 increased for increasing number of TiO_2 ALD cycles).

TOFs at 0 min and 500 min are both shown here for some of the catalysts. The 20c TiO_2 catalyst is more active than the uncoated catalyst based on TOFs at both the beginning of this reaction and after 500 min on stream. Therefore the TiO_2 ALD overcoating not only changes the number of active sites on the surface of Cu, but also modifies the electronic environment around copper surface. By comparing the TOFs between the uncoated catalyst and the TiO_2 overcoated catalysts, an electronic effect can be identified from TiO_2 overcoating samples. Except for 20c TiO_2 the TOFs at 0 min are higher than the TOFs at 500 min for each sample. For 20c TiO_2 , the peak TOF (based on Fig. 3a) occurs around 50 min TOS, indicating some deactivation during the reaction for all overcoated catalysts. The kinetics study in Figure 3a shows that increasing the ALD TiO_2 layer thickness beyond a certain point will decrease the TOF. The overcoating likely selectively covers the more active sites (step, edge or corner sites of Cu) first, leaving the less active sites (terrace sites), thus lowering the TOF compared to thinner layers in good agreement with our previous findings on the furfural hydrogenation reaction with ALD overcoated Pd catalysts.⁸

Figure 4. (a) N₂ adsorption/desorption isotherms and (b) their corresponding pore size distributions from desorption branch (equilibrium transition).

Figure 4a shows the nitrogen adsorption and desorption isotherms at 77 K for Cu-chromite, 40c TiO₂ and 45c Al₂O₃. This is a typical type five isotherm,²³ convex to P/P₀ axis at the low P/P₀ region resulting in pore condensation and hysteresis. The lack of an inflection point indicates when monolayer coverage is complete and multilayer adsorption begins to occur and 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 is over a P/P₀ range from 0.5 to 0.98 indicating the presence of a large pore volume and a relatively small surface area. The alumina ALD overcoating the Cu-chromite catalyst results in a surface area loss from 32.9 m²/g (Cu-chromite) to 9.3 m²/g (45c Al₂O₃). The 40c TiO₂ shows a surface area similar to the uncoated Cu-chromite implying that the TiO₂ ALD overcoating does not cover the surface as uniformly as Al₂O₃. The surface area for 40c TiO₂ is about 34.9 m²/g. The corresponding pore size distributions from desorption branch (equilibrium transition) are shown in Figure 4b. The pore diameters for uncoated and ALD overcoated catalysts range from about 2 to 100 nm. The peaks of the pore

volume distributions are between 10 nm and 20 nm. As we previously found, the pore size distribution becomes narrower after the alumina was applied,⁶ with small pores having a diameter of less than 3 nm lost after 45 cycles alumina ALD. On the other hand, the pore size distribution for 40c TiO₂ is similar to Cu-chromite before ALD overcoating with the only changes being the loss of some small pores consistent with a thinner layer of TiO₂ on the surface of Cu-chromite catalyst compared to the alumina coating for a similar number of cycles. This is in good agreement with the changes of the Cu loadings, which shows that the weight gain for TiO₂ ALD is much smaller than alumina ALD with similar ALD cycles. While both of these ALD processes increase the stability for furfural hydrogenation, the alumina overcoat covers and deactivates the surface Cu and results in a dramatic loss in activity.

Figure 5. Fourier transform magnitude of the Cu K-edge EXAFS spectra of (a) Cu-chromite, (b) 45c Al₂O₃, (c) 20c TiO₂ and (d) 40c TiO₂ calcined in air at 150 °C for 8h after reduction at 400 °C for 60 min. The interval between each nearest spectra is 17 min. (k -range from 2.0 Å⁻¹ to 12.8 Å⁻¹, $k\chi(k)$ EXAFS function). Note that the initial spectra are not at $t=0$ min and some reoxidation has occurred before the first measurement.

In situ XAFS during catalyst reoxidation

Figure 5 shows the evolution of the Cu K-edge EXAFS spectra during calcination in air at 150 °C for 8 h. Before calcination, the catalysts were pre-reduced at 400 °C for 60 min. It is

clear that the oxidation states of all the samples are a mixture of Cu and CuOx species. At the start, the predominant peak in the Fourier Transform (FT) is the Cu-Cu path: i.e., the nearest neighbor for Cu⁰ nanoparticles and indicated by the downward pointing arrow. As oxidation proceeds copper is slowly oxidized and magnitude of the Cu-O path (from Cu¹⁺ or Cu²⁺) increases, indicated by the upward pointing arrow. Over 8 h, large oxidation state changes are observed for all four catalysts. The corresponding XANES spectra are shown in Figure S3. The 45c Al₂O₃ coated material shows the least oxidation, implying that the redox properties of Cu-chromite were changed by alumina ALD similar to the previously reported results for a H₂-TPR experiment on alumina ALD overcoated catalysts.⁶ As stated above this oxidation resistance is most likely due to the formation of copper aluminate after alumina ALD overcoatings.

The oxidation profiles of the 20c TiO₂ and 40c TiO₂ are similar to Cu-chromite before ALD overcoating indicating that TiO₂ has a much smaller influence on the redox properties of Cu-chromite than alumina ALD overcoating as expected from the H₂-TPR experiments. Since the influence from TiO₂ ALD layer is smaller than alumina ALD and the processing conditions were fairly mild, we propose that no copper titanate is formed during TiO₂ ALD overcoating or the subsequent sample treatment.

It proved to be very useful to rigorously fit each XANES spectrum to a linear combination of the three assumed Cu reference spectra to try to determine in greater detail the constituent copper-containing phases. Figure 6 gives the percentage of the different Cu species as a function of time during *in-situ* oxidation from XANES spectra (shown in Fig. S3). Cu⁰, Cu¹⁺ and Cu²⁺ are present for all samples in different proportions. The species fractions observed in Cu-chromite after reduction at 400 °C are ~40% Cu⁰, ~50% Cu¹⁺ and ~10% Cu²⁺ changing to ~15% Cu⁰, ~60% Cu¹⁺ and ~25% Cu²⁺ after 8 h oxidation at 150 °C. However, since the first

spectrum for each of the sample was not collected at precisely the same time or, due to the measurement time, at $t=0$ min, it is not possible to compare the oxidation state of all the samples at the beginning of the TPO run. It is quite likely that the speciation immediately after reduction consisted of a much larger fraction of Cu^0 consistent with the observations in Fig. 2. The oxidation process is fairly slow at 150 °C under 20% O_2/He and, notably, Cu^{1+} is the dominant copper species. Recall that Cu^{1+} was not observed during reduction. All of these observations are also in good agreement with previous work by Rodriguez^{17, 20}

Figure S4 reduces the multiple species data shown in Fig. 6 to an average Cu oxidation state. The average Cu oxidation state for 40c TiO_2 is slightly lower than 20c TiO_2 , which may be due to higher TiO_2 coverage for 40c TiO_2 ; or, it may also be because of the influences on the diffusion of H_2 or water within TiO_2 layers, as seen from alumina ALD shown in supporting information (Figure S1). One example of the LC-XANES fit for copper K-edge XANES spectrum of Cu-chromite (from Figure S3 (a) _#14) under oxidation conditions is shown in Figure S5.

Figure 6. Fraction of Cu species as a function of time during *in-situ* oxidation at 150°C from Cu XANES for (a) Cu-chromite, (b) 45c Al₂O₃, (c) 20c TiO₂ and (d) 40c TiO₂

The oxidation profile for 45c Al₂O₃ is significantly different than the other three samples. The oxidation of 45c Al₂O₃ evolves from ~60% Cu⁰, ~30% Cu¹⁺ and ~10% Cu²⁺ to ~40% Cu⁰, ~45% Cu¹⁺ and ~15% Cu²⁺. Compared to the oxidation of uncoated Cu-chromite, 45c Al₂O₃ cannot be oxidized to nearly as high oxidation state as uncoated Cu-chromite, since the fraction of Cu⁰ remaining at 8 h is about 40%, compared to just 15%. In addition, the amount of Cu¹⁺ (45%) in 45c Al₂O₃ after calcination is also smaller than the other samples. This is consistent with copper aluminate phase formation during the heat-treatment process following deposition: a

consequence of the higher temperatures (700 °C) used to try to generate cracks and pores within ALD layers.

Comparing the point where the Cu^{2+} and Cu^0 traces are equal for Cu-chromite catalyst, 20c TiO_2 , and 40c TiO_2 , we can see that the crossover time for 20c TiO_2 occurs at nearly the same time as the uncoated Cu-chromite (~260 min) while the crossover time for 40c TiO_2 is greater than 400 min. That means 40c TiO_2 , in fact, has some influence on the rate of Cu oxidation, while 20c TiO_2 has virtually no effect. The slower oxidation may come from either the diffusion barrier created by thick or dense overlayers or from the electronic effect from TiO_2 layers attached to the copper nanoparticles.

Figure 7. *In situ* Cu K-edge spectra during furfural hydrogenation: (a) XANES and (b) Fourier transform modulus. (k -range from $2.0 \text{ \AA}^{-1}$ to $12.8 \text{ \AA}^{-1}$, $k\chi(k)$ EXAFS function).

In situ XAFS of the furfural hydrogenation reaction

Huber¹² and coworkers also found that the alumina ALD overcoating has a stronger influence over cobalt catalysts than TiO₂ ALD. They used *ex-situ* TPR and aqueous phase hydrogenation (APH) of furfuryl alcohol to elucidate the strong interaction between the cobalt nanoparticles and alumina and explain why the alumina ALD overcoated Co catalyst is so difficult to reduce and shows little activity for the reduction of furfuryl alcohol. The TiO₂ overcoated Co catalyst, in contrast, is easily reduced and very active in the APH experiment.

In-situ XAFS measurements were performed under furfural hydrogenation reaction conditions. The diluted copper catalyst was first reduced in 3.5% H₂/He at 200 °C. Then about 0.33% furfural was introduced into the reactor by passing 3.5% H₂/He through a bubbler containing pure furfural at room temperature. The hydrogenation reaction was carried out at 200 °C. The XAFS spectra after furfural injection were collected continuously every 15 min. Figure 7 shows the Cu K-edge XANES spectra and EXAFS Fourier transform modulus. The catalysts exhibit slightly different copper oxidation states, but in essence, all spectra are similar to Cu⁰ standard features shown in Figure 1b. Results of the LC-XANES fit are shown in Table 2. From the features of the *in-situ* Cu K-edge XANES, 45c Al₂O₃ is more oxidized than Cu-chromite, while there is an additional pre-edge feature for TiO₂ overcoated copper catalysts. Quantitative analysis of the pre-edge features is complex. However, it is generally understood that for 3d transition metals (i.e. copper) these features come from the 1s to 3d/4p transitions after absorption of the X-ray photon. The transition from 1s to 3d is dipole-forbidden by the symmetry around the central atom, but it is sometimes possible because of locally non-centrosymmetric structure.²⁴ This may happen when the local structure of the central atom has changed or a new oxidation state is formed by oxidation or reduction. The new pre-edge features shown

here on TiO₂ overcoated catalysts may be due to an intimate interaction between TiO₂ and Cu nanoparticles. TiO₂ is a reducible oxide, and can lose oxygen from its crystal structure under reducing conditions.^{24b} We therefore propose that the new pre-edge feature on TiO₂ overcoated Cu catalysts is due to the formation of CuO_x species after calcination (creating pores within the ALD layers at 500 °C). This hypothesis can be further tested by changing the experiment conditions. For example, this pre-edge feature disappears when the sample is reduced at higher temperatures (Figure S6 and Figure S7). Therefore, the primary difference between Al₂O₃ and TiO₂ overcoatings is the different copper species formed at the interface between ALD layers and the copper nanoparticles. At the interface between Al₂O₃ ALD layers and Cu nanoparticles, there is a thin layer of copper aluminate, while for TiO₂ ALD overcoatings, there may be a thin layer of copper oxide: probably Cu²⁺. The CuO_x species is easily reduced while copper aluminate is far more difficult to reduce. Therefore the reduction/oxidation profiles are very different between TiO₂ overcoated copper catalyst and Al₂O₃ overcoated ones; the activities for furfural hydrogenation are influenced accordingly.

It is important to point out that XAFS characterization is a bulk technique. Therefore, all Cu atoms are measured by XAFS including those atoms not at the surface. The subsurface Cu atoms are considered to be less important during the catalytic reaction. Certainly a large fraction of the Cu is not directly involved in the catalytic reaction. Therefore, the real difference between an uncoated catalyst and an ALD overcoated catalyst may be larger than what was observed, if we were able to isolate just the active Cu sites. The differences observed, nevertheless, indicate ALD overcoating can be a powerful technique to alter the working catalysts. The Cu K-edge EXAFS spectra of Cu-chromite, 20c TiO₂, 40c TiO₂ and 45c Al₂O₃ catalysts show results similar to the Cu-XANES (Figure 7b). All copper catalysts shown here are similar to Cu⁰ standard

spectrum in the supporting information (Figure S8). A small fraction of Cu-O bonding is observed at about 1.90-1.96 Å corresponding to the Cu-O bond lengths in CuO and Cu₂O.¹⁶ The TiO₂ overcoated catalysts exhibit a slightly higher Cu-O scattering strength (in the EXAFS Fourier transform magnitude) than the uncoated and alumina overcoated catalysts. Simple EXAFS calculation results are given in the supporting information (Table S2). The TiO₂ ALD overcoated catalysts are more oxidized compared to Cu-chromite and 45c Al₂O₃, which may be because of small electronic effect between TiO₂ ALD layers and Cu nanoparticles. Since the TiO₂ ALD layer is at least partially reducible it may lose its oxygen to the Cu at the interface. These results are in good agreement with those from *in-situ* H₂-TPR experiments. From the nearest neighbor coordination fit from EXAFS, it is clear that TiO₂ ALD overcoatings show a similar effect as Al₂O₃ for reducing agglomeration of the copper in the Cu-chromite catalyst during the reaction.

In the *in situ* furfural hydrogenation experiment the Cu oxidation state in TiO₂ overcoated catalysts is higher than either uncoated or the alumina ALD overcoated catalyst based on the Cu-O path amplitude in EXAFS spectra, in good agreement with the corresponding XANES results. However, due to the similarity of the Cu-O bond distance between Cu¹⁺ and Cu²⁺ standard materials, it is not possible to resolve the contributions to the nearest-neighbor Cu-O shell from Cu¹⁺ and Cu²⁺. The same linear combination fitting was performed for these XANES spectra as for the *in situ* oxidation experiment. The results, shown in Table 2, indicate predominantly Cu⁰, as expected. However, there is evidence of Cu¹⁺ along with a smaller contribution from Cu²⁺. The TiO₂ overcoated copper catalysts are clearly more oxidized than the uncoated and Al₂O₃ overcoated catalysts, while 40c TiO₂ shows a slightly higher Cu¹⁺ fraction than 20c TiO₂, probably due to the higher coverage of TiO₂.

Table 2. LC-XANES fit for the in-situ furfural hydrogenation experiment (0.33% furfural, T=200 °C, pre-reduced in 3.5% H₂/He (100 ml/min) at 200°C for 1 h.)

Cat.	Cu ⁰ (%)	Cu ¹⁺ (%)	Cu ²⁺ (%)
Cu-chromite	90.0	4.8	5.2
20c TiO₂	82.3	10.2	7.5
40c TiO₂	79.5	13.1	7.5
45c Al₂O₃	81.9	13.9	4.3

Speciation during Cu reduction and oxidation

We found no Cu¹⁺ during reduction, while a significant contribution from Cu¹⁺ is observed during oxidation. Several groups^{17, 20} have worked in this area and proposed that over hydrogen, CuO reduces directly to metallic Cu without forming an intermediate or suboxide (i.e., no Cu₄O₃ or Cu₂O). The apparent activation energy for the reduction of CuO is about 14.5 kcal/mol, while the value is 27.4 kcal/mol for Cu₂O; reducing CuO is easier than reducing Cu₂O. During CuO reduction, the system can reach metastable states (MS) and react with hydrogen instead of forming Cu₂O. To facilitate the generation of Cu¹⁺ in a catalytic process one can limit the supply of H₂ or mix with oxidizing agents (O₂, H₂O). CO shows the similar reduction trend. Cu¹⁺ species can be identified during reduction when the Cu ion is confined inside the channel of molecule sieve; this may limit diffusion similar to lowering the supply of H₂/CO.¹⁶ During oxidation of Cu⁰, Cu¹⁺ is a very stable transition state from Cu⁰ to Cu²⁺.^{17b} Another example on the existence of Cu¹⁺ during the reduction is when copper ions are inset into the skeleton of molecule sieve, like ZSM-5,¹⁶ diffusion within the molecular sieve is so strong that Cu¹⁺ ions can show up during the reduction. For our system, we see no formation of Cu¹⁺ during the TPR experiment, meaning there are no obvious diffusional limitations within the channels of ALD layers. Using TiO₂ ALD, the rate of oxidation or reduction was influenced only slightly, which

implies the pore size distribution within the ALD layers is not small enough to influence noticeably the diffusion of molecules to/from the surface of the active Cu particles.

Active species for furfural hydrogenation using copper catalyst

In the literature, researchers²⁵ have consistently proposed that Cu^{1+} and Cu^0 are both necessary for hydrogenation reactions with copper. CO and N_2O adsorption^{25a} were used to prove the existence of Cu^0 and Cu^{1+} after reduction. However, they did not see the active species during the reaction. From the current study, Cu^0 , Cu^{1+} and Cu^{2+} are all observed during furfural hydrogenation reaction with Cu^{1+} and Cu^0 being the most possible active species. Rao^{25a} 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 proposed that both Cu^0 and Cu^{1+} are necessary species for the furfural reduction reaction. Our previous operando experiment⁶ shows that the activity for furfural hydrogenation will decrease with a decreasing concentration of copper oxide species when the reduction temperature is increased. Dandekar et al.^{25b} showed that significantly higher TOFs were observed on Cu dispersed on a nitric acid-treated activated carbon and proposed that oxygen-containing acidic groups on the surface of the carbon enhance the activity by providing additional adsorption sites for crotonaldehyde that can react with hydrogen spilled over from Cu^0 sites. Unusually low TOFs were exhibited by Cu deposited on the graphitized fibers by an ion exchange technique.^{25b} However, more work would be needed to prove that Cu^{2+} is not active for this reaction.

4. Conclusions

TiO₂ ALD overcoating was applied to increase the stability of a Cu-chromite catalyst for the hydrogenation of furfural. TiO₂ shows less modification effect over Cu compared to the alumina from *in-situ* TPR/TPO experiments. This is likely due to the lack of a TiO₂ analog for Cu-aluminate after calcination at 500 °C. Nevertheless, small spectroscopic differences can be seen following TiO₂ ALD on reduction temperatures and oxidation rate of copper. Furthermore, TiO₂ ALD increases the stability of Cu-chromite catalyst for the furfural hydrogenation reaction and the catalyst remains active: a substantial improvement over alumina ALD. About 75% percent activity was preserved when 20 cycles of TiO₂ ALD were deposited. Cu¹⁺ is not a stable intermediate during reduction while it is much more stable during oxidation. Cu¹⁺/Cu⁰ should be the active species for furfural hydrogenation over copper nanoparticles based on XANES and a linear combination fit. A subtle electronic interaction was observed between the TiO₂ ALD layers and the Cu nanoparticles. ALD technique shows excellent modification effect against the heterogeneous catalysis.

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Graphical abstract