

## Article

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# The Role of the Cu-ZrO<sub>2</sub> interfacial sites for Ethanol Conversion to

## Ethyl Acetate and Methanol Synthesis from CO<sub>2</sub> and H<sub>2</sub>

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## Abstract

Well-defined Cu catalysts containing different amounts of zirconia were synthesized by controlled surface reactions (CSR) and atomic layer deposition methods and studied for the selective ethanol conversion to ethyl acetate and for methanol synthesis. Selective deposition of ZrO<sub>2</sub> on under-coordinated Cu sites or near Cu nanoparticles via the CSR method was evidenced by UV-Vis absorption spectroscopy, scanning transmission electron microscopy, and inductively coupled plasma-absorption emission spectroscopy. The concentrations of Cu and Cu-ZrO<sub>2</sub>

interfacial sites were quantified using a combination of sub-ambient CO Fourier transform infrared spectroscopy and reactive N<sub>2</sub>O chemisorption measurements. The oxidation states of the Cu and ZrO<sub>2</sub> species for these catalysts were determined using X-ray absorption near edge structure measurements, showing that these species were present primarily as Cu<sup>0</sup> and Zr<sup>4+</sup>, respectively. It was found that the formation of Cu-ZrO<sub>2</sub> interfacial sites increased the turnover frequency by an order of magnitude in both ethanol conversion to ethyl acetate and methanol synthesis from CO<sub>2</sub> and H<sub>2</sub>.

## 1. Introduction

Copper-based catalysts are used in a wide variety of reactions, such as methanol synthesis, methanol steam reforming, water gas shift (WGS), and ethanol conversion. The conversion of ethanol to ethyl acetate consists of a two-step process in which ethanol is first dehydrogenated to acetaldehyde, which then undergoes coupling to form ethyl acetate. Previous studies have investigated this reaction over copper-based catalysts on different supports and shown that the type of support used influences product selectivity.<sup>1</sup> For example, the rate of formation of ethyl acetate over Cu/ZrO<sub>2</sub> and Cu/ZnO is an order of magnitude faster than over Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/SiO<sub>2</sub> catalysts.<sup>1a, b</sup> This enhanced reactivity for production of ethyl acetate over Cu/ZrO<sub>2</sub> was attributed to the higher rate of coupling occurring on the ZrO<sub>2</sub> support in Cu/ZrO<sub>2</sub> compared to Cu sites in Cu/SiO<sub>2</sub>.<sup>1b</sup> In contrast, the presence of Cu<sup>0</sup>-ZrO<sub>2</sub> interfacial sites was proposed to be responsible for the higher rate of ethyl acetate formation over Cu/ZrO<sub>2</sub> compared to Cu/SiO<sub>2</sub> by other studies.<sup>1c, d</sup> The same reaction was also studied over Cu-Zn-Zr-Al-O catalysts, and it was found that the coupling of ethanol and acetaldehyde occurs over mixed metal-oxide sites.<sup>2</sup> In

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spite of a large volume of work, the nature of the active sites involved in selective ethanol conversion to ethyl acetate reaction over supported copper catalysts remains elusive.

Compared to ethanol conversion reactions, there have been a larger number of studies to understand the role of interfacial sites in methanol synthesis from synthesis gas  $(CO/CO_2/H_2)$ . It was reported that the active sites for methanol synthesis over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts are located at stepped (defective) Cu sites decorated with Zn atoms.<sup>3</sup> Similar work demonstrated the importance of Cu-ZnOx interfacial sites for methanol synthesis. It was found that the turnover frequency (TOF) of methanol formation over a Cu (111) surface decorated with Zn at a coverage of 19% ( $\theta_{Zn} = 0.19$ ) is an order of magnitude higher than that over a clean Cu (111) singlecrystal surface.<sup>4</sup> Interestingly, the promoting effect was only observed for Zn on Cu (111) but not on Cu (110) and Cu (100) surfaces, suggesting that a stepped Cu surface decorated with Zn is the active site for the methanol synthesis.<sup>4-5</sup> Besides promotion caused by the interaction between Cu and Zn, Bell and co-workers demonstrated the promoting effect of ZrO<sub>2</sub> on Cu/SiO<sub>2</sub>.<sup>6</sup> The rate of methanol formation over 30.5 wt% ZrO<sub>2</sub> deposited on Cu/SiO<sub>2</sub> is 25 times higher than the rate over Cu/SiO<sub>2</sub> for CO<sub>2</sub> hydrogenation. Higher activity over the ZrO<sub>2</sub>-promoted Cu/SiO<sub>2</sub> catalyst was ascribed to the effective adsorption of CO<sub>2</sub> on ZrO<sub>2</sub> and enhanced methanol synthesis on the ZrO<sub>2</sub> surface with hydrogen supplied by spillover from Cu.<sup>7</sup> In addition, it was concluded that the ZrO<sub>2</sub>-promoted Cu/SiO<sub>2</sub> catalyst behaves in a bifunctional manner.<sup>7c, 8</sup> Wokaun and coworkers suggested the importance of interfacial sites between Cu and ZrO<sub>2</sub> in the methanol synthesis reaction from CO<sub>2</sub>/H<sub>2</sub>.<sup>9</sup>

The nature of the active Cu phase under reaction conditions for both ethanol conversion to ethyl acetate and methanol synthesis is still a subject of controversy. Previous studies

demonstrated that a Cu<sup>1+</sup>/Cu<sup>0</sup> pair is responsible for the higher rate of ethyl acetate formation.<sup>1c, d</sup> The combination of Cu<sup>+</sup> and Cu<sup>0</sup> was also proposed to be active for the methanol synthesis reaction, in studies showing a change in the methanol formation rate as a function of oxygen coverage of Cu surface.<sup>10</sup> On the other hand, Wokaun and co-workers used X-ray diffraction (XRD) studies to show that metallic Cu (Cu<sup>0</sup>) is the predominant phase present during methanol production, which is consistent with the work of Topsøe and co-workers.<sup>9a, 11</sup> Cu<sup>1+</sup> was also suggested to be the active phase for the methanol synthesis reaction in other studies.<sup>12</sup>

In the present paper, we have studied  $Cu/SiO_2$  catalysts containing different zirconia amounts to probe the active sites for the selective conversion of ethanol to ethyl acetate and for the synthesis of methanol from  $CO_2$  and  $H_2$ . We have prepared these Cu catalysts with different amounts of  $ZrO_2$  using two approaches: controlled surface reactions (CSR) and atomic layer deposition (ALD). These synthesis methods allow us to prepare catalysts with well-defined Cu-ZrO<sub>x</sub> interfacial sites. We quantify the concentrations of Cu and Cu-ZrO<sub>x</sub> interfacial sites using a combination of sub-ambient CO Fourier Transform Infrared Spectroscopy (FT-IR) and reactive N<sub>2</sub>O chemisorption. Our objective is to use well-defined and well-characterized catalysts to probe the effect and role of interfacial sites on catalytic reactivity.

## 2. Experimental

## **2.1 Catalyst Preparation**

## 2.1.1 Monometallic catalyst

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A catalyst with a theoretical Cu loading of 10 wt% on SiO<sub>2</sub> was prepared by an ionexchange method described in detail elsewhere.<sup>13</sup> SiO<sub>2</sub> (Davisil grade 646, Sigma-Aldrich) was used as a support for the catalysts. This SiO<sub>2</sub> support was crushed and sieved to between 60 and 100 mesh (0.150-0.250 mm) and washed with 5% diluted nitric acid (HNO<sub>3</sub>, Sigma-Aldrich) for 24 h. The support was rinsed with milli-Q water until the water became neutral. The silica was dispersed in milli-Q water and tetra-ammine copper (II) sulfate monohydrate ( $Cu(NH_3)_4SO_4 \cdot H_2O_3$ ) Sigma-Aldrich) was added into the suspension under continuous mixing at room temperature. The pH was adjusted to 9 through dropwise addition of dilute solutions of nitric acid (HNO<sub>3</sub>, Sigma-Aldrich). The mixture was aged for 20 h under stirring at room temperature, and the solid material was then filtered and washed with deionized water. The sample was dried overnight at 383 K in air. The dried catalyst was pretreated in a flow-through cell at a temperature of 623 K (with a heating rate of 0.5 K min<sup>-1</sup>) under helium flow (30 cm<sup>3</sup>(STP) min<sup>-1</sup>) for 3 h, followed by air flow, and then reduced under hydrogen flow, and finally passivated at room temperature with 1% O<sub>2</sub> in He. The Cu reference catalyst was calcined at 1023 K (denoted as 1023K-C-Cu/SiO<sub>2</sub>) (with a heating rate of 2 K min<sup>-1</sup>) under air flow (30 cm<sup>3</sup> (STP) min<sup>-1</sup>) for 4 h. ZrO<sub>2</sub>/SiO<sub>2</sub> samples were prepared by incipient wetness impregnation method of silica with an aqueous solution of zirconium(IV) oxynitrate hydrate (ZrO(NO<sub>3</sub>)<sub>2</sub> xH<sub>2</sub>O, Sigma-Aldrich). In addition, a lower Cu loading (theoretical loading of 2 wt%) on SiO<sub>2</sub> was prepared by an ion-exchange method for elemental mapping of Cu and Zr species by scanning transmission electron microscopy/energydispersive X-ray spectroscopy (STEM/EDS).

## **2.1.2 Bimetallic catalyst**

CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts were prepared by controlled surface reactions (CSR) and atomic layer deposition (ALD) methods. CuZr/SiO<sub>2</sub> catalysts prepared by the CSR method were synthesized by following the procedure described elsewhere.<sup>14</sup> The Cu reference catalyst was reduced in a Schlenk tube, sealed, and then transferred to a glove box for ZrO<sub>2</sub> deposition without air exposure. A solution of Bis(cyclopentadienyl)dimethylzirconium (Strem Chemicals) in *n*-pentane was added onto the Cu reference catalyst in the Schlenk tube and stirred for 3 h. The mixture was transferred to a Schlenk line for evaporation of solvent left in the Schlenk tube. Then, the sample was reduced at 573 K (with a heating rate of 2 K min<sup>-1</sup>) under hydrogen flow (30 cm<sup>3</sup>(STP) min<sup>-1</sup>) for 2 h and then passivated at room temperature with 1% O<sub>2</sub> in He. Hereafter, CuZr/SiO<sub>2</sub> samples prepared by the CSR method with a theoretical Cu loading of 10 wt% on SiO<sub>2</sub> will be referred to as Cu<sub>1</sub>Zr<sub>x</sub>, where x is equal to the nominal Zr/Cu atomic ratio. In addition, CuZr/SiO<sub>2</sub> samples synthesized by the CSR method with a theoretical Cu loading of 2 wt% on SiO<sub>2</sub> for EDS mapping of Cu and Zr will be referred to as 2wt% Cu<sub>1</sub>Zr<sub>x</sub>, where x is equal to the nominal Zr/Cu atomic ratio.

Atomic layer deposition (ALD) of ZrO<sub>2</sub> on Cu/SiO<sub>2</sub> was carried out in a horizontal flowtube quartz reactor ALD system heated by a tube furnace. All depositions were carried out at 473 K, at a pressure of ~0.5 Torr. The powder was held in an aluminum tray and placed inside the heated zone of the reactor with no agitation applied to the powders during deposition. Tetrakis(dimethylamido)zirconium(IV) (TDMAZ, Strem) and deionized water (H<sub>2</sub>O) were used as precursors for Zr and O, respectively, with nitrogen (N<sub>2</sub>) used as purge gas. Powders were coated using the pulse sequence: TDMAZ – purge – H<sub>2</sub>O – purge. The TDMAZ was held in a bubbler at 353 K with a N<sub>2</sub> flow of 50 cm<sup>3</sup> (STP) min<sup>-1</sup> passing through the bubbler to entrain the precursor. The H<sub>2</sub>O bubbler outlet was connected to the carrier line through a metering valve

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which controls the precursor flow rate. A residual gas analyzer (SRS RGA 200) mass spectrometer connected to the downstream end of the reactor was used to monitor the reactor effluent before it exited the reactor into a roughing pump. The pulse and purge times of the precursors were selected based on the completion of a half-cycle surface reactions, as monitored by the decrease in the RGA signal intensity. All prepared ALD catalysts were calcined at 1023 K (with a heating rate of 2 K min<sup>-1</sup>) after ALD overcoating under air flow (30 cm<sup>3</sup>(STP) min<sup>-1</sup>) for 4 h to introduce pores in the ZrO<sub>2</sub> ALD overlayers, as reported in a previous study.<sup>15</sup> Hereafter, CuZr/SiO<sub>2</sub> samples prepared by an ALD method will be denoted as xALD-Cu/SiO<sub>2</sub>, where x is equal to the number of ZrO<sub>2</sub> ALD cycles. It should be noted that ZrO<sub>2</sub> deposited on Cu sites by ALD has different chemical and catalytic properties compared to those seen when bulk ZrO<sub>2</sub> is used as a support, as suggested in previous work.<sup>16</sup>

## 2.2 Reactivity Measurements.

Studies of ethanol conversion were conducted in a continuous flow, fixed-bed quarterinch stainless steel reactor with catalyst mass of 40 mg at 473 K and a pressure of 7.6 bar. Liquid phase ethanol (100%, Decon Labs, Inc.) was fed to the reactor system with a flow rate of 1.5  $\mu$ l/min at room temperature using a syringe pump (Havard Apparatus) and vaporized at the reactor inlet by passing into flowing He flow 40 cm<sup>3</sup>(STP)/min. The reaction condition of a low partial pressure of ethanol was chosen at which acetaldehyde becomes a dominant product, such that the effect of promotion for the formation of ethyl acetate could be more readily discernable. The reactor was filled to the top of the heating zone with fused SiO<sub>2</sub> chips, using a quartz wool plug at each end of the tubular reactor. Experiments without catalyst determined the absence of reactivity from the reactor. Control experiments to investigate the active sites for the coupling reaction were carried out by feeding acetaldhyde and ethanol simultaneosuly using a bubbler and

a syringe pump, respectively. The temperature of the reactor was measured using a K-type thermocouple attached to the outside of the reactor and adjusted by using a furnace connected to a variable autotransformer power source. Ultra-high purity (UHP) He and H<sub>2</sub> gas were used. Prior to reactivity measurements, catalysts were reduced in situ at 573 K (with a heating rate of 3 K min<sup>-1</sup>) under H<sub>2</sub> flow (30 cm<sup>3</sup>(STP) min<sup>-1</sup>) for 2 h. Reaction products were analyzed by an online gas chromatograph with a barrier discharge ionization detector (GC-BID) system equipped with an auto-sampling 6-port valve (Shimadzu). All lines from the reactor to the gas chromatographs (GC) were heat traced at 353 K to prevent the condensation of products and reactants inside the line. Conversion and selectivity were determined on the basis of carbon products. The reversibility of ethanol conversion reaction to ethyl acetate was calculated, and details for this calculation are shown in the Supporting Information.

Methanol synthesis was studied by feeding CO<sub>2</sub> and H<sub>2</sub> in a half-inch OD stainless steel fixed-bed reactor under a pressure of 30 bar, at 523 K and a total flow rate of 60 cm<sup>3</sup>(STP) min<sup>-1</sup>, in a down-flow configuration. Catalyst samples (150-300 mg) were diluted with crushed silica chips (Silicon dioxide, fused, 4-20 mesh, Sigma Aldrich) and placed in the center of the reactor, and the catalyst bed was positioned between plugs of quartz wool (Grace). A K-type thermocouple was positioned in the center of the catalyst bed for temperature measurement and control. The upstream and downstream portions of the reactor from the catalyst bed were filled with silica chips. The catalysts were reduced at 523 K (with a heating rate of 1.5 K min<sup>-1</sup>) under 20% H<sub>2</sub>/He flow (100 cm<sup>3</sup> (STP) min<sup>-1</sup>). The feed composition for CO<sub>2</sub> hydrogenation was  $CO_2/H_2=1/3$ . Products were maintained in gas phase and flowed to an online GC-FID (HP 6890 Plus) to detect methanol and methane. Product compositions at steady state were measured typically after 2-6 h on stream. All experiments were carried out at low conversion (e.g., less

than 35% of equilibrium). Internal mass transport limitations were predicted to be negligible for catalysts in both reactions according to the Weisz-Prater criterion.<sup>17</sup> Details for calculation of Weisz-Prater numbers are shown in the Supporting Information (Table S1).

## 2.3 Catalyst Characterization

## 2.3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

Catalyst samples were pressed into self-supporting pellets with a 0.9-1.1 cm die. Cu/SiO<sub>2</sub> and CuZr/SiO<sub>2</sub> pellets were mounted in the sample holder of a transmission cell described elsewhere<sup>14a, b, 18</sup> and reduced in flowing H<sub>2</sub> at 573 K. After reduction, the sample was cooled under  $H_2$  flow to room temperature and evacuated to  $10^{-5}$  Torr, and a background scan was then recorded. Fourier transform infrared (FTIR) (Nicolet 6700) spectra of adsorbed CO were obtained in transmission mode after dosing 300 Torr of 1% CO in He (Airgas). The spectra were collected after first cooling the sample to 113 K, and holding for 3 min, followed by collection of spectra at temperatures ranging from 113 K to 283 K. The temperature was measured by a Ktype thermocouple and heating was controlled by a PID controller (Love Controls Series 16A) connected to a variable autotransformer. The sample holder was designed for collecting spectra at sub-ambient temperatures using flowing liquid nitrogen, as described previously.<sup>14a, b, 18</sup> All spectra were collected by averaging 256 scans with a resolution of 4 cm<sup>-1</sup>. Spectral deconvolution was performed using Origin 9.1 to determine the areal contribution from each peak. The final spectrum of CO adsorbed on each catalyst was represented by two superimposed Gaussian curves, as described elsewhere.<sup>14b</sup>

## 2.3.2 N<sub>2</sub>O Reactive Chemisorption

The number of Cu surface sites was determined using the reactive  $N_2O$  chemisorption described elsewhere.<sup>18b</sup> Prior to the measurment, catalysts were reduced *in situ* at 573 K (with a heating rate of 3 K min<sup>-1</sup>) under H<sub>2</sub> flow for 2 h. After reduction the samples were cooled to 363 K and the cell was evacuated to 10<sup>-5</sup> Torr. Then, N<sub>2</sub>O was introduced and surface metallic Cu reacted with N<sub>2</sub>O to produce N<sub>2</sub> gas and O on the Cu surface. The stoichiometry for the adsorption of O on Cu surface was assumed to be 1:2 based on Eq. (1).

$$2Cu_s + N_2 O \to (Cu_s)_2 O + N_2$$
 Eq. (1)

where  $Cu_s$  denotes as Cu surface sites. The amount of O deposited on the surface was quantified by monitoring the N<sub>2</sub> pressure using a gas handling system and a volumetric system employing Baratron capacitance manometers for precision pressure measurement (5 × 10<sup>-5</sup> Torr) after condensation of N<sub>2</sub>O in a cold trap using liquid nitrogen.

## 2.3.3 Inductively Coupled Plasma-Absorption Emission Spectroscopy (ICP-AES)

The Cu and Zr loadings of catalysts were determined using a Perkin-Elmer Plasma 400 ICP Emission Spectrometer. Typically, 10-15 mg of catalyst samples were digested with a mixture of 2 mL of nitric acid (Fischer, 65 %) and 6 mL of hydrochloric acid (Fischer, 37 %) in a Teflon beaker at 383 K. Cu and Zr standards for the ICP analysis were prepared from Cu and Zr ICP standards (Fluka, 1000  $\pm$  2 mg L<sup>-1</sup>). The post-digestion mixture was cooled to room temperature, diluted in water, filtered and analyzed with ICP emission spectrometer.

## 2.3.4 Ultraviolet-Visible (UV-Vis) Absorption Spectroscopy

UV-Visible absorption spectra over the wavelength range 200-1100 nm were recorded using a Thermo Scientific Evolution 300 UV-Vis spectrometer with 1 cm path-length quartz cuvette.

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# 2.3.5 Scanning Transmission Electron Microscopy/Energy-dispersive X-ray Spectroscopy (STEM/EDS)

A FEI Titan STEM with Cs probe aberration corrector operated at 200 kV with spatial resolution < 0.1 nm was used for scanning transmission electron microscopy (STEM) studies. A high-angle annular dark-field (HAADF) mode, with HAADF detector angle ranging from 54 to 270 mrad, probe convergence angle of 24.5 mrad, and probe current of approximately 25 pA was used to record the images. Energy dispersive x-ray spectroscopy (EDS) data were collected using the same microscope with an EDAX SiLi Detector. Catalyst samples were suspended in ethanol and then dropped on a holey carbon Au TEM grid. Samples were plasma cleaned before being loaded into the microscope.

## 2.3.6 X-ray absorption near edge structure (XANES)

X-ray absorption near edge structure (XANES) measurements were collected at beamline 20-BM of the Advanced Photon Source (APS) at Argonne National Laboratory. Catalyst samples were crushed and diluted with boron nitride (Sigma-Aldrich). Self-supporting wafers were formed inside a 4 mm ID stainless steel sample holder. Sample weights were calculated to give a unit edge step. The sample holder was sealed in a 1" O.D. Kapton-windowed quartz tube fitted with Swagelok valves to allow for measurements without exposure to air. The sealed samples were heated to 573 K under 3.5% H<sub>2</sub>/Ar at 50 cm<sup>3</sup>(STP) min<sup>-1</sup>. After reduction, valves on the pretreatment tube were sealed and the samples were placed in the x-ray beam. XANES measurements of the Cu and Zr K-edge (7709 eV and 17998 eV) were collected in transmission mode. *In situ* TPR-XANES was collected for Cu<sub>1</sub>Zr<sub>0.5</sub>/SiO<sub>2</sub> during reduction while scanning the XANES every 5 min. Temperature was monitored by a thermocouple positioned near the

sample holder in the quartz tube. Energy calibration was performed with Cu and Zr reference foils. Oxidation states were quantified by comparison of the XANES with the experimental standards. Cu-based catalysts were fit with a linear combination of fully-reduced Cu nanoparticles, Cu<sub>2</sub>O, and CuO. All fittings were performed in the range of -20 to +30 eV from the edge energy using Athena software.<sup>19</sup>

## 3. Results and Discussion

Table 1 shows the Cu and Zr loadings of Cu/SiO<sub>2</sub>, Zr/SiO<sub>2</sub> and CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts determined by ICP and EDS measurements. The actual Zr/Cu molar ratio of CuZr<sub>x</sub>/SiO<sub>2</sub> (CSR) samples characterized by ICP analysis is close to the nominal molar ratio. All  $CuZr_x/SiO_2$ catalysts prepared by CSR and ALD methods were from the same Cu/SiO<sub>2</sub> catalyst batch. When Zr was deposited via the CSR method, UV-Vis absorption spectroscopy was carried out to monitor the extent of ZrO<sub>2</sub> deposition onto the Cu reference catalyst. As presented in Figure 1, the spectrum of Zr precursor solution after 3 h stirring became similar to that of *n*-pentane, indicating that the majority of Zr precursor was deposited on the supported Cu catalyst. Figure 2 (a) and (b) present the STEM image and EDS histrogram of the Zr content of the  $Cu_1Zr_{0.5}/SiO_2$ catalyst prepared by the CSR method. The Zr/Cu molar ratio of Cu<sub>1</sub>Zr<sub>0.5</sub>/SiO<sub>2</sub> (CSR) estimated by the STEM-EDS is 0.53, in agreement with nominal and actual loadings from ICP. This result suggests that the Zr precursor has been selectively deposited on or near the Cu nanoparticles with the CSR method. In addition, the atomic structure of the CuZrO<sub>2</sub> catalyst prepared by CSR was analyzed by EDS mapping, where red is the copper and green is the zirconium as shown in Figure 3. The EDS mapping results indicate that the CSR method leads to deposition of ZrO<sub>2</sub> onto Cu nanoparticle surfaces and to formation of some ZrO<sub>2</sub> clusters near Cu nanoparticles.

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Figure 4 (a) shows the Cu K edge XANES spectra of Cu/SiO<sub>2</sub>, 1023K-C-Cu/SiO<sub>2</sub>, and CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by CSR and ALD after reduction at 573 K, and the corresponding derivative XANES spectra are shown in Figure 4 (b). Normalized XANES and first derivative spectra of CuO, Cu<sub>2</sub>O, and Cu are also included for comparison. As shown in Figure 4 (b), the absorption edge of Cu, Cu<sub>2</sub>O and CuO appears at 8978.6, 8980.0, and 8984.1 eV as a characteristic fingerprint of Cu<sup>0</sup>, Cu<sup>1+</sup>, and Cu<sup>2+</sup>, respectively. These values for references are similar to those reported in the literature.<sup>1c, 20</sup> XANES spectra of all characterized catalysts are nearly identical, as evidenced by Figure 4 (a) and (b). The first derivative spectra of Cu/SiO<sub>2</sub>, 1023K-C-Cu/SiO<sub>2</sub>, and CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts exhibit a major peak at 8978.6 eV and a smaller peak at 8980.0 eV. Phase composition was determined by linear combination fitting of fullyreduced Cu nanoparticles, Cu<sub>2</sub>O and CuO standards. This analysis shows that the catalysts consist primarily of Cu<sup>0</sup> with approximately 10% Cu<sup>1+</sup>. In situ TPR XANES spectra along with evolution of Cu species as a function of temperature for Cu<sub>1</sub>Zr<sub>0.5</sub>/SiO<sub>2</sub> catalyst prepared by CSR are shown in Figure 5. As reduction temperature increased, the formation and subsequent reduction of CuO proceeded through two steps  $(Cu^{2+} \rightarrow Cu^{1+} \rightarrow Cu^{0})$ . The temperature of maximum Cu<sup>1+</sup> composition is 437 K as shown in Figure 5. Lercher and co-workers observed the trend that the degree of reduction increased as the Cu nanoparticle size increased.<sup>21</sup> According to their work, our supported Cu catalyst with Cu-Cu coordination number of 9 from EXAFS measurement would be reduced to nearly 90 %.<sup>21</sup> Other work studying Cu catalysts with similar particle size also suggests that the degree of reduction should be nearly 90-95%.<sup>1c, d, 21</sup> Thus it can be concluded that the dominant Cu phase is metallic Cu, but a small amount of Cu<sup>1+</sup> remained up to 573 K.

Figure 6 (a) shows the Zr K edge XANES spectra of  $CuZr_x/SiO_2$  catalysts prepared by CSR and ALD methods after reduction at 573 K. The corresponding derivative XANES spectra are shown in Figure 6 (b). Normalized XANES and first derivative spectra of  $ZrO_2$  and Zr are also included for comparison. The energies of Zr edges for all Zr-containing catalysts correspond with that of the  $ZrO_2$  reference, indicating that the oxidation state of the Zr for these catalysts is 4+. The apparent high oxidation state ( $Zr^{4+}$ ) of Zr in the bimetallic catalysts is in agreement with results reported in the literature.<sup>22</sup>

Figure 7 shows infrared spectra of CO chemisorbed on the reference Cu/SiO<sub>2</sub> and the CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by CSR and ALD methods, collected at 123 K and 263 K after insitu reduction in flowing H<sub>2</sub> at 573 K. The total area of the spectra becomes smaller after deposition of  $ZrO_2$  on the catalysts (Cu $Zr_x/SiO_2$ ) compared to the reference catalyst (Cu/SiO<sub>2</sub>), suggesting that ZrO<sub>2</sub> was deposited on Cu sites. The spectra of the reference Cu/SiO<sub>2</sub> and CSR catalysts collected at 123 K exhibited features around 2110 cm<sup>-1</sup> and 2157 cm<sup>-1</sup>. The feature at 2157 cm<sup>-1</sup> becomes weaker after the sample was warmed to 263 K. The main features of the ALD catalysts were a band at 2110 cm<sup>-1</sup> with a shoulder of 2157 cm<sup>-1</sup> at both temperatures. Spectral deconvolution was carried out to determine the contributions from two bands at 2110 and 2157 cm<sup>-1</sup> for the spectra collected at 123 K, and CO FT-IR peak areas at 2110 cm<sup>-1</sup> are shown in Table 2. As can be seen in Figure 7 (c) and (d), the Cu reference catalyst after calcination at 1023 K (1023K-C-Cu/SiO<sub>2</sub>) exibited a decrease in the intensity and a minor shift from 2110 to 2119 cm<sup>-1</sup> compared to the reference Cu catalyst. The change in the band intensity can be explained by sintering of the Cu nanoparticles after calcination at high temperature (1023 K), leading to a decrease in the concentration of Cu undercoordinated defect sites. This decrease in the CO intensity is in agreement with results from a previous study by Goodman and co-

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workers.<sup>23</sup> The peak shift to higher wavenumber with the increased Cu nanoparticle size is also accordance with the previous work.<sup>23-24</sup> The decease in Cu dispersion after calcination at high temperature (1023 K) was further evidenced by the decrease in the number of surface sites measured by N<sub>2</sub>O chemisorption, as shown in Table 2. The CO FT-IR areas of the spectrum decreased after a control experiment where CSR was performed without Zr precursor on the same Cu/SiO<sub>2</sub> catalyst (referred to control Cu/SiO<sub>2</sub>), as shown in Figure S1 (See Supporting Information).

Results from previous work by Hadjiivanov and co-workers, showing the spectra of CO (2 kPa equilibrium pressure) adsorbed on Cu/SiO<sub>2</sub> reduced at 573 K, are similar to our work.<sup>25</sup> As the temperature was increased, the two bands at 2128 cm<sup>-1</sup> and 2156 cm<sup>-1</sup> became weaker and the band at 2156 cm<sup>-1</sup> disappeared at 243 K, in agreement with our spectral behavior observed in Figure 7 (b).<sup>25</sup> They ascribed the bands at 2128 cm<sup>-1</sup> and 2156 cm<sup>-1</sup> to Cu<sup>0</sup>-CO and CO H-bonded to the surface Si-OH groups of the support, respectively.<sup>25</sup> Boccuzzi and co-workers assigned the band at 2152 cm<sup>-1</sup> to CO physisorbed on surface hydroxyls.<sup>26</sup> In agreement with this assignment, we also observed the band at 2157 cm<sup>-1</sup> with the SiO<sub>2</sub> support, as shown in Figure S2 (See Supporting Information), indicating that the band at 2157 cm<sup>-1</sup> can be assigned to the adsorption of CO on surface hydroxyl groups on the support. As shown in Figure 7 (c), CuZr<sub>x</sub> catalysts synthesized by the ALD method exhibited much smaller intensity at 2157 cm<sup>-1</sup> compared to catalysts prepared by our CSR method. Thus, whereas the CSR method leads to selective precursor deposition on under-coordinated Cu sites or near Cu nanoparticles, ALD overcoating leads to deposition of precursor over the entire catalyst surface.<sup>27</sup>

As mentioned above, Hadjiivanov and co-workers ascribed the band at 2129 cm<sup>-1</sup> to Cu<sup>0</sup>-CO.<sup>25, 28</sup> According to their study, decreasing intensity of the band at 2129 cm<sup>-1</sup> with

increasing temperature, such as seen in Figure 7 (b) and (d), is evidence that the band at 2129 cm<sup>-1</sup> is associated with Cu<sup>0</sup>-CO due to the low thermal stability of Cu<sup>0</sup>-CO.<sup>28</sup> In agreement with this assignment, Paffett and co-worker suggested that the feature observed at 2110 cm<sup>-1</sup> can be related to Cu<sup>0</sup>-CO.<sup>29</sup> Vannice and co-workers also showed that the band near 2110 cm<sup>-1</sup> in the spectrum of Cu/SiO<sub>2</sub> catalysts after reduction at 573 K is associated with Cu<sup>0</sup>-CO species.<sup>30</sup> Goodman and co-workers also showed that model silica supported copper catalysts without annealing exhibited a distinct band at 2091-2106 cm<sup>-1</sup> depending on the copper coverage, suggesting that the feature observed at 2110 cm<sup>-1</sup> can be attributed to CO adsorbed on Cu surface sites far from oxygen.<sup>31</sup> In single-crystal studies, they assigned bands at 2091-2116 cm<sup>-1</sup> and 2108-2110 cm<sup>-1</sup> to CO adsorbed on a Cu (100) and high-index Cu (211), and on a (311) surface perturbed by oxygen, respectively.<sup>31a, 32</sup> Similarly, Pritchard and co-worker assigned the band at 2117 cm<sup>-1</sup> to a Cu (111) surface near oxygen species. They also suggested that the band at 2111 cm<sup>-1</sup> can be associated with stepped (111) surface of metallic Cu (755). Based on these studies from the literature, the band at 2110 cm<sup>-1</sup> is mostly likely associated with metallic copper surface sites, considering that metallic Cu is the dominant Cu phase determined by in situ XANES, as shown in Figure 5.

Reactive N<sub>2</sub>O decomposition characterization was employed to estimate the number of metallic Cu (Cu<sup>0</sup>) sites of the reference Cu/SiO<sub>2</sub> and the CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by CSR and ALD methods, and these results are shown in Table 2. The number of Cu<sup>0</sup> sites of ZrO<sub>2</sub>-deposited catalysts (CuZr<sub>x</sub>/SiO<sub>2</sub>) was decreased compared to that of the reference catalyst (Cu/SiO<sub>2</sub>), in agreement with the decrease in CO FT-IR areas. Spectral deconvolution was performed with spectra collected at 123 K to obtain the spectral area of the CO band at 2110 cm<sup>-1</sup> (Cu<sup>0</sup>). Plots comparing the number of metallic Cu sites characterized by N<sub>2</sub>O uptake and FTIR

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spectral area of the CO band at 2110 cm<sup>-1</sup> for CuZr<sub>x</sub>/SiO<sub>2</sub> catalyts by CSR and ALD are shown in Figure 8 (a) and (b), respectively. There is a strong correlation between these results for CuZr<sub>x</sub>/SiO<sub>2</sub> catalyts (CSR), with a slope of 0.29. Data collected for the Cu/SiO<sub>2</sub> sample calcined at 1023 K also followed this trend, with a similar slope as shown a black dash line in Figure 8 (b). However, this correlation between two different characterizations does not hold for  $CuZr_x/SiO_2$ catalyts (ALD). The slope for CuZr<sub>x</sub>/SiO<sub>2</sub> catalyts (ALD) is 0.13. It is smaller than that for CuZr<sub>x</sub>/SiO<sub>2</sub> catalyts (CSR), as shown by a blue dash line in Figure 8 (b). This behavior suggests that a larger number of sites was estimated by  $N_2O$  decomposition characterization with respect to measurement using FTIR spectral area. Apparently, the extent of surface oxidation of metallic Cu by reactive  $N_2O$  decomposition is affected by the ALD process, suggesting that reactive  $N_2O$ characterization may not be as appropriate for measuring the number of Cu surface sites as is adsorption of CO.<sup>12a, 33</sup> It is possible that sub-surface oxidation of Cu can take place through diffusion along the interface between Cu and ZrO<sub>2</sub> ALD layers, leading to overestimation of Cu sites for ALD catalysts.<sup>34</sup> Hence, the number of metallic copper sites measured by the reactive N<sub>2</sub>O characterization is normalized to the CO FT-IR band area at 2110 cm<sup>-1</sup> of Cu/SiO<sub>2</sub> reference catalyst, and these values are denoted as corrected Cu<sup>0</sup> site in Table 2. The methodology to estimate the number of Cu-ZrO<sub>2</sub> interfacial sites is to assume that deposition of ZrO<sub>2</sub> on Cu sites occurs with 1:1 stoichiometry. The change in the CO FT-IR band area at 2110 cm<sup>-1</sup> with ZrO<sub>2</sub> addition can be ascribed to the number of under-coordinated Cu sites occupied by ZrO<sub>2</sub>. Hence, the number of Cu-ZrO<sub>2</sub> interfacial sites is determined from the change in the amount of corrected Cu<sup>0</sup> sites, as reported previosuly.<sup>14b</sup>

## 3.3. Catalytic Activity measurements

Table 3 shows the catalytic activity for ethanol conversion over Cu/SiO<sub>2</sub> and CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by CSR and ALD methods. The Cu/SiO2 catalyst exhibited higher selectivity to acetaldehyde, as seen in previous studies.<sup>1b, 1d</sup> The rate of ethyl aceate formation over Cu/SiO<sub>2</sub> at the reaction temperature of 473 K is in accordance with the rate reported by Beuno and coworkers.<sup>1d</sup> The TOF for ethyl acetate formation reported here is the site time yield (STY), defined as the number of molecules of ethyl acetate produced per surface site in the reactor per unit time, as the catalytic activity was obtained at a finite extent of conversion.<sup>35</sup> We find that deposition of ZrO<sub>2</sub> on Cu/SiO<sub>2</sub> via two different methods increased the selectivity to ethyl aceate in the ethanol conversion reaction. For the catalysts prepared by the CSR method, the selectivity toward ethyl acetate increases with ZrO<sub>2</sub> loading up to a Zr-Cu molar ratio equal to 0.5, with the Cu<sub>1</sub>Zr<sub>0.5</sub>/SiO<sub>2</sub> catalyst having almost 16 times higher TOF than that of the Cu/SiO<sub>2</sub> reference catalyst. Additional deposition of ZrO<sub>2</sub> onto the reference Cu catalyst (Cu<sub>1</sub>Zr<sub>0.75</sub>/SiO<sub>2</sub>) decreases the selectivity to ethyl acetate and the TOF of ethyl acetate formation. The decrease in the TOF of ethyl acetate formation can be explained by the smaller production of acetaldehyde due to the decreased number of Cu sites, which are active sites for the production of acetaldehyde over Cu<sub>1</sub>Zr<sub>0.75</sub>/SiO<sub>2</sub> catalyst. The CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts synthesized by ALD also exhibited higher selectivity to ethyl acetate and higher ethyl acetate formation TOF. The ethyl acetate formation TOF increased with ZrO<sub>2</sub> loading to 8 cycle ALD overcoating and levelled off above this ALD overcoating. The 8 and 15ALD-Cu/SiO<sub>2</sub> catalysts exhibited approximately 9 times higher TOF than that of the Cu/SiO<sub>2</sub> reference catalyst.

Interestingly,  $ZrO_2$  addition ( $Cu_1Zr_x/SiO_2$ ) on the  $Cu/SiO_2$  reference catalyst via the CSR method suppressed the formation of by-product, 2-butanone (methyl-ethyl-ketone, MEK). The formation of 2-butanone was also inhibited after calcination at 1023 K (1023K-C-Cu/SiO<sub>2</sub>) of

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the Cu reference catalyst, suggesting that under-coordinated Cu sites are responsible for the production of 2-butanone via acetaldehyde condensation. In fact, suppression of 2-butanone production from ethanol is beneficial in the industrial operation of ethyl acetate purification.<sup>2a, 36</sup> The mixture of 2-butanone and ethyl acetate forms an azeotrope, making it difficult to separate one from another. <sup>2a, 36</sup> However, deposition of ZrO<sub>2</sub> by ALD did not suppress the production of butanone, unlike ZrO<sub>2</sub> deposition by the CSR method. In fact, ZrO<sub>2</sub> deposition by an ALD method promotes the production of 2-butanone, which can be ascribed to highly dispersed ZrO<sub>2</sub> species on Cu/SiO<sub>2</sub> as reported in a previous study.<sup>1d</sup>

We also studied a physical mixture of  $Zr_{0.5}/SiO_2$  and the reference Cu/SiO<sub>2</sub> catalyst to determine whether separated Cu and ZrO<sub>2</sub> sites can lead to the production of ethyl acetate. As seen in Table 3, a physical mixture exhibited only a slight improvement in the rate of ethyl acetate formation, suggesting that Cu-ZrO<sub>2</sub> interfacial sites are responsible for the enhancement in the ethyl acetate production observed over our CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts. To further investigate the active sites for the coupling reaction, we studied reactions over  $Zr_{0.5}/SiO_2$  and  $CuZr_{0.5}/SiO_2$ catalysts by feeding acetaldehyde and ethanol simultaneously. The TOF of ethyl acetate formation over the Cu<sub>1</sub>Zr<sub>0.5</sub>/SiO<sub>2</sub> catalyst at atmosphere pressure is 12 h<sup>-1</sup>. However, there was no formation of ethyl acetate over the  $Zr_{0.5}/SiO_2$  catalyst, indicating that Cu-ZrO<sub>2</sub> interfacial sites are necessary for the dehydrogenative coupling reaction between ethanol and acetaldehyde.

Figure 9 show the activities for methanol synthesis from  $CO_2$  and  $H_2$  for the Cu/SiO<sub>2</sub> and CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by the CSR method. As shown in Figure 9, the of methanol formation rate over CuZr<sub>x</sub>/SiO<sub>2</sub> prepared by the CSR method increased with ZrO<sub>2</sub> loading up to a Zr-Cu molar ratio equals to 0.5, and it was not further increased above this Zr-Cu molar ratio.

 $Cu_1Zr_{0.5}/SiO_2 Cu_1Zr_{0.75}/SiO_2$  and catalysts exhibited approximately 12 times higher TOF than that of the Cu/SiO\_2 reference catalyst. The 15ALD-Cu/SiO\_2 catalyst synthesized by an ALD method also exhibited approximately 5 times higher TOF than that of Cu/SiO\_2 reference catalyst. In addition, a physical mixture of  $Zr_{0.5}/SiO_2$  and the reference Cu/SiO\_2 catalyst was studied for methanol synthesis, and this mixture exhibited only 20% higher TOF in methanol formation compared to the reference catalyst, indicating that Cu-ZrO\_2 interfacial sites are active sites for methanol formation reaction from CO<sub>2</sub>/H<sub>2</sub>.

The number of  $Cu^0$  and Cu-ZrO<sub>2</sub> interfacial sites shown in Table 2 (S<sub>Cu</sub> and S<sub>Cu-ZrO2</sub>) can be used to estimate the rate contributions from two different active sites. The reaction rates of the two active sites (under-coordinated Cu and Cu-ZrO<sub>2</sub> interfacial sites) were deconvolutated from the reaction kinetics data using Eq. (2):

$$R_{total} = R_{Cu} + R_{Cu-ZrO_2} = S_{Cu}r_{Cu} + S_{Cu-ZrO_2}r_{Cu-ZrO_2}$$
Eq. (2)

In this equation,  $r_{Cu}$  and  $r_{Cu-ZrO_2}$  refer to the turnover rates (the mole of methanol production per mole of Cu and Cu-ZrO<sub>2</sub> site per hour) for the under-coordinated Cu and Cu-ZrO<sub>2</sub> sites, respectively; and  $R_{Cu}$  and  $R_{Cu-ZrO_2}$  indicate the moles of methanol produced per mass of catalyst per hour from under-coordinated Cu sites and interfacial Cu-ZrO<sub>2</sub>, respectively. The experimental rate and model predicted rates are plotted in Figure 9. The model estimated the turnover rates to be  $r_{Cu} = 3.5$  h<sup>-1</sup> and  $r_{Cu-ZrO_2} = 28.5$  h<sup>-1</sup>. The rate per Cu-ZrO<sub>2</sub> site is approximately 8 times faster than the rate per Cu site.

A simplified reaction kinetics model for a plug-flow reactor was used to fit the experimental data for ethanol conversion by optimizing the rate constants  $(k_1, k_{2,Cu})$ , and

 $k_{2,Cu-ZrO_2}$ ) using nonlinear least squares regression in MATLAB (nlinfit function). The kinetic model developed for describing the two-step ethanol conversion reaction scheme is summarized in Eq. (3) and (4), and details for derivation of equations are shown in the Supporting Information.

$$r_{Acet} = k_1 P_{EtOH} S_{Cu} \qquad \text{Eq. (3)}$$

$$r_{EtAc} = P_{EtOH} P_{Acet} (k_{2,Cu} S_{Cu} + k_{2,Cu-ZrO_2} S_{Cu-ZrO_2}) \qquad \text{Eq. (4)}$$

Confidence intervals are reported as the 95% confidence level (nlinpaci function). The rate predictions from our model are shown in Figure 10. The rate constant for the first step reaction  $(k_1)$ , converting ethanol to acetaldehyde, is  $870 \pm 105 \text{ h}^{-1}$ . The model-predicted rate constants for the two different active sites (under-coordinated Cu and Cu-ZrO<sub>2</sub> interfacial sites) are estimated to be  $k_{2,Cu} = 24 \pm 220 \text{ bar}^{-1} h^{-1}$  and  $k_{2,Cu-ZrO2} = 17600 \pm 400 \text{ bar}^{-1} h^{-1}$ , suggesting that  $k_{2,Cu}$  is not statistically significant and the rate contribution of under-coordinated Cu sites is negligible compared to that of Cu-ZrO<sub>2</sub> interfacial sites.

## Conclusions

Well-defined Cu catalysts promoted with ZrO<sub>2</sub>-moieties were prepared by controlled surface reactions (CSR) and atomic layer deposition methods. Selective deposition of ZrO<sub>2</sub> on under-coordinated Cu sites or near Cu nanoparticles via the CSR method was evidenced by UV-Vis absorption spectroscopy, scanning transmission electron microscopy, and inductively coupled plasma-absorption emission spectroscopy. The concentrations of Cu and Cu-ZrO<sub>2</sub> interfacial sites were quantified using a combination of sub-ambient CO Fourier transform

infrared spectroscopy and reactive N<sub>2</sub>O chemisorption measurements. The oxidation states of the Cu and Zr species for these catalysts were determined by X-ray absorption near edge structure measurements to be primarily  $Cu^0$  and  $Zr^{4+}$ , respectively. It was found that the formation of Cu-ZrO<sub>2</sub> interfacial sites increased the turnover frequency by an order of magnitude in both ethanol conversion to ethyl acetate and methanol synthesis from CO<sub>2</sub> and H<sub>2</sub>. A physical mixture of Cu/SiO<sub>2</sub> and ZrO<sub>2</sub>/SiO<sub>2</sub> does not show enhancement in the rate of formation of ethyl acetate and methanol, indicating that the active sites for these reactions are Cu-ZrO<sub>2</sub> interfacial sites. In addition, the formation of ethyl acetate was not detected over  $Zr_{0.5}/SiO_2$  with feeding acetaldehyde and ethanol simultaneously, suggesting that Cu-ZrO<sub>2</sub> interfacial sites are necessary for the dehydrogenative coupling reaction between ethanol and acetaldehyde. We note that this paper does not address the exact nature of such sites. For example, interfacial sites may be composed of both metal and oxide working in tandem at the metal-oxide junction. Alternatively, the chemistry may take place only on the metal, adjacent to the interface, which has been modified by the oxide by creating index planes, or dislocations etc. that are active for the reaction.

#### **Associated Content**

## **Supporting Information.**

IR spectra of CO adsorbed on SiO<sub>2</sub>, Cu/SiO<sub>2</sub>, and Cu/SiO<sub>2</sub> after a control experiment; calculation of Weisz-Prater numbers; derivation of the reaction kinetics model for two-step ethanol conversion; and calculation of the reversibility for ethanol conversion to ethyl acetate. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Figure 1.** UV-Vis absorption spectra of Zr precursor (Bis-(cyclo-pentadienyl) dimethylzirconium) solution before/after deposition onto Cu/SiO<sub>2</sub>, 340 times diluted Zr precursor with *n*pentane, and *n*-pentane.



Figure 2. (a) STEM image of  $Cu_1Zr_{0.5}/SiO_2$  prepared by the CSR method and (b) EDS histrogram of Zr content for the  $Cu_1Zr_{0.5}/SiO_2$  catalyst.



**Figure 3.** STEM images of 2 wt%  $Cu_1Zr_{0.5}/SiO_2$  prepared by the CSR method with EDS mapping of Cu and Zr. Correspondence of colors and elements: red, Cu; green, Zr.



**Figure 4.** (a) *In situ* XANES spectra at the Cu *K* edge and (b) respective derivative of spectra of Cu/SiO<sub>2</sub>, 1023K-C-Cu/SiO<sub>2</sub>, and CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by CSR and ALD methods after reduction at 573 K. Spectra and derivative spectra of CuO, Cu<sub>2</sub>O, and Cu are included in both figures for comparison.



**Figure 5.** *In situ* XANES spectra showing evolution of Cu species as a function of temperature for  $Cu_1Zr_{0.5}/SiO_2$  catalyst prepared by CSR.



**Figure 6.** (a) *In situ* XANES spectra at the Zr *K* edge and (b) respective derivative of spectra of  $CuZr_x/SiO_2$  catalysts prepared by CSR and ALD methods after reduction at 573 K. Spectra and derivative spectra of ZrO<sub>2</sub> and Zr are included in both figures for comparison.



**Figure 7.** IR spectra of 3 Torr of CO on Cu/SiO<sub>2</sub> and CuZr<sub>x</sub>/SiO<sub>2</sub> prepared by CSR method collected at (a) 123 K and (b) 263 K and on Cu/SiO<sub>2</sub>, Cu/SiO<sub>2</sub> calcined at 1023K (1023K-C-Cu/SiO<sub>2</sub>), CuZr<sub>x</sub>/SiO<sub>2</sub> prepared by ALD method collected at (c) 123 K and (d) 263 K. Catalysts were *in situ* reduced in flowing H<sub>2</sub> at 573 K before spectra collection and the intensities are normalized by the pellet density.



**Figure 8.** Plot of the number of metallic Cu sites characterized by  $N_2O$  titration and CO FTIR band at 2110 cm<sup>-1</sup> of catalysts prepared by (a) CSR and (b) ALD methods.



**Figure 9.** Methanol formation rate of CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by CSR from CO<sub>2</sub>/H<sub>2</sub>. Dashed line indicates model predicted rates. The model predictions are  $r_{Cu} = 3.5$  h<sup>-1</sup> and  $r_{Cu-ZrO_2} = 28.5$  h<sup>-1</sup>. The rate per Cu-ZrO<sub>2</sub> site ( $r_{Cu-ZrO_2}$ ) is approximately 8 times greater than that of Cu site ( $r_{Cu}$ ).



**Figure 10.** (a) Total acetaldehyde formation rate of CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by CSR. The model-predicted rate constant  $(k_1)$  for the first step of ethanol conversion reaction is  $870 \pm 105$  h<sup>-1</sup>. (b) Ethyl acetate formation rate of CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts prepared by CSR. Dashed line indicates model predicted rates. The model predictions are  $k_{2,Cu} = 24 \pm 220$  h<sup>-1</sup> bar<sup>-1</sup> and  $k_{2,Cu-ZrO_2} = 17600 \pm 400$  h<sup>-1</sup> bar<sup>-1</sup>. The rate contribution of under-coordinated Cu sites  $(k_{2,Cu})$  is negligible compared to that of Cu-ZrO<sub>2</sub> interfacial sites  $(k_{2,Cu-ZrO_2})$  for converting acetaldehyde to ethyl acetate.

Sample	Nominal Zr/Cu molar ratio	Actual Zr/Cu molar ratio (ICP)	Actual Zr/Cu molar ratio (EDS)	Cu loading (%)	Zr loading (%)
Cu/SiO <sub>2</sub>	0	0	0	6.84	0
$Cu_1Zr_{0.25}/SiO_2$	0.25	0.32	-	6.19	2.88
$Cu_1Zr_{0.5}/SiO_2$	0.5	0.56	0.53	6.11	4.94
$Cu_1Zr_{0.75}/SiO_2$	0.75	0.79	0.79 -		6.87
5ALD-Cu/SiO <sub>2</sub> <sup>b</sup>	-	1.87	-	5.83	15.7
8ALD-Cu/SiO2 <sup>b</sup>	-	2.37	-	5.49	18.7
15ALD-Cu/SiO <sub>2</sub> <sup>b</sup>	-	4.03	-	4.91	28.4

Table 1. Characterization of Cu/SiO<sub>2</sub> and CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts

Sample	Cu <sup>0</sup> site <sup>a</sup> (µmol g <sup>-1</sup> )	CO FTIR peak area <sup>b</sup> (2110cm <sup>-1</sup> )	Corrected Cu <sup>0</sup> site <sup>d</sup> (µmol g <sup>-1</sup> )	Cu-ZrO <sub>2</sub> interfacial sites (µmol g <sup>-1</sup> )
 Cu/SiO <sub>2</sub>	208.9	62.2	208.9	N/A
$Cu_1Zr_{0.25}/SiO_2$	126.9	39.4	132.4	76.5
$Cu_1Zr_{0.5}/SiO_2$	96.0	26.2	87.9	121.0
Cu <sub>1</sub> Zr <sub>0.75</sub> /SiO <sub>2</sub>	95.1	23.0	77.3	131.6
 1023K-C-Cu/SiO <sub>2</sub> <sup>c</sup>	128.1	35.4 <sup>e</sup>	118.9	N/A
 5ALD-Cu/SiO <sub>2</sub> <sup>c</sup>	140.9	20.9	70.2	138.7
8ALD-Cu/SiO2 <sup>c</sup>	115.0	14.4	48.5	160.4
15ALD-Cu/SiO <sub>2</sub> <sup>c</sup>	115.0	13.8	46.5	162.4

Table 2. CO FT-IR and N<sub>2</sub>O characterization results of Cu/SiO<sub>2</sub> and CuZr<sub>x</sub>/SiO<sub>2</sub> catalysts

<sup>a</sup> Metallic copper sites were determined by N<sub>2</sub>O chemisorption. <sup>b</sup> Spectra deconvolution was performed with spectra collected at 123 K. <sup>c</sup> Catalysts were calcined at 1023 K, followed by *in-situ* reduced before activity measurement. <sup>d</sup> Number of metallic copper sites measured by the reactive N<sub>2</sub>O characterization (Cu<sup>0</sup> site) is normalized to the CO FT-IR band area at 2110 cm<sup>-1</sup> of Cu/SiO<sub>2</sub> reference catalyst. <sup>e</sup> The spectral area of the CO band measured at 2119 cm<sup>-1</sup> due to sintering of the Cu nanoparticles after calcination at high temperature (1023 K).

**Table 3.** Product distribution and ethyl acetate formation TOF for selective ethanol conversion acetate reaction.

Catalyst	Conversion (%)	S	Selectivity (%)	•		TOF Promotional factor <sup>d</sup>
		Acet- aldehyde	Ethyl acetate	2- butanone	Ethyl acetate formation TOF <sup>c</sup> (h <sup>-1</sup> )	
Cu/SiO <sub>2</sub>	45.1	77.8	3.3	18.8	$1.32\pm0.05$	1
$Cu_1Zr_{0.25}/SiO_2$	29.8	82.2	15.6	0	$7.37 \pm 1.16$	5.6
$Cu_1Zr_{0.5}/SiO_2$	30.2	64.8	32.9	0	$21.00\pm0.88$	16
$\operatorname{Cu}_{1}\operatorname{Zr}_{0.75}/\operatorname{SiO}_{2}$	16.3	68.8	35.1	0	$11.69 \pm 2.48$	8.9
Zr <sub>0.5</sub> /SiO <sub>2</sub> +Cu/SiO <sub>2</sub> <sup>a</sup>	33.2	78.4	9.2	12.9	$2.54 \pm 0.04$	1.9
1023K-C-Cu/SiO <sub>2</sub> <sup>b</sup>	27.1	100.0	0	0	0	-
5ALD-Cu/SiO2 <sup>b</sup>	35.0	55.2	4.4	40.3	$4.73 \pm 0.38$	3.6

8ALD-Cu/SiO <sub>2</sub> <sup>b</sup>	32.2	53.2	8.1	39.2	$10.84 \pm 2.83$	8.2
15ALD-Cu/SiO2 <sup>b</sup>	27.0	64.8	9.5	26.5	$11.50 \pm 1.50$	8.7

<sup>a</sup> Physical mixture of two catalysts and TOF was calculated with the number of site of Cu/SiO<sub>2</sub>. <sup>b</sup> Catalysts were calcined at 1023 K, followed by *in-situ* reduced before activity measurement. <sup>c</sup> TOF was calculated with corrected metallic copper sites shown in Table 2. <sup>d</sup> TOF promotional factor was calculated with respect to TOF of the Cu/SiO<sub>2</sub> reference catalyst.

*Note.* Reaction temperature: 473 K; pressure,  $P_{total} = 7.6$  bar,  $P_{ethanol} = 0.1$  bar.



Graphical Abstract

338x159mm (96 x 96 DPI)





214x180mm (300 x 300 DPI)







Figure 3 101x154mm (150 x 150 DPI)









217x91mm (300 x 300 DPI)



- 59
- 60



Figure 5 296x209mm (300 x 300 DPI)





Figure 7

247x182mm (300 x 300 DPI)













Figure 10 233x93mm (300 x 300 DPI)