Single-Site Zinc on Silica Catalysts for Propylene Hydrogenation and Propane Dehydrogenation. Synthesis and Reactivity Evaluation Using An Integrated Atomic Layer Deposition-Catalysis Instrument

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Abstract

Alkyl-zinc and zinc oxide-type sites were synthesized via atomic layer deposition on high-surface-area silica using an integrated atomic layer deposition-catalysis instrument (I-ALD-CAT). One-cycle ALD experiments using diethylzinc (DEZ) afforded Zn/SiO₂ systems that provided key insights into the reactivity and stability of Zn sites as a function of dispersion at the submonolayer level. The I-ALD-CAT tool design allowed for systematic comparison of the reactivity of different grafted zinc sites. Open-shell 16-electron, tricoordinate ethyl zinc-silica sites exhibit higher activity in propane hydrogenation-dehydrogenation compared to 18-electron, tetracoordinate zinc oxide-type centers. Silica surface saturation with Zn(II) sites (~75% of a monolayer) results in facile zinc agglomeration and catalyst deactivation under reaction conditions. Reduced DEZ dosing coupled with thermal substrate pretreatment techniques (e.g., dehydration under vacuum) resulted in increased Zn dispersion and produced Zn/SiO₂ catalysts with improved activity and stability under propylene hydrogenation (200°C) and propane dehydrogenation (550°C) conditions.

Introduction

Single-site heterogeneous catalysis remains a rapidly growing area due to its potential to combine the tunability of molecular catalysts with the stability of heterogeneous materials under a range of process conditions (e.g., temperature, pressure, solvent).^{1,2} Systematic investigation of

active site formation during synthesis and the transformations these species and reactive intermediates undergo during catalysis can harness key structural and mechanistic insights that are essential for the purposeful design of robust single-site catalysts with improved efficiency. However, systematic study of the transformations that these isolated sites undergo remains challenging due to the limitations of the synthesis procedures (e.g., formation of a distribution of sites), and the difficulty in handling sensitive catalytic species and intermediates from synthesis to the reactivity testing stage. Ideally, strategies integrating high-precision active site synthesis methods with immediate catalyst performance testing could allow for the systematic investigation of the catalytic properties of these supported sites without material decomposition from air- or moisture exposure.

In order to prepare single-site catalysts that are uniform-in-function, they must be synthesized using atomic-level control.^{3,4} Recent advances in synthesis techniques have produced catalytic materials with much improved activity, selectivity and stability.⁵⁻⁹ One thing all of these synthesis methods (e.g., impregnation, ion-exchange, precipitation, organometallic grafting) still lack in many cases is control of the structure, producing materials with a distribution of active sites, which in turn impacts performance. In principle, **Atomic Layer Deposition (ALD)** is a high-precision grafting technique that can synthesize a variety of supported catalytic sites (e.g., single atoms or clusters) at the atomic/monolayer level.^{3,10-11} ALD is a vapor-phase grafting method that relies on a stoichiometric and thus self-limiting reaction of chemical precursors with substrate surface functionalities.⁵⁻¹² The self-limiting nature of the ALD process presents a number of synthetic advantages that include (1) uniform active site dispersion, (2) high conformity to surface features which, in certain cases, allows for maximum utilization of the support surface area, and (3) high level of reproducibility.³

Although ALD as a catalyst synthesis tool has been applied mainly for the controlled synthesis of supported bulk – *nanoscale in size* – structures such as metal particles,¹³ films,¹⁴ alloys¹⁵ and core-shell nanoparticles,¹⁶ it comprises an ideal strategy for accessing supported single-site catalysts since *the initial nucleation of sites during ALD should consist of isolated sites*. So far, only a few reports of ALD for single-atom catalysts have appeared.¹⁷ Hence, improved understanding of synthesis mechanisms and optimization of key factors for the design of effective ALD synthesis methods to access single sites is warranted.

Our group recently reported the synthesis of isolated, low-coordinate Zn(II) sites on silica via strong electrostatic adsorption. These sites were shown active toward propylene hydrogenation (200 °C) and selective propane dehydrogenation (550 °C). Computational studies revealed the involvement of a tricoordinate Zn(II) sites and an alkyl-zinc intermediate in the catalytic cycle (**Fig 1**). However, systematic comparison of the intrinsic reactivity of these intermediates remains challenging due to difficulties in the synthesis, and the inherent instability of the species on oxide supports.

Figure 1. Proposed reactive intermediates for a previously reported single-site Zn(II)/SiO₂ catalyst for propylene hydrogenation and propane dehydrogenation: **(a)** three-coordinate Zn(II) site and **(b)** alkyl-zinc species.

In this paper, we report the use of an **Integrated Atomic Layer Deposition-Catalysis** (I-ALD-CAT, Figure 2)¹⁸ synthesis and catalyst reaction testing tool for the synthesis of isolated alkyl-zinc and zinc oxide-type sites via one-cycle ALD methods and immediate *in situ*

evaluation of the reactivity of these sites at the atomic-scale/submonolayer level under propylene hydrogenation and propane dehydrogenation conditions.¹⁸ The I-ALD-CAT tool – *the first of its kind* – has the capability of (1) ALD synthesis on a support loaded into a plug-flow reactor, a design element that allows for (2) immediate *in situ* catalyst performance evaluation under plug-flow conditions *without material exposure to air or moisture* (Figure 2).

Figure 2. Schematic diagram for the I-ALD-CAT tool. Lower left: Metal precursors (PR₁–PR₁₂). Upper left: Oxidizing/reducing reagents (O₁–O₄). Upper right: Catalysis reagents (C₁–C₄). Middle right: Plug-flow reactors (R₁, R₂). Middle far-right: Product manifold (LM). The I-ALD-CAT has the capability of providing gaseous reagents comprised of 12 different ALD precursors, 4 oxidizing or reducing agents, and 4 catalytic reaction feeds to the two plug-flow reactors. The reactor is able to immediately test these single site catalysts (or any newly synthesized materials) on a wide range of reactions and process conditions. Volatile products of the ALD synthesis and catalytic reactions can be analyzed by both GC and mass spectrometry.¹⁸

The approach presented in this report provides key insights into the mechanism of zinc grafting on hydroxylated supports, and the reactivity and stability of these alkyl-zinc and zinc oxide-type sites as a function of zinc dispersion and nuclearity. Additionally, this study presents the use of an organo-zinc pre-catalyst where the initial pre-catalyst ligand (ethyl, C₂) is well differentiated from the reacting alkene/alkane (propylene and propene, both C₃ species). This

approach allowed for the unambiguous monitoring of the activation pathways that the pre-catalyst undergoes during catalysis. Based on this understanding, optimized synthesis of Zn/SiO₂ catalysts with improved activity and stability have been achieved by ALD.

Experimental Section

General ALD Synthesis Conditions. Silica (SiO₂, Davisil 646, 40–50 mesh, 300 m²/g (BET surface area) and 1.1 cc/g, Sigma-Aldrich) was used as substrate for the gas-phase grafting of Zn catalysts. The synthesis was performed using an ARRADIANCE Integrated ALD-Catalysis tool (model ARR-100000 GEMSTAR-CAT Dual System). A series of ALD experiments were carried out to ensure the self-limiting nature of the gas-phase deposition reaction (see details in the Supporting Information). 160 to 320 milligrams of SiO₂ was loaded into a 406 mm x 7 mm (i. d.) stainless steel, plug-flow tube reactor. Unless otherwise stated, the silica substrate for each ALD synthesis experiment was purged with N₂ (10 sccm) for 30 minutes after reactor tube installation, and subsequently heated at 200 °C for 1 h under vacuum (0.1 Torr). (Note: Silica pretreated under the given conditions is reported to have surface hydroxyl (4.9 α-OH/nm²; 2.44 mmol α-OH/g)).¹⁹⁻²¹ Diethylzinc (DEZ, >52 wt.% Zn basis, Sigma-Aldrich) as ALD precursor and, in some cases, deionized H₂O was used to protonate the organo-zinc intermediates. Reported thermal growth windows for DEZ–H₂O ALD range from 25 to 200 °C;²² The ALD experiments in this study were carried out at 100 and 175 °C (Note: The substrate temperature reported in this study is temperature reading of the thermocouple attached to the reactor chamber. The actual silica bed temperature is not measured during the ALD process). During the course of ALD synthesis, the manifold upstream of the reactor chamber (**M₁–M₃**, **UM**) was maintained at 135 °C, the valves downstream of the reactor (**LM**) at 175 °C. Both the DEZ and H₂O bottles were kept at ambient temperature during the synthesis. Each ALD precursor pulse

was carried out in a three-step sequence: (1) manifold evacuation to 1 Torr base pressure (30 s), (2) precursor pulse (10-25 ms) at 1 Torr pressure, and (3) 50 sccm N₂ purge (30 s). The progress of the deposition experiment was monitored by detection of ethane using an online residual gas mass spectrometer. (Note: The rate of DEZ delivery is estimated to be 110 mg (0.89 mmol) DEZ/Torr-s. This number is based on the consumption of 5 grams of DEZ over 45 Torr-s). ICP-AES analysis of Zn/SiO₂ samples was conducted by Galbraith Laboratories, Inc. (Knoxville, TN) to determine the zinc loading (per weight basis).

Zn_A [(60x25 ms) DEZ–(60x25 ms) H₂O; 175 °C]. One cycle deposition of ZnO was carried out using 60 consecutive 25 ms (1 Torr) pulses of DEZ followed by 60 consecutive 25 ms (1 Torr) pulses of H₂O on 160 mg SiO₂ (0.39 mmol α-OH).^{19,21} Ethane generation during the DEZ pulsing experiments indicates that saturation coverage of the SiO₂ substrate by DEZ is achieved within the first 30 pulses.

Zn_B [(30x25 ms) DEZ–(30x25 ms) H₂O; 175 °C]. One-cycle ZnO deposition was carried out using 30 consecutive 25 ms (1 Torr) pulses of DEZ followed by 30 consecutive 25 ms (1 Torr) pulses of H₂O on 160 mg SiO₂ (0.39 mmol α-OH).

Zn_C 3[(30x25 ms) DEZ–(30x25 ms) H₂O; 175 °C]. Three cycles of zinc oxide deposition were carried out on 160 mg SiO₂ (0.39 mmol α-OH) 30 consecutive 25 ms (1 Torr) DEZ pulses followed by 30 consecutive 25 ms (1 Torr).

Zn_D 10[(30x25 ms) DEZ–(30x25 ms) H₂O; 175 °C]. Ten cycles of zinc oxide deposition were carried out on 160 mg SiO₂ (0.39 mmol α-OH) 30 consecutive 25 ms (1 Torr) DEZ pulses followed by 30 consecutive 25 ms (1 Torr) H₂O.

Zn_E (30x25 ms DEZ; 175 °C). One-cycle DEZ deposition was carried out using 30 consecutive 25ms (1 Torr) pulses of DEZ on 160 mg SiO₂ (0.39 mmol α -OH).

Zn_F (30x10 ms DEZ; 175 °C). One-cycle DEZ deposition was carried out using 30 consecutive 10 ms (1 Torr) pulses of DEZ on 320 mg SiO₂ (0.78 mmol α -OH).

Zn_G (30x10 ms DEZ; 175 °C). The silica substrate for this experiment was dehydrated at 600 °C under vacuum (0.1 Torr) for 1.5 h prior to the ALD experiment. SiO₂ dehydration at 600 °C results in α -OH concentration of 1.5/nm² (0.75 mmol α -OH/g). One-cycle DEZ deposition was carried out using 30 consecutive 10ms (1 Torr) pulses of DEZ on 320 mg SiO₂ (0.24 mmol α -OH).

Zn_H (30x10 ms DEZ; 100 °C). One-cycle DEZ deposition was carried out using 30 consecutive 10 ms (1 Torr) pulses of DEZ on 320 mg SiO₂ (0.78 mmol α -OH).

Zn_{Et} , SiO₂-Zn-CH₂CH₃ Synthesis by Solution Grafting. Solution grafting of DEZ on silica was conducted inside a N₂ glove box. A 20 mL scintillation vial was charged with 500 mg SiO₂ (1.22 mmol α -OH); SiO₂ dehydrated at 200 °C prior to solution grafting).^{19,21} A 2 mL mixed hexanes solution containing 176 mg (1.42 mmol) DEZ was then added to the resulting mixture dropwise with constant stirring at room temperature. The reaction mixture was allowed to stir for three hours after the complete addition of DEZ. The resulting mixture was then filtered through a ceramic filter frit and washed three times with 5 mL portions of hexane. The residue was then dried *in vacuo* for six hours. The product was characterized by elemental analysis (%Zn and C), infrared spectroscopy, X-ray absorption spectroscopy and solid-state, multinuclear (¹H, ¹³C, ²⁹Si) magic-angle spinning NMR spectroscopy.

I-ALD-CAT *In Situ* Catalysis Studies. The *in situ* catalyst reactivity experiments were conducted immediately after each ALD catalyst synthesis by switching the I-ALD-CAT tool to “catalysis mode.” On-line GC analyses were performed using an Agilent 7890 equipped with a 6-port injection valve, a split/splitless injector and a flame ionization detector. A 60m x 0.32 mm GS GasPro capillary column was employed for the separation. GC cycle times were typically 8 minutes. In a typical test, 160 to 320 mg of catalyst generated from the *in situ* ALD synthesis was tested.

Propylene Hydrogenation. The ALD-synthesized ZnO-type catalyst candidates ($\text{Zn}_{\text{A-D}}$) and the reference catalyst Zn_{SEA} , were activated with 2.5 mol% H_2 in He (Airgas USA, LLC), purified using an oxygen trap, at 40 mL/min at 200 °C for 30 min. After the H_2 -treatment, the catalyst was fed with 10 mL/min 3.0 mol% propylene in N_2 , maintaining the initial 40 mL/min H_2 flow. Since the study aims to differentiate the activity of ZnO- and organozinc-type sites, the supported ethyl-zinc catalysts ($\text{Zn}_{\text{E-H}}$) were tested immediately after the ALD synthesis without a H_2 pretreatment step. After the ALD synthesis of the catalyst, the reactor temperature was increased to the desired temperature and was fed with 10 mL/min 3.0 mol% propylene in N_2 and 40 mL/min H_2 flow.

Propane Dehydrogenation. The reference catalyst Zn_{SEA} was heated to 200 °C for 30 minutes, maintaining a 40 mL/min flow of a 2.5 mol% H_2 feed. The reactor was then heated to 550 °C until the temperature is stable, and then fed with 2.5% propane/Ar at 10 mL/min. The supported ethyl-zinc catalyst (Zn_{F}) were tested immediately after the ALD synthesis. The reactor temperature was increased to 550 °C with a constant 40 mL/min flow of N_2 . When the temperature stabilized, the reactor was fed with 2.5% propane/Ar at 10 mL/min.

Infrared Spectroscopy. Infrared (IR) spectra were collected using a Bruker Alpha FTIR spectrometer (Bruker Optics, Billerica, MA) under DRIFTS mode. Spectra at 4 cm^{-1} resolution were obtained in absorbance mode over the $375\text{--}4000\text{ cm}^{-1}$ range. Air-sensitive samples were characterized in a glove box under a nitrogen atmosphere. All IR data were normalized, baseline-corrected, and analyzed using OPUS (v7.0, Bruker Optics, Billerica, MA) software.

Solid-state Proton Magic-Angle Spinning (^1H MAS) NMR Spectroscopy. Air-sensitive samples were packed into a 1.3 mm rotor post vacuum dry under an Argon atmosphere. $^1\text{H}/^{13}\text{C}$ Cross-Polarization (CP) and ^1H Single Pulse Magic Angle Spinning (MAS) Solid-State NMR experiments were performed at 11.7 Tesla on a Bruker Avance spectrometer, operating at Larmor frequencies of 500.13 MHz for ^1H and 125.76 MHz for ^{13}C , using a 2.5mm MAS probe. $^1\text{H}/^{13}\text{C}$ CP MAS spectrum was measured at a spinning speed of 20 kHz, with a contact time of 4 ms and a recycle delay of 2 s. The RF field strengths for ^1H - ^{13}C CP experiment were ~ 83.3 and ~ 73.5 kHz for ^1H and ^{13}C , respectively. SPINAL-64 was applied as a heteronuclear decoupling sequence. ^1H single pulse experiment was performed at a spinning speed of 20 kHz, with a $\pi/2$ pulse of $2.5\text{ }\mu\text{s}$ and a recycle delay of 2s. $^1\text{H}/^{29}\text{Si}$ Cross Polarization (CP) and ^{29}Si Single Pulse Magic Angle Spinning (MAS) Solid-State NMR experiments were performed at 7.05 Tesla on a Bruker Avance III HD spectrometer, operating at Larmor frequencies of 300.13 MHz for ^1H and 59.62 MHz for ^{29}Si , using a 3.2mm MAS probe. $^1\text{H}/^{29}\text{Si}$ CP MAS spectrum was measured at a spinning speed of 10 kHz, with a contact time of 4 ms and a recycle delay of 2 s. The RF field strengths for ^1H - ^{29}Si CP experiment were ~ 72 and ~ 42.5 kHz for ^1H and ^{29}Si , respectively. SPINAL-64 was applied as a heteronuclear decoupling sequence. ^{29}Si single pulse experiment was performed at a spinning speed of 10 kHz, with a $\pi/2$ pulse of $5\text{ }\mu\text{s}$ and a recycle delay of 30s.

In all experiments ^1H , ^{13}C and ^{29}Si chemical shifts were referenced to TMS at 0 ppm and the sample was packed into NMR rotor under an inert atmosphere in a glovebox.

X-ray Absorption Spectroscopy. X-ray absorption spectroscopic characterization (XAS) of various Zn/SiO_2 samples was conducted by Zn K-edge (9.659 keV) measurements on the bending magnet beamline of the Materials Research Collaborative Access Team (MRCAT, 10-BM) at the Advanced Photon Source (APS), Argonne National Laboratory. The Zn/SiO_2 samples were pressed into 4 mm self-supporting wafers and placed in a stainless steel holder. The air-sensitive $\text{SiO}_2\text{-Zn-CH}_2\text{CH}_3$ sample prepared by solution grafting was prepared inside a glove box under a N_2 atmosphere, and maintained under air-free conditions throughout the course of the XAS measurement. Each stainless steel holder was placed into a quartz tube (1 in. o.d., 10 in. length) reactor capped with Ultra-Torr fittings equipped with shut-off valves. Both ends of the reactor were sealed with Kapton windows. Samples that required pretreatment prior to XAS measurements were placed in reactors with an internal thermocouple directly touching the sample holder; this thermocouple provided feedback control for the clam-shell furnace used to heat the reactor. The Zn/SiO_2 samples were tested at room temperature after synthesis and under two pretreatment conditions: (1) flowing H_2/He (100 cc/min) at 200 °C, and (2) flowing $\text{H}_2/\text{propylene/He}$ (100 cc/min) at 200 °C. After sample pretreatment at 200 °C, the XAS measurements were obtained after the catalysts were cooled in He to room temperature without exposure to air. Ionization chambers were optimized at the midpoint of the Zn spectrum for the maximum current with linear response ($\sim 10^{10}$ photons detected s^{-1}) using 5% Ar in N_2 (15% absorption) in the incident X-ray detector and a mixture of $\sim 25\%$ Ar in N_2 (70% absorption) in the transmission X-ray detector. A third detector in the series simultaneously collected a Zn foil reference spectrum with each measurement for energy calibration. A cryogenically cooled

double-crystal Si(111) monochromator was used and detuned to 50% to minimize higher harmonics. The X-ray beam was 0.5 x 1.5 mm, and data were collected in transmission geometry over 10 min in step-scan mode.

The Zn K-edge XANES energy was determined from the inflection point of the leading edge by determination of the energy of the maximum in the first peak of the first derivative. Extended X-ray absorption fine structure (EXAFS) fits of the Zn/silica catalysts were determined from experimental phase shift and backscattering amplitudes using standard procedures within WINXAS 3.1 software. The EXAFS coordination parameters were obtained by least-squares fit in r-space of the first shell nearest neighbor, k^2 -weighted Fourier transform data. Zn-O phase and amplitude were obtained from a Würtzite ZnO reference (3 Zn-O bonds at 1.974 Å and 1 Zn-O bond at 1.988 Å): the k^2 -weighted Fourier transformed spectrum was reverse-transformed over the range 0.96 – 2.16 Å to select for first-shell Zn-O scattering, and the resulting phase and amplitude used to define a scattering reference for 4.0 Zn-O bonds at 1.98 Å. Zn-C phase and amplitude were obtained from ZnEt₂ (2 Zn-C bonds at 1.95 Å): the k^2 -weighted Fourier transformed spectrum was reverse-transformed over the range 0.84 – 2.04 Å, and the resulting phase and amplitude used to define a scattering reference for 2.0 Zn-C bonds at 1.95 Å. These scattering references were then used to fit Zn-O and Zn-C scattering contributions to samples of interest. Reported $\Delta\sigma^2$ values are defined as $\Delta\sigma^2 = \sigma^2(\text{sample}) - \sigma^2(\text{reference})$, where the value of $\sigma^2(\text{reference})$ is implicitly contained within the reference phase and amplitude data. A $\Delta\sigma^2$ value near zero indicates that sample and reference have similar values for the pseudo-Debye Waller factor. Absolute values of σ^2 were not determined in general; examination of selected spectra applying FEFF 6.0 calculations within the Artemis software package to experimental crystal structures suggested absolute values for σ^2 of 0.0025 for Zn-C first shell scattering in ZnEt₂ and

0.0031 for Zn-O first shell scattering in ZnO. Transfer of experimentally measured backscattering amplitudes from references to samples directly accounts for the energy-dependent variation in scattering amplitude for each scattering path, obviating the need for the S_o^2 correction factor. Examination of selected spectra within Artemis suggested an $S_o^2 = 0.80$ for both Zn-O and Zn-C.

X-ray diffraction. Crystalline phase compositions of the ALD-synthesized Zn/SiO₂ samples were determined by powder X-ray diffraction using a Bruker Diffractometer D8 Advance operating with the following parameters: Cu K α radiation of 40 mA, 40 kV, $K_\lambda = 0.15418$ nm, 2θ scanning range of 5-70°, a scan step size of 0.005° and a time of 3s per step. The samples were ground and placed on a zero background silicon holder (MTI Corp.) for analysis.

Transmission Electron Microscopy (TEM). High Resolution TEM images were obtained at the University of Illinois-Chicago's Research Resources Center facility using the JEM-3010 (a 300kV transmission electron microscope with a LaB₆ electron source). The JEM-3010 is an ultrahigh resolution analytical electron microscope with a point resolution of 0.17 nm. Each sample was dispersed in deionized water and sonicated for 20 min. A drop of the suspension was added to a holey-carbon copper grid and dried under a heat lamp for 10 min. Imaging was performed in bright field mode with an objective aperture selected to permit lattice imaging. A minimum of 100 particles were counted to get an accurate representation of the particle size distribution for each catalyst using Digital Micrograph software.

Density Functional Theory Computational Methods. First-principles calculations based on the hybrid density functional theory (B3LYP)²³ were conducted to simulate the mechanism of ethyl group activation on zinc under catalytic conditions. The catalyst surface was simulated using cluster models representing silsesquioxane cage structures. Such models have been successfully

used in our previous studies.^{4a} The structure optimizations and free energy calculations of different reaction intermediates and transition states were performed using the Gaussian-09 quantum chemistry software.²⁴ The accuracy of the transition state (TS) calculations was verified through intrinsic reaction coordinate (IRC) scans²⁵ and frequency analysis. TZVP basis sets were used to perform the calculations (B3LYP/TZVP).²⁶

Results and Discussion

Catalyst synthesis by ALD. Various zinc on silica catalysts were synthesized by ALD using diethylzinc (DEZ) as precursor and, in some cases, water in a subsequent synthesis step (Figure 4). The self-limiting nature of the gas-phase grafting technique was verified through a series of ZnO deposition experiments under surface saturating conditions. Table 1 summarizes the results of these ALD synthesis experiments on silica pre-dried at 200 °C ($4.9 \alpha\text{-OH}/\text{nm}^2$).^{19,21} In this paper, a complete zinc oxide monolayer is defined as the material generated from the reaction of one equivalent of DEZ with one equivalent of surface hydroxyl groups ($\alpha\text{-OH}$). One-cycle ZnO deposition experiments employing total DEZ doses of 0.75 Torr-s and 1.5 Torr-s on 160 mg SiO₂ (0.39 mmol $\alpha\text{-OH}$) afforded Zn_A and Zn_B (Table 1), respectively. ICP-AES analysis of Zn_A and Zn_B revealed identical zinc loadings of 10% (per weight basis; 0.29 mmol). The identical zinc loading despite the difference in total DEZ dosage employed in the ALD synthesis confirms the self-limiting nature of the zinc oxide deposition.²⁷⁻²⁹ The self-limiting deposition reaction is also supported by findings from the mass spectrometric monitoring of the reaction between silica and excess amount of DEZ at 100 °C and 175 °C (see Figures S1 to S3 in the Supporting Information).

The observed 10% Zn loading (0.29 mmol Zn) suggests that, during the first ALD half-reaction, silica surface saturation by ethyl-zinc(II) species constitutes ~75% of a theoretical

monolayer (0.39 mmol Zn). This coverage limit is attributed to steric crowding of ethyl-zinc(II) fragments on the silica surface. (Note: The 0.75 Torr-s ALD method for Zn_B is estimated to deliver ~83 mg (0.67 mmol) DEZ. The 0.29 mmol Zn on Zn_B constitutes to 43% of the total Zn pulsed. The rate of DEZ delivery is estimated to be 110 mg (0.89 mmol) DEZ/Torr-s. This number is based on the consumption of 5 grams of DEZ over 45 Torr-s). Analysis of the top and bottom regions of the Zn_B bed revealed Zn loadings of 12% and 10%, respectively, both of which are consistent with submonolayer coverage by Zn species and an ALD-type deposition mechanism. Three successive ZnO cycles gave Zn_C (Table 1) with 27% Zn. This Zn content suggests that, on the average, 19 mg (0.29 mmol) Zn is deposited per ZnO deposition cycle. This result is a demonstration of the reproducibility of the ALD synthesis method.

Scheme 1. (1) Synthesis of Zn/SiO₂ via atomic layer deposition at 175 °C. (2) Synthesis of H₃CH₂-Zn/SiO₂ (**Zn_{Et}**) via solution grafting.

Table 1. Zn/SiO₂ synthesis by atomic layer deposition.

ALD Synthesis Method	ALD Cycle(s)	Temperature (°C)	SiO ₂ (mg)	Zn (wt %)	Type of Zn species formed
Zn_A [1.5 Torr-s DEZ) + (1.5 Torr-s H ₂ O)]	1	175	160	10	Monodispersed zinc oxide sites (submonolayer)
Zn_B [(0.75 Torr-s DEZ)	1	175	160	10	

+ (0.75 Torr-s H ₂ O)]					
Zn_C [(0.75 Torr-s DEZ) + (0.75 Torr-s H ₂ O)]	3	175	160	27	film
Zn_D [(0.75 Torr-s DEZ) + (0.75 Torr-s H ₂ O)]	10	175	160	49	
Zn_E (0.75 Torr-s DEZ)	1	175	160	10	ethylzinc(II) sites
Zn_F (0.3 Torr-s DEZ)	1	175	320	2.2	
Zn_G (0.75 Torr-s DEZ)	1	175	320	4.5	
Zn_H (0.3 Torr-s DEZ)	1	100	320	3.7	

The zinc oxide-type sites generated from the ALD synthesis were characterized via diffuse-reflectance infrared Fourier-Transform spectroscopy (DRIFTS) and X-ray absorption spectroscopy (XAS), and were found to be isolated tetracoordinate Zn(II) sites on silica (**b**, Figure 4). On the other hand, since the product of the first ALD half reaction (**b**, Eq. 1 in Scheme 1) is air-sensitive and cannot be transported out of the I-ALD tool under inert-atmosphere conditions, spectroscopic characterization of ethyl-zinc on silica was carried out using the product generated from the room-temperature solution grafting of DEZ on silica (Zn_{Et}, Eq. 2, Scheme 1). Spectroscopic characterization of Zn_{Et} (*vide infra*) revealed a tricoordinate configuration for the ethyl-zinc/SiO₂ species. Detailed discussion of the spectroscopic data for both zinc species will be presented in the latter section of this paper.

Catalytic Propylene Hydrogenation Activity. The catalytic activities of the ALD-synthesized Zn/SiO₂ systems were investigated for propylene hydrogenation and propane dehydrogenation under plug-flow conditions, with the I-ALD-CAT tool in “*catalysis mode*”. Each catalyst performance evaluation was carried out immediately after the *in situ* catalyst synthesis by ALD. This feature of the I-ALD-CAT tool allows for systematic comparison of the catalytic reactivity of zinc oxide and alkyl zinc-type active sites without exposure to air and moisture during the course of the experiment. Our group recently reported a single-site Zn/SiO₂ catalyst prepared by strong electrostatic adsorption (SEA) of [Zn(NH₃)₄]²⁺ **Zn_{SEA}** that hydrogenates propylene at 200

°C with the Zn(II) sites functioning as Lewis acid centers that heterolytically activate H–H and C–H bonds under hydrogenation and dehydrogenation conditions, respectively.^{4a} Homogeneous and heterogeneous zinc materials that either catalytically or stoichiometrically hydrogenate olefins are rare.^{31-33,36} Of the few stoichiometric systems that insert an olefin into a Zn–H bond, promoter complexes of Ti or Ni are necessary.³⁶⁻³⁷ Zn/ZSM-5, on the other hand, lacks olefin hydrogenation activity since olefin polymerization by the protons in the catalyst framework is more favorable.^{4a} Similar to Zn_{SEA}, the ALD-synthesized catalysts required high hydrogenation temperatures (> 150 °C; Note: Propylene hydrogenation results presented in this section were obtained at 200 °C).^{4a} The catalysts are 100% selective to propane, with no other hydrocarbon products observed. The SiO₂ support is unreactive under the given conditions while the ALD-synthesized Zn/SiO₂ catalysts exhibit various rates of deactivation as influenced by Zn loading and SiO₂ pretreatment conditions. Interestingly, the ALD catalyst synthesis methods that involve water treatment of the ethyl zinc submonolayer on SiO₂ generate unstable, low-reactivity materials. For example, a submonolayer of monodispersed ZnO on SiO₂ (Zn_B), hydrogenates propylene but deactivates completely in the first 30 minutes of the reaction. The low activity and stability of Zn_B is attributed to the facile agglomeration of the Zn sites, forming ZnO clusters which are inactive for hydrogenation under the given conditions.³⁰⁻³⁴ This is consistent with TEM images of Zn_B which show the presence of ~20 nm ZnO particles (a, Figure 3). This mode of ZnO speciation is consistent with reported island-like nucleation of ZnO on oxide supports.³⁰ Our work shows that the formation of island-nuclei appears to occur during the *water* pulse, with the initial ethyl-zinc surface species being well-dispersed. Conformal ZnO sub-monolayer deposition cannot be completely ruled out since the observed particles may have formed upon exposure to the atmosphere prior to TEM imaging. Moreover, varying degrees of particle

formation were also observed in several spent Zn/SiO₂ catalysts (*vide infra*) further confirming the mobility of Zn(II) sites on the silica surface.

Figure 4. Hydrogenation of propylene reactivity of Zn_B, Zn_E, Zn_F, Zn_G and Zn_H at 200 °C. The apparent TOF was calculated based on the total amount of Zn present in the catalyst.

a (<20 nm)

b (3-5 nm)

Figure 3. Bright Field TEM images of Zn/SiO₂ synthesized by ALD. (a) Zn_B, (b) Zn_E (spent), (c) Zn_F (spent) and (d) Zn_G (spent).

The propylene hydrogenation activity of ethyl zinc sites on silica was also evaluated. Zn_E, with Zn loading identical to Zn_B (Table 1), is catalytically inactive at room temperature and exhibits hydrogenation activity above 150 °C. Zn_E hydrogenates propylene at 200°C (TOF_{0h} = 0.159 h⁻¹, TOF_{3h} = 0.012 h⁻¹; Fig. 4), however, it completely deactivates in ~3 h due to Zn agglomeration (3-5 nm particles; b, Figure 3). Notably, Zn_E exhibits higher initial hydrogenation activity compared to Zn_B. The observed disparity in the *initial hydrogenation activities* (t < 80 min) between these Zn/SiO₂ with identical Zn loadings (~75% of a monolayer) is attributed to differences in the precatalyst structure: One-cycle DEZ–H₂O experiment generates Zn_B with closed shell 18-electron, tetracoordinate Zn(II) centers. The higher *initial* activity of Zn_E, on the other hand, is expected for the open-shell 16-electron, tricoordinate ethyl zinc(II) sites present. These open-shell Zn(II) sites are expected to exhibit enhanced substrate binding affinity while the zinc–ethyl functionality is a reactive site that can heterolytically activate hydrogen (*vide infra*). In contrast to Zn_B, Zn_{SEA} and bulk ZnO, catalyst Zn_E *does not require high-temperature pretreatment conditions*, consistent with the higher reactivity for supported alkyl zinc species under similar conditions. Overall, the hydrogenation activity of Zn_E confirms that supported alkyl zinc species provide a convenient entry into the catalytic cycle.

The observed facile deactivation of Zn_B and Zn_E suggests that *Zn(II) isolation is the key factor to access stable catalysts*. Hence, optimization of ALD synthesis conditions (e.g. substrate preparation, DEZ dose) was conducted to increase active site dispersion and, in turn, produce catalysts with improved activity and stability. Reducing the DEZ dosing time from 0.75 Torr-s to 0.3 Torr-s and doubling the substrate loading (320 mg) afforded catalyst Zn_F (2.2% Zn; Table 1) with increased activity ($\text{TOF}_{0\text{h}} = 0.650 \text{ h}^{-1}$, $\text{TOF}_{12\text{h}} = 0.280 \text{ h}^{-1}$, Fig. 4) and longer catalyst life. Zn_F deactivates, retaining only 31% of its initial activity after a 12-hour reaction period. TEM imaging of spent catalyst Zn_F revealed the formation of smaller ZnO particles (2 nm; **c** in Figure 3), indicative of slower agglomeration and retained monodispersity of majority of the Zn(II) sites. The single-site nature of majority of the Zn sites in catalyst Zn_F post-catalysis is confirmed by EXAFS data where second-shell scattering due to sintered Zn sites were not observed.

Silica dehydration *in vacuo* at 600 °C to reduce surface hydroxyl concentration also resulted in improved organo-zinc site dispersion. A 0.75 Torr-s DEZ deposition on 320 mg SiO_2 -600 °C generates catalyst Zn_G (4.5% Zn, Table 1) with improved hydrogenation activity compares to Zn_E ($\text{TOF}_{0\text{h}} = 0.318 \text{ h}^{-1}$, $\text{TOF}_{12\text{h}} = 0.137 \text{ h}^{-1}$). Zn_G exhibits improved stability, retaining 42% of the initial activity after 12 hours of testing (Fig. 7). Post-catalysis images of Zn_G support improved Zn dispersion based on the smaller particles observed (1-2 nm; **d** in Figure 3).

The effect of the deposition temperature on catalytic reactivity was also explored. 0.3 Torr-s DEZ was grafted at 100 °C, affording Zn_H (Table 1) with 3.7% Zn (wt). The resulting material exhibits lower hydrogenation activity ($\text{TOF}_{0\text{h}} = 0.393 \text{ h}^{-1}$, $\text{TOF}_{0\text{h}} = 0.167 \text{ h}^{-1}$) relative to Zn_F (2.2% Zn), which was synthesized at 175 °C. The observed lower zinc deposition at 175 °C suggests that self-decomposition of DEZ that can lead to CVD is *not a major factor during the one-cycle Zn deposition experiments* employed in this study. An earlier report by Weimer and

coworkers suggests that DEZ-H₂O at 177 °C resulted in variations in Zn loading due to DEZ self-decomposition at high temperatures.³⁸ However, they also emphasized that self-decomposition only becomes a challenge under conditions where overexposure of DEZ to decomposing temperatures (e.g., 10 cycle DEZ-H₂O deposition or more) occurs.³⁸ The higher zinc loading (3.7%) at a lower temperature (100 °C) is attributable to higher surface hydroxyl concentration on the silica substrate resulting in the formation of catalytically inactive zinc clusters. This aspect presents the advantage of high-temperature, gas-phase organometallic grafting for the nucleation of single-atom sites over traditional liquid- and gas-phase techniques under ambient conditions; *isolated catalytic sites can be grafted under conditions that allow for thermal control of surface hydroxyl concentrations*. Reference catalyst Zn_{SEA}, with Zn loading similar to Zn_H (4% Zn), show lower activity under the given conditions (TOF_{0h} = 0.107 h⁻¹, TOF_{12h} = 0.043 h⁻¹) Note: Due to instrument design limitations, the conditions employed in the previously reported Zn_{SEA}-catalyzed hydrogenation study^{4a} cannot be implemented in the present study. Slower flow rates were employed in the catalysis experiments. The slower Zn_{SEA} hydrogenation rates reported in this study are due to a shorter contact time employed (1.3 s); This is almost half of that employed in our previous report (~2.0 s).^{4a}

Interestingly, the period where higher initial activity with catalysts Zn_{E-H} was observed (t < 80 min) coincides with active generation of C₂ and C₄ hydrocarbons, further confirming that supported alkyl zinc species provide reasonable entry into the catalytic hydrogenation cycle. Notably, systems with increased Zn dispersity (Zn_{F-G}) exhibit long-term activity (t > 12 h) with Zn_F and Zn_G exhibiting enhanced activity over time. This is an indication of the dynamic nature of these surface sites under reaction conditions, however, no definitive explanation can be offered yet for this phenomenon.

Catalytic Propane Dehydrogenation Activity. Catalytic propane dehydrogenation activity was determined at 550 °C as equilibrium conversion is reasonable (~30%), while thermal cracking contributions at this temperature are minimal.^{4a} Both zinc oxide- and ethylzinc(II)-saturated SiO₂ catalysts (Zn_B and Zn_E, respectively) are inactive for propane dehydrogenation at 550 °C. The lack of activity is attributable to Zn sintering to ZnO clusters that are known to be inactive for propane dehydrogenation.³⁹ The more dispersed ethylzinc(II) sites in Zn_F, on the other hand, selectively dehydrogenates propane (TOF_{0h} = 0.103 h⁻¹, TOF_{12h} = 0.042 h⁻¹; Fig. 5) over a 12 hour period. Since the study aims to differentiate the dehydrogenation activity of ZnO (e.g., Zn_{SEA}) and ethyl-zinc-type sites (Zn_F), catalyst Zn_F was tested for propane dehydrogenation immediately after the ALD synthesis without the pre-activation with H₂ step implemented for Zn_{SEA}. Lower selectivities for propylene (30-70 %) were observed for Zn_F in the first ~90 minutes of testing since this period coincides with the generation of ethane and ethylene from the activation of the ethyl-zinc/SiO₂ precatalyst. At t>90 min, higher selectivities to propylene (78% selectivity to propylene) were observed; however, propylene selectivity decreases to 65% by the end of the 12 hour reaction period. Under identical conditions, Zn_{SEA} exhibits lower activity (TOF_{0h} = 0.071 h⁻¹, TOF_{12h} = 0.020 h⁻¹) and propylene selectivity (Fig. 5).

Figure 5. Dehydrogenation selectivity of Zn_F (red) and Zn_{SEA} (green) to propylene. The calculated TOF was calculated based on the total amount of Zn present in the catalyst.

The dehydrogenation reaction also produces ethylene, methane and butane, which are products of competing C–C bond activation pathways. The Zn/SiO₂ catalyst dehydrogenation selectivity originates from the preference of these Lewis acidic centers for primarily activating C–H bonds over C–C bonds.^{4a} The observed catalyst selectivity for C–H bond activation is consistent with the greater propensity of Zn(II) propyl species to undergo β–hydrogen elimination over β–methyl elimination. The energy of activation for the former pathway (C–H bond activation) is ~10 kcal lower than the energy barrier for the latter process (C–C bond scission).^{4a,40} The activation of catalyst Zn_F can proceed through protonation of the zinc-ethyl functionality by adjacent surface hydroxyls, producing ethane and a three-coordinate Zn(II) active site – the proposed active site in Zn_{SEA}.

Infrared Spectroscopy. Figure 9 shows the infrared spectra of the Zn/SiO₂ catalysts prepared by ALD and solution grafting methods. One-cycle ZnO deposition on SiO₂ affords materials (e.g., Zn_B) that exhibit infrared spectral features identical to that of the silica substrate.⁴¹ The spectra of

SiO₂ and Zn_B show strong, broad absorptions at 3700 cm⁻¹ to 2900 cm⁻¹ (Si–OH stretching), 1650 cm⁻¹ (H₂O adsorbed by siliceous materials), and 1250 cm⁻¹ (Si–O bond stretching). The deposition of three and ten cycles of ZnO produces Zn_C and Zn_D (10 ZnO cycles; 0.75s DEZ–0.75s H₂O) that exhibit shifted Si–O absorption in the 1200 cm⁻¹ region. Zn_C, Zn_D and bulk ZnO exhibit weak O–H stretching bands (3700 cm⁻¹ to 2900 cm⁻¹),⁴² potentially indicative of lower O–H concentration. On the other hand, the spectrum of Zn_{Et} (solution grafting) shows strong absorption at 2900 cm⁻¹ which is attributable to C(sp³)–H bond stretching, confirming the presence of zinc-bound ethyl functionality after the solution-phase grafting.

Figure 6. Infrared spectra of SiO₂ (red), Zn_A (blue), Zn_C (green), Zn_D (purple), bulk ZnO (brown) and Zn_{Et} (orange).

Multinuclear (¹H, ¹³C, ²⁹Si) Solid-state MAS NMR Spectroscopy. Figure 10a shows the solid-state ¹H MAS NMR spectra of the Zn_{Et}, Zn_B and non-metalated silica substrate. The upfield chemical shift at 0.31 ppm for Zn_{Et} is indicative of zinc-bound methylene protons (Zn–CH₂) based on reported solution-phase ¹H-NMR spectral data for DEZ with the Zn–CH₂–CH₃ chemical shift at 0.30 ppm.⁴³ The Zn–CH₂ chemical shift overlaps with a broad signal ranging from 3 to -1 ppm, and with peak at 0.79 ppm. This broad peak could arise from the terminal methyl protons

of Zn-CH₂-CH₃, Si-OH, Si-OCH₂CH₃ and Si-CH₂CH₃ groups.⁴⁴ The absence of SiCH₂CH₃ groups in Zn_{Et} is further confirmed by direct-pulse ²⁹Si and cross-polarization ¹H-²⁹Si MAS NMR experiments where only chemical shifts in the -100 to -115 ppm range, corresponding to tetrahedral Si centers typically observed in mesoporous silica materials, were observed (Figure 7b). ¹³C MAS NMR experiments on Zn_{Et} (Figure 7c) shows only two chemical shifts occurring at 0.7 (Zn-CH₂) and 10 ppm (ZnCH₂CH₃), confirming the presence of zinc-bound ethyl groups. The absence of downfield ¹³C chemical shifts expected for silyl ethers and upfield signals for silanes (e.g., SiCH₂CH₃) is indicative of the absence of Si-O-CH₂CH₃ and SiCH₂CH₃ groups.

One-cycle DEZ deposition under surface-saturating conditions (0.75 Torr-s) followed by water treatment affords Zn_B (10% Zn, w/w). Zn_B shows a major proton chemical shift at 7 to 2 ppm (silica O-H functionalities, Fig. 7a). Interestingly, the broad chemical shifts from 0.8 to 0 ppm were observed at a lower intensity, indicating that the intense chemical shifts in the Zn_{Et} spectrum could be mainly due to zinc-bound ethyl groups that can undergo protonolysis upon water treatment. Elemental analysis of Zn_{Et} revealed 10.5% Zn loading (0.16 mmol) and 3.5 wt% C (0.29 mmol). The corresponding molar composition translates to a 1.1 : 1.0 Zn-to-ethyl group ratio. Under the assumption that no unreacted DEZ is present in Zn_{Et}, this ratio indicates that 91% of all Zn sites have metal-bound ethyl groups, while the remaining 9% underwent complete protonolysis of the two Zn-C bonds to form ZnO-type centers.

Figure 7. (a) Solid-state ^1H MAS NMR spectra of ZnEt (green), ZnB (red), and SiO_2 (blue); (b) ^{29}Si direct pulse and $^1\text{H}/^{29}\text{Si}$ cross polarization MAS NMR spectrum of ZnEt ; and (c) ^{13}C MAS NMR spectrum of ZnEt .

X-ray Absorption Spectroscopy (XAS) and Powder X-ray Diffraction (PXRD). X-ray absorption spectroscopy (XAS) was employed to elucidate the zinc oxidation state and coordination environment in the Zn/SiO₂ systems. The X-ray absorption near edge spectra (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) are considered separately. XANES is sensitive to both coordination number (CN) and the electronegativities of the nearest neighbors around Zn(II): absorption edge energies shift to higher energies with larger CN, greater nearest neighbor electronegativity, and higher formal oxidation state of the absorbing atom, while post-edge features (EXAFS) provide an additional structural fingerprint. EXAFS provides information about the number of, and distance to, near neighbors of the scattering atom.

XAS characterization of Zn_{Et} (DEZ solution grafting) and Zn_B (one-cycle ZnO deposition) was carried out to elucidate the nature of the Zn sites generated from the two ALD half reactions: (1) DEZ grafting and (2) the subsequent H₂O treatment step. The latter is discussed first. The XANES spectrum of Zn_B closely resembles that of a single site Zn²⁺/SiO₂ catalyst previously reported by our group (Zn_{SEA}), suggesting similar coordination environments around Zn in both materials (Figure 8). The edge energies for these materials are 9.6644 keV and 9.6646 keV respectively, slightly greater than the 9.6637 keV edge energy of the Wurtzite ZnO standard and consistent with four-coordinate, divalent Zn. However, the relative intensities of the first two absorption maxima above the edge in Zn_{SEA} and Zn_B differ from those of ZnO, supporting the conclusion that the Zn in these samples is not located in Wurtzite-structured domains. While precise assignment of XANES absorption features is in general not possible without high level electronic structure theory calculations, the absorption spectrum of ZnO roughly mirrors the conduction band density of states in this well-studied semiconductor, while the pair of absorption maxima for Zn_{SEA} and Zn_B can reasonably be assigned to Zn 4p-derived

states of A_1 (p_z) and E (p_x, p_y) symmetry for single site $\text{Zn}(\text{OSi})_2(\text{HOSi})_2$ centers of approximate C_{2v} symmetry.^{4a}

As in ZnO , zinc in DEZ is also formally divalent. However, the lower electronegativity of carbon vs. oxygen and the two-coordinate linear geometry in DEZ give rise to significant differences between their XANES spectra. In particular, the edge energy of 9.6618 keV is closer to that of Zn metal foil (9.6608 keV) than to that of ZnO . However, the maximum absorption in the DEZ spectrum at 9.6625 keV makes DEZ readily distinguishable from Zn metal, which lacks this feature. In DEZ, the strong absorption at the XANES edge is a result of the allowed photoexcitation of a Zn 1s electron into the two unoccupied, nonbonding Zn 4p orbitals provided by the linear coordination geometry. The third Zn 4p orbital in DEZ is of $\sigma^*(\text{Zn-C})$ character and its energy is well above the ionization energy for the Zn 1s electron; the resulting short lifetime of this state gives rise to a broad, low intensity feature near 9.675 keV.

The value of the edge energy for Zn_{Et} (9.6624 keV) is intermediate between that of ZnO (9.6637 keV) and DEZ (9.6618 keV), consistent with a bonding environment intermediate between these references. The first absorption maximum above the edge is of lower intensity than that of DEZ and more comparable to that of ZnO , suggesting smaller contribution from nonbonding Zn 4p orbitals and therefore a coordination number greater than 2. This interpretation is supported by a fit to the EXAFS region of Zn_{Et} , which yields $\text{CN} \approx 3$. While the edge energy of 9.6624 keV is lower than that of ZnO , it is greater than that of DEZ and remains consistent with Zn in the 2+ oxidation state. (A more detailed investigation into the effects of coordination number, ligand electronegativity, and ligand-metal bond character in main group organometallic compounds has recently been completed by our group and will be reported separately.)

Table 2. Summary of XAS data for Zn/SiO₂ species and reference compounds.

Treatment	Edge Energy, keV	N _{Zn-O/C}	R, Å	$\Delta\sigma^2$ (x10 ³)	E0, eV
ZnO Standard	9.6637	4.0	1.98	0.0	-0.1
DEZ Standard	9.6618	2.0	1.95	0.0	0.3
H ₃ CH ₂ C–Zn/SiO ₂ (Zn _{Et})	9.6624	2.9	1.95	5.9	1.1
ZnO (1 cy)/ SiO ₂ (Zn _B)	9.6644	3.9	1.97	2.3	-2.0
Zn(NH ₃) ⁺² /SiO ₂ Calcined 300°C (Zn _{SEA})	9.6646	3.8	1.98	2.5	0.2

Figure 9 shows the extended X-ray absorption fine structure (EXAFS) spectra recorded for Zn_{Et} and Zn_B, and the Zn(II) standards DEZ and ZnO. DEZ is monomeric both in solution⁴⁵ and in the solid phase,⁴⁶ with the two-coordinate Zn center exhibiting an average Zn–C bond distance of 1.95 Å. DEZ exhibits a relatively small first shell Zn–C scattering centered near 1.4 Å (phase-uncorrected distance) and no meaningful higher shell scattering. Bulk zinc oxide, on the other hand, adopts the Würtzite structure with each four-coordinate Zn(II) center surrounded by four oxygen atoms in a nearly tetrahedral environment (average Zn–O bond distance of 1.98 Å).^{4a,47} ZnO exhibits a more intense first shell scattering centered near 1.5 Å (phase uncorrected distance). The observed greater intensity of the first shell scattering peak for ZnO compared to DEZ results from differences in (1) Zn coordination numbers (ZnO = 4; DEZ = 2) and (2) intrinsic scattering amplitude of the zinc-bound atoms (O scattering > C scattering).

Figure 8. XANES spectra of DEZ, Zn foil, Zn_{Et}, Zn_B, and bulk ZnO.

Figure 9. EXAFS spectra of DEZ, Zn_{Et}, Zn_B and ZnO.

The first shell scattering peak intensity for Zn_{Et} is consistent with tri-coordinate Zn(II) centers; each 16-electron Zn center is bound to two O atoms and one C atom (average bond distance of 1.95 Å). No significant higher shell scattering was observed for Zn_{Et} , confirming the uniformity of ethyl zinc(II) species on silica. Zn_{B} , on the other hand, exhibits first shell scattering with amplitude almost equal to that of ZnO , consistent with the presence of 18-electron, four-coordinate Zn(II) sites with a 1.97 Å average Zn–O bond distance.^{4a} Zn_{B} exhibits a very weak second-shell scattering peak and no significant higher shell scattering, indicative of isolated ZnO species. In addition, the XAS spectrum of Zn_{B} resembles that of the single-site Zn (II) on silica catalyst that we reported earlier, prepared via strong electrostatic adsorption of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ on silica followed by calcination (Zn_{SEA} , Table 2). The $\Delta\sigma^2$ values for Zn_{B} and Zn_{SEA} are somewhat greater than zero (i.e. somewhat greater than those of ZnO), consistent with the greater diversity of Zn–O–Si geometries likely to exist on the surface of amorphous silica vs. the crystallographically well-defined Zn–O–Zn environment in ZnO . The unusually large $\Delta\sigma^2$ value for Zn_{Et} may also reflect differences between Zn–O and Zn–C bond lengths; however, attempts to fit Zn–O and Zn–C contributions separately in a single scattering shell lead to mathematically overspecified fits with no unique solutions.^{4a} Furthermore, ZnO as isolated species in Zn_{B} is also supported, albeit inconclusively, by the absence of higher nuclearity crystalline phases based on PXRD characterization (Figure S8 in the Supporting Information (SI)). The PXRD spectrum of Zn_{B} resembles that of the amorphous SiO_2 support.

Figure 10. EXAFS spectra of bulk ZnO, Zn_B (1 cycle ZnO/SiO₂) and Zn_D (10 cycles ZnO/SiO₂).

The EXAFS spectrum of Zn_D (10-cycle deposition of ZnO) features stronger scattering near 3.0 Å and hints of higher shell peaks near 4.0 Å and 5.5 Å (Figure 10). These higher shell scattering peaks are indicative of higher nuclearity Zn assemblies (e.g., clusters, particles) with structural features similar to bulk ZnO.^{47,48} Interestingly, the first shell scattering peak is much weaker in Zn_D, with an average coordination number of 2.7 and bond distance of 1.96 Å. The lower apparent Zn-O coordination number is attributable to the presence of interstitial metallic zinc, also detected by PXRD analysis (Figure S7b in SI). PXRD analysis of Zn_C (3 ZnO cycles/SiO₂) and Zn_D (10 ZnO cycles/SiO₂) revealed the presence of Zn(0) based on the peaks at $2\theta=36.3^\circ$, 39.0° , 43.2° and 54.3° .

Mechanism of Zn–CH₂CH₃ Activation. Since the active sites in catalysts Zn_{E-G} contain ethyl zinc functionalities, the transformations of the ethyl group can be unambiguously monitored, as the incoming substrate (propylene) and hydrogenation product (propane) are both C₃-

hydrocarbons. Gas chromatographic monitoring of the C₂ (ethane and ethene) and C₄ (butane) hydrocarbon generated under reaction conditions suggests multiple ethyl-zinc activation pathways. In order to understand the mechanisms of ethyl-zinc activation, Density Functional Theory (DFT) calculations were performed (Figure 11). Two contributing non-redox pathways are predicted for the observed rapid generation of ethane, which include (1) protonation of the zinc-bound ethyl groups (**2-TS**) by adjacent surface hydroxyls with an intrinsic energy barrier of 35.9 kcal/mol, and (2) direct hydrogenolysis of the Zn–Et bond by molecular hydrogen (**3-TS**) with an intrinsic energy barrier of 57.5 kcal/mol, suggesting that pathway 2 is relatively less favorable. The proposed ethane-generating zinc-ethyl activation pathways are considered *productive organometallic transformations* as they both generate Zn(II) species that are proposed key intermediates in the catalytic cycle. Protonation of the zinc-carbon bond by adjacent surface hydroxyls forms a three-coordinate 16e[−] Zn(II) center (**2**) which is the same active site proposed to be responsible for propane dehydrogenation activity of Zn_{SEA}.^{4a} Zn–Et bond hydrogenolysis, on the other hand, generates ethane and a 16e[−] Zn(II) hydride (**3**), which was proposed to be a key intermediate in the hydrogenation of propylene by Zn_{SEA}.^{4a}

Figure 11. Different activation mechanisms of Zn-CH₂CH₃ to form C₂ and C₄ hydrocarbons predicted by DFT calculations. The intrinsic activation energy (E_a, kcal/mol) associated with each step is shown.

The slower generation of ethylene under reaction conditions is consistent with the resistance of zinc alkyl species to β-hydrogen elimination (Figure 4; **4-TS**, E_a = 50.9 kcal/mol). In

addition to ethylene, this pathway also generates a three-coordinate $16e^-$ Zn(II) hydride (**3**). Butane formation, on the other hand, presumably proceeds via non-reductive route; ethylene generated *in situ* can insert into a Zn–CH₂CH₃ group (Figure 14; **5-TS**, E_a (calc) = 56.5 kcal/mol), followed by protonation of the resulting zinc-bound butyl group. Activation of the catalyst Zn_E generates ethane, ethylene and butane in a 13:2:1 ratio within the first 20 minutes of exposure to hydrogen and propylene at 200 °C (Figure 12). The observed selectivity to ethane, ethylene and butane is consistent with the calculated activation energies at 200 °C for the non-redox ethyl zinc activation pathways discussed above i.e., E_{a2-TS} (alkyl protonation) > E_{a4-TS} (alkyl protonation) > lcE_{a5-TS} (ethylene insertion).

Alternatively, butane formation could proceed through homolytic activation of the ethyl-zinc groups, generating ethyl radicals than can eventually recombine to produce butane, and lower oxidation state zinc species such as metallic zinc. Interestingly, hydrogen activation of the ALD-synthesized catalysts with improved active site dispersion (Zn_F and Zn_G) gives ethane as the main activation product. This supports the hypothesis that higher ethyl zinc loading favors the formation of neighboring zinc alkyl sites that are prone to reductive decomposition and zinc agglomeration.

Figure 12. Plot of $\text{H}_3\text{CH}_2\text{C-Zn}$ activation selectivity to ethane (green), ethylene (red), butane (blue).

Summary and Conclusions

Controlled gas-phase grafting of zinc oxide and organo zinc active sites on high-surface-area silica was achieved using an integrated atomic layer deposition-catalysis (I-ALD-CAT) tool. This approach has provided key insights into the mechanism of zinc grafting on silica supports at the monolayer level, and the reactivity and stability of these Zn sites as a function of dispersion. The I-ALD tool design allowed for the systematic reactivity comparison of different ALD-grafted zinc sites; *in situ* catalysis experiments confirmed much higher reactivity for the open shell 16-electron, tri-coordinate ethyl zinc-silica sites compared to 18-electron, tetra-coordinate zinc oxide-type centers. However, silica surface saturation with Zn(II) sites (~75% of a monolayer) results in facile zinc agglomeration and catalyst deactivation under catalysis conditions. Improved active site dispersion was achieved through reduced DEZ dosing and substrate pretreatment (e.g., dehydration under vacuum), producing Zn/SiO_2 catalysts that are active and stable under propylene hydrogenation (200°C) and propane dehydrogenation (550°C) conditions.

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