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**Author(s):** Yim, Jihong; Haimi, Eero; Mäntymäki, Miia; Kärkäs, Ville; Bes, René; Gutierrez, Aitor Arandia; Meinander, Kristoffer; Brüner, Philipp; Grehl, Thomas; Gell, Lars; Viinikainen, Tiia; Honkala, Karoliina; Huotari, Simo; Karinen, Reetta; Putkonen, Matti; Puurunen, Riikka L.

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# Atomic Layer Deposition of Zinc Oxide on Mesoporous Zirconia Using Zinc(II) Acetylacetonate and Air

Jihong Yim, Eero Haimi, Miia Mäntymäki, Ville Kärkäs, René Bes, Aitor Arandia Gutierrez, Kristoffer Meinander, Philipp Brüner, Thomas Grehl, Lars Gell, Tiia Viinikainen, Karoliina Honkala, Simo Huotari, Reetta Karinen, Matti Putkonen, and Riiikka L. Puurunen\*



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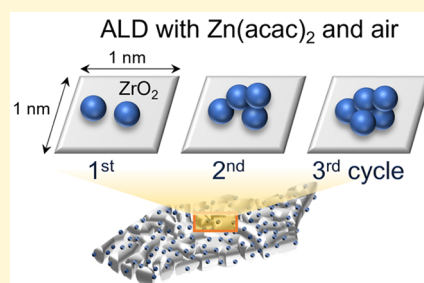


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**ABSTRACT:** The self-terminating chemistry of atomic layer deposition (ALD) ideally enables the growth of homogeneously distributed materials on the atomic scale. This study investigates the ALD of zinc oxide (ZnO) on mesoporous zirconium oxide (ZrO<sub>2</sub>) using zinc acetylacetonate [Zn(acac)<sub>2</sub>] and synthetic air in a fixed-bed powder ALD reactor. A broad variety of methods, including thermogravimetry analysis, scanning electron microscopy with energy-dispersive X-ray spectroscopy, low-energy ion scattering, X-ray absorption near-edge structure, X-ray photoelectron spectroscopy, in-situ diffuse reflectance infrared Fourier transform spectroscopy–mass spectrometry, and density functional theory calculations, were used to analyze the reactant and the resulting samples. The factors affecting the zinc loading (wt %) on ZrO<sub>2</sub> were investigated by varying the ALD reaction temperature (160–240 °C), the calcination temperature of zirconium oxide (400–1000 °C), and the ALD cycle number (up to three). The studied process showed self-terminating behavior with the areal number density of zinc of approximately two atoms per square nanometer per cycle. Zinc was distributed throughout ZrO<sub>2</sub>. After the Zn(acac)<sub>2</sub> reaction, acac ligands were removed using synthetic air at 500 °C. In the following cycles, already-deposited ZnO acted as nuclei for further ZnO growth. This study demonstrates the potential of Zn(acac)<sub>2</sub> as an ALD reactant and provides an initial understanding of ZnO growth via ALD on high surface area porous particles as an example for catalytic applications.



## 1. INTRODUCTION

The self-terminating chemistry of the atomic layer deposition (ALD) process enables the synthesis of well-defined surface structures. Theoretically, ALD can be used to obtain conformal coatings on high surface area materials, such as porous powders.<sup>1–4</sup> The amount of material deposited can be controlled at an atomic scale by repeating the number of ALD cycles.<sup>5</sup> However, conformality of the ALD process is not self-guaranteed, especially for coatings in high aspect ratio (HAR) features.<sup>1,6–10</sup> Higher exposure is required to saturate the surface of high surface area porous supports compared to coating planar substrates.<sup>6–8,10–16</sup> Various experimental and modeling approaches have been developed to investigate the effect of process parameters on the conformality of ALD with HAR features.<sup>1,6,7,9,10,12,15,17–22</sup> A recent simulation study reported that growth per cycle (GPC) and molar mass of reactant, in addition to the exposure (exposure = partial pressure × reactant pulse time), influence the penetration depth of the ALD coating in a microchannel.<sup>10</sup>

Preparation of heterogeneous catalysts via ALD has attracted increasing global interest, as evident from recent review articles.<sup>23–29</sup> However, the use of ALD for catalysis is not new. ALD has been independently invented two times: as “molecular layering” (ML) in the 1960s by Aleskovskii and

Koltsov<sup>30,31</sup> and as “atomic layer epitaxy” (ALE) in 1974 by Suntola.<sup>32,33</sup> Suntola received the Millennium Technology Prize for his invention in 2018.<sup>5</sup> Researchers in both pioneering ALD development branches experimented with catalyst preparation; however, this history has not been well documented in recent review articles. While an exhaustive review of ALD is beyond the scope of this study, the scientific community should be aware of its history. The following paragraph highlights some of the early studies and better-known, more recent studies on ALD-made catalysts.

ALD-made catalysts have been studied in the past 50 years for various applications. Lakomaa et al.<sup>34</sup> summarized the Suntola-related early history of ALE-made catalysts in a book chapter in 2013.<sup>31,35</sup> In the first ALE experiment on porous particles in the late 1980s, elemental zinc was vaporized at 400 °C to react on Zeolite Socony Mobil-5 (ZSM-5).<sup>34</sup> In the following research study, over 40 metal reactants were tested,

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and scale-up demonstrated up to a 17 kg scale in a circulating fluidized bed for silica–alumina catalysts.<sup>34</sup> Suntola and collaborators patented the apparatus for preparing a heterogeneous catalyst via ALE<sup>36,37</sup> and published reports on, for example, how to control the metal loading via ALE,<sup>4</sup> preparation of nickel-on-alumina catalysts for toluene hydrogenation,<sup>38,39</sup> and preparation of chromia-on-silica catalysts for alkene polymerization.<sup>40</sup> Early studies on ML made catalysts include invention reports on silica modification via sequential adsorption of CrO<sub>2</sub>Cl<sub>2</sub> and PCl<sub>3</sub> vapors and water to make catalysts, for example, for dehydrogenation and dehydrocyclization,<sup>41</sup> and VOCl<sub>3</sub> and water to make V<sub>2</sub>O<sub>5</sub> catalysts for the oxidation of benzol to maleic anhydride.<sup>42</sup> Pioneering investigations on ML (sometimes called “molecular deposition”)-made catalysts were also performed by Damyanov and co-workers.<sup>35,43</sup> More recent studies on catalyst preparation via ALD are as follows: the overcoating of Al<sub>2</sub>O<sub>3</sub> on palladium nanoparticles via ALD to prevent coking and sintering during the oxidative dehydrogenation of ethane into ethene;<sup>44</sup> addition of Ni nanoparticles on high surface area alumina via ALD to improve hydrogenolysis selectivity compared to that of catalysts made via incipient wetness impregnation method;<sup>45</sup> modification of zeolites, such as ZSM-5,<sup>46,47</sup> and the Pt–SiO<sub>2</sub> interface<sup>48</sup> via ZnO ALD for catalytic applications such as dehydrogenation of propane to propene<sup>47,48</sup> and methanol to aromatics;<sup>46</sup> the modification of V<sub>2</sub>O<sub>5</sub> via phosphorus ALD to improve selectivity for oxidation of *n*-butane to maleic anhydride;<sup>49</sup> and the synthesis of TiO<sub>2</sub> on  $\gamma$ -alumina to prepare high surface area titania catalyst supports for hydroprocessing.<sup>50</sup> Recently, Ingale et al.<sup>51</sup> used an extension of ALD, molecular layer deposition, to grow alucone on Ni/SiO<sub>2</sub> catalysts to prevent their deactivation during methane dry reforming. Copper-based catalysts have also been modified via ALD ZrO<sub>2</sub>,<sup>52</sup> Ni,<sup>53</sup> and ZnO<sup>54,55</sup> to enhance their catalytic activity and selectivity for the hydrogenation of carbon dioxide to methanol. The well-defined surface structure of ALD-made catalysts provides a better understanding of the relationship between the catalytic performance and structural properties of the ALD-made catalysts.<sup>26,27,45,52–58</sup>

ZnO is a functional material that can be used in various applications, including optical sensors, solar cells, transparent conductive layers, and heterogeneous catalysts.<sup>13,48,59–62</sup> Interestingly, in the works by Suntola and co-workers on ALD-made catalysts, zinc was the first element whose growth on ZSM-5 was attempted via ALD.<sup>34</sup> ZnO can be coated via ALD mostly using diethylzinc (DEZ) and water owing to the good reactivity and high vapor pressure of DEZ.<sup>13,14,47,62</sup> However, DEZ is pyrophoric and environmentally hazardous.<sup>63</sup> Additionally, a study reported the decomposition of DEZ at a temperature above 80 °C.<sup>14</sup> Other ALD reactants and oxygen sources, such as Zn and water,<sup>64</sup> Zn and O<sub>2</sub>,<sup>65</sup> zinc acetate [Zn(OAc)<sub>2</sub>] and water,<sup>66–68</sup> dimethylzinc [Zn(CH<sub>3</sub>)<sub>2</sub>] and water,<sup>46,69,70</sup> zinc chloride (ZnCl<sub>2</sub>) and water,<sup>71</sup> ZnCl<sub>2</sub> and O<sub>2</sub>,<sup>65,72,73</sup> and DEZ and O<sub>2</sub> plasma,<sup>74</sup> have been reported for ZnO ALD.

To the best of our knowledge, zinc acetylacetonate [Zn(acac)<sub>2</sub>] has not been reported as a zinc source in experimental ALD studies, although it has been suggested in a computational study.<sup>75</sup> Zn(acac)<sub>2</sub> is nontoxic and stable in air, has a relatively low vapor pressure compared to DEZ, and exists as a solid at normal temperature and pressure.<sup>14,76</sup> In a recent study, Zn(acac)<sub>2</sub> was used as a preferential chemical vapor deposition reactant to promote the Cu/Al<sub>2</sub>O<sub>3</sub> catalyst for hydrogenation

of carbon dioxide to methanol.<sup>58</sup> In another study, a ZnO film was grown via CVD using Zn(acac)<sub>2</sub> and O<sub>3</sub>.<sup>77</sup> A recent study by Arandia et al.,<sup>55</sup> related to the current study, reported the beneficial effect of adding ZnO after copper impregnation on catalytic performance for hydrogenation of carbon dioxide to methanol. The study by Arandia et al.<sup>55</sup> used Zn(acac)<sub>2</sub> and synthetic air to deposit ZnO via ALD, which is explored in more detail in this study.

This study aimed to demonstrate the potential of Zn(acac)<sub>2</sub> as an ALD reactant, especially for modifying the surface of mesoporous supports. Mesoporous zirconium oxide (ZrO<sub>2</sub>) supports were treated with Zn(acac)<sub>2</sub> in a fixed-bed powder ALD reactor. The suitability of Zn(acac)<sub>2</sub> as an ALD reactant was investigated via thermogravimetric (TG) analysis, and the saturating nature of the Zn(acac)<sub>2</sub> reaction under our reaction conditions was also investigated. Additionally, the effects of the ALD reaction temperature, calcination temperature, and number of ALD cycles on zinc loading were also investigated. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectrometry (EDS), inductively coupled plasma–optical emission spectrometry (ICP-OES), carbon content analysis, in-situ diffuse reflectance infrared Fourier transform spectroscopy–mass spectrometry (DRIFTS-MS), DFT calculations, X-ray absorption near-edge structure (XANES) analysis, X-ray photoelectron spectroscopy (XPS), and low-energy ion scattering (LEIS) were used to obtain information on the deposited zinc and surface species.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** A mesoporous monoclinic zirconium oxide powder (ZrO<sub>2</sub>, Saint-Gobain, 99.0%, grinded and sieved particle size of 250–420  $\mu$ m) was used as a support for ALD. ZrO<sub>2</sub> was calcined in synthetic air (99.999%, Oy AGA Ab) typically at 600 °C for 5 h at a heating rate of 5 °C/min. To study the effect of the calcination temperature on zinc loading, ZrO<sub>2</sub> was calcined at various temperatures of 400, 600, 800, and 1000 °C.

Zn(acac)<sub>2</sub> (Voltec, 99.99%) and synthetic air (99.999%, Oy AGA Ab) were used as the ALD reactants. Acetylacetone (Hacac, 2,4-pentanedione, Merck, >99%) was used to prepare Hacac bound to ZrO<sub>2</sub> (sample labeled Hacac/ZrO<sub>2</sub>) for comparative purposes. Nitrogen (N<sub>2</sub>) generated from air (<10 ppm of oxygen) using a Parker HPN2-5000 high-purity nitrogen generator was used as carrier and purge gases.

**2.2. Nitrogen Physisorption.** The physical properties of ZrO<sub>2</sub> calcined at different temperatures and samples prepared with different ALD cycles were analyzed via nitrogen physisorption (77 K, liquid nitrogen) using a Thermo Scientific SURFER. Before measurements, around 200 mg of the sample was degassed at 180 °C for 2 h. The quantity of adsorbed nitrogen was given under the standard temperature and pressure conditions (STP). From the physisorption isotherm (Figure S1a), the specific surface area and Barrett–Joyner–Halenda (BJH) pore size distribution (Figure S1b) were calculated using the Brunauer–Emmett–Teller (BET) method<sup>78</sup> and the BJH method,<sup>79</sup> respectively. The specific surface area, total pore volume, and median pore diameter of calcined ZrO<sub>2</sub> are given in Table 1.

**2.3. Thermal Analysis of the Zn(acac)<sub>2</sub> Reactant.** The TG analysis of Zn(acac)<sub>2</sub> was performed by using a Netzsch STA 449F3 Jupiter simultaneous thermal analyzer. Zn(acac)<sub>2</sub> was heated in a flowing nitrogen atmosphere (40 mL/min) at ambient pressure from room temperature to 600 °C. The heating rate was 10 °C/min. The mass of the sample in the 90  $\mu$ L pan was approximately 10 mg. Samples were measured with and without a lid. Using a lid with a small orifice slows down the evaporation of the sample, thus making any decomposition more visible in the resulting TG curve.

**2.4. Chemisorption of Zn(acac)<sub>2</sub> on ZrO<sub>2</sub>.** The reaction of Zn(acac)<sub>2</sub> with mesoporous ZrO<sub>2</sub>, typically at 200 °C, was performed

**Table 1. BET Surface Area, Cumulative Pore Volume, and Median Pore Diameter of ZrO<sub>2</sub> Calcined at Varied Temperatures Analyzed Using N<sub>2</sub> Physisorption Measurements**

calcination temp (°C)	BET surf. area (m <sup>2</sup> g <sup>-1</sup> )	total pore vol (cm <sup>3</sup> g <sup>-1</sup> )	median pore diam (nm)
400	99.2	0.34	9.8
600	53.5	0.26	16.6
800	28.6	0.19	26.0
1000	14.5	0.033	8.0

in a flow-type ALD reactor (F-120, ASM Microchemistry Ltd., Finland) equipped with a powder chamber (Figure S2). Typically, after preheating ZrO<sub>2</sub> with N<sub>2</sub> at 250 °C for 10 h in the reactor, 2 g of calcined ZrO<sub>2</sub> was used as a support. Typically, 1.9 mmol of Zn(acac)<sub>2</sub> per gram of ZrO<sub>2</sub> was sublimed at 120 °C and ca. 5 mbar, and the reactant vapor was carried by N<sub>2</sub> (the 100 sccm of inlet N<sub>2</sub> flow was divided into six different inlet tubes within the reactor). To ensure the saturation of the reaction with ZrO<sub>2</sub>, a sufficient pulse time of 3 h was used with different dose of Zn(acac)<sub>2</sub> [0.2, 0.5, 1.0, and 1.9 mmol Zn(acac)<sub>2</sub> per gram of ZrO<sub>2</sub> by placing 0.0625, 0.125, 0.25, and 0.5 g of Zn(acac)<sub>2</sub> per gram of ZrO<sub>2</sub> into the reactor, respectively]. Leftover reactants and byproducts were purged for 2 h, followed by cooling in N<sub>2</sub> at approximately room temperature. After the reaction, sampling was performed twice by tilting the powder bed. (Samples a and b were mostly collected from the top and bottom parts of the powder bed, respectively.) For the samples prepared with 1.0 mmol of Zn(acac)<sub>2</sub> per gram of ZrO<sub>2</sub>, the experiment was repeated five times (an average sample was taken after mixing the powder and denoted by "Repeat"). To study the effect of ALD temperature on zinc loading on ZrO<sub>2</sub>, the deposition temperature was varied as follows: 160, 180, 200, 220, and 240 °C. To study the effect of the calcination temperature of ZrO<sub>2</sub> on zinc loading, the ZrO<sub>2</sub> powder calcined at various temperatures was used as a support. Herein, one full reaction cycle includes the reaction of Zn(acac)<sub>2</sub> with ZrO<sub>2</sub>, followed by purging for 2 h with N<sub>2</sub> in the ALD reactor and the removal of acetylacetonate (acac) ligands via oxidative treatment at 500 °C for 2 h (5 K/min) in a tube furnace in synthetic air (100 mL/min) (Figure S3). The zinc loading on ZrO<sub>2</sub> was controlled by repeating the number of reaction cycles up to three. These samples with two or three ALD cycles were prepared from the same batch. For a comparison, a Hacac/ZrO<sub>2</sub> sample was prepared via ALD. Hacac was evaporated at 55 °C and reacted with ZrO<sub>2</sub> at 200 °C for 3 h in the reactor followed by purging for 2 h and cooling to room temperature in N<sub>2</sub>.

**2.5. Characterization.** The zinc loading on the sample was analyzed via ICP-OES. Approximately 100 mg of the sample weighed in a Teflon vessel was dissolved in a mixture of nitric acid (HNO<sub>3</sub>, 65%, 2.5 mL) and hydrochloric acid (HCl, 37%, 7.5 mL) by heating it at 200 °C for 1 h in a microwave oven (Milestone, Ethos) and cooling it to room temperature. The dissolved sample was diluted by using Milli-Q-grade water. The zinc loading on the sample was determined using an F-AAS instrument (Varian 220 F) with an air-acetylene burner.

The zinc distribution within several ZrO<sub>2</sub> particles was analyzed via cross-sectional SEM-EDS. The sample, which was stored in ambient air, was vacuum-impregnated in epoxy resin, and its cross section was revealed by manual target polishing. The polished sample was carbon-coated using a LEICA EM SCD050 to prevent charging under the electron beam. SEM-EDS was performed using a Tescan Mira3 SEM fitted with a Thermo Scientific EDS. The EDS line scan was measured at an accelerating voltage of 15 keV. Irrespective of variation in particle cutting planes, similar results were attained. One representative image was selected to be discussed further in this work.

The crystalline phase of ZrO<sub>2</sub> calcined at an elevated temperature of 1000 °C was analyzed via powder X-ray diffraction (XRD) using a PANalytical X'Pert Pro MPD Alpha 1 device with Cu K $\alpha$  radiation.

A X-ray scanning range from 5 to 100° (2 $\theta$ ), a step size of 0.026°, and a time per step of 99.45 s were applied.

The carbon content of the Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> and nonmodified ZrO<sub>2</sub> reference was determined using a FlashSmart elemental analyzer. The sample was weighed in a tin container and introduced into the combustion reactor using a MAS Plus Autosampler with 250 mL/min of oxygen. After combustion up to 950 °C the evolved gases were carried by 140 mL/min of a helium flow to a copper-filled layer, swept through a gas chromatography column that separated the combustion gases, and finally detected using a thermal conductivity detector.

XANES spectra were acquired using the laboratory-scale XANES instrument Hel-XAS at the University of Helsinki Center for X-ray Spectroscopy.<sup>80</sup> Briefly, the instrument is based on a spherically bent Ge(555) crystal monochromator using Johann geometry with a curvature radius (Rowland circle diameter) of 0.5 m. The X-ray source was a water-cooled X-ray tube (XRD Eigenmann), and the detector was a silicon drift diode (Amptek X-123SDD). Approximately 10 mg of each powder sample was mixed with a buffer material (starch) to make 2 mm thick pellets for transmission XANES.

The surface composition of the samples was studied via XPS using a Kratos AXIS Ultra DLD spectrometer with a monochromated Al K $\alpha$  X-ray source (1486.7 eV). The base pressure of the system was typically below 1 × 10<sup>-9</sup> Torr. During measurements the source was run at a power of 100 W, and photoelectrons were collected at a 90° takeoff angle, with a pass energy of 80 eV and a step size of 1.0 eV for survey spectra and a pass energy of 20 eV and a step size of 0.1 eV for high-resolution spectra. All spectra were charge-corrected relative to the position of the C–C bonding of adventitious carbon at 284.8 eV. The homogeneity of the samples was confirmed by collecting spectra from three separate spots on the surface of each sample, and results from all three spots were used to calculate average values for elemental concentrations.

LEIS measurements were used to analyze the elemental composition of the first atomic layer of the sample. The measurements were performed at IONTOF GmbH (Münster, Germany) by using a Qtac100 LEIS spectrometer. The instrument is equipped with a double toroidal electrostatic analyzer simultaneously optimized for maximum sensitivity and high mass resolution. The analysis ion beam hits the sample surface at normal incidence, and all ions scattered at a 145° angle are transmitted to the energy analyzer. The samples were compacted into flat pellets for introduction into the vacuum system of the instrument. Before LEIS analysis, the samples were cleaned by exposure to atomic oxygen extracted from oxygen plasma. This cleaning procedure removes all atmospheric contaminants and completely oxidizes the surface of the sample. <sup>4</sup>He<sup>+</sup> and <sup>20</sup>Ne<sup>+</sup> primary ions were used for the analysis, with a 2 × 2 mm<sup>2</sup> analysis field of view. The analysis ion dose density was limited to 5 × 10<sup>13</sup> and 1 × 10<sup>13</sup> ions/cm<sup>2</sup> for He and Ne ions, respectively. This ensures that the analysis stays below the static limit; that is, the top atomic layer is not significantly altered by ion beam damage during analysis.

## 2.6. Temperature-Controlled Oxidation of Acac Ligands.

The oxidation of the acac ligands remaining on Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> samples prepared at ALD temperatures of 200 and 240 °C was observed via in-situ DRIFTS-MS. DRIFTS was measured by using a Nicolet Nexus FTIR spectrometer and a high-temperature Spectra-Tech reactor chamber with a deuterated triglycine sulfate detector. The DRIFTS setup was coupled with a mass spectrometer (OmniStar GSD 301 by Pfeiffer Vacuum) with a faraday cup detector. 100 scans were collected in the wavenumber of ranging from 4000 to 600 cm<sup>-1</sup> at a scan resolution of 4 cm<sup>-1</sup>. Before the experiment, a background spectrum was measured using an aluminum mirror (scan resolution of 4 cm<sup>-1</sup>, 200 scans) under an Ar flow (99.999%, Woikoski). The DRIFT spectra of Hacac/ZrO<sub>2</sub>, ZrO<sub>2</sub>, and Zn(acac)<sub>2</sub> were measured as references. The DRIFT spectrum of the Zn(acac)<sub>2</sub> reference was measured at 30 °C with 50 mL/min Ar (99.999%, Woikoski). Zn(acac)<sub>2</sub>/ZrO<sub>2</sub>, ZrO<sub>2</sub>, and Hacac/ZrO<sub>2</sub> references were placed in an in-situ cell and heated from 30 to 180 °C for 2 h with 50 mL/min of Ar (99.999%, Woikoski) and at a heating step of 15 °C (Figure S5). The heating process was followed by cooling to 30 °C with Ar. DRIFT spectra were recorded at 30 and 180 °C (0, 60, and 115 min)

and after cooling. Next, the oxidative removal of acac ligands from the  $\text{Zn}(\text{acac})_2/\text{ZrO}_2$  sample was performed by heating the sample up to 500 °C (heating in steps of 5 °C) in synthetic air (25 mL/min synthetic air mixed with 25 mL/min Ar) and keeping the sample at 500 °C for 30 min. The oxidation step was followed by cooling to 30 °C in 50 mL/min of Ar. DRIFT spectra were recorded every 25 °C during heating, at 500 °C, and at 500 °C after 30 min. The DRIFT spectra were obtained as % reflectance and converted to Kubelka–Munk units using the following equation:<sup>81</sup>

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s} \quad (1)$$

where  $R$  is the diffuse reflectance,  $k$  is the absorption coefficient of the sample, and  $s$  is the scattering coefficient.<sup>81</sup>

**2.7. Areal Number Density Calculation.** The areal number density of metal  $c_M$  ( $\text{nm}^{-2}$ ) represents how many metal atoms (herein, zinc) are deposited per unit surface area,<sup>5</sup> obtained as follows (eq 25 in ref 82):

$$c_M = \frac{w_M N_A m_t}{M_M S m_s} \quad (2)$$

Here,  $W_M$  is the metal weight fraction (–),  $N_A$  is Avogadro's number ( $\text{mol}^{-1}$ ),  $M_M$  ( $\text{g}_{\text{metal}} \text{mol}^{-1}$ ) is the molar mass of metal  $M$ ,  $S$  ( $\text{m}^2 \text{g}_{\text{support}}^{-1}$ ) is the specific surface area of the support,  $m_t$  ( $\text{g}_{\text{sample}}$ ) is the total mass of the sample including the amount of the deposited material, and  $m_s$  ( $\text{g}_{\text{support}}$ ) is the mass of the original support. This calculation assumes that the mass of  $\text{ZnO}$  is added to the sample after the  $\text{Zn}(\text{acac})_2$  reaction without affecting the total surface area of the sample ( $\text{m}^2$ ). (After each ALD cycle, the specific surface area expressed as  $\text{m}^2/\text{g}$  decreases because of the mass gain.<sup>82</sup>) The mass of oxygen deposited on the sample was determined assuming a 1:1 stoichiometry of  $\text{MO}$  ( $M = \text{Zn}$ ). Note that areal number density counts all metal atoms added via ALD, and it does not reveal how individual species are arranged (e.g., how many metal atoms are on the outermost surface).<sup>5</sup>

The GPC expressed as the areal number density of metal  $\Delta c_M$  ( $\text{nm}^{-2}$ ) can be calculated from the GPC in thickness increment  $\Delta h$  (nm) as follows (eq 12 in ref 83):

$$\Delta h = \frac{M}{\rho N_A} \Delta c_M \quad (3)$$

Here,  $\rho$  ( $\text{g m}^{-3}$ ) is the mass density of the  $\text{MZ}_x$  material, and  $M$  ( $\text{g mol}^{-1}$ ) is the molar mass of one unit of  $\text{MZ}_x$ .

For an average bulk monolayer of the  $\text{MZ}_x$  material,<sup>5</sup> the areal number density of metal can be obtained as follows (eq 16 in ref 83):

$$\bar{c}_M^{\text{ml}} = \left( \frac{\rho N_A}{M} \right)^{2/3} \quad (4)$$

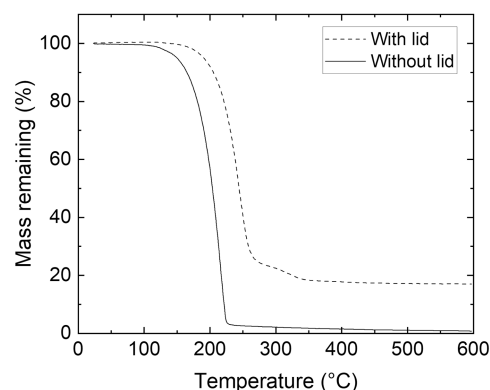
**2.8. Computational Methods.** DFT calculations were performed using the projector-augmented wave (PAW)<sup>84</sup> formalism as implemented in the grid-based PAW (GPAW) package.<sup>85</sup> The Bayesian error estimation functional (BEEF)–vdW exchange–correlation functional<sup>86</sup> was assumed, and the core electrons of all elements were described by PAW setups in the frozen-core approximation. A maximum spacing of 0.20 Å was used for the real-space grid basis, and the reciprocal space was sampled at  $2 \times 2 \times 1$  k-points for structure optimization and at  $16 \times 16 \times 1$  k-points for IR frequency calculations. We applied a Hubbard  $U$  correction<sup>87,88</sup> of 2.0 eV to the d-orbitals of zirconium atoms. Geometry optimizations were performed using the Fast Inertial Relaxation Engine algorithm as implemented in the Atomic Simulation Environment.<sup>89,90</sup> IR frequencies were calculated using the Frederiksen method.<sup>91</sup>

A monoclinic  $\text{ZrO}_2$  (–111) surface was modeled with a  $1 \times 1 \times 2$  unit cell and periodic boundary conditions in  $x$  and  $y$  directions together with a 6 Å vacuum on the top and bottom of the surface. The computational cell measures  $6.9 \times 7.4 \times 25.9 \text{ Å}^3$  with angles of  $90^\circ \times 90^\circ \times 116.5^\circ$ , resulting in a surface area of  $0.455 \text{ nm}^2$ . During geometry optimization, the two bottom layers of the  $\text{ZrO}_2$  slab were

kept frozen in its initial bulk geometry while all other atoms were allowed to relax until the maximum residual force was reduced below  $0.005 \text{ eV Å}^{-1}$ . To understand the impact of  $\text{ZnO}$  ALD on the structure and IR spectrum of the  $\text{ZrO}_2$  surface, a monoclinic  $\text{ZrO}_2$  (–111) surface covered with adsorbed water was compared to a surface with  $\text{ZnO}$  and adsorbed water. One  $\text{ZnO}$  per computational unit cell was considered, which corresponds to an experimentally measured areal number density of  $\text{ZnO}$  of  $2.2 \text{ nm}^{-2}$  after one ALD cycle. We also considered two distinct water concentrations on the surface: (a) two water molecules per unit cell (areal number density  $4.4 \text{ OH/nm}^2$ ) and (b) three water molecules per unit cell (areal number density  $6.6 \text{ OH/nm}^2$ ).

### 3. RESULTS

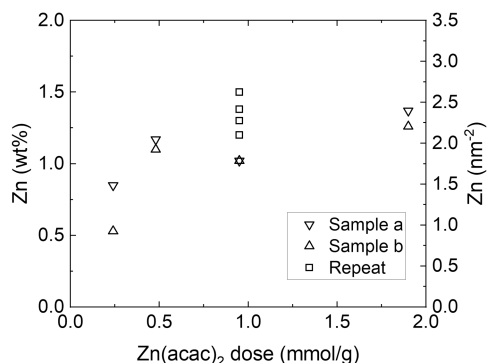
**3.1. Thermal Analysis of  $\text{Zn}(\text{acac})_2$ .** The behavior of the  $\text{Zn}(\text{acac})_2$  reactant during heating was observed via TG analysis. The sample was measured without and with a lid on the top of the sample at atmospheric pressure under a  $\text{N}_2$  flow. The lid with a small orifice made any decomposition more visible. Figure 1 shows the  $\text{Zn}(\text{acac})_2$  mass remaining versus



**Figure 1.** TG analysis of  $\text{Zn}(\text{acac})_2$  under a  $\text{N}_2$  flow (40 mL/min) at ambient pressure from room temperature to 600 °C. The heating rate was 10 °C/min. The sample was heated without (solid line) and with a lid (dashed line).

temperature [differential scanning calorimetry (DSG) and derivative thermogravimetric (DTG) curves were depicted in Figure S4]. The  $\text{Zn}(\text{acac})_2$  reactant evaporated with only a small residue until about 200–220 °C when heated without a lid (solid line, Figure 1). When the reactant was heated with a lid, some decomposition was observed above 275 °C (dashed line, Figure 1). Therefore, the highest deposition temperature was limited below 250 °C. Based on the weight loss onset observed, a sublimation temperature of 120 °C was selected for ALD experiments.

**3.2. Chemisorption of  $\text{Zn}(\text{acac})_2$  on  $\text{ZrO}_2$ .** To investigate the  $\text{ZrO}_2$  surface saturation with the  $\text{Zn}(\text{acac})_2$  reaction, the amount of the  $\text{Zn}(\text{acac})_2$  reactant sublimed per gram of  $\text{ZrO}_2$  was varied. Figure 2 shows the zinc loading (wt %) and zinc areal number density ( $\text{nm}^{-2}$ ) versus the amount of  $\text{Zn}(\text{acac})_2$  sublimed. Samples a and b were collected mostly from the top and bottom parts of the bed, respectively. With a low amount of  $\text{Zn}(\text{acac})_2$ , the zinc loading on sample b is significantly lower than that on sample a, indicating that the reactant dose is not sufficient to saturate the surface throughout the powder bed. When the amount of  $\text{Zn}(\text{acac})_2$  increases, the zinc loading on  $\text{ZrO}_2$  settles to an almost constant value of ca.  $2.2 \text{ nm}^{-2}$ . Concurrently, the zinc loading from sample b is close to that of sample a. These results



**Figure 2.** ICP-OES analysis of the zinc loading on  $\text{ZrO}_2$  as a function of the  $\text{Zn}(\text{acac})_2$  dose. An ALD temperature of  $200\text{ }^\circ\text{C}$  was used. The areal number density of zinc ( $\text{nm}^{-2}$ ) was calculated by using a specific surface area of calcined  $\text{ZrO}_2$  of  $53.5\text{ m}^2\text{ g}^{-1}$ .

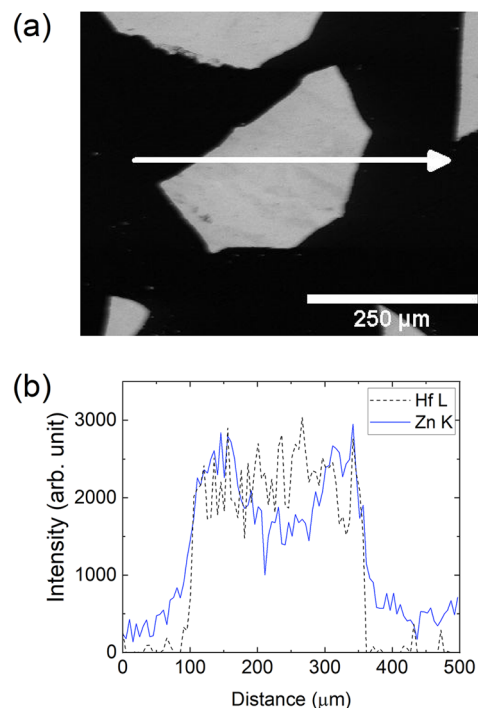
indicate that the reaction of  $\text{Zn}(\text{acac})_2$  on  $\text{ZrO}_2$  is a self-terminating process<sup>1</sup> that can be used in an ALD process under our reaction conditions.

The  $\text{Zn}(\text{acac})_2$  process under conditions typically used in this study [ $1.0\text{ mmol}$  of  $\text{Zn}(\text{acac})_2$  per gram of  $\text{ZrO}_2$ , ALD temperature =  $200\text{ }^\circ\text{C}$ ] was tested five times to investigate the repeatability among different ALD runs. For most of these samples, sampling was performed once (marked as “Repeat” in Figure 2). Different runs showed somewhat different zinc loadings (average of six observations =  $1.2\text{ wt } \%$ , standard deviation =  $0.19\text{ wt } \%$ , relative standard deviation =  $15.8\%$ ). Small differences in the surface area of  $\text{ZrO}_2$  calcined in different batches and uncertainty in ICP-OES measurement (relative standard deviation  $<5\%$ ) are likely the sources for the difference in zinc loadings.

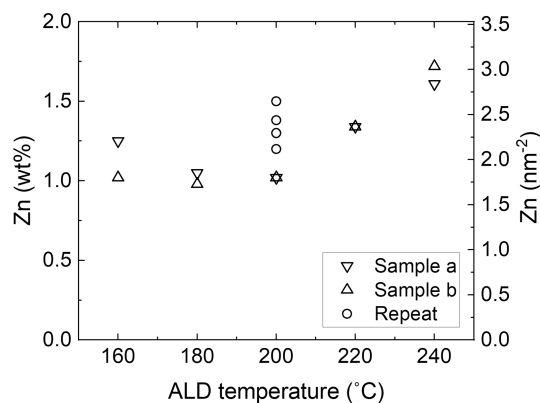
**3.3. Distribution of Zinc within a  $\text{ZrO}_2$  Particle.** The presence of Zn within several  $\text{ZrO}_2$  particles was observed via EDS analysis. Figure 3a illustrates the position of the EDS line scan on top of the backscattered electron image of a particle, and Figure 3b shows the X-ray intensities of Zn and Hf along the line scan. Hf is an evenly distributed impurity in  $\text{ZrO}_2$ , and it serves as a reference. The measured X-ray intensities are proportional to the concentrations of Zn and Hf, respectively. Therefore, Zn was present throughout the  $\text{ZrO}_2$  particle. However, less Zn is present in the central part of the particle compared to that on the outermost surface.

**3.4. Effect of ALD Temperature and Calcination Temperature on Zinc Loading.** The effect of the ALD temperature on the zinc loading was investigated. Figure 4 shows the zinc loading versus ALD temperature ( $160\text{--}240\text{ }^\circ\text{C}$ ). [The data marked as “Repeat” is already discussed in Subsection 3.2, and the spread was discussed there.] The zinc loading is almost constant up to an ALD temperature of  $200\text{ }^\circ\text{C}$ . Above  $200\text{ }^\circ\text{C}$ , a slight increase in zinc loading is observed with an increase in the ALD temperature.

To investigate the effect of the support calcination temperature on zinc loading, the ALD reaction at  $200\text{ }^\circ\text{C}$  was performed on  $\text{ZrO}_2$  calcined at various temperatures from  $400$  to  $1000\text{ }^\circ\text{C}$ . Figure 5 shows the zinc loading and specific surface area of  $\text{ZrO}_2$  versus the calcination temperature. Both the zinc loading and the specific surface area of  $\text{ZrO}_2$  decrease with an increase in  $\text{ZrO}_2$  calcination temperature. Interestingly, the zinc areal number density ( $\text{nm}^{-2}$ ) is almost constant as ca.  $2\text{ nm}^{-2}$  with an increase in the calcination temperature. After



**Figure 3.** Zinc distribution in a  $\text{Zn}(\text{acac})_2/\text{ZrO}_2$  sample [ $1.0\text{ mmol}$  of  $\text{Zn}(\text{acac})_2$  per gram of  $\text{ZrO}_2$ ] analyzed via SEM-EDS. (a) Backscattered electron image showing the location of EDS line scan. (b) EDS line scans showing the intensity of zinc relative to that of hafnium in  $\text{ZrO}_2$ .

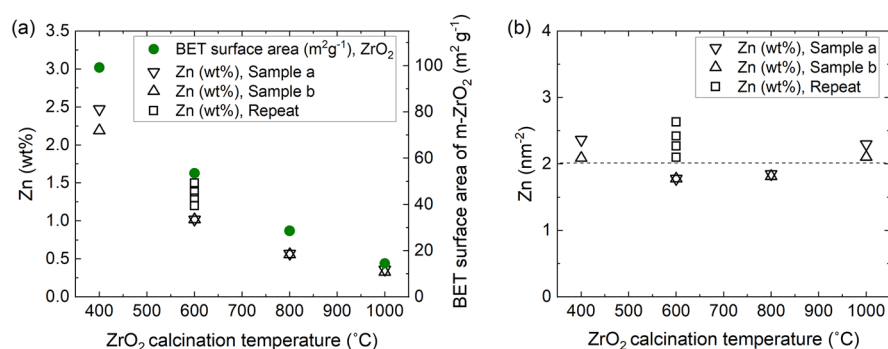


**Figure 4.** Zinc loading on the  $\text{Zn}(\text{acac})_2/\text{ZrO}_2$  samples vs ALD temperatures. The areal number density of zinc ( $\text{nm}^{-2}$ ) was calculated by using the BET surface area of  $\text{ZrO}_2$  ( $53.5\text{ m}^2\text{ g}^{-1}$ ) calcined at  $600\text{ }^\circ\text{C}$ . A  $\text{Zn}(\text{acac})_2$  dose of  $1.0\text{ mmol}$  per gram of  $\text{ZrO}_2$  was used.

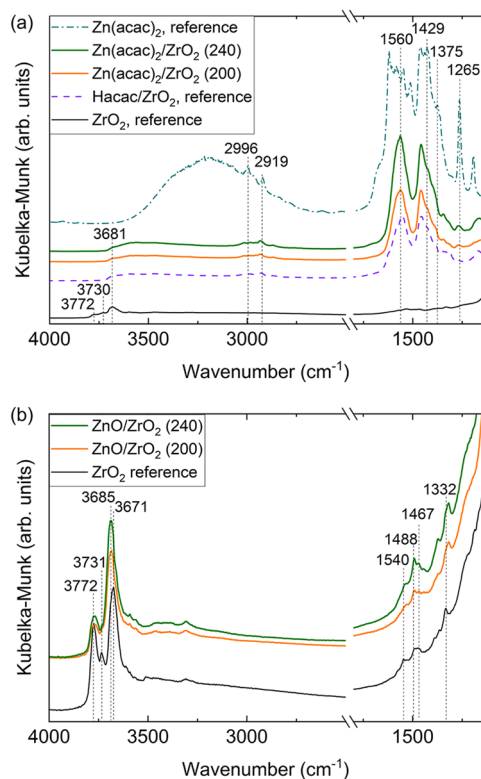
calcination at  $1000\text{ }^\circ\text{C}$ , the crystalline phase of  $\text{ZrO}_2$  is still monoclinic, as observed via XRD (Figure S9).

**3.5. Temperature-Controlled Oxidation of Acac Ligands.** After the chemisorption of  $\text{Zn}(\text{acac})_2$  on  $\text{ZrO}_2$  (the first step in the ALD cycle<sup>5</sup>), some acac ligands were attached on the sample surface. These remaining ligands were removed before the next ALD cycle, via thermal oxidation. The surface species after the  $\text{Zn}(\text{acac})_2$  reaction with  $\text{ZrO}_2$  and the removal of remaining ligands via thermal oxidation in synthetic air were investigated via in-situ DRIFTS-MS.

Figure 6 shows the in-situ DRIFT spectra of  $\text{Zn}(\text{acac})_2/\text{ZrO}_2$  prepared at  $200$  and  $240\text{ }^\circ\text{C}$  and those for  $\text{Zn}(\text{acac})_2$ ,  $\text{Hacac}/\text{ZrO}_2$ , and bare  $\text{ZrO}_2$  for comparison. Before oxidative



**Figure 5.** Zinc loading on Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> as a function of the ZrO<sub>2</sub> calcination temperature. The Zn(acac)<sub>2</sub> reaction temperature was 200 °C. (a) Specific surface area of ZrO<sub>2</sub> and zinc loading versus calcination temperature. (b) Areal number density of zinc (nm<sup>-2</sup>) versus calcination temperature. A Zn(acac)<sub>2</sub> dose of 1.0 mmol per gram of ZrO<sub>2</sub> was used, unless stated otherwise.



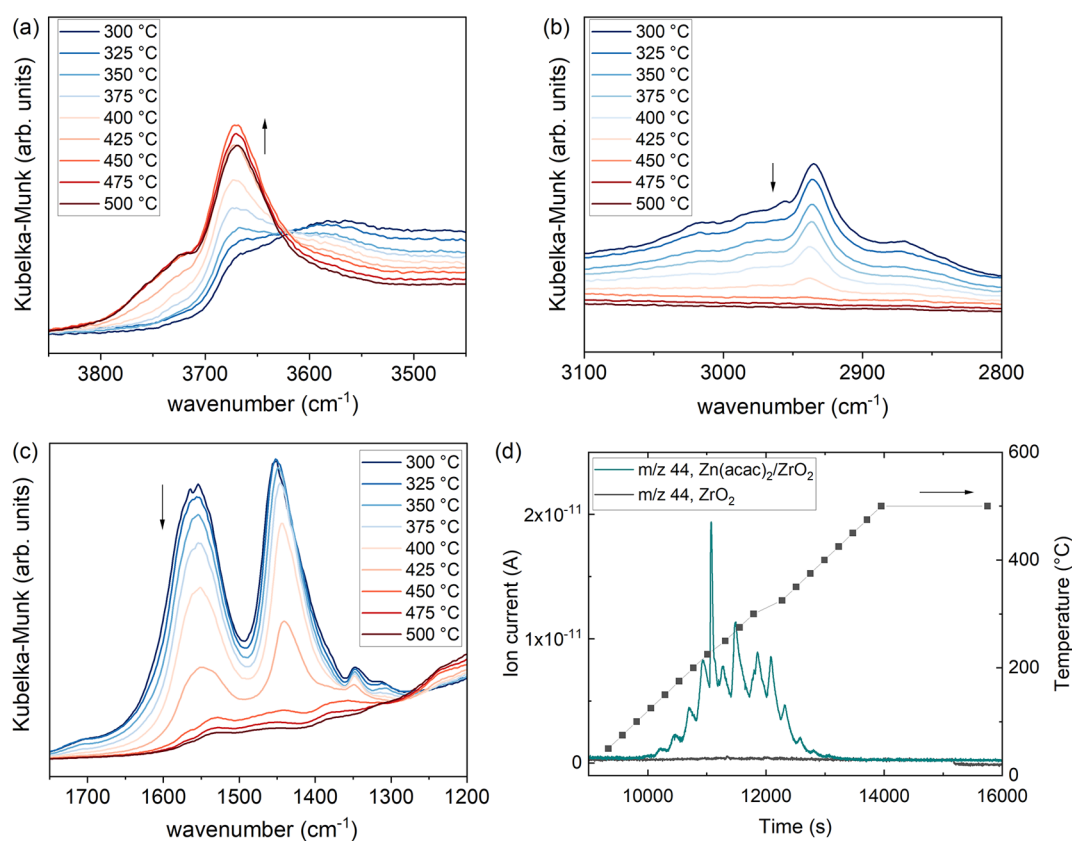
**Figure 6.** DRIFT spectra of Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> samples prepared at different ALD temperatures (ALD temperature in parentheses) (a) before and (b) after oxidative removal of acac ligands at 500 °C in synthetic air followed by cooling to 30 °C with Ar. The spectra of bare ZrO<sub>2</sub>, Hacac/ZrO<sub>2</sub>, and Zn(acac)<sub>2</sub> reactant are shown as a reference in (a).

removal of acac ligands, DRIFT spectra were measured at 30 °C in the presence of Ar and after the pretreatment at 180 °C with Ar. The DRIFT spectrum of bare ZrO<sub>2</sub> exhibits three bands at 3772, 3730, and 3681 cm<sup>-1</sup>, corresponding to different kinds of  $\nu(\text{OH})$  (terminal, bridged, and tribridged hydroxyl groups, respectively).<sup>92,93</sup> After Zn(acac)<sub>2</sub> reactions with ZrO<sub>2</sub> at different temperatures, the first two bands at 3772 and 3730 cm<sup>-1</sup> disappear. The DRIFT spectra of Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> and Hacac/ZrO<sub>2</sub> exhibit a broad band at 3550–3500 cm<sup>-1</sup>, which can be assigned to hydrogen-bonded hydroxyl group.<sup>92,94,95</sup> This broad band was not observed in the DRIFT spectrum of ZrO<sub>2</sub>.

The Zn(acac)<sub>2</sub> and Hacac/ZrO<sub>2</sub> reference DRIFT spectra exhibit bands at ca. 3000–2910, 1560, 1429, 1375, and 1265 cm<sup>-1</sup>. The bands at ca. 3000–2910 cm<sup>-1</sup> can be assigned to  $\nu(\text{C-H})$  of methyl groups.<sup>38</sup> The bands at ca. 1560, 1375, and 1265 cm<sup>-1</sup> can be assigned to  $\nu_s(\text{C=O})$ ,  $\nu_{as}(\text{C=O})$ , and  $\nu_s(\text{C=C})$  from acac ligands, respectively.<sup>94,96,97</sup> The band at 1429 cm<sup>-1</sup> is mostly from  $\delta(\text{C-H})$  from acac ligands.<sup>96</sup> Similar bands, especially in the fingerprint region, are observed in the DRIFT spectra of the Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> samples, indicating the presence of acac ligands in prepared samples. The DRIFT spectrum of the sample prepared at the ALD temperature of 240 °C is similar to that of the sample prepared at the ALD temperature of 200 °C with higher peak intensities near 1560 and 1429 cm<sup>-1</sup>.

The carbon content of the Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> sample was determined after the Zn(acac)<sub>2</sub> reaction with ZrO<sub>2</sub> at 200 °C. The carbon content in the Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> sample was 0.96 wt %. For comparison, the carbon content measured for the nonmodified ZrO<sub>2</sub> reference was almost negligible as 0.12 wt %. The areal number density of the acac ligand was calculated from the measured carbon content and specific surface area of 53.5 m<sup>2</sup> g<sup>-1</sup>. Around 1.8 nm<sup>-2</sup> of the acac ligand was bound to the Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> sample.

Figure 7 shows the DRIFT spectrum of Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> prepared at 200 °C during oxidative removal of the remaining acac ligands in synthetic air at an elevated temperature. Figure 7a shows a band at about 3670 cm<sup>-1</sup>, which can be attributed to  $\nu(\text{OH})$ . In Figures 7b and 7c, bands at ca. 2950, 1700, 1550, and 1450 cm<sup>-1</sup> can be attributed to  $\nu(\text{C-H})$  of the methyl group, combined  $\nu(\text{C=C})$  and  $\nu(\text{C=O})$  of the conjugated chelate ring, and  $\delta(\text{C-H})$ , respectively.<sup>94,98</sup> The intensity of these peaks decreases with an increase in temperature, indicating the removal of acac ligands. A broad band (3550–3500 cm<sup>-1</sup>) in the DRIFT spectra measured at 300 °C can be from strongly hydrogen-bonded OH groups, and the intensity of this band decreases with an increase in temperature.<sup>92,94,99</sup> During oxidation of remaining acac ligands, the intensity of the band at 3670 cm<sup>-1</sup> increases with increasing oxidation temperature up to 500 °C, as shown in Figure 7a, indicating the formation of new surface hydroxyl groups.<sup>56</sup> MS analysis supports the results of DRIFTS. Figure 7 shows the oxidation product monitored via MS against the treatment time and temperature. The signal for the mass/charge ratio of  $m/z = 44$ , which is most likely from CO<sub>2</sub>, is observed from below 100 °C, and the intensity increases at approximately 250 °C. The signal intensity decreases to almost 0 at around 450 °C, suggesting



**Figure 7.** In-situ DRIFT spectra (a–c) of  $\text{Zn}(\text{acac})_2$ -modified  $\text{ZrO}_2$  at 200 °C during the oxidation of acac ligands from 300 to 500 °C in synthetic air (the arrow indicates the direction of increasing temperature). (d) Mass spectra of  $\text{Zn}(\text{acac})_2$ -modified  $\text{ZrO}_2$  and pure  $\text{ZrO}_2$  during the same treatment as (a–c).

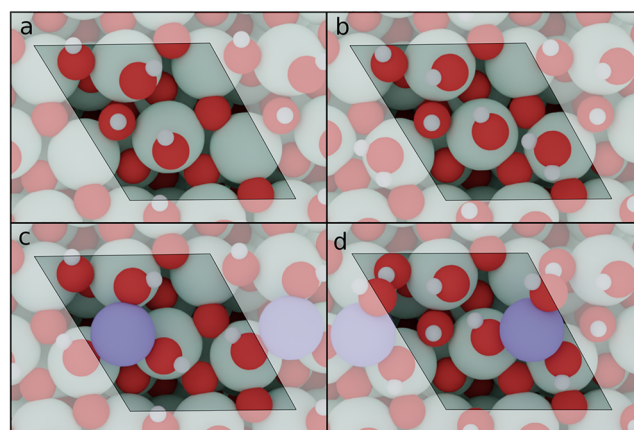
that all acac ligands on the samples are removed above this temperature. The mass spectrum of the  $\text{ZrO}_2$  reference was also recorded while heating, and no signal for  $m/z = 44$  was observed.

After the thermal oxidation of acac ligands in synthetic air, the samples were cooled to 30 °C with Ar. Figure 6b exhibits in-situ DRIFT spectra of samples prepared at different ALD temperatures (200 and 240 °C) and calcined  $\text{ZrO}_2$  as a reference after the cooling process. The DRIFT spectrum of  $\text{ZrO}_2$  exhibits bands at 3772, 3731, and 3671  $\text{cm}^{-1}$ , which can be attributed to terminal, bibridged, and tribridged  $\nu(\text{OH})$ , respectively.<sup>92,93</sup> When  $\text{ZnO}$  is deposited on  $\text{ZrO}_2$ , the intensity of the bands at 3772 and 3731  $\text{cm}^{-1}$  decreases, indicating that  $\text{Zn}(\text{acac})_2$  reacts with some of the terminal and bibridged hydroxyl groups on  $\text{ZrO}_2$ . In the DRIFT spectrum of  $\text{ZnO}/\text{ZrO}_2$ , a peak shift is observed from 3671 to 3685  $\text{cm}^{-1}$ , compared to those of  $\text{ZrO}_2$ , while the peak intensity is almost similar. Small bands are observed in the region of ca. 1330–1550  $\text{cm}^{-1}$ . These bands correspond to bidentate (1540 and 1330  $\text{cm}^{-1}$ ) and monodentate (1488  $\text{cm}^{-1}$ ) carbonate and bicarbonate (1467  $\text{cm}^{-1}$ ) species.<sup>100</sup> These species may be formed by  $\text{CO}_2$  produced during the decomposition of acac ligands; however, these bands are also observed in the DRIFT spectrum of bare  $\text{ZrO}_2$ .

After each reaction of  $\text{Zn}(\text{acac})_2$  with the support in the ALD reactor, the sample was calcined in a tube furnace to remove acac ligands and stored in a desiccator before the next reaction. The DRIFT spectrum of the calcined  $\text{ZnO}/\text{ZrO}_2$  sample (ALD cycle number of one) exhibits bands at ca. 1500

$\text{cm}^{-1}$ , corresponding to bicarbonates and carbonates, indicating the presence of adsorbed  $\text{CO}_2$  on the surface (Figure S6).<sup>93</sup>

**3.6. DFT Calculations of Different Bands of Hydroxyl Group.** The effect of  $\text{ZnO}$  ALD on the structure and IR spectrum of the  $\text{ZrO}_2$  surface was investigated via DFT calculations. Figure 8 shows the minimum-energy structures for all of the studied systems. In the case of two water molecules, Figure 8a shows that the adsorption is dissociative,



**Figure 8.** Obtained minimum-energy structures for (a) two  $\text{H}_2\text{O}$  molecules, (b) three  $\text{H}_2\text{O}$  molecules, (c) one  $\text{ZnO}$  and two  $\text{H}_2\text{O}$  molecules, and (d) one  $\text{ZnO}$  and three  $\text{H}_2\text{O}$  molecules adsorbed on a monoclinic  $\text{ZrO}_2$  (–111) surface. Colors: O, H, Zr, and Zn are colored red, white, light green, and blue, respectively.



with hydroxyl groups occupying Zr-top positions and the hydrogen atoms sitting on two- and three-coordinated oxygen anions. Figure 8b shows that the third water molecule adsorbs molecularly to a Zr cation via oxygen. Both water adsorption structures well agree with the previously computed adsorption structures on  $\text{ZrO}_2$  ( $-111$ ).<sup>101</sup>

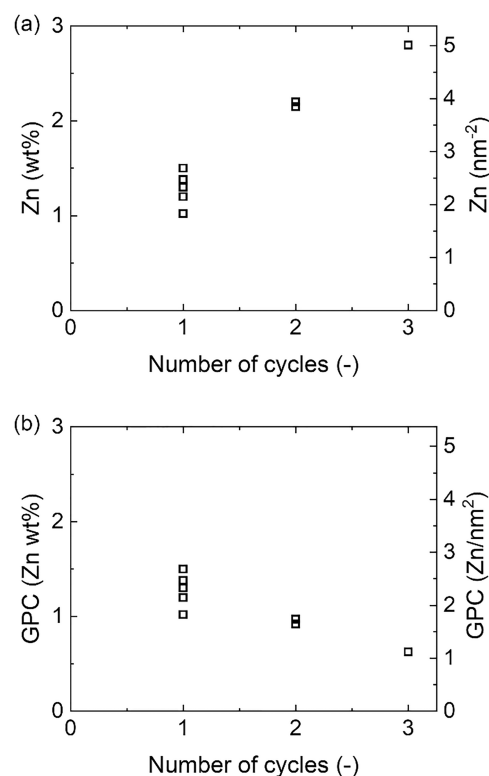
When ZnO is added on the surface having two dissociated water molecules, the Zn atom replaces hydrogen that was previously bound to the three-coordinated oxygen of  $\text{ZrO}_2$ . This hydrogen atom is instead attached to oxygen in the ZnO species. Figure 8c shows that ZnO addition leads to surface-bound  $\text{Zn}(\text{OH})_3$  with each OH group sitting in a Zr-top position. Figure 8 shows that the presence of three water molecules on the surface also results in the formation of a  $\text{Zn}(\text{OH})_3$  complex, but the Zn atom and one hydroxyl group are slightly farther away from the surface than the other two hydroxyls, which reside over Zr cations. Analyzing adsorption energies of water, we find that the dissociative adsorption energy of two water molecules on bare  $\text{ZrO}_2$  is exothermic by  $-2.11$  eV (or  $-1.05$  eV on average per water molecule), whereas that on the ZnO-modified surface adsorption is exothermic by  $-3.39$  eV (or  $-1.69$  eV on average per water molecule) owing to the formation of the Zn complex. In addition, the adsorption of a third water molecule on the ZnO-modified zirconia is endothermic by  $0.35$  eV, whereas on  $\text{ZrO}_2$ , the adsorption is exothermic by  $-1.03$  eV.

O–H IR frequencies of the surfaces for each surface structure were calculated together with the corresponding OH binding environment (Table S1). For the two-water molecule system, we identify four bands (at  $3872$ ,  $3831$ ,  $3733$ , and  $3688$   $\text{cm}^{-1}$ ) with the highest two frequencies standing for the hydroxyl group on a Zr-top position and the lowest two frequencies representing two- and three-coordinated lattice –OH groups. For three adsorbed water molecules, we see six frequencies (ranging from  $4020$  to  $3041$   $\text{cm}^{-1}$ ). Comparison of calculated and measured frequencies shows that lower water coverage is closer to the experimental system, as the number of peaks above  $3500$   $\text{cm}^{-1}$  matches better, and the calculated frequencies are red-shifted with respect to the measured values.

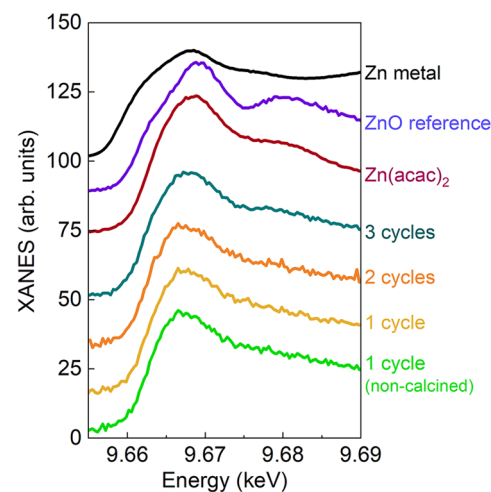
### 3.7. Effect of Number of ALD Cycles on Zinc Loading.

Figure 9 shows zinc loading versus the number of ALD cycles. Here, one full cycle includes the  $\text{Zn}(\text{acac})_2$  reaction with  $\text{ZrO}_2$ , followed by removal of the ligand by air. The zinc loading increases with increasing ALD cycles up to three. After the first ALD cycle, zinc loading is ca. 1.2 wt %. The uptake of zinc loading decreases to 0.95 and 0.62 wt % in the second and third ALD cycle, respectively. The zinc loading was converted to the areal number density of zinc ( $\text{nm}^{-2}$ ), assuming the mass gain from zinc addition and no change in the sample surface area between ALD cycles. The GPC of each cycle shown in  $\text{nm}^{-2}$  also decreased with an increasing number of ALD cycles.

**3.8. XANES.** The electronic structure of the zinc of the samples prepared with one–three ALD cycles was analyzed using XANES. Figure 10 shows the Zn K-edges of the ALD samples and Zn metal, bulk ZnO (wurtzite), and  $\text{Zn}(\text{acac})_2$  as references. The XANES spectrum of the Zn metal is a reference standard, using which the energy axis is calibrated so that the peak of its first derivative (inflection point) is at  $9.659$  keV. The most obvious information from XANES related to the oxidation state and the local coordination geometry. The XANES spectra of ZnO (wurtzite) and  $\text{Zn}(\text{acac})_2$  reference are rather similar, with the main edge peak at  $9.669$  keV, and they represent spectra of tetrahedrally coordinated  $\text{Zn}^{2+}$ . The



**Figure 9.** Controlling the zinc loading on  $\text{ZrO}_2$  by repeating the  $\text{Zn}(\text{acac})_2$  ALD process. One ALD cycle comprises the reaction of  $\text{Zn}(\text{acac})_2$  with  $\text{ZrO}_2$ , followed by ligand removal by air at  $500$  °C. (a) Zinc loading on  $\text{ZrO}_2$  after each cycle and (b) GPC (wt % and  $\text{nm}^{-2}$ ) of the ALD process.



**Figure 10.** Zn K-edge XANES spectra for different numbers of  $\text{Zn}(\text{acac})_2$  ALD cycles. The XANES spectra of the  $\text{Zn}(\text{acac})_2$  reactant, wurtzite ZnO, and Zn metal are included as references.

XANES spectra of samples with different numbers of ALD cycles are very similar, with a slight difference to the  $\text{Zn}^{2+}$  references that their main peak has slightly shifted toward lower energies, to  $9.667$  keV. Similar behavior is observed in nanoscale  $\text{Zn}^{2+}$  oxides.<sup>102</sup> Otherwise, overall, all their spectra resemble the peaks of  $\text{Zn}^{2+}$  in the spectra of the  $\text{Zn}(\text{acac})_2$  reference, having somewhat broader features than those of the crystalline ZnO (wurtzite) reference. We can conclude that the

zinc species in our samples are present as  $\text{Zn}^{2+}$  and are independent of the number of ALD cycles.

**3.9. XPS Analysis.** The elemental composition of samples prepared with one to three ALD cycles was determined by XPS. Table 2 shows the elemental composition and relative

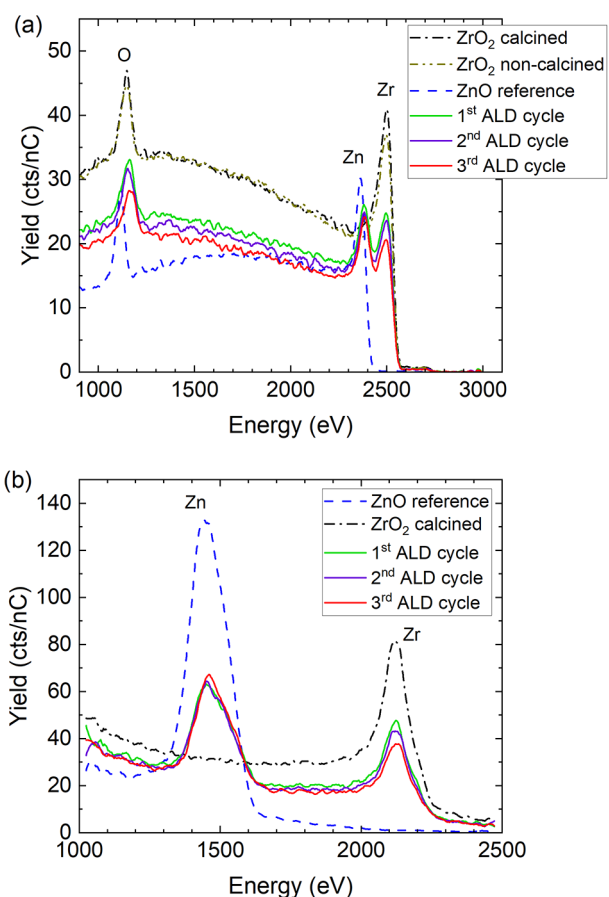
**Table 2. Relative Concentration of Elements and Different Components of Zinc in the Samples with Different ALD Cycle Numbers Determined via XPS**

ALD cycle number	elemental composition (atom %)					relative components of zinc (%)	
	Zn 2p	Zr 3d	O 1s	F 1s	C 1s	ZnO	Zn mixed state a + b
0	0.0	32.4	55.1	1.6	10.9		
1	3.8	29.7	54.5	2.1	9.9	78.2	20.6 + 1.1
2	4.6	29.4	51.3	1.9	12.8	72.2	23.2 + 4.6
3	5.2	29.2	52.0	2.2	11.5	71.0	28.2 + 0.8

amounts of different zinc components. The surface concentration of zinc increases from ca. 3.8 to 5.2 atom %, while that of zirconia decreases with increasing ALD cycle numbers. Zinc was in the  $\text{Zn}^{2+}$  state in all samples. The maximum of the Zn 2p<sub>3/2</sub> peak appears at a binding energy of approximately 1021.8 eV, and the L<sub>3</sub>M<sub>45</sub>M<sub>45</sub> Auger peak appears at a kinetic energy of 987.7 eV, giving a modified Auger parameter of approximately 2009.5 eV, which corresponds well with the expected literature value.<sup>103</sup> Shifts in the binding energy of the 2p<sub>3/2</sub> peak are generally rather small for different chemical states of Zn, but a broadening of the peak and appearance of a shoulder at higher binding energies can be generally attributed to the presence of several different chemical species. The Zn 2p<sub>3/2</sub> peak was deconvoluted into three components at binding energies of 1021.5, 1023.1, and 1024.4 eV, most likely corresponding to ZnO and two different zinc mixed-oxide states a and b, respectively (Figure S10). The total concentration of the zinc mixed states a and b increases with increasing zinc loading. The maximum intensity of the O 1s peak appears at approximately 529.9 eV, with a considerable shoulder in the peak appearing at a higher binding energy. The peak was deconvoluted using three Gaussian components at approximately 529.8, 531.2, and 532.5 eV. These peaks were attributed to lattice oxygen in ZrO<sub>2</sub>, oxygen in sub- or mixed-oxides, and surface hydroxyls, respectively. Most of the oxygen was found to be lattice oxygen in ZrO<sub>2</sub> (Table S2). According to this analysis, the concentration of hydroxyls decreases with increasing ALD cycle numbers.

**3.10. LEIS Analysis.** LEIS measurements were performed to determine the relative surface area of ZnO from different ALD cycle number samples along with bare ZrO<sub>2</sub> calcined at 600 °C. In addition, a pure ZnO powder sample was analyzed as a Zn reference. The 3 keV He<sup>+</sup> spectra in Figure 11a allow detection of all elements heavier than 10 Da, that is, carbon and heavier elements. Only the expected surface peaks for O, Zn, and Zr were detected, indicating the absence of any impurities. Surface peak areas are proportional to the surface fraction of the respective elements. Figure 11b shows 5 keV Ne<sup>+</sup> spectra. Only elements heavier than Ne were detected. In these spectra, the Zn and Zr peaks are properly separated, and peak areas are easily evaluated by subtracting the baseline.

The results are summarized in Table 3. Assuming that the pure ZnO sample is a suitable reference, the surface fraction of ZnO after a single ALD cycle is quantified as 35%. With



**Figure 11.** LEIS spectra of ZnO ALD samples deposited on ZrO<sub>2</sub> with different ALD cycle numbers. (a) 3 keV He<sup>+</sup> and (b) 5 keV Ne<sup>+</sup> were used as the primary ions. The LEIS spectra of the nontreated ZrO<sub>2</sub>, ZrO<sub>2</sub> calcined at 600 °C, and ZnO powder as references. In 5 keV Ne<sup>+</sup> spectra, only elements heavier than Ne are detected, but the mass resolution is vastly improved compared to the He<sup>+</sup> spectra.

**Table 3. Summary of the LEIS Results**

sample	Zn intensity (cts/nC)	Zr intensity (cts/nC)	surface fraction of ZnO <sup>a</sup> (%)
ALD 1st cycle	5830	4620	35
ALD 2nd cycle	6150	4300	37
ALD 3rd cycle	6540	3700	39
ZnO reference	15830	0	100

<sup>a</sup>Quantified by comparison to ZnO reference.

additional ALD cycles, the surface fraction of ZnO only slightly increases up to 39%. Thus, the initial ALD cycle leads to a good surface fraction of ZnO. The additional ZnO added during the second and third cycles is mostly located on the existing ZnO phase from the first cycle. Decreasing LEIS signal of Zr with increasing ALD cycle numbers indicates that some extent of ZnO was added on unoccupied reactive sites of ZrO<sub>2</sub>.

## 4. DISCUSSION

**4.1. Factors Affecting the Amount of Zinc Added by ALD.** In this work, we investigated the effect of the ALD temperature and calcination temperature of the support on the

**Table 4. Areal Number Density of Zinc Obtained in This Work Using Zn(acac)<sub>2</sub> Compared to That of Other Studies That Use Other Zinc Sources**

support	BET surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	zinc source (reactant A)	oxygen source (reactant B)	ALD temp (°C)	no. of cycles (–)	zinc loading (wt %)	GPC (nm)	GPC as Zn/nm <sup>2</sup>	ref
porous ZrO <sub>2</sub>	53.5	Zn(acac) <sub>2</sub>	synthetic air	200	1	1.2		2.2	this work
porous ZrO <sub>2</sub>	53.5	Zn(acac) <sub>2</sub>	synthetic air	220	1	1.3		2.3	this work
porous ZrO <sub>2</sub>	53.5	Zn(acac) <sub>2</sub>	synthetic air	240	1	1.7		3.0	this work
porous ZrO <sub>2</sub>	70.0	Zn(acac) <sub>2</sub>	synthetic air	200	1	1.4		1.9	55
porous CuO/ ZrO <sub>2</sub>		Zn(acac) <sub>2</sub>	synthetic air	200	1	1.1		1.5	55
porous Cu/SiO <sub>2</sub>	264	DEZ	H <sub>2</sub> O	150	1	1.5		0.5	54
HZSM-5 zeolite	320	DEZ	H <sub>2</sub> O	120	1	5.8		1.8	47
HZSM-5 zeolite	432	DMZ	H <sub>2</sub> O	210	50	0.01 <sup>b</sup>		0.002 <sup>b</sup>	46
HY zeolite	532	DEZ	H <sub>2</sub> O	120	1	11.9		2.4	47
porous SiO <sub>2</sub>	505	DEZ	H <sub>2</sub> O	80	1	12.0		2.1	14
porous SiO <sub>2</sub>	505	DEZ	H <sub>2</sub> O	80	1	16.1		2.8	13
Cu(OH) <sub>2</sub> nanowire		DEZ	H <sub>2</sub> O	50	20		0.19	7.9	106
Si(100)		DEZ	H <sub>2</sub> O	150	250 <sup>c</sup>		0.25	10.4	69
Si(100)		DEZ	H <sub>2</sub> O	70–200			0.19	7.9	107
Si(100)		DMZ	H <sub>2</sub> O	150	300 <sup>c</sup>		0.28	11.6	69
Si wafer		DEZ	H <sub>2</sub> O	150	100		0.20	8.3	108
glass		DEZ	H <sub>2</sub> O	105–165	1600 <sup>d</sup>		0.28 <sup>d</sup>	11.6	104
glass		DEZ	H <sub>2</sub> O	130–170	200		0.13	5.4	70
glass		DMZ	H <sub>2</sub> O	120–170	300		0.14	5.8	70
sapphire(0001)		Zn(OAc) <sub>2</sub>	H <sub>2</sub> O	350	100		0.30	12.4	67
sapphire(0001)		Zn(OAc) <sub>2</sub>	H <sub>2</sub> O	350	250		0.24	10.0	67
sapphire(0001)		ZnCl <sub>2</sub>	O <sub>2</sub>	450–550	200		0.26	10.8	72
GaN/Al <sub>2</sub> O <sub>3</sub>		ZnCl <sub>2</sub>	O <sub>2</sub>	480	4000		0.050	2.1	73

<sup>a</sup>BET surface area of supports before the addition of zinc. <sup>b</sup>The total zinc loading (wt %) was calculated from the ZnO content of 0.59 wt %.<sup>46</sup> The GPC (wt %) was estimated by dividing the total loading by 50 cycles. <sup>c</sup>The number of cycles was determined from Figure 1 in ref 69. <sup>d</sup>The number of cycles and GPC (nm) were determined from Figures 3 and 2 in ref 104, respectively.

zinc loading on mesoporous monoclinic ZrO<sub>2</sub> in one ALD cycle using Zn(acac)<sub>2</sub> and synthetic air. Approximately a constant zinc loading is obtained up to an ALD temperature of 200 °C, after which the loading slightly increases with increasing ALD temperature (Figure 4). This increase in zinc loading may indicate a change in favorable adsorption sites or reaction pathways at an elevated temperature or slight decomposition of Zn(acac)<sub>2</sub>.<sup>5,82</sup> TG analysis (Figure 1) confirms the partial decomposition of the Zn(acac)<sub>2</sub> reactant at 240 °C. However, no color change is observed in samples formed at different ALD temperatures, and zinc loadings are rather uniform in different parts of the powder bed. These results suggest only a minor effect of Zn(acac)<sub>2</sub> decomposition at 240 °C. DRIFTS results support this idea: the spectrum of the 240 °C sample shows bands similar to those of the 200 °C sample, indicating that decomposition of Zn(acac)<sub>2</sub> barely occurs under our reaction conditions. With an increase in ALD cycle numbers up to three, the zinc loading (wt %) increases, while the GPC slightly decreases (Figure 9). This result suggests a substrate-enhanced growth<sup>5</sup> at least in the first ALD cycle: the GPC on the starting surface, ZrO<sub>2</sub>, was slightly higher than on ZnO-modified ZrO<sub>2</sub>. Meanwhile, the zinc loading (wt %) decreases with increasing calcination temperature of ZrO<sub>2</sub>, as shown in Figure 5. This decrease in zinc loading is mainly due to the decrease of the ZrO<sub>2</sub> specific surface area from 99.2 to 14.5 m<sup>2</sup> g<sup>-1</sup>. Interestingly, the areal number density of zinc remains constant at ca. 2 nm<sup>-2</sup>.

Table 4 presents the areal number density of zinc deposited via the Zn(acac)<sub>2</sub> reaction at 200 °C compared to various ALD processes reported earlier. The zinc areal number density values were calculated from data given in the publications using eqs 2 and 3. Interestingly, the areal number density of zinc reported in this article (2.2 nm<sup>-2</sup>) is similar to that of zinc deposited on high surface area porous supports via the DEZ reaction,<sup>13,47,14</sup> except for one study that reported a relatively low areal number density of zinc (ca. 0.5 nm<sup>-2</sup>) via the DEZ reaction with a Cu/SiO<sub>2</sub> support.<sup>54</sup> A study on the ZnO ALD on HZSM-5 zeolite with DMZ and water also reported a rather low GPC value (ca. 0.01 wt %).<sup>46</sup> When the same DEZ reactant was used as the zinc source for coating nonporous planar substrates, the areal number density of zinc tends to be significantly higher than that of zinc deposited on porous supports. A study with the DEZ reaction on glass reported a GPC value of 0.28 nm,<sup>104</sup> which gives an areal number density of zinc of 11.6 nm<sup>-2</sup> (eq 3). This value is higher than a typical GPC value of <5 nm<sup>-2</sup> for ALD<sup>5,105</sup> and close to the areal number density of zinc for an average bulk monolayer of 12.0 nm<sup>-2</sup> (eq 4).

In conclusion, a rather wide range of areal number densities of zinc (0.002–12.4 nm<sup>-2</sup>) has been reported in the literature for ZnO ALD processes. The areal number density of zinc obtained in this work (2.2–3.0 nm<sup>-2</sup>) is in the middle of this range and comparable to that obtained on porous supports via the DEZ reaction.

**Table 5. Summary of the Elemental Analysis of Materials Deposited via ALD with Various Metal Acetylacetonate Reactants**

M(acac) <sub>n</sub> reactant	n in M(acac) <sub>n</sub>	support	pretreatment temp (°C)	reaction temp (°C)	metal atoms (nm <sup>-2</sup> )	acac ligands (nm <sup>-2</sup> )	acac/metal ratio after adsorption	ref
Zn(acac) <sub>2</sub>	2	ZrO <sub>2</sub>	600	200	2.2	1.8	0.8	this work
Ni(acac) <sub>2</sub>	2	Al <sub>2</sub> O <sub>3</sub>	200	200	2.4	2.4	1.0 <sup>a</sup>	38
Co(acac) <sub>3</sub>	3	Al <sub>2</sub> O <sub>3</sub>	600	180	1.5	2.6	1.7	110
Cr(acac) <sub>3</sub>	3	Al <sub>2</sub> O <sub>3</sub>	600	200	0.8	1.8 <sup>b</sup>	2.2 <sup>b</sup>	109
Cr(acac) <sub>3</sub>	3	SiO <sub>2</sub>	200	200	0.8	1.6	2.0	99
Ir(acac) <sub>3</sub>	3	Al <sub>2</sub> O <sub>3</sub>	200	200	0.7 <sup>c</sup>	1.8 <sup>c</sup>	2.6	111
Ir(acac) <sub>3</sub>	3	Al <sub>2</sub> O <sub>3</sub>	200	250	0.9 <sup>c</sup>	1.9 <sup>c</sup>	2.1	111
Ir(acac) <sub>3</sub>	3	SiO <sub>2</sub>	200	250	0.6 <sup>c</sup>	0.7 <sup>c</sup>	1.2	111
Ir(acac) <sub>3</sub>	3	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	200	200	0.7 <sup>c</sup>	1.6 <sup>c</sup>	2.3	111
Ir(acac) <sub>3</sub>	3	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	200	250	1.1 <sup>c</sup>	1.5 <sup>c</sup>	1.4	111

<sup>a</sup>The acac/metal ratio was estimated from the C/Ni ratio of 5 from the sample with Al<sub>2</sub>O<sub>3</sub> preheated at 200 °C.<sup>38</sup> <sup>b</sup>The amount of acac ligands and acac/metal ratio were estimated from the C/Cr ratio of 11.<sup>109</sup> <sup>c</sup>The amount of acac ligands and Ir obtained were determined from Figure 2 in ref 111.

**4.2. Distribution of Zinc within a ZrO<sub>2</sub> Particle.** In SEM-EDS analysis of the sample prepared with one ALD cycle, zinc was present throughout the ZrO<sub>2</sub> particle (Figure 3). No accumulation of zinc at the edges of the zirconia particles was observed. This contrasts a recent study, where in addition to rather homogeneously distributed TiO<sub>2</sub> inside  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles, enrichment of TiO<sub>2</sub> was observed at the edges of the particles.<sup>50</sup>

The zinc intensity near the center was somewhat lower than that on the outer surface (Figure 3). In this work, we made a reference experiment to investigate the reaction of the Hacac byproduct with ZrO<sub>2</sub> (for details see the Experimental Section). Figure 6 shows the DRIFT spectrum of Hacac/ZrO<sub>2</sub> which is similar to those of the Zn(acac)<sub>2</sub>/ZrO<sub>2</sub> sample and Zn(acac)<sub>2</sub> reference suggesting that Hacac, too, reacts with ZrO<sub>2</sub>. As Zn(acac)<sub>2</sub> gets consumed during the reaction of Zn(acac)<sub>2</sub> with the ZrO<sub>2</sub> support, Hacac byproducts form and diffuse to the center of the ZrO<sub>2</sub> particles before the Zn(acac)<sub>2</sub> reactant, consuming reactive sites. DRIFTS and SEM-EDS results suggest that during the reaction of Zn(acac)<sub>2</sub> with ZrO<sub>2</sub>, the competitive adsorption of Hacac on ZrO<sub>2</sub> might occur, decreasing the intensity of zinc inside the ZrO<sub>2</sub> particle.

**4.3. Reaction Mechanism and Saturation-Determining Factor.** In this section, we analyze the reaction mechanism of Zn(acac)<sub>2</sub> with ZrO<sub>2</sub> and compare it to earlier studies using other metal acetylacetonates [M(acac)<sub>n</sub>]. The acac to metal ratios obtained by elemental analysis in this work and the literature are given in Table 5 (calculated from the carbon content by assuming one acetylacetonate ligand contains five carbon atoms). After adsorption via the ligand exchange reaction, one acac ligand from the M(acac)<sub>n</sub> reactant is released, leaving  $n - 1$  ligands on the surface. In our samples prepared by using Zn(acac)<sub>2</sub> ( $n = 2$ ), the ratio of acac to zinc is approximately 0.8. This ratio is close to one, indicating that at least one acac ligand is released into the gas phase during the Zn(acac)<sub>2</sub> reaction with the surface OH groups. Earlier ALD studies on other metal acetylacetonates have also reported the acac to metal ratio of ca. one for the Ni(acac)<sub>2</sub> reaction with Al<sub>2</sub>O<sub>3</sub> and two for Co(acac)<sub>3</sub> and Cr(acac)<sub>3</sub> reactions with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, resulting from the ligand exchange reaction.<sup>38,99,109,110</sup> Silvennoinen et al.<sup>111</sup> reported an acac to metal ratio of higher than two for the reaction of Ir(acac)<sub>3</sub> with Al<sub>2</sub>O<sub>3</sub>. They suggested that this ratio closed to three might

have been caused by the competitive adsorption of Hacac byproducts on the Al<sub>2</sub>O<sub>3</sub> surface or molecular associative adsorption.<sup>111</sup>

The amount of metal obtained by ALD can be defined by steric hindrance of bulky ligands.<sup>5,82,83,99,112</sup> Puurunen<sup>83</sup> demonstrated via a ball model that the GPC (nm<sup>-2</sup>) decreases with increasing ligand size, and the GPC is typically less than 50% of a monolayer because of steric hindrance of ligands. Gu et al.<sup>113</sup> showed the effect of bulky reactants on areal coverage (%) by Monte Carlo simulations using various reactants such as trimethylaluminum (TMA) and dimethylaluminum isopropoxide (DMAI). The areal coverage of DMAI was lower than that of TMA because DMAI has a larger size. Li et al.<sup>114</sup> demonstrated using random sequential adsorption simulations that the surface density (nm<sup>-2</sup>) covered by inhibitor molecules decreases with increasing radius of inhibitors. Lakomaa<sup>4</sup> reported 0.47 nm<sup>2</sup> as the filling area of one acac ligand. By taking the reciprocal of this filling area (eq 7 in ref 83), the theoretical maximum for the acac ligand packing can be estimated to be 2.1 nm<sup>-2</sup>. Herein, the amount of acac ligands measured by carbon analysis (1.8 nm<sup>-2</sup>) almost reached its theoretical maximum, suggesting that the steric hindrance of acac ligands acted as a saturation-determining factor.<sup>5</sup> Silvennoinen et al.<sup>111</sup> also concluded that steric hindrance is the saturation-determining factor<sup>5</sup> for the ligand exchange reaction of Ir(acac)<sub>3</sub> with Al<sub>2</sub>O<sub>3</sub> because the amount of acac (1.6–1.9 nm<sup>-2</sup>) is close to the maximum ligand packing value.

To support the idea that steric hindrance is the key to surface saturation, the areal number density of zinc was compared to the total number of surface OH groups. This work obtained ca. 2.2 nm<sup>-2</sup> as the areal number density of zinc after one ALD cycle. Kouva et al.<sup>92</sup> reported ca. 6 nm<sup>-2</sup> as the number of surface OH group on ZrO<sub>2</sub> calcined at 700 °C. Therefore, we can estimate the ratio of the amount of zinc atoms to that of surface OH groups to be approximately 0.4. This relatively low ratio likely indicates that the steric hindrance of acac ligands and not a limited number of OH groups defines surface saturation.

**4.4. Growth Mode.** The ZnO growth was studied by LEIS for samples prepared with up to three ALD cycles. LEIS results show the surface fraction of roughly one-third of ZnO after the first ALD cycle. This ZnO was well spread and acted as nuclei to cluster ZnO during the following ALD cycles. Thus, our

results indicate an two-dimensional growth mode during the first ALD cycle and island growth thereafter.<sup>5</sup>

Our results were compared to an earlier study by Jacobs et al.<sup>39</sup> on the NiO growth mode in the reaction of Ni(acac)<sub>2</sub> and ambient air with Al<sub>2</sub>O<sub>3</sub>. Jacobs et al.<sup>39</sup> performed ten ALD cycles and concluded that the Ni signal obtained by LEIS increases with increasing ALD cycles, but the rate of increase decreases after the first cycle. Meanwhile, the Ni XPS signal rather linearly increases. By comparing LEIS and XPS analyses, Jacobs et al.<sup>39</sup> concluded that atomically distributed Ni atoms obtained after the first ALD cycle acted as nuclei for the further cycles.<sup>39</sup> In conclusion, the ZnO ALD using Zn(acac)<sub>2</sub> and air shows a growth mode similar to that of the NiO ALD using Ni(acac)<sub>2</sub> and air.

## 5. CONCLUSIONS

This study investigated the deposition of ZnO on mesoporous high surface area ZrO<sub>2</sub> via ALD using Zn(acac)<sub>2</sub> and synthetic air and a fixed bed powder ALD reactor. The reaction of Zn(acac)<sub>2</sub> with ZrO<sub>2</sub> showed a saturating behavior. TG analysis showed good thermal stability of Zn(acac)<sub>2</sub> up to a temperature of ca. 240 °C. The areal number density of zinc had a constant value (ca. 2.2 nm<sup>-2</sup>) with an increase in the amount of Zn(acac)<sub>2</sub>. A similar value (ca. 2 nm<sup>-2</sup>) was obtained on ZrO<sub>2</sub> calcined at various temperatures (400–1000 °C) with different surface areas (99.2–14.5 m<sup>2</sup> g<sup>-1</sup>). The elemental carbon and zinc analyses suggest that Zn(acac)<sub>2</sub> reacts with ZrO<sub>2</sub> most probably via ligand exchange with surface OH groups. This finding is supported by the DFT results, which further indicate the formation of zinc-bonded OH groups. Comparison to the literature indicates that the steric hindrance of acac ligands likely defines saturation. XANES and XPS analyses showed that zinc species are present as Zn<sup>2+</sup>. The zinc loading in different parts of the powder bed was rather constant. However, SEM-EDS analysis revealed that the intensity of zinc near the center of a ZrO<sub>2</sub> particle was somewhat lower than that on the outer part of the particle. In-situ DRIFTS analysis shows that Hacac reacts with ZrO<sub>2</sub> suggesting the possible readsorption of some Hacac byproduct on the ZrO<sub>2</sub> surface, causing the lower intensity of zinc near the particle center. According to LEIS, the surface fraction of roughly one-third of ZnO was obtained from the first ALD cycle. In the following cycles, the already-deposited ZnO acted as a nucleation center for further ZnO growth. In conclusion, this study shows the potential of Zn(acac)<sub>2</sub> as an ALD reactant for coating high surface area porous ZrO<sub>2</sub> particles with ZnO.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.3c00668>.

Nitrogen physisorption isotherm of ZrO<sub>2</sub> calcined at various temperatures, photographs of samples inside the powder bed of the F-120 reactor and the tube furnace, thermal analysis of Zn(acac)<sub>2</sub>, temperature program used for the in-situ DRIFTS-MS analysis, DRIFT spectra, XRD on ZrO<sub>2</sub>, DFT calculations results, XPS spectra, a table for the relative amount of different components of oxygen determined by XPS, and nitrogen physisorption isotherm and physical properties of ZnO ALD samples (one and three ALD cycles) and nondecorated zirconia reference (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

**Riikka L. Puurunen** – School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Aalto University, FI-00076 Aalto, Espoo, Finland; [orcid.org/0000-0001-8722-4864](https://orcid.org/0000-0001-8722-4864); Email: [riikka.puurunen@aalto.fi](mailto:riikka.puurunen@aalto.fi)

### Authors

**Jihong Yim** – School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Aalto University, FI-00076 Aalto, Espoo, Finland

**Eero Haimi** – School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Aalto University, FI-00076 Aalto, Espoo, Finland

**Miia Mäntymäki** – Department of Chemistry, University of Helsinki, 00014 Helsinki, Finland; [orcid.org/0000-0003-0880-0427](https://orcid.org/0000-0003-0880-0427)

**Ville Kärkäs** – School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Aalto University, FI-00076 Aalto, Espoo, Finland

**René Bes** – Department of Physics, University of Helsinki, 00014 Helsinki, Finland; [orcid.org/0000-0003-4206-1525](https://orcid.org/0000-0003-4206-1525)

**Aitor Arandia Gutierrez** – School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Aalto University, FI-00076 Aalto, Espoo, Finland

**Kristoffer Meinander** – School of Chemical Engineering, Department of Bioproducts and Biosystems, Aalto University, FI-00076 Aalto, Espoo, Finland

**Philipp Brüner** – IONTOF GmbH, 48149 Münster, Germany

**Thomas Grehl** – IONTOF GmbH, 48149 Münster, Germany

**Lars Gell** – Department of Chemistry, Nanoscience Center, University of Jyväskylä, FI-40014 Jyväskylä, Finland

**Tiia Viinikainen** – School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Aalto University, FI-00076 Aalto, Espoo, Finland

**Karoliina Honkala** – Department of Chemistry, Nanoscience Center, University of Jyväskylä, FI-40014 Jyväskylä, Finland; [orcid.org/0000-0002-3166-1077](https://orcid.org/0000-0002-3166-1077)

**Simo Huotari** – Department of Physics, University of Helsinki, 00014 Helsinki, Finland

**Reetta Karinen** – School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, Aalto University, FI-00076 Aalto, Espoo, Finland

**Matti Putkonen** – Department of Chemistry, University of Helsinki, 00014 Helsinki, Finland; [orcid.org/0000-0002-4166-2890](https://orcid.org/0000-0002-4166-2890)

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.chemmater.3c00668>

### Author Contributions

J.Y. planned the experiments together with R.L.P., prepared the samples, made the physisorption measurements and XRD measurements, and performed DRIFTS-MS experiments together with T.V. and V.K. E.H. performed SEM-EDS analysis, M.M. the TG analysis, K.M. the XPS analysis, P.B. and T.G. the LEIS analysis, L.G. and K.H. the DFT calculations, and R.B. and S.M. the XANES analysis. J.Y. was responsible for writing the first version of the manuscript under the supervision of R.L.P. All the coauthors contributed to the final manuscript.

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## Notes

The authors declare no competing financial interest.

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