



Interface engineering of Pt–ZnO–CeO₂ by atomic layer deposition for advanced applications

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ABSTRACT

The precise design of metal-oxide interfaces in heterogeneous catalysts is crucial for optimizing activity and selectivity in reactions such as ethanol decomposition. In this study, Pt₁ZnO₁CeO₂ composite catalysts were synthesized via atomic layer deposition (ALD) with systematically varied ZnO loadings to investigate the influence of support structure on platinum nucleation, interfacial properties, and catalytic performance. High-resolution TEM, XPS, ICP-MS reveal that ZnO strongly affects Pt growth, leading to non-monotonic trends in nanoparticle size, dispersion, and loading. These structural effects translate into distinct electronic interactions at Pt/CeO₂, ZnO/CeO₂ and Pt/ZnO interfaces, as reflected by XPS analysis. To probe the catalytic relevance of these interfaces, ethanol decomposition was employed as an interface-sensitive reaction. The results demonstrated that moderate ZnO loading (3–5 cycles) generated a Pt/ZnO/CeO₂ interface, that significantly increased ethanol conversion and promoted C₁-product formation. At higher ZnO coverage (30 cycles), the catalyst surface was dominated by Pt/ZnO interactions, resulting in reduced C–C bond cleavage activity. These trends were supported by in situ DRIFTS by identifying the suppression of acetate formation and promotion of aldehyde intermediates at Pt–ZnO surfaces. These findings underscore the critical role of interfacial engineering via ALD in modulating catalyst structure, metal-support interactions, and reaction pathways.

1. Introduction

Atomic layer deposition (ALD) is increasingly recognized as a powerful method to engineer catalyst interfaces with atomic-scale precision. Beyond thin-film growth, the self-limiting surface reactions characteristic of ALD provide independent control over thickness, composition, and spatial distribution of metal and oxide layers, enabling the deliberate construction of specific metal/oxide and oxide/oxide interfaces [1,2]. Recent studies have demonstrated that such ALD-generated interfaces can drastically modify the electronic structure and adsorption properties of supported metals and oxides, and thereby tune catalytic performance in reactions such as CO oxidation [3]. While ALD technique has been successfully used to tune interfacial structure for ethanol electro-oxidation [4–6], its application to interface engineering in thermally driven ethanol reforming processes remains limited.

In thermal ethanol conversion, numerous studies have demonstrated

that metal-oxide interfaces critically determine reaction pathways, particularly on Pt/CeO₂ [7,8]. Beyond binary systems, interface effects have also been reported in multi-component catalysts. Davidson *et al.* investigated Co/CeO₂ catalysts promoted with ZnO for ethanol steam reforming (ESR) and showed that ZnO addition alters the Co–CeO₂ interface by enhancing the oxygen mobility of the ceria support, which in turn suppresses C–C bond cleavage and modifies the product distribution [9]. Chiou and Galicia *et al.* demonstrated that ZnO morphology influences Pt dispersion and alcohol reforming performance in Pt/ZnO systems [10,11]. Ternary Pt/ZnO/CeO₂ systems have also been explored but primarily in photocatalysis, where enhanced activity was attributed to interfacial Pt–ZnO–CeO₂ sites [12–14].

Despite these advances, there is still a lack of model systems with atomic-level control in which distinct interfaces can be tuned independently and systematically under otherwise comparable conditions. In this work, we address this gap by using ALD to construct a series of Pt/ZnO/CeO₂ catalysts, in which ZnO overlay coverage is varied (0–30

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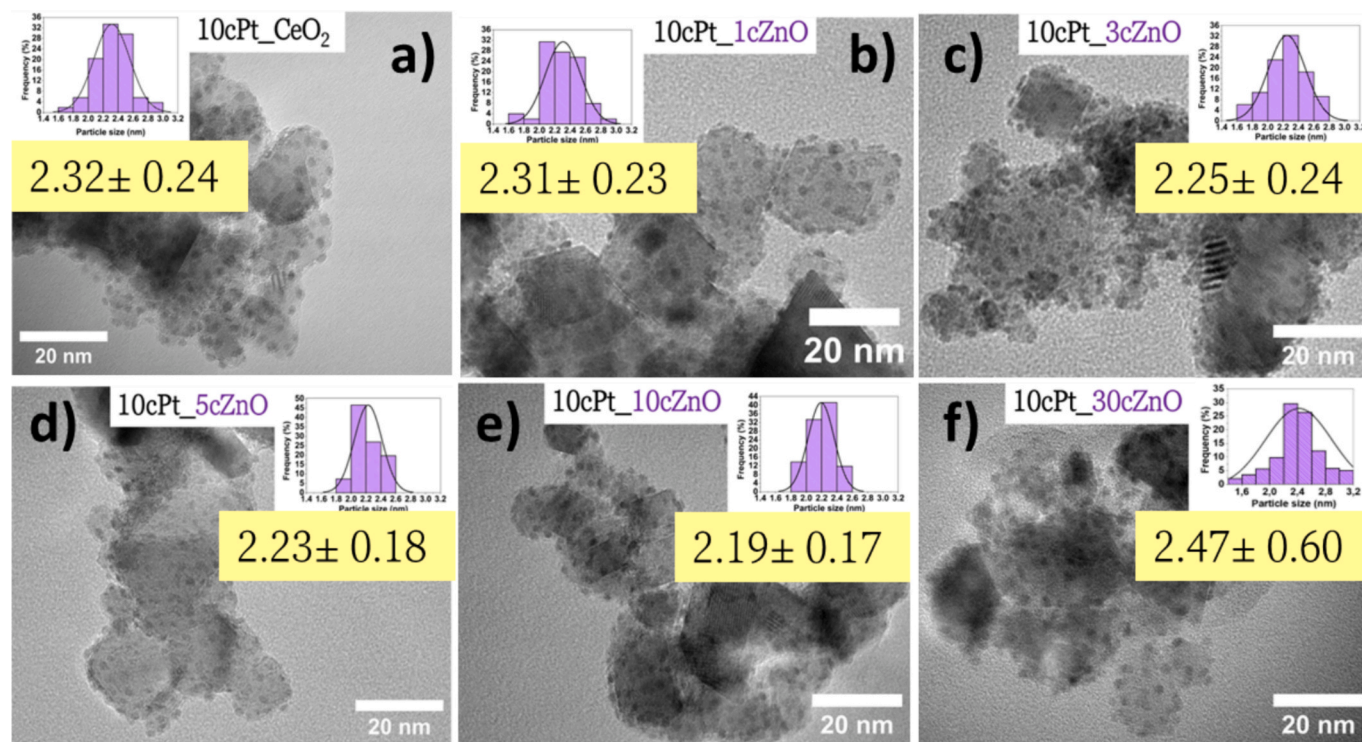


Fig. 1. HR-TEM images and corresponding size distribution histograms of the as-prepared 10cPt_XcZnO_CeO₂ samples with 0cZnO (a); 1cZnO (b); 3cZnO (c); 5cZnO (d); 10cZnO (e), and 30cZnO loading (f).

cycles) while Pt loading is held constant (10 cycles). ZnO deposition partially covers the spincoated bulk ceria surface, generating tunable ZnO/CeO₂ interfaces. Subsequent Pt ALD deposition generates Pt nanoparticles that nucleate on both bare CeO₂ and ZnO-covered regions, allowing the relative abundance of Pt/CeO₂ and Pt/ZnO interfaces to be modulated by design. XPS, TEM, and ICP-MS analyses establish how ZnO coverage influences Pt nucleation, particle size, and dispersion at the atomic scale.

In the second part of the study, these ALD-fabricated Pt/ZnO/CeO₂ materials were evaluated as model catalysts for thermal ethanol decomposition. Ethanol is an industrially relevant probe molecule that can undergo dehydrogenation to acetaldehyde, dehydration to ethylene, and deeper C–C bond scission to C₁ products such as methane and CO, as well as hydrogen formation, where conversion and selectivity are governed by surface composition and chemistry.

Building on established knowledge that Pt favors dehydrogenation pathways [15], CeO₂ provides redox-active Lewis acid/base sites [16–18], and ZnO exhibits amphoteric behavior with oxygen-vacancy-dependent basicity [19,20], we exploit our interface-controlled series to disentangle the roles of the Pt/CeO₂, ZnO/CeO₂, and Pt/ZnO interfaces in steering ethanol conversion. By combining precise ALD synthesis with detailed structural characterization and catalytic testing, we establish direct connections between atomic-scale interface tuning and macroscopic activity/selectivity, thereby providing a general framework for rational interface engineering in multi-component oxide/metal catalysts.

2. Experimental part

2.1. Synthesis of the catalysts

The silicon wafers were first cut into 1.7 × 1.7 cm substrates and cleaned by sonication in acetone to eliminate surface contaminants. A ceria layer was introduced by preparing a 10 mg·mL^{−1} CeO₂ nanopowder (Aldrich) suspension in ethanol and depositing 4 sequential 25

μL aliquots by spincoating. The surface was air-dried between applications to ensure uniform distribution.

The as prepared samples were coated with zinc oxide and platinum nanoparticles by using a Beneq TFS-200 atomic layer deposition (ALD) equipment. In each case, the high aspect ratio chamber was used with a 10 s residence time and N₂ gas purge between each step. ZnO films were grown at 443 K using diethyl zinc (DEZ, STREM, 99.9998 % Zn) and Milli-Q water. Each ALD cycle consisted of a 150 ms DEZ pulse, a 5 s N₂ purge, a 150 ms H₂O pulse, followed by another 5 s N₂ purge. Platinum deposition was carried out at 573 K using trimethyl(methylcyclopentadienyl)platinum(IV) (MeCpPtMe₃, Strem Chemicals) and high-purity O₂ (Messer 5.0). Each Pt cycle used a 500 ms precursor pulse, an 8 s N₂ purge, a 500 ms O₂ pulse, and a second 8 s purge.

The resulting catalyst series follows the nomenclature 10cPt_XcZnO_CeO₂, where c denotes the number of ALD cycles. Pt loading was fixed at ten cycles (10cPt) throughout the study, while ZnO loading was deliberately varied between 0 and 30 cycles (X = 0, 1, 3, 5, 10, 30) to isolate the role of ZnO in modulating Pt dispersion and metal-oxide interactions. Although the designation of “SiO₂” is omitted for brevity, it is implicitly present in all sample names because every film is grown on the same rigid SiO₂ support. The preparation procedure of the 10cPt_0-30cZnO_CeO₂ samples is schematically illustrated in Fig. S1.

2.2. Catalytic activity tests

The silica supported catalysts were tested in ambient pressure ethanol decomposition reaction in the gas phase in a batch mode. The batch reactor (0.1–1100 mbar pressure range) constituted a stainless-steel chamber of ~900 cm³ in volume equipped with a heating/cooling system (Fig. S2). In a typical experiment, 25 mbar of ethanol balanced with N₂ was introduced into the reactor, and the gas composition was circulated with a metal bellows pump. The decomposition of ethanol was monitored by flame ionization (FI) and thermal conductivity (TC) detectors integrated into the Agilent 6890 N gas chromatograph. During the pre-treatment, the sample stage was first heated to

573 K, and thereafter 250 mbar of O₂ or H₂ balanced with N₂ were introduced into the chamber and circulated for 30 min and 60 min, respectively for oxidation and reduction. Before the reaction, the chamber was flushed with N₂ for 10 min and evacuated. The ethanol conversion was calculated on the basis of carbon material balance and the consumption of the ethanol was also considered (Eq. (1)).

$$X_{EtOH} = \frac{\sum n_i \cdot \vartheta_i}{\vartheta_0 + \sum n_i \cdot \vartheta_i} \cdot 100\% \quad (1)$$

where ϑ_i corresponds to the amount of a given product (nmol); n_i is the number of carbon atoms in product (i); ϑ_0 indicates the amount of unconverted ethanol. Selectivity was calculated according to the Eq. (2):

$$S_i = \frac{\vartheta_i \cdot n_i}{\sum \vartheta_i \cdot n_i} \cdot 100\%; S_{H_2} = \frac{\vartheta_{H_2}}{\sum \vartheta_i \cdot (n_i/2)} \quad (2)$$

2.3. Characterization of the catalysts

High-resolution TEM (FEI Tecnai G2 20 X-Twin, 200 kV, with electron diffraction) was used to images the as-synthesized and spent samples. The samples were released from the silicon wafer by 10 min sonication in ethanol and drop-casted onto carbon coated copper grids.

For X-ray photoelectron spectroscopy (XPS) analysis, silica wafer pieces (60 × 60 mm) were co-fabricated with the regular samples during ALD to fit the XPS sample holder. The pre-treatment (in O₂ at 573 K for 30 min; in H₂ at 573 K for 60 min) was executed in the modified pre-chamber of a Kratos XSAM800. The high-resolution XP spectra were obtained with a non-monochromatized Mg K α X-ray source (1253.6 eV) at 40 eV pass energy (0.1 eV energy resolution) and referenced to the aliphatic component of the C1s spectrum region at 284.8 eV.

Metal ion ratios were measured by an inductively coupled plasma mass spectrometer (ICP-MS) (Agilent 7700x). Catalyst pieces were digested in 3 mL concentrated aqua regia for 24 h, followed by 10 min sonication. Aliquots of 75 or 750 μ L were diluted to 25 mL (final acid content ~1.5 %). A multielement internal standard was applied. Pt and ZnO surface loadings were calculated from the ICP-MS-derived amounts normalized to the Si wafer area.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted using a Bruker Invenio-R FTIR spectrometer, coupled with a Harrick Praying Mantis™ diffuse reflectance attachment (ZnSe window). Samples were heated to 573 K at a rate of 10 °C·min⁻¹ in He, oxidized in O₂ for 0.5 h, followed by reduction in H₂ for 1 h. After flushing with helium, the background spectrum was recorded. Ethanol was introduced into the cell with nitrogen flow, and spectra were recorded every 10 min for one hour after the system reached a steady state. To simulate batch conditions, spectra were also collected every 10 min for an additional hour after ethanol flow was discontinued.

3. Results and discussion

3.1. Growth mechanism

To investigate the morphology of ALD synthesized platinum nanoparticles on ceria particles with varying ZnO coverage, the coated silica wafers were sonicated in ethanol for 10 min, and the dislodged particles were subsequently analysed. Fig. 1 shows the obtained TEM images and corresponding size distribution histograms of structured 10cPt-0-30cZnO/CeO₂ thin-films.

Interestingly, the particle size exhibited a non-monotonic trend with increasing ZnO cycle number, contrary to initial expectations. In the absence of ZnO, the average platinum particle size was 2.32 ± 0.24 nm. After 10 ZnO cycles, the size slightly decreased to 2.19 ± 0.17 nm. However, following 30 ZnO cycles, the trend shifted, with the average particle size significantly increasing to 2.47 ± 0.60 nm.

To investigate the nucleation process in ALD-synthesized 10cPt-XcZnO/CeO₂ thin films, ICP-MS measurements were performed

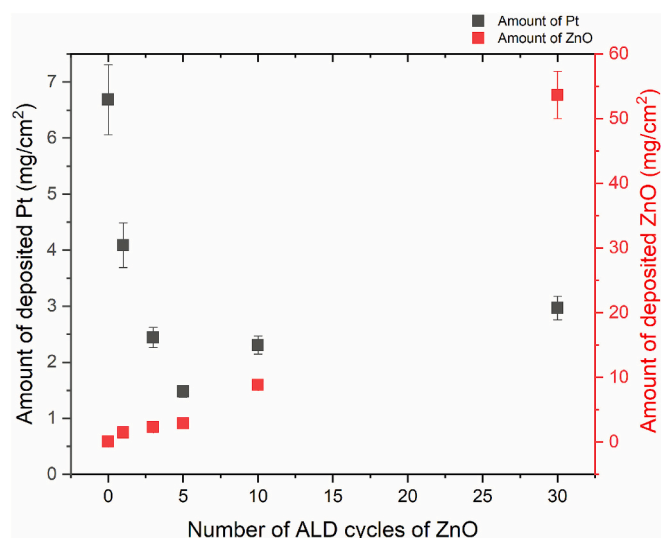


Fig. 2. The amount of deposited platinum per square cm and the amount of deposited zinc oxide per square cm versus the number of zinc oxide cycles.

on previously dissolved samples (Fig. 2).

The quantity of ZnO deposited per unit area shows an approximately linear correlation with the number of ALD cycles in the first 5 cycles and grows slightly faster after 10 and 30 cycles. In contrast, the platinum loading decreases from 6.69 ± 0.62 mg·cm⁻² on a pure ceria to a minimum of 1.48 ± 0.11 mg·cm⁻² after 5 ALD cycles, meanwhile, later increases again, reaching 2.97 ± 0.21 mg·cm⁻² in the case of 30 cycles of zinc oxide.

The observed non-monotonic Pt particle size evolution suggests that the Pt growth is influenced by ZnO and overlayer structure. The deposition of ZnO by ALD often proceeds by Volmer-Weber (island) growth with a “nucleation delay”, where early cycles deposit only fractional monolayers and full CeO₂ coverage requires multiple cycles [21]. This phenomenon is highly dependent on the substrate and the temperature of the deposition [22–24]. The initial decrease in Pt particle size and loading indicates that ZnO islands restrict Pt nucleation by blocking ceria sites. This competition for active sites explains the reduced Pt content at low ZnO cycles. After ZnO coverage becomes continuous (~30 cycles), Pt particle size and loading increase, implying that a stabilized ZnO overlayer facilitates improved Pt nucleation and dispersion.

The nucleation delay phenomenon is well documented on various oxide substrates, including SiO₂, Al₂O₃, and ZnO, driven by low density of chemisorption sites, particularly surface hydroxyl groups [25]. While both ZnO and CeO₂ typically exhibit some amount of surface hydroxyl groups that facilitate precursor adsorption [26,27], the additional ability of ceria to cycle between Ce⁴⁺ and Ce³⁺ oxidation states enhances precursor decomposition and Pt nucleation via oxygen vacancies [28,29,30]. However, the introduction of ZnO may partially block these sites, reducing early Pt nucleation density. Additionally, Lee et al. have shown that Pt ALD growth rates can vary depending on the phase and thickness of the underlying oxide layer. Specifically, Pt ALD nucleates more readily on crystalline, catalytically active surfaces than on amorphous ones [31]. A similar amorphous-to-crystalline transition can occur during ZnO deposition. At lower deposition temperatures, such as those used in this study, the ZnO tends to form small, amorphous islands that lack the thermal energy required to organise into the hexagonal wurtzite structure [24]. Although the crystalline ZnO phase could not be directly detected by XRD due to its low amount, this structural evolution likely accounts for the observed increase in Pt loading at 30 ZnO cycles compared to 10 cycles, despite both exhibiting near-complete surface coverage. The enhanced crystallinity and order in the thicker ZnO layer may facilitate more favorable Pt nucleation and growth.

Table 1

XPS results: characterization of surface species after the pre-treatment at 573 K: ceria through $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ ratio; ZnO and Pt phases through peak position of main components.

Catalyst	Probed interface	$\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$, %	Zn 2p _{3/2} , eV	Pt 4f _{7/2} , eV
CeO ₂	CeO ₂	12.0	–	–
30cZnO	ZnO	–	1021.8	–
30cZnO_CeO ₂	ZnO	–	1022.1	–
10cPt_CeO ₂	Pt/CeO ₂	40.1	–	71.6
3cZnO_CeO ₂	ZnO/CeO ₂	23.1	1021.3	–
10cPt_3cZnO_CeO ₂	Pt/ZnO/	27.6	1021.4	71.6
	CeO ₂			
10cPt_10cZnO_CeO ₂	mostly Pt/ ZnO	26.2	1022.3	71.9
10cPt_30cZnO_CeO ₂	Pt/ZnO	–	1022.2	71.6

3.2. The role of interfaces and practical applications

ALD is a precise and reproducible technique for preparing 2D structures composed of various materials in controlled combinations. In this study, 10cPt_0-30cZnO_CeO₂ thin assemblies were prepared. Characterization of these structures with TEM and ICP-MS revealed a distinct evolution in material deposition behavior with increasing ZnO ALD cycles. As ZnO loading increases, different interfaces become exposed, allowing for the tuning of material properties.

This tunability is particularly valuable in heterogeneous catalysis, where distinct surface-active sites govern different steps of complex industrial reactions. One such process is ethanol decomposition, which produces a range of value-added products, including hydrogen, ethylene, acetaldehyde, CO, and methane. We employed ethanol decomposition as a model reaction to demonstrate the catalytic potential of the prepared thin films as well as to emphasize the critical role of interfacial structures in catalytic processes. Ethanol was chosen as a probe molecule since it contains both C–C and C–O single bonds, where bond cleavage selectivity combined with intrinsic activity can provide a mechanistic basis to differentiate between contributions from Pt/CeO₂, Pt/ZnO, and ZnO/CeO₂ interfaces.

Before the catalytic measurements, all thin films were in-situ pre-treated under identical activation procedure: 30 min in O₂ followed by 60 min in H₂ at 573 K. To gain deeper insight into surface composition, and assist interpretation of catalytic results, the pre-treated structures were studied with X-ray Photoelectron Spectroscopy (XPS) as a surface-sensitive characterization technique.

3.2.1. XPS interface Probing

Fig. S3 shows the Pt 4f, Zn 2p and Ce 3d core spectra of 3cZnO_CeO₂ and 10cPt_XcZnO_CeO₂ with 3cZnO, 10c ZnO and 30cZnO thin films collected after in-situ activation procedure. In addition to this, a series of reference samples was prepared – CeO₂; 30cZnO; 30cZnO_CeO₂; 10cPt_CeO₂ – and high resolution XPS spectra of corresponding regions were recorded after identical activation process to elucidate the role of separate interfaces (Fig. S4).

The Ce 3d spectrum is usually complex due to the mixed-valence nature of cerium. It is typically deconvoluted into ten components: six peaks attributed to Ce^{4+} – v, v', v'' (3d_{5/2}) and u, u', u'' (3d_{3/2}), and four to Ce^{3+} – v₀, v' (3d_{5/2}) and u₀, u' (3d_{3/2}), reflecting the coexistence of both oxidation states in the near-surface region of ceria [30,32]. For deconvolution, the intensity ratio between the 3d_{5/2} and 3d_{3/2} components was constrained to 1.5 [33]. The spin-orbit splitting between each pair of satellite peak varied in the range of 18.3–18.4 for u'' and v'' and 18.6–18.7 for u' and v', which is consistent with spin-orbit splitting rules and prior literature [34,35].

Observing the Ce 3d peak in the 10cPt_3cZnO_CeO₂ – 10cPt_10cZnO_CeO₂ – 10cPt_30cZnO_CeO₂ row (Fig. S3), it can be clearly seen that with the increasing amount of deposited ZnO, the intensity of the Ce 3d signal decreased gradually before it nearly

disappeared when ZnO amount reached 30 cycles. This strongly suggests that the surface region probed by XPS (~5–10 nm depth) is entirely covered by 30 cycles of ZnO, effectively eliminating any direct Pt/CeO₂ interfacial exposure in agreement with TEM and ICP-MS results.

The presence of Ce^{3+} features in the deconvoluted spectra arises from intrinsic surface defects, particularly oxygen vacancies (V_O). The relative concentration of oxygen vacancies was estimated using the $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$ ratio. These values are summarized in Table 1 for all samples where the Ce signal was detectable. A higher Ce^{3+} fraction is indicative of a greater density of oxygen vacancies, which can play a crucial role in catalytic activity and metal-support interactions.

The Pt 4f spectra of the reference 10cPt_CeO₂ sample exhibited binding energies of 71.6 eV (Pt 4f_{7/2}) and 74.9 eV (Pt 4f_{5/2}) (Fig. S4, Table 1), which are slightly higher than the literature-reported values for bulk metallic Pt and zero valent Pt nanoparticles on chemically inert BN support (typically ~71.2–71.4 eV and 74.6 eV, respectively) [36,37]. The observed positive shift of ~0.2–0.4 eV can be primarily originated from the imperfect core-hole screening of small Pt nanoparticles (Fig. 1), and partial charge transfer to the ceria support as the result of metal-support interactions [38].

When 3 cycles of ZnO were deposited (10cPt_3cZnO_CeO₂), the Pt 4f peak positions remained unchanged, indicating no significant alteration in the electronic environment of Pt. However, with 10 ZnO cycles (10cPt_10cZnO_CeO₂), the Pt 4f peaks shifted to higher binding energies, observed at 71.9 eV (Pt 4f_{7/2}) and 75.3 eV (Pt 4f_{5/2}) (Fig. S3, Table 1). This suggests a decrease in electron density around Pt atoms, which can be attributed to electron transfer from Pt to the ZnO layer. This interaction likely reflects the formation of Pt/ZnO interfacial sites, where ZnO withdraws electron density from Pt, stabilizing a slightly more oxidized Pt state or inducing partial charge depletion at the surface [39].

Interestingly, in the sample with 30 cycles of ZnO (10cPt_30cZnO_CeO₂), the Pt 4f peaks shifted back slightly to lower binding energies (71.5 and 74.8 eV), approaching the values for metallic Pt. This reversal may be linked to increased Pt loading, leading to particle agglomeration (Fig. 1). Moreover, thickness and possibly crystallinity of the ZnO layer is different at 30 cycles and may screen or reduce direct Pt-ZnO interaction, thereby restoring a more metallic character of Pt (Chapter 3.1).

For all ZnO-containing thin films, the Zn 2p region exhibited a clear doublet structure with spin-orbit splitting of 23.0–23.1 eV, which is consistent with the oxidation state of Zn²⁺ in ZnO [40] (Figs. S3 and S4). When comparing substrates, the 30cZnO sample showed a Zn 2p_{3/2} binding energy of 1021.8 eV, which closely matches the reported value for stoichiometric ZnO (Table 1). However, in the 30cZnO_CeO₂ system, this binding energy increased to 1022.1 eV, which hints to a stronger electronic interaction between ZnO and the ceria support, likely involving oxygen extraction from CeO₂ by ZnO.

In the case of 3 cycles ZnO, the Zn 2p_{3/2} binding energy dropped to 1021.3–1021.4 eV, both in the bare 3cZnO_CeO₂ and Pt-containing (10cPt_3cZnO_CeO₂) samples (Table 1). In these cases, the ZnO amount is low and the ZnO coverage is incomplete (Fig. 2). The presence of Pt, which itself interacts strongly with CeO₂ and can stabilize surface oxygen vacancies, may help maintain a reduced Zn chemical state.

For the 10cPt_10cZnO_CeO₂ sample, the Zn 2p_{3/2} peak shifts significantly to 1022.3 eV (Table 1). The simultaneous increase in binding energies for both Zn and Pt strongly suggests intense Pt-ZnO interfacial interactions and oxidative charge redistribution. In contrast, in the 10cPt_30cZnO_CeO₂ sample, while the Zn 2p_{3/2} BE remains high at 1022.2 eV, the Pt 4f_{7/2} BE decreases back to 71.6 eV, indicating a partial restoration of metallic Pt character. This decoupling suggests that the thicker ZnO layer (30 cycles) could reduce the extent of direct Pt-ZnO interaction, perhaps due to Pt nanoparticle aggregation or spatial separation from the support interface. In this regime, Pt likely grows atop the ZnO, reducing its sensitivity to the underlying electronic structure of the oxide, while ZnO itself remains in a more oxidized state due to persistent interaction with the ceria substrate.

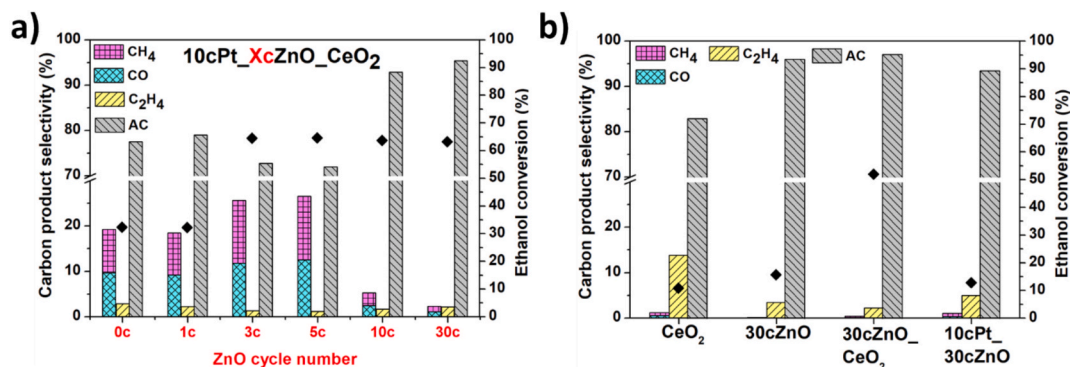
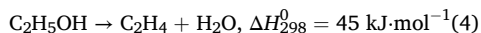
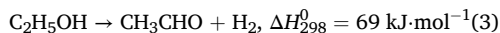


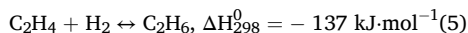
Fig. 3. Catalytic activity of a series of structured thin-film materials: (a) 10cPt_XcZnO_CeO₂/SiO₂, where X corresponds to 0, 1, 3, 5, 10, or 30 ALD cycles of ZnO; (b) CeO₂; 30cZnO; 30cZnO_CeO₂; 10cPt_30cZnO reference samples in the ethanol decomposition reaction in the batch mode at 573 K after 14 h TOS.

3.2.2. Ethanol decomposition and its mechanism for the Pt/ZnO/CeO₂

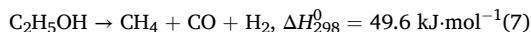
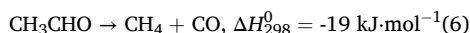
Depending on the active surface sites, ethanol decomposition proceeds through distinct elementary steps that are sensitive to the nature of the catalyst support and metal-oxide interactions [41]. Two main reaction channels dominate the primary decomposition of ethanol: dehydrogenation, yielding acetaldehyde and hydrogen (Eq. (3)) and dehydration, yielding ethylene and water (Eq. (4)):



Ethylene can be hydrogenated by hydrogen formed during the dehydrogenation reaction (Eq. (5)):

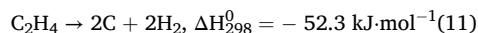
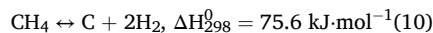
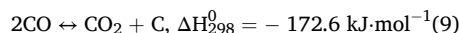


The C–C bond cleavage leading to syngas components may occur via acetaldehyde decomposition (Eq. (6)) or direct C–C scission (Eq. (7)):



Beyond these primary routes, several secondary and side reactions

may occur under the tested thermal conditions. The main reactions include water–gas shift (WGS) reaction (Eq. (8)) and coke-formation reactions: Boudouard reaction (Eq. (9)); methane dehydrogenation (Eq. (10)) and ethylene decomposition (Eq. (11)) [42].



The prepared structures were subjected to ethanol decomposition at 573 K to ensure substantial ethanol conversion while allowing for the observation of both dehydrogenation (Eq. (3)) and dehydration (Eq. (4)) products [43]. Fig. 3a presents the ethanol decomposition performance of 10cPt_XcZnO_CeO₂ structured thin-film materials. In addition to this, a series of reference samples was tested under identical reaction conditions – CeO₂; 30cZnO; 30cZnO_CeO₂; 10cPt_ZnO (Fig. 3b). The carbon-containing products detected in significant concentrations included CO, CH₄, CO₂, C₂H₄, C₂H₆, and acetaldehyde (AC). Independent replicate runs showed extremely small variations, and the resulting uncertainties do not influence the observed activity or selectivity trends. In Fig. 3, the

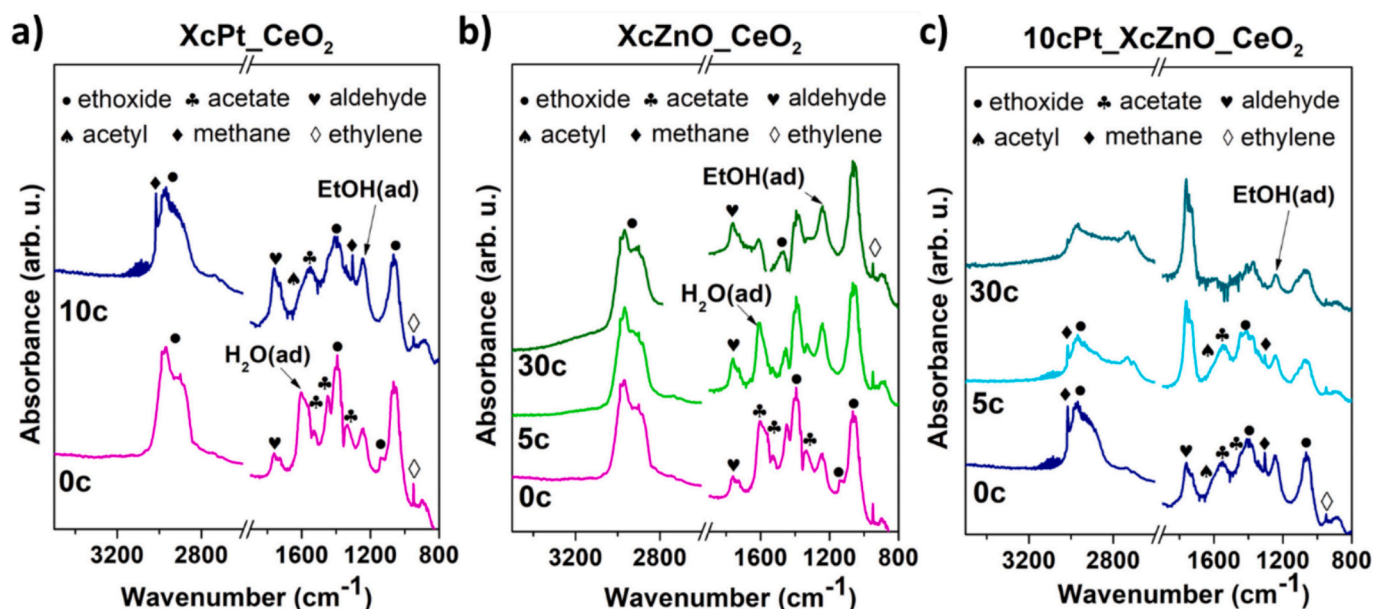


Fig. 4. In situ DRIFTS spectra of evolution of surface species after ethanol exposure at 573 K for: (a) XcPt_CeO₂, (b) XcZnO_CeO₂, and (c) 10cPt_XcZnO_CeO₂ systems, where X = 0; 5; 10; 30 ALD cycles.

catalytic results are presented and compared after 14 h of time on stream (TOS). In the beginning of the reaction ($t \leq 3$ h), the slope of the conversion curve is big and strongly affected by transient activation, which makes it difficult to separate intrinsic activity from stability effects (Fig. S6). In contrast, after 14 h the systems have passed the rapid-change region and reached a representative regime that reflects both the initial activity and the resistance to deactivation. Since the selectivity trends remain unchanged between 3 h and 14 h, comparison after 14 h does not include interference from changes in reaction pathway (Fig. S8). A short discussion on deactivation pathway is included in the SI.

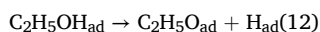
For clarity, three major pathways were monitored using key product markers: C_2H_4 selectivity was used to represent dehydration activity, acetaldehyde selectivity indicated dehydrogenation performance, and the combined selectivity of CO and CH_4 were used as a measure of C–C bond cleavage. Side reactions such as the water–gas shift (CO_2 formation) and ethylene hydrogenation were not included in the simplified reaction map.

To complement the catalytic and XPS studies, in situ DRIFTS experiments were performed on selected samples – CeO_2 , $10Pt_{CeO_2}$, $5cZnO_{CeO_2}$, $30cZnO_{CeO_2}$, $10Pt_{5cZnO_{CeO_2}}$, and $10Pt_{30cZnO_{CeO_2}}$ – to investigate ethanol adsorption and reaction pathways at different interfaces. The experiments were conducted at 573 K, initially under a continuous flow of ethanol (in N_2 carrier gas) for one hour. To simulate batch-mode conditions within the DRIFTS cell, the ethanol supply was then discontinued while maintaining the cell at reaction temperature for one hour. This effectively created a closed environment that allowed reaction intermediates and products to accumulate on the catalyst surface. The resulted spectra are presented in Fig. 4.

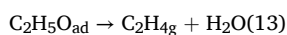
3.2.2.1. Pt/CeO₂ interface. The $10Pt_{0cZnO_{CeO_2}}$ sample provides direct evidence of the catalytic properties of the Pt/CeO₂ interface in ethanol decomposition. In this configuration, the ethanol conversion reached ~20 % and the product distribution was dominated by acetaldehyde, alongside significant amounts of CO and methane, indicating that both dehydrogenation and C–C bond cleavage pathways are active.

In contrast, the reference CeO_2/SiO_2 (Fig. 3b), which does not contain Pt, exhibited nearly 2x less activity and a markedly different product profile. The ethylene formation was much more enhanced, with only minor amounts of CO and CH_4 . On its own, CeO_2 was reported to catalyze both dehydration to ethylene and dehydrogenation to acetaldehyde [44]. In the case of ceria, ethanol dehydration to ethylene most likely follows an E_{1CB} -type mechanism, consistent with its moderate basicity and the presence of Lewis acidic Ce^{4+} centers and oxygen vacancies [45].

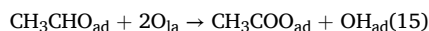
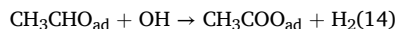
This pathway is further supported by in situ DRIFTS, which provided evidence of ethoxide intermediates through IR bands at 2976, 2929, and 2898 cm^{-1} , corresponding to the asymmetric and symmetric stretching modes of CH_3 and CH_2 groups. Additional features at 1065 and 1132 cm^{-1} were attributed to mono- and bidentate ethoxide $\nu(CC-O)$ modes, accompanied by CH_3 deformation vibrations ($\delta_{as}(CH_3)$ and $\delta_s(CH_3)$) of CH_3 at ~1450 and 1390 cm^{-1} [32,46–48] (Fig. 4a). Ethoxide species form via heterolytic cleavage of the O–H bond in ethanol, and the $\delta(OH)$ mode of adsorbed molecular ethanol appeared at 1240 cm^{-1} (Fig. 4a). The proton is then accepted by a basic site, while the resulting ethoxide binds to a surface metal center (Eq. (12)).



The sharp peak at 950 cm^{-1} , assigned to the CH_2 wagging mode of gas-phase ethylene, together with a band around 1600 cm^{-1} attributed to adsorbed water species, further supports the dehydrogenation pathway observed on several oxides, including CeO_2 and ZnO [49,50] (Fig. 4a) (Eq. (13)).



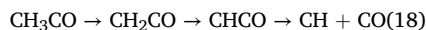
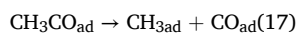
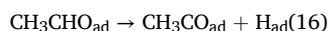
Acetate species – $_{as}(OCO)$, $_{as}(CH_3)$ and $_{s}(OCO)$ – were also detected at ~1557, ~1430, and 1333 cm^{-1} [46,48], indicating partial oxidation of ethanol via aldehyde and transient acetyl (CH_3CO) intermediates [51,52]. This is further supported by a weak aldehyde $\nu(C=O)$ band at 1745 cm^{-1} [53,54] (Eqs. 14, 15).



These findings show that alongside dehydration, the dehydrogenation pathway proceeds as a stepwise mechanism: ethanol $\rightarrow$ ethoxide $\rightarrow$ acetaldehyde $\rightarrow$ acetate, where acetate is a terminal, and non-reactive product under the examined conditions. The acetate species were identical regardless of the supported metal (Pt, Pd, Ir, Rh, Ru), indicating that the formation of acetate species takes place on the oxide support [51].

The improved activity observed in the Pt_{CeO_2} system most likely arises from the synergy of the metal-oxide interface. The XPS analysis revealed a notable increase in the degree of ceria reduction after O_2 - H_2 pre-treatment: the $Ce^{3+}/(Ce^{3+} + Ce^{4+})$ ratio increased to 40.1 % in Pt_{CeO_2} compared to 12.0 % in the CeO_2 sample, which can be attributed to the ability of Pt to promote H_2 -spillover, thus creating oxygen vacancies [8,55]. These vacancies, in turn, promote redox-driven steps such as H-abstraction and C–C bond cleavage, contributing to enhanced formation of acetaldehyde, CO, and CH_4 .

This mechanistic pathway is further supported by in situ DRIFTS results, which reveal the emergence of bands assigned to gaseous CH_4 (1305 and 3016 cm^{-1}), as well as gaseous CO at 2143 cm^{-1} (not shown) (Fig. 4a). The overall spectral profile remained similar to that of CeO_2 with ethoxide and acetate species being predominant intermediates. However, the Pt_{CeO_2} system showed a notably increased aldehyde signal (Fig. 4a). Adsorbed acetaldehyde can transform to CH_4 and CO through the breaking C–C bond in aldehyde. DFT calculations, however indicated that C–H bond scission with concomitant formation of acetyl species is the energetically favored route [56]. Moreover, the formation of an acetyl intermediate over different metal surfaces has been experimentally confirmed at 1610 cm^{-1} for $\nu(CO)$ [57]. Therefore, it was proposed that acetyl formation and C–C bond scission proceeds sequentially through the following series of steps: (Eqs. 16, 17, 18):



Due to the shortlived acetyl on the surface, its detection is not easy. In our case at the Pt/CeO_2 a visible shoulder at 1610 cm^{-1} may indicate its presence (Fig. 4a).

The sample with 1 ALD cycle of ZnO ($10Pt_{1cZnO_{CeO_2}}$) showed very similar activity and product distribution profile compared to that of the Pt_{CeO_2} system (Fig. 3a). This suggests that at such low ZnO coverage, the ceria surface remains largely accessible and the Pt/CeO_2 interfacial environment is mostly preserved. At the same time, platinum concentration is reduced in the $1cZnO$ sample compared to bare Pt_{CeO_2} (Fig. 2), which may explain the slightly higher selectivity toward acetaldehyde in this case.

3.2.2.2. ZnO/CeO₂ interface. The incorporation of 3 ALD cycles of ZnO increased ethanol conversion to ~60 %, boosted C_1 selectivity, and lowered AC production compared to the Pt_{CeO_2} (Fig. 3a). These trends indicate that while most of the Pt appears to remain in contact with the CeO_2 surface, the deposited ZnO begins to participate in the reaction environment, and a cooperative interface involving Pt, ZnO, and CeO_2 forms. Notably, further ZnO deposition did not lead to a proportional increase in the catalytic activity.

To evaluate the intrinsic contribution of ZnO, a $30cZnO$ benchmark

was tested (Fig. 3b). This system displayed much lower ethanol conversion and almost exclusive acetaldehyde selectivity. This behavior confirms that pure ZnO does not promote C–C cleavage, and probably has a low amount of acidic surface hydroxyl groups required for strong ethylene selectivity [58]. It is important to emphasize, however, that ZnO deposition on SiO₂ is limited. The spatial maps revealed non-uniform ZnO coverage on SiO₂ wafer after 30 cycles most likely due to its low surface area (Fig. S5a). In contrast, ZnO nucleation CeO₂ is faster and more homogeneous (Fig. S5b). While this affects total conversion, the product selectivity pattern remains informative, reinforcing the conclusion that ZnO alone is not accountable for the observed changes.

To isolate and study the effect of zinc-ceria interactions, a 30cZnO_CeO₂ control sample was also tested (Fig. 3b). This sample exhibited over 50 % ethanol conversion, indicating synergistic ZnO-CeO₂ activity. This synergy effect can be attributed to interface-induced defect chemistry: Zn²⁺ ($r \approx 0.74 \text{ \AA}$) is a smaller divalent cation which can partially substitute Ce⁴⁺ ($r \approx 0.97 \text{ \AA}$) within the ceria lattice, leading to oxygen vacancy formation [59]. The redox tuning of ceria by ZnO was confirmed by XPS. The Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratio after pre-treatment increased from 12.0 % in bare CeO₂ to 23.1 % in the 3cZnO_CeO₂ system. Moreover, Zn 2p binding energy in ZnO_CeO₂ shifted to higher values relative to ZnO, (from 1021.8 to 1022.1 for the 3/2 Zn 2p component), reflecting lattice oxygen uptake from ceria, Zn has less electron density when it interacts with ceria (Table 1).

DRIFTS showed that the introduction of ZnO altered the product distribution. In the case of ZnO_CeO₂, ethoxide species remained, but acetate formation was significantly suppressed, particularly at higher ZnO content (Fig. 4b). Aldehyde accumulation was slightly more pronounced. Interestingly, even though ZnO is electronically more oxidized (for the 30cZnO_CeO₂ sample) as evidenced by XPS (Table 1), the availability of labile surface oxygen for C–H activation and aldehyde oxidation is reduced. This suggests that incorporated into ZnO lattice oxygen is in a relatively immobile form. The concentration of dehydration products, H₂O and C₂H₄ is greatly diminished with higher ZnO loading, which is in line with catalytic results (Fig. 3b; 4b).

3.2.2.3. Pt/ZnO/CeO₂ interface. While ZnO-CeO₂ interface was shown to participate in the ethanol decomposition by improving overall catalyst reactivity, it was not active in splitting the C–C bond (Fig. 3b). High activity of zinc-ceria combination for the dehydrogenation of alcohols has been highlighted in the literature as well [60].

The enhanced selectivity toward CO and methane in the case of 10cPt_3cZnO_CeO₂ compared to either 10cPt_CeO₂ or ZnO_CeO₂ points to a distinct Pt/ZnO/CeO₂ interfacial effect. The XPS results indicated, the oxygen mobility is further improved in the presence of Pt: after the oxidation–reduction treatment, the Ce³⁺/(Ce³⁺ + Ce⁴⁺) ratio is further increased to 27.6 for the 10cPt_3cZnO_CeO₂. Thus, while the ZnO-CeO₂ interface is primarily responsible for the high ethanol turnover, Pt clearly contributes an additional promotional effect: the integration of Pt increases the conversion from ~50 % in ZnO/CeO₂ to ~60 % in the ternary system.

When a ternary interface is present, it appears that acetaldehyde, once formed, is more readily converted to C₁ products via mobile surface oxygen interactions. CH₃CHO and C₂H₄ can react with oxygen ions to form CO₂ and H₂O. Similar behavior has been reported in ZnO-Co/CeO₂ system, where ZnO promoted cobalt oxidation (Co⁰ → Co²⁺) and excess oxygen transfer led to over-oxidation of CO and CH_x species to CO₂ [9]. In our system, however, Pt did not get more oxidized, as confirmed by identical Pt 4f binding energies in both 10cPt_CeO₂ and 10cPt_3cZnO_CeO₂ samples. This suggests that Pt supplies sufficient atomic hydrogen to prevent complete oxidation of CH_x fragments, enabling partial C–C scission instead of total oxidation.

The in-situ DRIFTS spectra change markedly after platinum introduction and formation of the Pt/ZnO/CeO₂ (Fig. 4c). Ethoxide bands diminished, indicative of rapid reaction turnover. Acetate bands

decreased while aldehyde-related features intensified, including the characteristic $\nu(\text{C}=\text{O})$ band at 1745 cm^{−1}. A weak IR band at 1604 cm^{−1} suggested the presence of acetyl intermediate. Similar spectral features were reported for Pt/CeZrO₂ and Rh/oxide systems [61,62]. In static (non-flow) conditions, methane formation was detected alongside CO and CO₂. These observations suggest that, when a tertiary Pt/ZnO/CeO₂ interface is present, aldehyde oxidation to acetate is hindered, allowing acetyl species to undergo C–C bond cleavage, consistent with catalytic behavior (Eqs. 16, 17, 18) (Fig. 3a).

In Pt/ZnO_CeO₂, the carbonate bands (1409 and 1377 cm^{−1}) were also more pronounced (Fig. 4c). While these bands are present in all spectra, they were largely masked by the strong ethoxide adsorptions in other cases (Fig. 4a, 4b). These carbonate species most probably result from the stabilization of formed at 573 K CO₂ on basic CeO₂ or ZnO-CeO₂ sites, making its transient production less apparent in catalytic measurements, where minimal CO₂ was detected in the gas phase (data not shown) [63]. The CO₂-TPD-DRIFTS spectra (Fig. S9) further confirm the evolution of surface basicity with ZnO addition. The intensity and thermal stability of carbonate bands (~1400 and 1530 cm^{−1}) increase with ZnO content: while in 10cPt_CeO₂ these species desorb below 473 K, they remain stable up to ~573 K in 10cPt_30cZnO_CeO₂.

3.2.2.4. Pt/ZnO interface. At 10 ALD cycles of ZnO, the selectivity shifts again, with acetaldehyde emerging as the predominant product (Fig. 3a). This reversal in trend indicates a significant alteration of the surface environment. The suppression of deeper decomposition suggests that the ternary Pt/ZnO/CeO₂ interface is largely diminished, and the catalyst surface is now dominated by Pt particles deposited on ZnO. This interpretation is strongly supported by ICP-MS data, which show that ZnO loading saturates the surface at this point, displacing Pt from ceria and leading to its preferential nucleation on the ZnO overlayer.

Additional insight comes from XPS analysis, where the Pt 4f binding energy increases from 71.6 eV in Pt_CeO₂ to 71.9 eV in 10cPt_10cZnO_CeO₂, indicating that Pt is more oxidized when in contact with ZnO. This change implies a reduction in the electron density of Pt, which can weaken its ability to cleave C–C bonds, thereby suppressing its activity for deeper decomposition pathways.

However, the presence of a small amount of CH₄ and CO in the 10cPt_10cZnO_CeO₂ sample indicates that Pt/CeO₂ interfacial contact is not completely eliminated at this stage (Fig. 4a). This contrasts with the 10cPt_30cZnO_CeO₂ system, where the deposition of 30 cycles of ZnO likely forms a continuous overlayer, fully separating Pt from the CeO₂. This structural change is corroborated by XPS measurements, which show the absence of cerium surface signals in all samples containing 30cZnO, confirming that ceria is no longer accessible at the outer surface (Fig. S3; Fig. S4). As a result, the formation of C₁ products is lowest in this sample. Supporting this, the reference 10cPt_30cZnO catalyst showed low conversion and C–C splitting capability (Fig. 3b).

In the 10cPt_30cZnO_CeO₂ sample, DRIFTS spectra showed a strong reduction in ethoxide intensity, similar to the tertiary Pt/ZnO_CeO₂ system, indicating accelerated consumption of surface intermediates (Fig. 4c). No acetate species were detected while a small shoulder at 1611 cm^{−1} indicates transient acetyl formation. From the gaseous products, CO is clearly observed while methane remains only in small amounts. This pattern indicated a shift from C–C bond breaking to consecutive hydrogen abstraction mechanism (Eq. 18). In this stepwise sequence, CH_{3-x}CO intermediates formed, which eventually undergo C–C bond scission and give rise to CO and carbonaceous residues as the dominant decomposition products. At the same time, the exceptionally strong acetaldehyde signal highlights that acetaldehyde remains the primary reaction product, reflecting the dominance of the hydrogen abstraction pathway under high ZnO coverage (Fig. 3a, 3b).

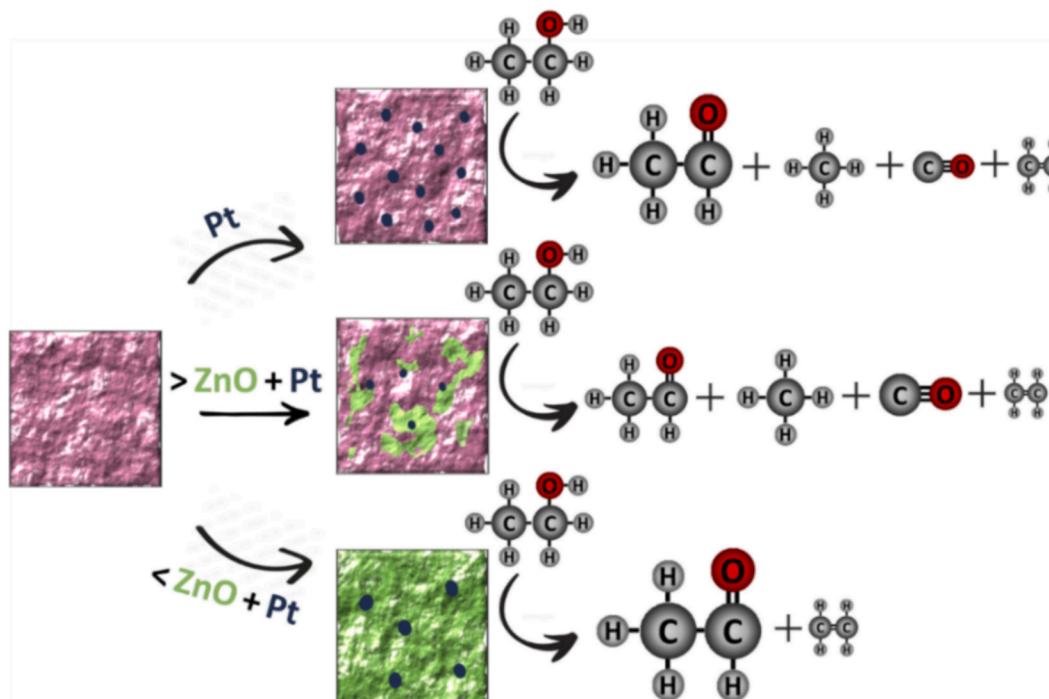


Fig. 5. A schematic illustrating the correlation between the structure of ALD-modified CeO₂ films with varying ZnO content and selectivity in ethanol decomposition reaction at 573 K. Colour code: purple – spincoated CeO₂ overlayer; green – ZnO modification (0–30 ALD cycles); dark blue dots – Pt nanoparticles (10 ALD cycles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

This study demonstrates that ALD provides a powerful and precise method for engineering metal-oxide interfaces to fine-tune the catalytic properties of the sample. By systematically varying the ZnO surface coverage on CeO₂ via ALD cycles, we modulated Pt-support interactions in a controlled manner, influencing Pt dispersion, electronic structure, and oxygen mobility. These interactions were carefully studied by a combination of techniques such as TEM, ICP-MS, XPS, and in situ DRIFTS, allowing us to determine the active interfaces and establish direct structure–function relationships in the thermal ethanol decomposition (Fig. 5).

In the absence of ZnO, Pt nanoparticles nucleated directly on CeO₂, establishing strong Pt-ceria interactions. These structures showed moderate ethanol conversion with acetaldehyde as the dominant product, and a limited contribution from C–C bond cleavage pathways. Partial ZnO overlayers (3–5 cycles) promoted Pt dispersion and generated a ternary Pt–ZnO–CeO₂ interface. This configuration increased Ce³⁺ concentrations and oxygen mobility, as confirmed by XPS, which allowed for maximum ethanol conversions. The selectivity shifted toward C₁ products (CO and CH₄) due to the suppression of acetate formation and the enhanced transformation of aldehyde intermediates. Excessive ZnO loadings (30 ALD cycles), however, isolated Pt particles from CeO₂, reducing the extent of Pt-ceria contact, which resulted in diminished activity. As revealed by in-situ DRIFTS, the acetate formation was strongly suppressed, and mainly the aldehyde intermediate accumulated, consistent with minimal deep decomposition activity (Fig. 5).

CRedit authorship contribution statement

Anastasiia Efremova: Writing – original draft, Visualization, Validation, Investigation, Conceptualization. **Gergő Ballai:** Writing – original draft, Validation, Investigation, Conceptualization. **Ákos Szamosvölgyi:** Supervision, Investigation. **Imre Szent:** Writing –

review & editing, Validation, Investigation, Conceptualization. **Bence Kutus:** Validation, Investigation. **János Kiss:** Writing – review & editing, Conceptualization. **András Sági:** Supervision, Project administration. **Ákos Kukovecz:** Resources, Funding acquisition. **Zoltán Kónya:** Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2026.115640>.

Data availability

Data will be made available on request.

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