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Gallium-Assisted Platinum Isolation: Formation of Multiple Pt Species in Ga-Pt Liquid Metal Catalysts

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ABSTRACT

Ga-Pt liquid metal catalysts have emerged as promising catalysts, offering improved catalytic performance compared to pure platinum for reactions such as propane dehydrogenation. Previous studies suggest that the active species formed in Ga-Pt catalysts differ from traditional metallic Pt. In this study, we explore multiple potential active Pt species by focusing on the surface-derived electronic and chemical structures assessed via X-ray photoelectron spectroscopy (XPS) and the correlating structural composition analyzed by scanning transmission electron microscopy (STEM). While XPS indicates that Pt is present in different chemical environments, STEM reveals different topographic structures varying from Pt single atom to Pt agglomerates and Ga-Pt intermetallic compounds (IMCs). The variation in the chemical, electronic, and topographic structure of Pt depends on its amount, as well as on the surrounding environment (e.g., gallium-oxide shell versus liquid Ga matrix). Further, XPS and STEM in situ investigations at elevated temperature (T) shed light on the high dynamic surfaces, demonstrating the dissolution of Ga-Pt IMCs due to the enhanced solubility of Pt in Ga with increasing T. The chemical and electronic structure of the Pt species is discussed in conjunction with density-functional theory and molecular dynamics simulations, providing an unprecedented conceptual understanding of Ga-Pt catalysts.

1 | Introduction

Over the past few decades, the advancement of thermocatalytic dehydrogenation has become a vivid area of research. Dehydrogenated organic compounds serve as crucial intermediates in the synthesis of polymers and various chemicals. For example, the rising demand for propylene, a key building block for polypropylene and formaldehyde [1], has intensified

significantly. This surge in demand has led to a disparity, referred to as the “propylene gap,” between global propylene demand and its traditional supply derived from by-products of steam cracking and fluid catalytic cracking processes [2]. However, existing industrial processes remain energy-intensive [3] and largely reliant on expensive and/or toxic catalysts, e.g., supported Pt or CrO_x nanoparticles, respectively [1]. In this context, propane dehydrogenation (PDH) emerges as a promising route to bridge

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the propylene gap. Accordingly, PDH is promoted due to its simplicity: propane serves as the sole feedstock, which is converted into propylene and hydrogen as the primary product, which can be utilized as fuel or redirected for other applications [1, 4].

Recent developments in catalysts for PDH have shown that supported alloys can be potentially well-performing alternatives. Sn-Pt and Sn-Ni alloys are more active in PDH with respect to the corresponding pure metal catalysts, i.e., supported Pt and Ni [5, 6]. In addition, Ga-Pt intermetallic compounds (IMCs) with defined crystalline structure demonstrated a promoted reactivity compared to pure Pt [7]. Recently, the family of alloy catalysts was further extended from the crystalline to the amorphous (and even liquid) system where, e.g., trace amounts of transition metals are located in a matrix of (liquid) host metals [8, 9]. A prominent example are Ga-Pt supported catalytically active liquid metal solutions (SCALMS), as catalyst candidates for PDH. Ga-Pt SCALMS are characterized by low concentrations of platinum (<2%) embedded within a liquid Ga matrix and supported by oxide substrates, e.g., SiO₂, Al₂O₃ [10]. SCALMS exhibit exceptional catalytic performance and superior resistance to poisoning and coking compared to conventional Pt/Al₂O₃ catalysts [10–13]. According to the investigations on Ga-Pt SCALMS [14, 15], the outstanding catalytic performance can be attributed to a dissolution of Pt in the liquid Ga matrix at elevated temperatures during reaction conditions resulting in active sites at the liquid Ga/gaseous reactant interface.

While the extraordinary properties of SCALMS have been attributed to the highly dynamic nature of the liquid metal surface containing isolated transition metals [16, 17], examining the structure-function relationship of SCALMS surfaces required for deliberate optimization becomes a major challenge. Specifically, the relationship between observed Pt species and their dependence on PDH-related reaction conditions, e.g., resolving the morphological and chemical/electronic structural changes upon Pt deposition and catalyst liquefaction, has not yet been fully explored. Furthermore, recent studies utilizing correlative identical location nano-computed tomography and analytical transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) have discovered the complex nature of SCALMS catalysts [14, 18]; particularly, the inevitable emergence of a GaO_x shell and its consequence for Pt agglomeration during PDH is multifaceted [18]. On one hand, the structural evolution of the GaO_x shell surrounding the SCALMS particles during PDH, air-exposure, and/or calcination, as well as the segregation of Pt in the oxide shell, leading to the formation of Ga-Pt IMCs, which might play a significant role as active species, has been reported. On the other hand, phenomena such as cracking of the said oxide shell have been observed, allowing the release of liquid Ga-Pt on to the porous support [18]. Accordingly, the perspective of SCALMS has evolved from being described as idealized pristine single atom catalysts dispersed in a liquid metal matrix, to mixed-phase active materials containing amorphous Ga-Pt, crystalline Ga-Pt IMCs, and GaO_x. This zoo of possible present species suggests that more than one active species may be involved in catalyzing PDH complicating the identification of the reactivity decay mechanism observed in Ga-Pt SCALMS [19].

In this study, we aim to bridge and correlate the knowledge gained from IMC- and model system- derived studies and the reactivity

performance of SCALMS. Several investigations of SCALMS model systems in reaction conditions are reported in literature [16, 20, 21]. The combination of X-ray photoelectron spectroscopy (XPS) and correlative analytical TEM has enabled insightful examinations of surface segregation of the active transition metal, precipitation/dissolution of IMCs, and oxide shell formation as a function of temperature in well-controlled conditions [16, 22, 23]. Thus, correlative ex situ and in situ XPS and STEM methodologies are employed in this study for detection and detailed investigation of the Pt species present in both sequential deposited Pt-on-Ga and codeposited Ga-Pt SCALMS model systems as function of Pt content and SCALMS temperature, to identify the microscopic and spectroscopic fingerprints that can be attributed to different present Pt species. The well-defined SCALMS model system prepared through co- as well as sequential deposition allows us to examine the transformation of present Pt species depending on the morphology and local chemical environments. Our observations indicate a transformation in the morphology and chemical structure of present Pt species upon interacting with the Ga matrix and/or the SiO_x/Si support at elevated temperature. We find indications for the presence of Pt species best described by isolated Pt atoms, undercoordinated Pt rafts, and Ga-Pt IMCs. According to analogous studies of Pt deposited on TiO₂ thin-films, a strong relation of the sample morphology and Pt 4f XPS peak position is observed and explained by metal-support interactions and particle size [24–26]. Our results provide a correlation of Pt 4f spectral fingerprints to the observed Pt species in electron microscopy allowing a monitoring of their evolution at PDH-related conditions, to get experimental insight into the distribution and evolution of Pt species under relevant conditions and to identify which species are most plausibly associated with catalytic function in Ga-Pt SCALMS. The resulting implications are discussed in conjunction with static density-functional theory (DFT) calculations and molecular dynamics (MD) simulations with machine-learned force fields (ML-FFs) to assess the significance of the observed spectroscopic changes to the chemical structure of the probed material and consequently to the reported PDH activity [19, 27], paving the way for knowledge-driven modifications of liquid metal catalysts.

2 | Material and Methods

Fully exploiting the synthesis and characterization capacities of the Energy Materials In situ Laboratory Berlin (EMIL) that is composed of an interconnected system of different UHV chambers [28], sample preparation, oxidation/annealing treatments, and spectroscopic measurements have been performed “in-system,” i.e., without exposing the sample to ambient conditions to avoid undesired surface oxidation and contamination of the studied Ga-Pt samples by air and/or moisture.

2.1 | Sample Preparation

Gallium (powder, 99.99%) and platinum (wire, 99.9%) were purchased from Sigma-Aldrich/Alfa Aesar, respectively. The Ga-Pt model system samples were prepared via physical vapor deposition (PVD) using a SPECS EBE-4 e-beam evaporator. All Ga-Pt samples were prepared in ultra-high vacuum (UHV) at a base pressure <1×10^{−8} mbar by coevaporation of Ga and Pt on a

silicon wafer (Boron doped, Czochralsky tech. prepared, 2–4 Ω -cm resistance) with native silicon oxide (SiO_x/Si). Substrates were annealed to 500°C to clean the surface and desorb water before deposition. During deposition, the substrate was kept at room temperature. Pt was evaporated using a 2 mm thick wire, and Ga was evaporated from a BN crucible. The deposition rate was monitored using a quartz crystal microbalance. For photoemission measurements, samples were transferred under UHV conditions in-between preparation and analysis chamber after deposition and oxidation/annealing treatments.

In this study, two sample preparation methods are utilized, i.e., sequential deposition and codeposition. The sequential deposition approach is used to prepare the Pt-on- SiO_x and Pt-on-Ga model system samples. The Pt-on- SiO_x and Pt-on-Ga samples are prepared by step-wise Pt deposition, resulting in an increasing Pt thickness (0.5–3 Å) on SiO_x/Si substrate and on PVD-prepared 300 Å Ga film, respectively. The codeposition approach is used for the preparation of Ga-Pt model system samples. During the preparation, the evaporation of Ga and Pt occurred simultaneously with elevated rates, resulting in the deposition Pt amounts that are equivalent to nominal Pt thickness of 0.3 Å, 1.2 Å, and 20 Å Pt intermixing with 300 Å Ga. This results in nominal Pt concentrations of 0.1 at%, 0.5 at%, and 6.5 at% in Ga, respectively. Note that the corresponding samples have been analyzed by XPS before breaking the vacuum for sample transfer to the TEM and hence the STEM analysis was done on air-exposed samples.

The sample for STEM-EDXS mapping measurements shown in Figure S1 are prepared with sequential PVD (using the same process as used for synthesizing the samples for the XPS studies but includes sample transfer induced exposure to air) on SiO_x terminated SiN_x TEM-grids. The parameters of sample preparation are summarized in Table 1.

2.2 | Lab-Based Photoelectron Spectroscopy

X-ray (XPS) and ultraviolet (UPS) photoelectron spectroscopy measurements were conducted using nonmonochromatized Mg K_α (1253.56 eV) irradiation from a SPECS XR 50 X-ray source and He II (40.8 eV) irradiation from a Prevac UVS 40A2 gas discharge lamp, respectively. The photoelectrons were detected by a ScientaOmicron Argus CU electron analyzer. The pass

energy for the core level detail spectra measurements was set to 20 eV, resulting in a total experimental energy resolution of approximately 0.7 ± 0.1 eV for Mg K_α -XPS. For the He II-UPS measurements, a pass energy of 5 eV was used, resulting in a total experimental resolution of approximately 0.2 ± 0.1 eV.

2.3 | Synchrotron-Based Photoelectron Spectroscopy

[In situ annealing monitored by XPS measurements of Ga-Pt samples were conducted in the SISSY-1 endstation using highly brilliant soft X-ray radiation from the UE48-PGM undulator/monochromator combination and hard X-ray radiation from the U17-DCM setup of the two-color EMIL beamline [28]—located at the BESSY II synchrotron, which is operated by the Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB). The SISSY-1 endstation (at a base pressure $< 2 \times 10^{-9}$ mbar) is equipped with a Scienta EW 4000 hemispherical electron analyzer. The endstation is designed with a magic angle geometry for photoelectron spectroscopy measurements [29]. Pt 4f core levels were measured using 570 eV photon energies having a kinetic energy (KE) of approximately 500 eV (resulting in a inelastic-mean-free-path of 1.4 nm) [30]. A pass energy of 20 eV was used for recording the detail spectra resulting in a total experimental resolution of 0.4 ± 0.1 eV. All spectra are energy-calibrated using the Fermi-edge (of metallic Pt) acquired with same photon energy.

2.4 | XPS Data Analysis

The Pt 4f core levels were simultaneously fit using Winspec by Doniach-Sunjic profiles including a Shirley background. The fits were constraint using a fixed spin-orbit splitting (3.33 eV [31]), a 5/2-to-7/2 doublet area ratio of 3-to-4 as governed by the multiplicity rule ($2j + 1$), and coupled peak shapes ensuring that the XPS Pt 4f doublet signatures of all Pt species had the same spectral width.

2.5 | STEM

In situ and ex situ energy dispersive X-ray spectroscopy (EDXS) STEM studies were performed using a ThermoFisher Scientific (TFS) Titan Themis microscope operated at 300 kV. The samples sequentially deposited by PVD (similarly prepared as those used

TABLE 1 | Summary of synthetic protocols used to prepare the studied Pt and Ga-Pt samples.

Sample name	Preparation approach	Substrate/characterization method	Pt thickness	Ga thickness
Pt-on- SiO_x	Sequential deposition	SiO_x/Si (XPS/STEM)	0.5, 1, 2, 3 Å	300 Å
Pt-on-Ga	Sequential deposition (Ga first)	SiO_x/Si (XPS)	0.5, 1, 2, 4 Å	300 Å
Ga-Pt (0.1 at%)	Codeposition	SiO_x/Si (XPS)	0.3 Å	300 Å
Ga-Pt (0.5 at%)		SiO_x/SiN (STEM)	1.2 Å	300 Å
Ga-Pt (6.5 at%)			20 Å	300 Å
Pt-on-Ga	Sequential deposition (Ga first)	SiO_x/SiN (STEM/EDS, Figure S1)	3 Å	40 Å

for XPS studies) on DENSsolution wildfire chips are inserted in a DENSsolution single tilt heating holder and inserted in the TEM for in situ heating observations. The TEM is equipped with Cs-correctors both at the illumination and imaging side, along with a Super-X EDXS system. In the STEM imaging experiments, the probe-forming semiangle was set to a value of 15.7 mrad. A probe current of ~60 pA and dwell times of 5–10 μ s were applied for high-angle annual dark-field (HAADF) STEM imaging; an increase probe current of 150–200 pA and a dwell time of 30 μ s were applied for EDXS-maps. For in situ studies, the beam damage to the sample was carefully evaluated by direct comparison with unobserved areas in ~100°C steps.

Ex situ STEM imaging was performed utilizing an aberration-corrected Thermo Fisher Scientific Spectra 200 at 200 keV. Images were taken at 1.9 Mx with 3 μ s dwell time (for single atom (SA) – like Pt topographies on Pt-on-SiO₂ samples) and at 3.8 Mx with 5 μ s dwell time (for SA-like Pt topographies on Pt-on-Ga samples) at a camera length of 98 mm. For that a beam convergence angle of 15 mrad, a collection angle of 56–200 mrad, and a beam current below 20 pA were used. To avoid charging of the Pt-on-SiO₂ samples, a Carbon Coater (Leica EM ACE200) was used to deposit C on the backside of the TEM-Grid (2 pulses).

Segmentation of STEM images: for statistical analysis of the SA-like and different agglomeration-type Pt topographies (for Pt-on-SiO₂, cf. Figure 1), STEM images (2024 × 2024 sample size with 18.17 pm pixel size) were segmented (with preceding binning 2) using the software ArivisVision 4D (v. 4.1.1.) utilizing a machine-learned segmentation. The segmentation was trained with respect to three classes, namely, SAs, agglomerates, and background/substrate. For segmentation purposes and the following discussion all segmented Pt features with <4 pixels were assigned to a SA-like Pt topography.

The STEM-EDXS measurement displayed in Figure S1 was acquired at a Titan Themis microscope equipped with a Super-X EDXS detector and a GIF Quantum ERS (spectrometer) operated at 300 keV with 30 μ s dwell-time, a probe current of 250–300 pA, and a pixel-size of 0.38 nm. The probe-forming semiangle was set to a value of 15.7 mrad. Spectrum image quantification was optimized with the help of the *Thermo Scientific Velox* Software (3.8.1.14) using prefiltering of 1.0 gaussian blur and limiting Pt to the peak fractions of its M-lines to avoid overlapping peak fractions of Ga. Selected area electron diffraction (SAED) data was acquired using an Selected Area (SA) aperture including a round area with diameter of about 3.4 μ m.

2.6 | DFT and ML-FF Calculations

All first-principles calculations and all molecular dynamics simulations with machine-learned force fields were performed with the VASP (Vienna Ab Initio Simulation Package) code, version 6.4.2, where the valence electrons are described with plane waves and the projector augmented wave (PAW) method is used to represent the atomic cores [32–34]. Exchange-correlation effects were described with the exchange-correlation functional developed by Perdew, Burke, and

Ernzerhof (PBE) [35]. The convergence criterion for the electronic minimizations were always set to 10^{−7} eV; in geometry optimizations, atomic positions were relaxed until a maximum force component criterion of 5 × 10^{−3} eV/Å was met for the crystalline intermetallic compounds and a criterion of 1 × 10^{−2} eV/Å was met for the Pt clusters adsorbed on a SiO₂ surface.

2.7 | Pt Clusters of Different Sizes

Pt₁, Pt₄, Pt₇, Pt₁₀, Pt₁₅, Pt₂₄, Pt₃₃, Pt₄₀, and Pt₅₂ were placed on a crystalline α -Ga surface slab that was used as a computational model to represent the local coordination environment of metallic Ga. Acknowledging that the PVD prepared Ga is rather amorphous or poorly crystalline. Importantly, however, as the conclusions drawn from these simulations rely on local geometric and electronic descriptors (e.g., Pt coordination, charge transfer, and bonding characteristics), which are expected to be relatively insensitive to long-range crystallinity, we consider, in this context, α -Ga to serve as a reasonable approximation for capturing the essential physics of Pt–Ga interactions.

In the first step, the gas phase clusters, whose initial structures were obtained from Ref. 33, were optimized in cubic 30 × 30 × 30 Å unit cells [36]. In the second step, they were placed on the α -Ga slab and (together with the upper half of the slab) reoptimized (see Table S1 for cluster formation energies of Pt clusters on a Ga surface). Then, core level shifts were calculated for all Pt atoms in the clusters to investigate the influence of the size of a cluster and the position of the current atom in the cluster on its initial and final state core level energies. In order to manage the calculations efficiently (one separate final state calculation is needed for each Pt atom in each system), an automated CLS setup and evaluation algorithm was developed and added to the program `analyze_dft` in our `utils4VASP` repository on github [https://github.com/Trebonius91/utils4VASP; DOI: 10.1021/acs.jctc.5c01491]. It generates a separate final state calculation folder for each atom of a chosen element (Pt in this case) and evaluates the results by generating pseudo-XPS spectra of Gauss-broadened final state energies and PDB files with CLS energies assigned to atoms, allowing a spatial visualization of the energies. The same strategy was applied to place Pt rafts of different sizes (Pt₃, Pt₆, Pt₁₀, Pt₁₅, and Pt₃₀) on a hexagonal SiO₂ surface slab with two defect sites (missing Si atoms). For Pt₁₅, a one-atom layer and a two-atom layer raft were placed; the Pt₃₀ raft had two layers.

Finally, **diffusion coefficients** of Pt atoms on SiO₂ and liquid Ga were calculated at different temperatures. For Pt on SiO₂, different local adsorption minima were optimized and connected via nudged elastic band (NEB) calculations using the VASP TST tools add-on [37]. The transition state along the most favorable diffusion path (highest point of the respective NEB path) has been optimized thereafter with the dimer method [38]. Based on the found TS, the diffusion rate along the path has been calculated using the simple approximation

$$k(T) = \nu \exp\left(-\frac{E_{\{\text{TS}\}} - E_{\{\text{min}\}}}{k_B T}\right) \quad (1)$$

where ν is the vibrational frequency at the TS, E_{TS} the potential energy at the TS, and E_{min} the potential energy at the local minimum, where the diffusion path starts.

The diffusion coefficient was then approximately obtained by

$$D(T) \approx a^2 k(T) \quad (2)$$

where a is the distance covered by one diffusion step, estimated to be 3.88 Å from the geometry of the diffusion NEB path.

The calculation of static NEB diffusion paths turned out to be difficult for the Pt on α -Ga, since a significant rearrangement of the Ga atoms takes place during the diffusion step. Since this hardly suits the model of a fixed surface, on which the Pt atoms are moving, we decided to move to a fully dynamic picture. For this, we calculated the Pt diffusion coefficients from the mean square displacement of Pt atoms during a ML-FF MD simulation of a Ga-Pt slab containing 171 Ga and 9 Pt atoms. Since we are interested in the diffusion parallel to the slab surface, we only calculated the mean square displacement with respect to x and y coordinates

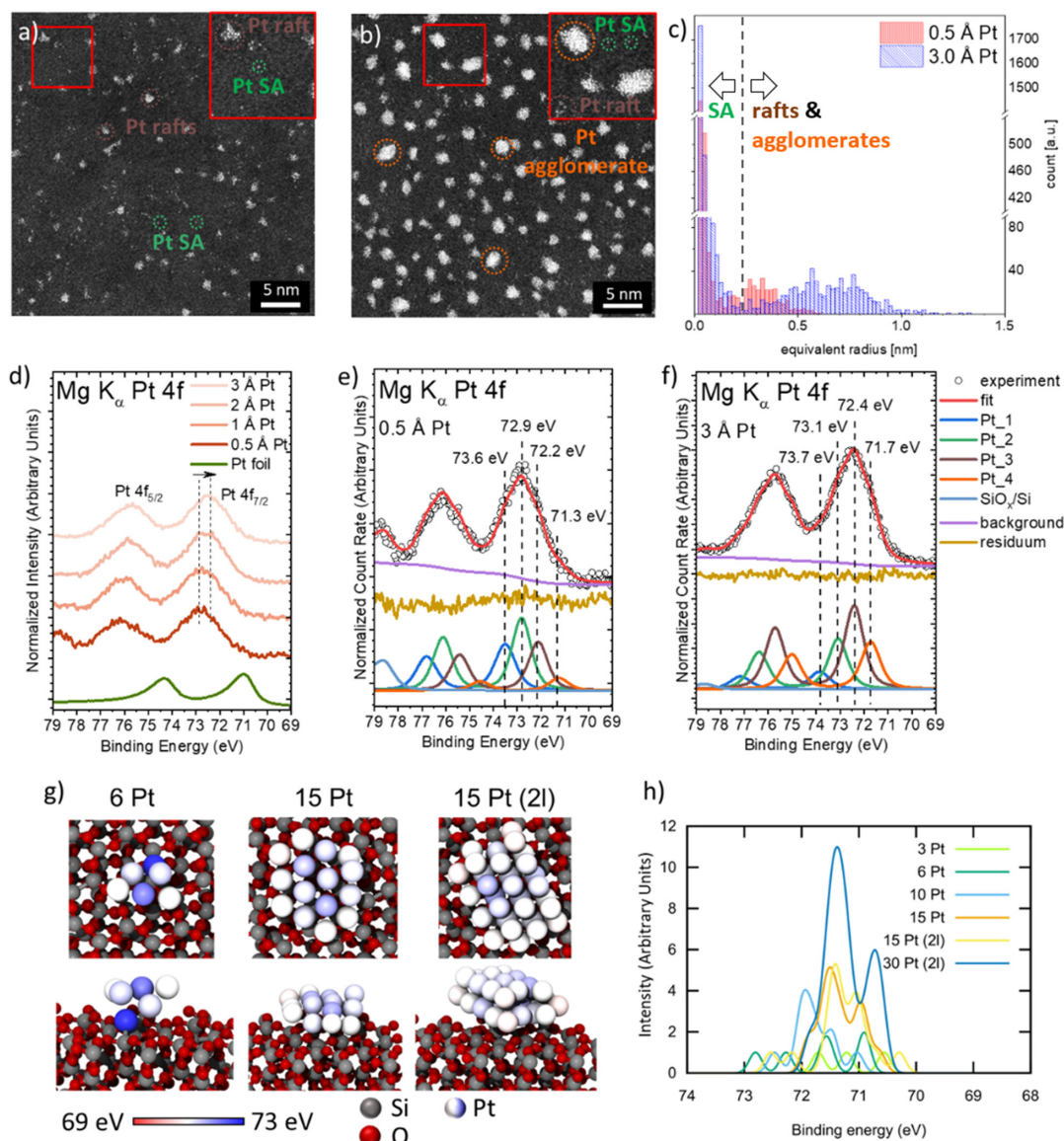


FIGURE 1 | STEM images of nominal 0.5 Å (a) and 3 Å (b) Pt deposited on a SiO₂ TEM grid with native SiO_x featuring Pt single atoms (SAs) and agglomerated rafts with increasing deposition amount summarized in the segmented histogram displayed in (c). (d) Mg K_α-excited XPS Pt 4f detail spectra for different Pt loadings equivalent to a nominal thickness of 0.5 Å to 3 Å Pt, exhibiting a continuous shift towards lower binding energy (BE). The Pt 4f spectrum of sputter cleaned Pt foil is also plotted as a reference of metallic Pt. (e, f) Fit analysis of Pt 4f XPS detail spectra of sequentially deposited 0.5 Å and 3 Å Pt on SiO_x/Si support. A reasonable fit requires 4 different Pt 4f spin-orbit split fit components (Pt₁, Pt₂, Pt₃, Pt₄) of which the position of the Pt 4f_{7/2} is indicated. The SiO_x/Si fit component at 78.5 eV BE refers to the Si 2p excitation satellite peak resulting from Mg K_α emission of the nonmonochromatized Mg K_α source [31]. Below each fit, the residuum (i.e., the difference between data and fit) is shown to visualize the quality of the fit. (g) Optimized DFT geometries of Pt agglomerations (6 to 30 atoms) on a defective SiO_x surface. 15 Pt (2l) model represents the 2D morphology of Pt clusters with 2 layers of 15 Pt atoms. The calculated Pt 4f_{7/2} BE of Pt atoms is visualized by the color code of red → white → blue to represent the BE from 69 to 73 eV. Calculated final state Pt 4f_{7/2} core level spectra calculated for Pt clusters of different sizes (3 atoms to 30 atoms) is summarized in (h), indicating a shift to higher BE with decreasing number of present Pt atoms, i.e., increasing Pt isolation.

$$\Delta^2(t) = \frac{1}{N} \sum_{i=1}^N ((x_i - x_0) + (y_i - y_0))^2 \quad (3)$$

where N is the number of Pt atoms in the system. The diffusion coefficient was then obtained by the usual expression, now only over two dimensions

$$k = \lim_{t \rightarrow \infty} \frac{D_k^2(t)}{4t}$$

Five ML-FF trajectories were sampled for 0.4 ns each at 27°C, 127°C, 227°C, 327°C, 427°C, and 527°C, and the diffusion coefficients calculated for each run were averaged at the respective temperatures.

3 | Results and Discussion

3.1 | Pt on SiO_x

Note that unambiguous identification of different Pt species is challenging. This is why we combine in this paper three different analysis approaches and in addition, our conclusions are not based on a single dataset but on the consistency between XPS (chemical and electronic state), STEM (topological structure), and DFT (energetics and electronic structure as a function of topography) derived information of different (also model) sample series and cross validation with literature. Thus, before investigating the more complex Ga-Pt systems, we first focus on the spectroscopic and microscopic characteristics of Pt species on silicon oxide surfaces, i.e., Pt-on-SiO_x, as derived by XPS and STEM. For this, Pt was deposited at room temperature onto silicon TEM grids with a natively formed silicon oxide layer at the surface (SiO_x/Si) with two different loadings, i.e., Pt amounts that would result in a nominal (equivalent) thickness of 0.5 Å and 3 Å when assuming a complete homogeneous coverage of the support, which aimed at mimicking the miniscule amount of Pt in SCALMS (cf. method section). As a first result the STEM analysis of Pt-on-SiO_x reveals the presence of dispersed Pt rather than homogeneous coverage of the support (cf. Figure 1a,b), as expected. Directly visible in Z-enhancing high angle annular dark field (HAADF) STEM contrast [39] is the presence of three major species: Pt single atom (SA), 2D plate-like Pt rafts, and Pt agglomerates with different sizes on the support. The presence of all these topographic species is observed on both samples. However, for the sample with higher Pt loading, a trend towards larger and more rafts can be observed. These findings align well with established literature indicating a tendency for Pt to agglomerate, which can be attributed to the inherent (lower) surface energy and thus increased thermodynamic stability of such formed agglomerations [25, 26, 40, 41]. Examinations of the Pt rafts suggest that they mostly exhibit a distinct 2D morphology, lacking observable lattice fringes that indicates the formation of crystalline Pt nanoparticles (hence named “2D Pt rafts”) [24]. Nevertheless, larger Pt rafts consisting of several Pt layers with increased Pt–Pt coordination are also observed in the 3 Å Pt sample (i.e., the sample with higher loading), which we refer to as “Pt agglomerates” (Figure 1a,b). This observation is consistent with previous studies on Pt deposited on TiO₂ [24, 42], which reported on similar topographies under

various conditions, such as different loadings or applied currents [25], as well as light-induced or thermal agglomeration [24, 26]. Moreover, examples from literature, including the behavior of Au as a Pt subgroup element, also display a comparable agglomeration behavior [43]. The STEM images shown in Figure 1a,b are further segmented for a quantitative evaluation of the size distribution of the detected Pt topographies (cf. Figure 1c). The analysis (cf. method part) reveals i) decrease of the SA to raft ratio, ii) a broadening of the size distribution, and iii) a larger average Pt-raft size (and thus development of Pt agglomerates) upon higher loading. However, it is notable that while the ratio between the SAs and rafts changes drastically, the total amount of SAs appears to be roughly similar for both samples. This observation can be attributed to the sequential formation of Pt SAs on the SiO_x/Si support during deposition.

The spectroscopic fingerprints of the present Pt species on SiO_x/Si are further elucidated by XPS (cf. Figure 1d–f). A sequential Pt deposition from nominal 0.5–1, 2, and 3 Å Pt on a SiO_x/Si support is studied by XPS (corresponding survey spectra of the samples are shown in Figure S2). As a first consideration of the consecutive Pt deposition below nominal monolayer thickness on SiO_x/Si support (cf. methods part), the XPS spectra reveal a shift of the Pt 4f core level peak to lower binding energy (BE) as a function of deposited Pt contents (cf. Figure 1d). Nevertheless, the peak position remains at significantly higher BEs compared to the feature of sputter-cleaned Pt foil, i.e., metallic Pt, indicating the absence of a metallic character. The broader spectral features from Pt deposited on SiO_x/Si compared to those of Pt foil indicate a multi-species chemical structure profile of different Pt species on SiO_x, consistent with the STEM finding of the presence of various Pt topographies (with different Pt–Pt coordination). This peak shift is also corroborated by the literature, where a shift toward lower binding energy serves as a fingerprint for Pt agglomeration occurring below monolayer coverage [44, 45]. According to previous studies on Pt nanoparticles, the larger agglomerates correspond to a more metallic character, resulting in lower BEs [45–47]. By applying the fit analysis routines shown in Figure 1, it is possible to identify at least four distinct Pt 4f_{7/2} fit components (cf. Figure 1e–f): Pt₁ at 73.6 ± 0.1 eV, Pt₂ at 73.0 ± 0.1 eV, Pt₃ at 72.3 ± 0.1 eV, and Pt₄ at 71.5 ± 0.2 eV. Note that a three-component fit did not result in a reasonably good representation of the data (see Figure S3), corroborating the presence of at least four Pt species. By comparing the fit analysis of the XPS spectra and the Pt SAs/Pt rafts ratio derived by segmentation of the STEM results (cf. Figure 1c), a strong correlation between the ratio of the spectral components and the microscopy-derived Pt topographies is observed. Upon increasing the total Pt amount from 0.5 Å to 3 Å, the mean size distribution changes from ~0.3 nm to ~0.7 nm equivalent radius (cf. Figure 1c), indicating that Pt rafts become the dominant species for higher Pt loadings. Along with this transition, the relative intensity of components Pt₁ and Pt₂ at around 73.6 eV and 73.0 eV, respectively, decreases with respect to the intensity of the components Pt₃ and Pt₄ at around 72.3 eV and 71.5 eV, respectively. In combination with previous findings indicating that the Pt 4f_{7/2} component around 73.5 eV can be associated with oxidized platinum (PtO_x) [48, 49], we tentatively attribute the observed Pt 4f_{7/2} spectral contributions to the different microscopy-derived Pt topographies, as follows: Pt₁ is ascribed to Pt SAs pinned at defect sites of SiO_x support presumably forming PtO_x, Pt₂ is attributed to Pt SAs on SiO_x,

Pt_3 corresponds to undercoordinated Pt atoms present in 2D Pt rafts, and Pt_4 represents increased coordinated Pt atoms in Pt agglomerates.

Furthermore, DFT geometry optimizations (cf. method part) simulating Pt distribution on a defective SiO_x surface missing Si atoms directly visualize the effects of size-dependent Pt-agglomeration, revealing the formation of 2D-like structures and the pinning of Pt SAs on defect sites (cf. Figure 1g–h and methods of DFT calculations). The BE shifts obtained from the calculated DFT Pt 4f_{7/2} final state core level energies, referenced towards the experimental value of metallic Pt with a separate calculation, support the assignment of XPS fingerprints: there is a visible general trend towards higher BEs upon Pt isolation and oxidation with BE values between 70 and 73 eV. The incorporation of Pt atoms at SiO_x defect sites leads to a BE shift up to 73 eV (Figure 1g). In contrast, the Pt 4f_{7/2} BE of Pt contributing to Pt rafts located on the SiO₂ support shifts to lower BEs around 71.5 eV. In short, based on the STEM images and XPS spectra a Pt structure-size-dependent Pt 4f_{7/2} peak shift is observed. Notably, DFT core level shift calculations reveal that Pt atoms at different positions relative to both the substrate and the borders of the agglomerates exhibit different BEs. In this context, undercoordinated Pt atoms at the edges of agglomerates also exhibit different BEs as compared to those in the center (Figure 1g).

3.2 | Pt in Ga-Pt SCALMS at Room Temperature

To shed light on which Pt species are present in Ga-Pt SCALMS, Pt was sequentially deposited after initial Ga deposition (cf. method part). The primary aim was to develop a straightforward Ga-Pt model system without the presence of GaO_x, to unravel the potentially active Ga-Pt species in a SCALMS related context. To facilitate this, the Pt-on-Ga model systems (at loadings of 0.5 Å and 4 Å nominal Pt thickness on top of 300 Å Ga) were prepared directly in ultra-high vacuum conditions (UHV), i.e., $\leq 1 \times 10^{-8}$ mbar, to avoid the formation of a GaO_x shell that would have a significant impact on emerging BE shifts in XPS [50, 51].

The contaminant- and oxide-free surface of Pt-on-Ga samples is corroborated by survey spectra examination (cf. Figure S4, S5). The Pt 4f detail spectra of Pt-on-Ga samples were fitted (summarized in Figure S6) following the identical approach as employed for the Pt-on-SiO_x system, revealing again the presence of four components (cf. Figure 2), with slightly different characteristics. For 0.5 Å Pt on Ga, both the relative fractions of the components and the BE in particular of component Pt_4 slightly change as compared to the Pt-on-SiO_x system (cf. Figure 1e). We find Pt_1 at 73.7 ± 0.1 eV, Pt_2 at 73.0 ± 0.1 eV, Pt_3 at 72.3 ± 0.1 eV, and Pt_4 at 71.9 ± 0.1 eV.

According to the discussion above, these four components may still, to some extent, be attributed to PtO_x (Pt_1), Pt SAs (Pt_2), Pt rafts (Pt_3), and Pt agglomerates (Pt_4), respectively. However, the 0.4 eV higher BE of component Pt_4 may indicate the absence of Pt atoms with high Pt–Pt coordination, favoring the formation of a different Pt species depicted as Pt_5 in later discussions, for example those associated with Ga-Pt IMCs [52, 53].

For the 4 Å Pt-on-Ga sample the Pt 4f peak narrows. The comparison of the Pt 4f core level spectra for the 3 Å Pt-on-SiO_x and 4 Å Pt-on-Ga samples is plotted in Figure S7, corroborating this observation. The narrower Pt 4f peak of the 4 Å Pt-on-Ga sample indicates the formation of a single dominant Pt species. Indeed, the Pt_3 component at 72.3 eV prevails over the other three species, with Pt_1 (associated with PtO_x) completely disappearing (cf. Figure 2b). Here, partial Pt dissolution up to its solubility limit in Ga may play a key role. Accordingly, DFT geometry optimizations also suggest a limited Pt dissolution on Ga surfaces (cf. Figure 2c). Pt clusters arranged on the Ga surface (α -Ga serves here as a reasonable approximation model for the rather amorphous or poorly crystalline PVD Ga; see details in the Material and Methods section above) become partially dissolved into the Ga matrix, leading to a Pt 4f core-level shift towards higher BEs with increasing site isolation. With increasing Pt cluster size, the undercoordinated Pt agglomerations present in a Ga-containing environment cause the core-level shift towards lower BE. It should be noted that the Ga deposition in this study results in a Ga film that is not completely closed on the SiO_x/Si support [50]. This dewetting

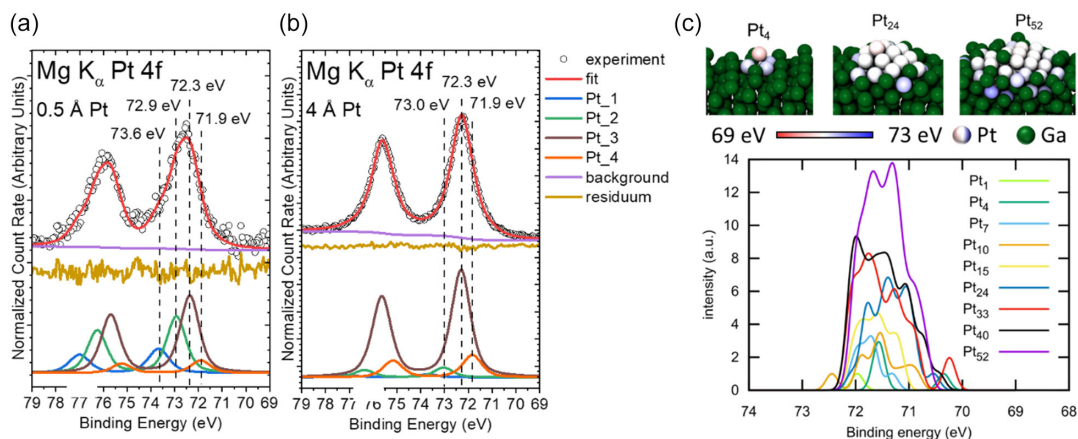


FIGURE 2 | Fit analysis of Mg K_α-excited XPS Pt 4f detail spectra of sequentially deposited nominal 0.5 Å (a) and 4 Å (b) Pt on 300 Å Ga. A reasonable fit requires 4 different Pt 4f spin-orbit split fit components (Pt_1, Pt_2, Pt_3, and Pt_4) of which the position of the Pt 4f_{7/2} is indicated. (c) DFT geometry optimized structures of three example clusters (Pt₄, Pt₂₄, and Pt₅₂) deposited on α -Ga. Shown are the optimized structures (top), where the Pt atoms are colored according to their 4f final state BE (red: 69 eV, blue: 73 eV, cf. color bar) as well as pseudo-XPS spectra (bottom), where the final state energies of all Pt atoms in the clusters are broadened by a Gaussian (FWHM: 0.08 eV) and summed up for each cluster, respectively.

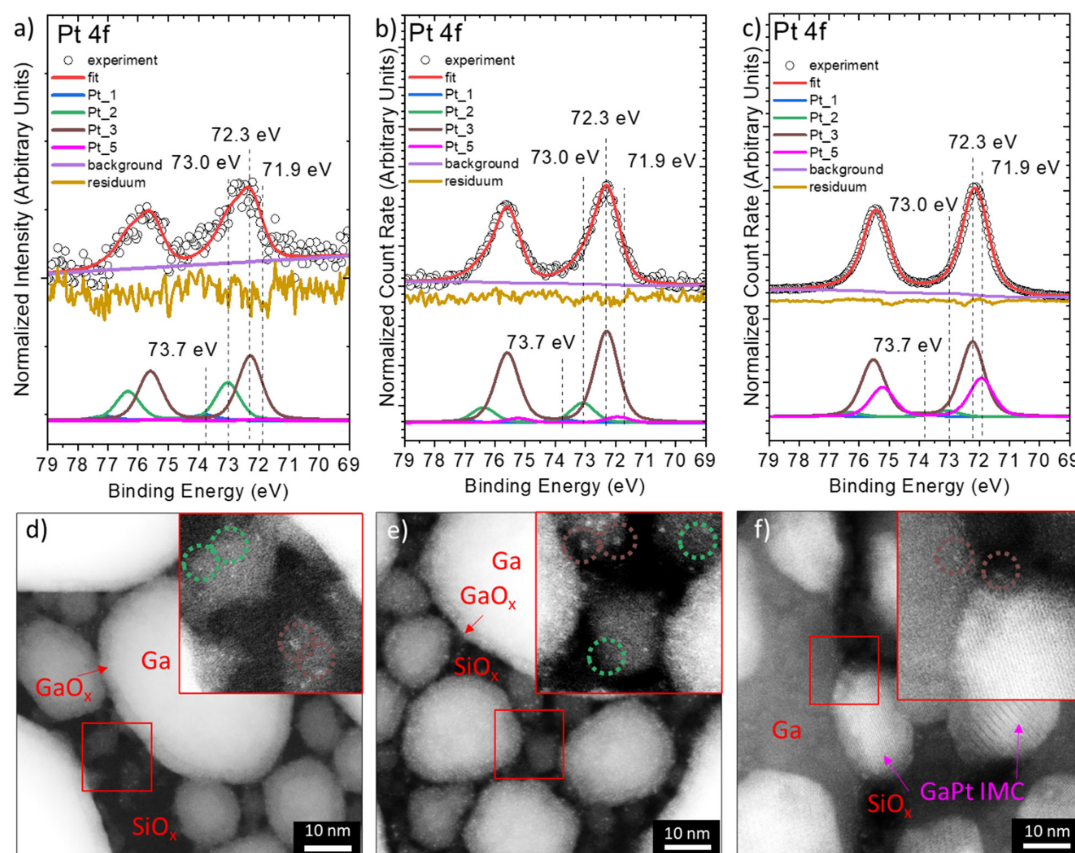


FIGURE 3 | Fit analysis of Mg K α -excited XPS Pt 4f detail spectra of codeposited Ga-Pt alloys of (a) 0.3 Å, (b) 1.2 Å, and (c) 20 Å Pt with 300 Å Ga, leading to nominal Pt concentrations of 0.1 at%, 0.5 at%, and 6.5 at%, respectively. The Pt 4f peaks are fitted with Doniach-Sunjic profiles with 0.94 eV FWHM. (d–f) Correlative STEM images in Z-dependent HAADF contrast of the same Ga-Pt samples (after sample transfer in ambient conditions), featuring Pt SAs, undercoordinated Pt rafts, and Ga-Pt IMCs (in f) near the O-terminated SiN_x support (SiO_x), the amorphous Ga, and the GaO_x shell, respectively.

implies that, to some extent, minor contributions from Pt-on-SiO_x regions are also present in the spectra shown in Figure 2.

The analyzed data highlight two factors influencing the Pt 4f_{7/2} BE of the present Pt species: i) the degree of Pt isolation, either at isolated (defect) sites—most likely located at cluster corners or in proximity to the support—and ii) the type of underlying substrate, which clearly affects the agglomeration behavior, including morphological changes of the Pt rafts, and consequently the Pt 4f_{7/2} BE.

Unfortunately, STEM imaging of the same Pt-on-Ga sample after each sequential deposited step was not possible, as the high oxophilicity of Ga causes immediate surface oxidation during transfer from the deposition chamber to the microscope. This oxidation may significantly alter the morphology of the Pt species predominantly located at the sample surface [54].

Thus, in the following, we will further elucidate the nature of the Pt species and their XPS fingerprints by investigating first the loading and subsequently the temperature-dependent behavior of codeposited Ga-Pt model systems. Here, the system is intermixed due to the codeposition approach, leading to a lower impact of surface (oxidation) effects on the Ga-Pt and Pt species in the model system. We codeposited Ga and Pt onto SiO_x-terminated silicon nitride

(SiN_x) micro-electromechanical systems (MEMS) chips using three different Pt loadings, corresponding to nominal Pt thicknesses of 0.3 Å Pt, 1.2 Å Pt, and 20 Å Pt (in parallel with 300 Å Ga) and to Pt concentrations of 0.1 at%, 0.5 at% and 6.5 at%, assuming complete and homogeneous coverage of the MEMS chip. Using MEMS chips with electron-transparent windows as support allows us to investigate nominal *identical* samples by XPS and HAADF STEM (cf. Figure 3); however, note that while XPS was performed before breaking the vacuum to transfer the samples to the TEM, the STEM measurement was done on air-exposed samples. The codeposition was designed to create a model system closely resembling real-world Ga-Pt SCALMS by purposely intermixing Ga and Pt, analogous to their intended configuration in catalytic applications, while remaining suitable for in situ TEM heating experiments (vide infra). Here, the formation of an oxide layer during transfer to the TEM likewise reflects the application case, where such oxides form either natively during transfer to the reactor or more prominently during calcination steps in the synthesis of real-world SCALMS [18]. Following the same fit approach of the XPS spectra as presented above for the Pt-on-SiO_x and Pt-on-Ga samples, four Pt 4f_{7/2} components are required to describe the data properly. We find Pt₁ at 73.7 ± 0.1 eV, Pt₂ at 73.0 ± 0.1 eV, Pt₃ at 72.3 ± 0.1 eV, and Pt₅ at 71.9 ± 0.1 eV (see Table S2 for an overview of the Pt 4f spectral fit contributions, corresponding Pt speciation, and semiquantitative occurrence).

Three key aspects will be discussed in the following: i) the very weak contribution of Pt₁ (at 73.7 eV), ii) the appearance of a new Pt species (Pt₅), and iii) the evolution of the XPS Pt 4f_{7/2} spectral contributions with increasing Pt content, from an initially rather balanced occurrence of Pt₂ and Pt₃ towards a Pt₃-dominated signal with distinct Pt₂ contributions, and finally to a more balanced Pt₃ and Pt₅ scenario. The minor Pt₁ species can again be attributed to PtO_x formed on the exposed oxide-terminated support, as also observed in the investigations discussed above (cf. Figures 1 and 2). The PtO_x component in the codeposited Ga-Pt samples is much less prominent than in the sequentially deposited Pt-on-Ga model systems (cf. Figure 2a,b). This observation is reasonable, as during codeposition, Pt atoms—unlike in sequential deposition—do not impinge on the bare substrate but are always accompanied by Ga, which exhibits a higher affinity for oxygen bonding [55].

The assignment of the other three species is aided by atomically resolved STEM images (cf. Figure 3d–f), which reveal isolated Pt species on the support, within the Ga matrix, and near the GaO_x shell, while Pt agglomerates and/or IMCs additionally form within the Ga droplets. Notably, Ga-Pt IMCs are suggested to only form in the Ga-Pt sample with highest Pt content (6.5 at%; Figure 3f), similar to the Pt-on-Ga model system. Thus, the increased peak at 71.9 eV can be attributed to Pt present in Ga-Pt IMCs, which also explains the deviation between the Pt₅ BE (71.9 ± 0.1 eV) observed for codeposited Ga-Pt samples and the BE of fit component Pt₄ (71.5 ± 0.2 eV) in the Pt-on-SiO_x samples, where it is assigned to coordinated Pt atoms within Pt agglomerates. Such Pt agglomerates on SiO_x cannot be found in the Ga-Pt samples. The assignment of the 71.9 eV peak to Ga-Pt IMCs is also consistent with relative BE shifts reported in literature [56].

In short, STEM imaging, corroborated by XPS, of the codeposited Ga-Pt samples reveals a transition from isolated Pt SA to Pt rafts and Ga-Pt IMCs, along with an evolution in the relative fraction of detectable Pt SAs and Pt rafts as the Pt loading increases. While the SA density is comparable for the 0.3 Å Pt (0.1 at%) and 1.2 Å Pt (0.5 at%) sample, more rafts are present with increasing Pt concentration. This allows us to assign the Pt₂ fraction as a fingerprint for Pt SAs in Ga, whereas the Pt₃ fraction represents the fingerprint of Pt rafts in Ga and on the support (vide supra), in good agreement with the conclusions drawn from the discussion of the sequentially deposited samples. It should be noted, as depicted by the DFT simulations, an exact correlation of specific Pt species to a precise BE is not feasible, since Pt atoms in both 2D rafts and 3D agglomerates exhibit a wide spread of BEs (Figure 1g). Nevertheless, based on the correlation between the XPS data and the STEM images, it appears reasonable to conclude that, a pronounced Pt₂ signal serves as a fingerprint of Pt isolation, including the presence of SAs. Based on the Ga-Pt phase diagram [55, 57], one would expect that, in thermodynamic equilibrium, dissolved Pt species (SAs) coexist with IMCs. In the present case, however, at least three factors are expected to cause deviations from the phase diagram: i) the presence of the GaO_x shell (in STEM measurements), ii) the confinement within liquid Ga droplets and the associated Laplace pressure, which may promote the formation of unexpected phases [58], and iii) the nonequilibrium nature of the system due to the as-deposited state of the sample. During deposition, the Ga atoms possess high kinetic energy, which facilitates the dissolution of Pt to a much greater extent

than under room temperature conditions. During cooling, Pt will enter a supersaturated state, leading to Pt agglomeration. Under thermodynamic equilibrium, this would result in the formation of IMCs; however, such phase formation may be suppressed in a nonequilibrium, nanoscale system that includes a GaO_x shell.

3.3 | Towards Catalytic Conditions: Elucidating the Temperature Effect on the Presence of the Different Pt Species

Since Ga-Pt SCALMS exhibit catalytic PDH activity at around 550°C, understanding the impact of temperature and alloy liquefaction on the formation and evolution of the Pt species is crucial for a deeper insight into the catalytically active Ga-Pt surfaces. Therefore, in situ heating experiments were performed on the dedicated model systems to examine the previously assigned fractional changes upon annealing to 550°C (cf. Figure 4). For the Pt-on-Ga sample, a slight increase in the minor component Pt₂ at 73.0 eV (attributed to Pt SAs) at the expense of the major component Pt₃ at 72.3 eV (ascribed to 2D Pt rafts) is observed upon annealing to 550°C (Figure 4a), while component Pt₄ remains largely unaffected. The increase in Pt₂ relative to Pt₃ is illustrated in Figure 4b, indicating a pronounced increase of Pt SAs upon annealing. In the context of the previous results, this increase can be attributed to the partial dissolution of surface Pt rafts into the liquid Ga matrix, leading to a formation of Pt SAs at the surface of the Ga droplet at elevated temperature due to the increased solubility limit [55, 57], thereby revealing the high dynamic nature of the liquid metal system. In direct comparison, the Pt-on-SiO_x sample shows a distinct shift of three major components by −0.4 eV towards lower BE upon heating (Figure S8b), which can be attributed to thermally induced Pt agglomeration, as reported in the literature, and is correspondingly observed in the STEM images after heating (Figure S8a). This observation further confirms the previous peak assignment of Pt₂ (at 73.0 eV) to Pt SAs and Pt₃ (at 72.3 eV) to undercoordinated Pt rafts, as well as the observed correlation with the fractional changes in XPS peaks.

Furthermore, in situ STEM (cf. Figure 5 and Figures S9–13) reveals that, upon heating the codeposited Ga-Pt sample (same sample for which data is shown in Figure 3), Pt rafts and Ga-Pt IMCs partially dissolve while in parallel an increasing appearance of Pt SAs is observed, supporting the previous assignment of the Pt₂ fit component at 73.0 eV BE to isolated Pt species. The representative line scans supporting the differentiation of Pt rafts and Pt SAs are demonstrated in Figures S12 and S13. This process is driven by the entropic gain at elevated T, leading to a larger fraction of Pt rafts and agglomerates dissolving into the Ga matrix, as also highlighted by DFT calculations (cf. Figure S14). The new Pt SAs are likely generated through the dissolution of Pt rafts and IMCs, emphasizing that the as-deposited Pt species does not necessarily represent the species contributing to the activity under PDH-like conditions. In addition, the DFT calculations and ML-FF MD simulation results further confirm the higher mobility of Pt on Ga and Ga₂O₃ surfaces compared to SiO_x (cf. Figure S15). The diffusion coefficient of Pt on the Ga surface remains at approximately 1×10^{10} nm²/s, independent of annealing, suggesting a high mobility of Pt atoms (also see Video S1) that promotes Pt isolation. In contrast, Pt on defective SiO₂ exhibits a much lower diffusion coefficient of about 1 nm²/s at 550°C. Furthermore, an energy

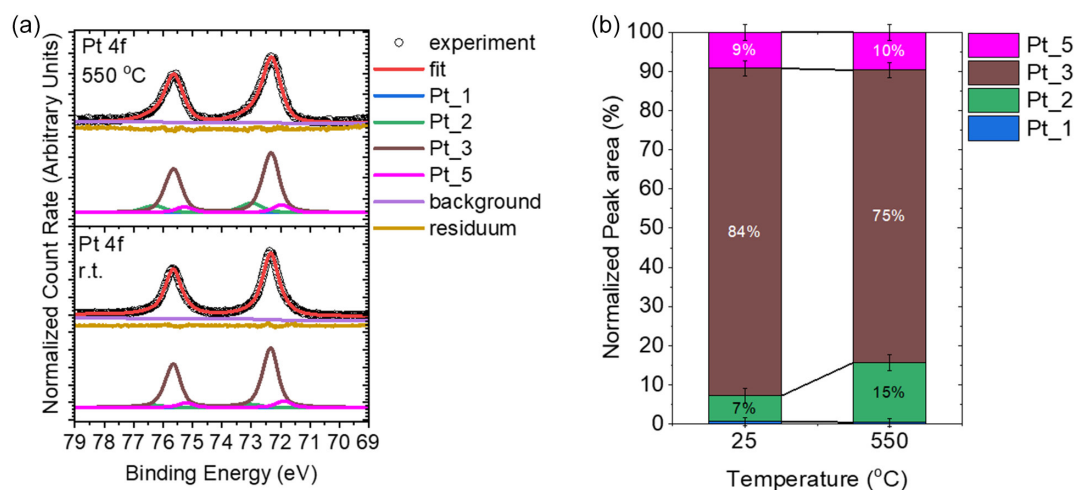


FIGURE 4 | (a) Synchrotron-based (excitation energy = 570 eV) Pt 4f XPS spectra and fit analysis of sequential deposited Ga-Pt alloys with 4 Å Pt on 300 Å Ga measured at room temperature (r.t. = 25°C) and 550°C. (b) Relative Pt 4f peak area of the four Pt species (Pt_1, Pt_2, Pt_3, and Pt_5) for the two different measurement temperatures. In the analysis results, the contribution of Pt_1 is negligible, i.e., <1% of total peak area.

barrier of 1.4 eV was calculated for the migration of a Pt atom between defect sites on the SiO_x surface (Figure S15c), explaining the low mobility of Pt on SiO_x which can lead to Pt agglomeration. By comparing the different behaviors of Pt species deposited on

Ga and SiO_x upon annealing, we propose that the presence of liquid Ga matrix promotes Pt isolation at elevated temperatures, consistent with the increased solubility of Pt in Ga. These comprehensive investigations underscore the complexity and dynamic

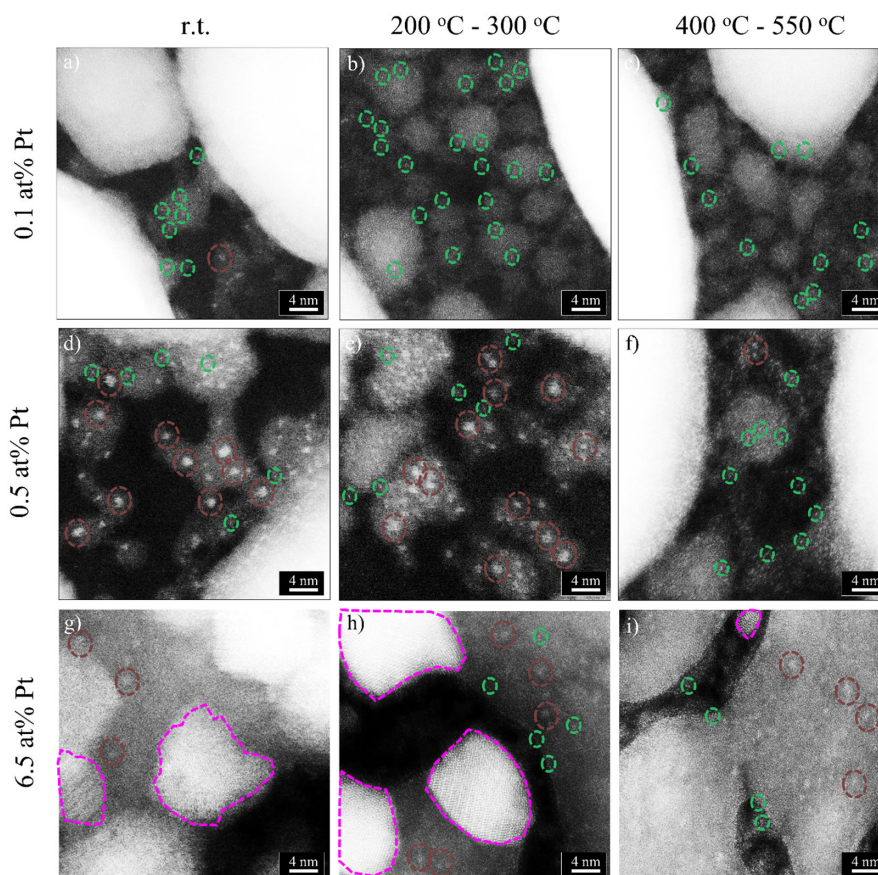


FIGURE 5 | In situ STEM HAADF images of the 0.3 Å Pt/300 Å Ga (0.1 at% Pt) codeposited sample at r.t., 200°C, and 400°C (a-c), the 1.2 Å Pt/300 Å Ga (0.5 at% Pt) codeposited sample at r.t., 200°C, and 400°C (d-f), and the 20 Å Pt/300 Å Ga codeposited sample (6.5 at% Pt) at r.t., 300°C, and 550°C (g-i), visualizing the (partial) dissolution of Pt rafts (brown) and of Ga-Pt IMCs (purple) and the increasing appearance of Pt SAs (green) upon increasing temperature.

nature of the Ga-Pt SCALMS system, providing critical insights into the underlying catalytic mechanisms. The observed XPS peak shifts can be attributed to the relative fractional changes in the populations of the different Pt species. Thus, SCALMS may be regarded as a statistical catalyst, in which a dynamic ensemble of active species is present at the catalyst surface and collectively governs and stabilizes the catalytic behavior.

4 | Conclusion

This study presents a comprehensive and correlative XPS and STEM investigation of Pt-on-SiO_x, sequentially deposited Pt-on-Ga, and codeposited Ga-Pt samples, elucidating the chemical and electronic structures of Pt with the aim of understanding the formation mechanism of the (multiple) active Pt species in Ga-Pt SCALMS. Corresponding DFT calculations support the interpretation of the spectroscopic and microscopic results by providing optimized adsorbate structures and atom-resolved core-level binding energies. For Pt-on-SiO_x samples, the formation of multiple Pt species on the SiO_x/Si support—namely, Pt SAs, Pt rafts, and Pt agglomerates—is revealed. Upon increasing the Pt content, the ratio of the number of Pt rafts and Pt agglomerates relative to that of Pt SAs increases, leading to a shift of the Pt 4f peak towards lower BE. This shift can be explained by variations in the local coordination environment of the Pt atoms, that is, by a transition from low to high Pt–Pt coordination. In contrast, the species that evolve in the presence of Ga exhibited greater diversity, including the formation of Ga-Pt IMCs, thereby highlighting the influence of the underlying support on Pt morphology. Due to the complex nature of these species and the inherent dynamics of SCALMS, the experiments were systematically designed to gradually approach a more representative SCALMS environment, ultimately providing essential insights into the electronic structural changes observed in the XPS measurements. The key findings indicate that the XPS shifts can be attributed to changes in the ratio of Pt SAs to undercoordinated Pt rafts, leading to variations in the local Pt concentration. In addition, changes in the chemical environment of the Pt species—such as the presence of the GaO_x shell, the SiO_x support, or the liquid Ga matrix—as well as morphological modifications of Pt agglomerates were found to influence the BEs observed in the DFT calculations. However, it is evident that other Pt species, including Ga-Pt IMCs, PtO_x, and undercoordinated Pt rafts, also coexist within this highly dynamic catalytic system. These observations refine the current understanding of the potential active species present in real-world Ga-Pt SCALMS. Our findings suggest that, rather than focusing on a single active entity, attention in SCALMS should be directed toward identifying statistical changes in the populations of multiple species that give rise to corresponding shifts in the XPS signals. Nevertheless, our data illustrates a clear tendency for the XPS shifts observed in our experiments to serve as potential fingerprints of Pt in Ga under SCALMS operating conditions. In essence, SCALMS can be characterized as a highly dynamic catalyst system—featuring continuously evolving surfaces and multiple possible active species—which makes it challenging to pinpoint individual active centers. Future work can build on these findings to fine-tune the ratios of various Pt species, guided by a deeper understanding of the oxidation processes and the influence of interfacial surface dynamics on Pt species formation.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Zenodo at <https://doi.org/10.5281/zenodo.18390841>.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. Detailed description of qualitative and quantitative analysis of the XPS data, additional XPS/UPS spectra and SEM/STEM images (in particular of the in-situ annealing experiment), details on the Pt cluster stability considerations and diffusion dynamics calculations.