Silica-Supported PdGa Nanoparticles: Metal Synergy for Highly Active and Selective CO₂-to-CH₃OH Hydrogenation

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ABSTRACT: The direct conversion of CO₂ to CH₃OH represents an appealing strategy for the mitigation of anthropogenic CO₂ emissions. Here, we report that small, narrowly distributed alloyed PdGa nanoparticles, prepared via surface organometallic chemistry from silica-supported Ga³⁺ isolated sites, selectively catalyze the hydrogenation of CO₂ to CH₃OH. At 230 °C and 25 bar, high activity (22.3 molMeOH molPd⁻¹ h⁻¹) and selectivity for CH₃OH/DME (81%) are observed, while the corresponding silica-supported Pd nanoparticles show low activity and selectivity. X-ray absorption spectroscopy (XAS), IR, NMR, and scanning transmission electron microscopy—energy-dispersive X-ray provide evidence for alloying in the as-synthesized material. In situ XAS reveals that there is a dynamic dealloying/realloying process, through Ga redox, while operando diffuse reflectance infrared Fourier transform spectroscopy demonstrates that, while both methoxy and formate species are observed in reaction conditions, the relative concentrations are inversely proportional, as the chemical potential of the gas phase is modulated. High CH₃OH selectivities, across a broad range of conversions, are observed, showing that CO formation is suppressed for this catalyst, in contrast to reported Pd catalysts.

KEYWORDS: CO₂ hydrogenation, Heterogeneous catalysis, Alloys, Nanoparticles, Operando spectroscopy, Hydrogenation

INTRODUCTION

The conversion of CO₂ to liquid fuels has garnered significant attention in recent years, as a strategy to mitigate anthropogenic CO₂ emissions and an alternative source of platform chemicals to fossil fuels.¹ In particular, the direct hydrogenation of CO₂ to CH₃OH (eq 1−Scheme 1a) has been highlighted as an appealing target.²−⁵ For this purpose, metallic nanoparticles supported on oxide supports, modified with various promoters, have been extensively studied. For the most part, efforts have focused on copper particles combined with zinc oxide/alumina (Cu/ZnO/Al₂O₃)⁶⁻⁸ or supported on zirconia (Cu/ZrO₂).⁹⁻¹¹ However, these Cu-based catalysts show limited activity, decreasing selectivity with increasing conversion, and suffer from deactivation.¹² Therefore, alternative metals, oxide promoters, and supports have been investigated.³ In this context, Pd-containing systems (Pd/MOX)¹³⁻¹⁸ show superior activities to those based on Cu in the hydrogenation of CO₂ to CH₃OH when supported on reducible oxides (ZnO or Ga₂O₃). In particular, Pd−Ga-based systems have attracted attention in recent years, as highly active catalysts for the hydrogenation of CO₂ to methanol.¹³,¹⁴,¹⁹⁻²⁵ These systems, based on Pd/Ga₂O₃, Pd−Ga/ SiO₂, Pd/Ga₂O₃/SiO₂ or PdGa colloidal nanocrystals, often show superior activity when compared to Cu-based catalysts. However, Pd-based catalysts display low CH₃OH selectivity.
(<60%, Scheme 1b) due to the competing reverse water gas shift (RWGS) reaction (eq 2). As such, molecular insights into the origin of the high activity of these systems as well as the underlying cause of the undesired RWGS reaction is critical to the design of improved CO2 hydrogenation catalysts.

Our group has recently shown that surface organometallic chemistry (SOMC) can be an ideal approach to control metal−support interfaces and to improve the catalytic performance for various reactions including CO2 hydrogenation. We thus reasoned that SOMC could provide a tool to tune the CO2 hydrogenation activity and selectivity of Pd by tailoring the interface between Pd and Ga. Herein, we report the synthesis of a bimetallic PdGa system, consisting of small PdGa alloy nanoparticles generated by grafting a tailored Pd molecular precursor, Pd(COD)Me(OSi(OtBu)3), (Supporting Information S2 and S3). We first evaluated the grafting of 1 on silica dehydroxylated at 700 °C (SiO2−700), followed by reduction under H2. This material (PdGa@SiO2, Scheme 1b), characterized by transmission electron microscopy (TEM), chemisorption, X-ray absorption spectroscopy (XAS), energy-dispersive X-ray (EDX) mapping as well as CO-adsorption infrared (IR) spectroscopy, shows high activity and unprecedented selectivity in the hydrogenation of CO2 to CH3OH when compared to reported Pd-containing catalysts and conventional Cu-based systems. The PdGa nanoparticles undergo partial dealloying under CO2 hydrogenation as confirmed by XAS, but Pd remains metallic throughout the reaction, and Ga is partially oxidized but remains highly dispersed. The absence of large domains of Ga2O3, which are known to promote the RWGS (forming CO), probably explains the high methanol selectivity. An analysis of strongly bound surface adsorbates by nuclear magnetic resonance (NMR) spectroscopy and IR suggests the presence of mostly methoxy moieties. Transient operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and multivariate curve resolution (MCR) analyses show that methoxy and carbonyl species are preferentially stabilized under CO2-rich conditions, while formate moieties are only detected under H2-rich conditions. These observations parallel the alloying−dealloying of PdGa, indicating that the catalyst is highly dynamic, with implications for its reactivity and selectivity in CO2 hydrogenation.

### RESULTS AND DISCUSSION

**Synthesis and Characterization of Supported Materials**

We first developed a tailored Pd precursor that is amenable to grafting on silica and nanoparticle formation while releasing all its organic ligands: Pd(COD)Me(OSi(OtBu)3), (Supporting Information S2 and S3). We then grafted 1 on silica dehydroxylated at 700 °C (SiO2−700), followed by reduction under H2. This material (PdGa@SiO2, Scheme 1b), characterized by transmission electron microscopy (TEM), chemisorption, X-ray absorption spectroscopy (XAS), energy-dispersive X-ray (EDX) mapping as well as CO-adsorption infrared (IR) spectroscopy, shows high activity and unprecedented selectivity in the hydrogenation of CO2 to CH3OH when compared to reported Pd-containing catalysts and conventional Cu-based systems. The PdGa nanoparticles undergo partial dealloying under CO2 hydrogenation as confirmed by XAS, but Pd remains metallic throughout the reaction, and Ga is partially oxidized but remains highly dispersed. The absence of large domains of Ga2O3, which are known to promote the RWGS (forming CO), probably explains the high methanol selectivity. An analysis of strongly bound surface adsorbates by nuclear magnetic resonance (NMR) spectroscopy and IR suggests the presence of mostly methoxy moieties. Transient operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and multivariate curve resolution (MCR) analyses show that methoxy and carbonyl species are preferentially stabilized under CO2-rich conditions, while formate moieties are only detected under H2-rich conditions. These observations parallel the alloying−dealloying of PdGa, indicating that the catalyst is highly dynamic, with implications for its reactivity and selectivity in CO2 hydrogenation.

### Table 1. Physicochemical Properties of Reduced Materials

| Material       | EA wt % | Particle Size, nm | CO Chemisorption, molCO molPd−1 | H2 Chemisorption, molH2 molPd−1 | H/CO Ratio | Terminal CO Stretch, cm−1 | Bridging CO Stretch, cm−1 |
|---------------|---------|------------------|-------------------------------|-------------------------------|------------|---------------------------|---------------------------|
| PdGa@SiO2     | Pd: 1.08 Ga: 1.66 | 1.6 ± 0.4        | 0.55 (55%)                    | 0.56                          | 2.0        | 2086                      | 1960                      |
| Pd@SiO2       | Pd: 1.61 | 1.6 ± 0.3        | 0.61 (61%)                    | 0.91                          | 3.0        | 2094                      | 1967                      |

*Particle size determined by TEM. Dispersion assumes 1:1 ratio CO/Pd surface.*
The dispersion from TEM indicates a 1:1 CO/Pd stoichiometry,32 the dispersion from CO adsorption at 13C CP-MAS NMR shows signals at 126, 95, 29, 20, and 11 ppm, which is consistent with the spectrum of the molecular precursor. The signals at 126 and 94 ppm are assigned to C-sp² carbons of COD lying trans- to Me and OSi, respectively.31 The peak at 11 ppm is assigned to Pd-Me, which is consistent with a displacement of the large ((tBuO)₃Si—ligand by a surface siloxy ligand upon grafting. Reduction under a flow of H₂ (1 bar) at 500 °C yields Pd nanoparticles with a size of 1.6 ± 0.4 nm, as shown by TEM, while IR reveals the re-emergence of the isolated silanol band, alongside the disappearance of all bands associated with organic ligands (Supporting Information S5). H₂ and CO chemisorption show an uptake of 0.91 molH₂ molPd⁻¹ and 0.61 molCO molPd⁻¹, respectively (Table 1, Supporting Information S6). Considering a 1:1 CO/Pd stoichiometry,32 the dispersion from CO chemisorption (D₁₃C) equals 61%, in a reasonable agreement with the dispersion from TEM (DTEM ≈ 70%; Supporting Information S9).33 While H₂ chemisorption is not effective for a determination of the metal dispersion of Pd nanoparticles due to the formation of a stable bulk hydride with larger particles (>2.6 nm),32 a comparison of the H₂ uptake and D₁₃C would correspond to approximately three hydrogen atoms per surface Pd.

With these encouraging results in hand, the molecular precursor (1) was next grafted on Ga@SiO₂ (Figure 1a), a surface-doped silica prepared via SOMC that contains 0.8 Ga nm⁻², to generate a grafted material, Pd(COD)Me@Ga@SiO₂. In this case, 1.9 equiv of isobutene per Pd (quantified by NMR, Supporting Information S4) was evolved during grafting. The formation of isobutene in place of HOSi(OBu₃) is consistent with the presence of Lewis acid sites, which catalyze the decomposition of HOSi(OBu₃).29 An IR analysis of the grafted material indicates the presence of C—H stretching and bending bands, alongside a decreased intensity for the isolated ᵃ⁻SiOH band (Supporting Information S5), indicative of grafting through the silanol groups. The elemental analysis of the grafted material indicates the presence of 11 equiv of C and 25 equiv of H per Pd, in agreement with the proposed structure (Supporting Information S4). Furthermore, the ¹³C CP-MAS NMR shows signals at 126, 95, 29, 20, and 11 ppm (Supporting Information S5), consistent with a chemical environment akin to that of the molecular precursor and the surface species grafted on silica; that is, the chemical shift of the olefinic protons and carbons confirms that all surface species are PdⅡ with a methyl and a siloxy ligand. Treatment under a flow of H₂ (1 bar) at 500 °C yields nanoparticles with a size of 1.6 ± 0.3 nm, as shown by TEM (Figure 1b), while H₂ and CO chemisorption show an uptake of 0.56 molH₂ molPd⁻¹ and 0.55 molCO molPd⁻¹ (D₁₃C = 55%, Table 1, Supporting Information S6). The H₂ uptake, which corresponds to two H per surface Pd, is significantly lower than the three H per surface Pd that is observed for Pd@SiO₂, despite the near-identical particle size according to TEM, and suggests a different electronic structure of Pd in the presence of Ga. Furthermore, the transmission IR of a self-supporting pellet of PdGa@SiO₂ exposed to a pressure of CO (10 mbar) at room temperature reveals a strong vibrational band at 2086 cm⁻¹ and a much weaker band at 1960 cm⁻¹, assigned to a terminal bound CO on Pd (μ₁-CO₃Pd) and bridged CO species (μ₂-CO₃Pd), respectively (Figure 1c, Supporting Information S7). This observation contrasts with what is observed for Pd@SiO₂, where two bands of similar intensity at 2094 and 1967 cm⁻¹ are attributed to terminal and bridging species,16,33 and is consistent with the formation of a PdGa alloy, where the presence of a bridging CO species is suppressed through a dilution of surface Pd species.34 This disparity highlights the intrinsic difference in the interaction of the particles with CO, which can be explained by the dilution of surface Pd by Ga centers. Furthermore, the red-shifted terminal CO bands (ca. 8 cm⁻¹) observed for the bimetallic system provides further evidence for alloying.34,35

To gain a greater understanding of the structure of the as-synthesized materials, XAS was performed. For PdGa@SiO₂, Ga K edge X-ray absorption near edge structure (XANES) shows two edge features (identified by the two maxima of the first derivative at 10367.5 and 10371.8 eV, Figure 2a,b, Supporting Information S8), indicating the presence of two distinct species—one metallic, at an energy typical for Ga(0), and one GaIII with an edge energy typical of tetracoordinate Ga sites.16 The absence of any species with the energy expected for octahedral Ga sites indicates that the material formed does not correspond to bulk Ga₃O₅—an observation that contrasts with materials prepared using impregnation techniques.13,14 The linear combination fit (LCF) of the XANES indicates a ratio of 67:33 for the two species (metallic/oxidic, Supporting Information S8). This ratio is consistent with the formation of...
a Ga-rich alloyed phase. The corresponding Pd K edge XANES (Figure S2c, Supporting Information S8) shows a strong shift to lower energy for PdGa@SiO2 (24 348.1 eV) from that of bulk Pd (24 350.0 eV), while a smaller shift is observed for Pd@SiO2 (24 348.8 eV), consistent with earlier literature describing the edge energy of supported Pd nanoparticles.32

An in situ study of the reduction process, by XAS-TPR (temperature-programmed reduction (H2)) at the Pd K edge, in combination with an MCR analysis, indicates that PdII in Pd(COD)Me@Ga@SiO2 is reduced to Pd0 under a flow of H2 at room temperature (Supporting Information S8, Figures S27–S30), highlighting the facile reduction of the molecular precursor employed. Conversely, Ga is gradually reduced and intercalated into palladium nanoparticles as temperature is increased (vide infra), as evidenced by a continuous measurement of both the Ga K and Pd K edges (see Supporting Information S8 for an extended discussion). For comparison, the Pd K edge EXAFS for Pd@SiO2 was fitted with a Pd–Pd scattering path (Figure 2e, N = 8.1 ± 0.4, R = 2.73 ± 0.002 Å).

The emergence of a feature consistent with Ga0 in the Ga K edge XANES as well as EXAFS fitting at the Pd K edge indicate that an alloy forms upon reduction under H2. Furthermore, STEM-EDX mapping indicates the coexistence of Pd and Ga in the nanoparticles, in agreement with the observed configuration from XAS (Supporting Information S9). Overall, the CO adsorption IR, XAS, and EDX show that intimate domains of Pd and Ga, in the form of a PdGa alloy, are present upon reduction of the grafted material at 500 °C.

**Catalytic Performance**

The catalytic performance of PdGa@SiO2 and Pd@SiO2 was then evaluated in the hydrogenation of CO2 to CH3OH (3:1:1 H2/CO2/Ar, 25 bar, 230 °C) (Figure 3, Table 2, Supporting Information S10). For PdGa@SiO2, an intrinsic rate of 6.40 mmol s–1 molPd–Cu1 was observed, while Pd@SiO2 displays a much lower intrinsic rate for CH3OH (0.14 mmol molPd–Cu1 s–1). Under the same conditions, Ga@SiO2 is inactive. The catalyst slowly deactivates (25%) over 36 h on stream.

Table 2. Summary of Formation Rates and Selectivities for Materials Investigated, Alongside Reference Data for Materials Previously Tested in the Same Conditions

| material, (wt% Pd/Cu) | formation rate, mmol s–1 molPd–Cu1 | selectivity |
|------------------------|------------------------------------|-------------|
|                        | CH3OH + DME | CO | CH2 | $S(\text{CH}_3\text{OH+DME})/\underline{\text{S(CO)/S(CH}_2\text{)}}$ |
| PdGa@SiO2 (1.08)       | 6.40 1.57 <0.01 | 81/19/n/a |
| Pd@SiO2 (1.61)         | 0.14 0.50 0.03 | 20/75/5 |
| Ga@SiO2 (n/a)          | n/a b  n/a b  n/a b | n/a |
| CuGa@SiO2 (4.5)        | 0.23 0.24 <0.01 b | 49/51/n/a |
| Cu@ZrO2 (2.33)         | 0.51 0.30 n/a | 67/33/n/a |
| CuGa@SiO2 (3.88)       | 0.72 0.06 n/a | 93/7/n/a |

*Conditions: 3:1:1 (H2/CO2/Ar), 25 bar, 230 °C, 200 mg of catalyst, 5 g of SiC, 6–100 sccm.*

Conversion, Figure 3), in contrast to Cu/ZrO2 or Cu/ZnO/AI2O3, where a significant drop in selectivity is observed as conversion increases (Table S7).5 This increased CH3OH selectivity at higher conversion was already observed in the related Cu–Ga@SiO2 system (~90%) prepared via SOMC, though the latter shows ca. 1 order of magnitude lower CH3OH formation rates (0.72 mmol CH3OH molCu1 s–1).27

**In Situ and Postreaction Catalyst States**

To assess changes to PdGa@SiO2 under reaction conditions, the material was first analyzed after the reaction. The TEM of PdGa@SiO2 after the reaction reveals that the particle size does not change after the reaction (1.6 ± 0.4 nm, Figure S11), indicating that the as-synthesized material does not sinter significantly under reaction conditions. Similarly, the XANES of the spent catalyst (PdGa@SiO2) indicates no significant
changes in the edge energy or the white line intensity for the Pd K edge (24 348.0 eV vs 24 348.1 eV), while the Ga K edge XANES reveals the presence of both a metallic component and a GaIII component (10 367.2 and 10 371.5 eV, Supporting Information S11). The LCF of the Ga K edge gives a GaII/GaIII ratio of 46:54, suggesting that part of the alloyed gallium is oxidized under reaction conditions. Notably, the oxidized Ga appears to be exclusively tetracoordinated Ga (Supporting Information S8 and S11). The absence of octahedral Ga sites, typical of Ga2O3, is consistent with the formation of highly dispersed Ga sites or small GaO4 clusters upon the segregation of Pd and Ga from the alloy present in the as-synthesized material. The absence of bulk Ga2O3 is also consistent with the low formation rate and selectivity for CO2, which can readily occur on Ga2O3 via RWGS.30 A study of the material, by Ga K edge XANES under a flow of H2/CO2 (5 bar, 230 °C), demonstrates that the material undergoes a partial oxidation under reaction conditions, which is demonstrated by both the increase in the white line intensity and the partial disappearance of the feature at 10 367.5 eV (Supporting Information S11 Figures S54 and S55). The change is, however, reversible; under H2 at 230 °C, a partial rereduction of a proportion of tetracoordinate Ga is observed, as evidenced by the re-emergence of the feature at 10 367.5 eV (Supporting Information S11 Figures S56 and S57), highlighting the dynamic nature of the dealloying/redealloying process for this material.

**Study of Bound Surface Adsorbates and Reaction Intermediates**

To further understand the divergent reactivity of the mono- and bimetallic systems, the nature of surface adsorbates was probed by IR and NMR spectroscopy. PdGa@SiO2 and Pd@SiO2 were contacted with a H2/CO2 mixture (3:1) at 230 °C for 12 h in a high-pressure glass reactor at 5 bar. When cooled, volatiles were removed under reduced pressure, and the solid was analyzed by transmission IR (Figure 4). Analysis of the IR spectrum of the exposed PdGa@SiO2 shows the emergence of peaks at 2996, 2959, 2857, and 1466 cm−1, assigned to surface methoxy species (Supporting Information S12). PdGa@SiO2 was also contacted with a H2/13CO2 mixture (3:1) at 230 °C for 12 h in a high-pressure glass reactor at 5 bar. 13C CP-MAS, 1H MAS, and 1H−13C heteronuclear correlation (HETCOR) spectra of the exposed PdGa@SiO2 show signals at 49 ppm (13C) and 3.6 ppm (1H), consistent with the presence of surface methoxy groups (Supporting Information S12). In contrast, IR spectroscopy on Pd@SiO2 after treatment with H2/CO2 at 230 °C and 5 bar shows exclusively peaks at 2091 and 1644 cm−1, assigned to linear and bridged CO species (vide supra, Figure 1c), suggesting that strongly bound carbonyl species may suppress the formation of CH3OH on Pd@SiO2. In the corresponding experiment using H2/13CO2, only a very weak signal was observed in the CP-MAS spectrum at 49 ppm (Supporting Information S12), indicating a very low concentration of surface methoxy groups.

To have a better understanding of the reaction intermediates at play under reaction conditions, operando DRIFTS on the PdGa@SiO2 catalyst was performed. Under a flow of H2/CO2 (3:1) at 20 bar and 230 °C, at steady-state, bands assigned to C=H stretching modes at 2960, 2920, and 2860 cm−1 are observed (Figure 5a). The intense bands at 2960 and 2860 cm−1 are assigned to methoxy species, while the weak band at 2920 cm−1 is assigned to bidentate formate species, consistent with earlier literature.19 Note that a second peak typically observed for bound formate species, at ~2860 cm−1, is obscured by the dominant methoxy band (vide infra). Between 2200 and 1200 cm−1 (Figure 5b), three kinetically distinct bands are observed, with maxima at 2085, 1920, and 1588 cm−1, which are assigned to terminal CO bound to Pd (μ1−COμ2p), bridging CO species bound to Pd (μ2−COμ3), and the OCO asymmetric stretch of formate species bound to metallic sites, respectively.37 In contrast to observations from ex situ experiments, both surface carbonyl species and formate species are observed in reaction conditions. Consistent with observations from ex situ experiments, methoxy species are the dominant surface oxygenate species.

To probe the relevance of the observed surface species, we then turned to transient experiments (Figure 5c,d). MCR analysis of switching experiments, between CO2/He (1:3) and H2/He (3:1) at 20 bar and 230 °C, reveals three distinct species in the C=H stretching region, assigned to formate and two kinetically distinguishable methoxy species. In addition, the evolution of the bound terminal carbonyl species is observed. In CO2/He, a rapid buildup of methoxy and terminally bound carbonyl species is observed, alongside a drop in the relative concentration of formate species. When switched to H2/He, the concentration of methoxy species and carbonyl species falls rapidly, while the concentration of formate increases, with a concomitant increase in methanol formation (Supporting Information S13). These data support that the formation of methanol from methoxy surface species likely involves H2. In sum, both methoxy and carbonyl species are preferentially stabilized at the catalyst surface under CO2-rich conditions, while a greater fraction of bound formate species are observed in H2-rich conditions. The observation that surface formate concentrations are inversely correlated with the concentrations of methoxy and carbonyl species highlights the facile interchange between the two species and the dynamic nature of this catalyst.

**Proposed Role of Ga and Implications for Mechanism**

Both DRIFTS and XAS indicate that PdGa@SiO2 is a dynamic catalytic system, where the chemical state of Ga and the observed surface intermediates are highly dependent on the chemical potential of the gas phase. Under H2-rich conditions, an increased proportion of GaII is observed by XAS, with a
concomitant emergence of formate species according to IR, which could indicate that formate surface species are preferentially stabilized by metallic sites, as previously proposed in the literature.\textsuperscript{38} In contrast, under CO\textsubscript{2}-rich conditions, an increased proportion of tetracoordinate Ga\textsuperscript{III} is observed, alongside an increase in surface methoxy species, which are most likely stabilized by the Ga\textsuperscript{III} species. This change of preponderant surface intermediates as a function of chemical potential, the low abundance (and stability) of formate species, and the high methanol selectivity at high conversion for this PdGa@SiO\textsubscript{2} catalyst contrasts what is observed for Cu/ZrO\textsubscript{2} and related materials, where formates are invariably observed as stable surface adsorbates and methanol selectivity deteriorates with increasing conversion.\textsuperscript{39} Furthermore, it has been shown that the over stabilization of formate intermediates, clearly observed for Cu/Al\textsubscript{2}O\textsubscript{3} and related materials, where formates are invariably observed as stable surface adsorbates and methanol selectivity deteriorates with increasing conversion. Furthermore, it has been shown that the over stabilization of formate intermediates, clearly observed for Cu/Al\textsubscript{2}O\textsubscript{3} and related materials, where formates are invariably observed as stable surface adsorbates and methanol selectivity deteriorates with increasing conversion.\textsuperscript{39} Hence, the lower stability of formate intermediates is likely linked to the higher observed methanol selectivity at an elevated conversion for PdGa@SiO\textsubscript{2} catalysts. These results support that an efficient methanol synthesis from CO\textsubscript{2} should involve a fast conversion of CO\textsubscript{2} to formate, formate to methoxy intermediates, before formation and desorption of methanol. Overall, the results discussed above could indicate that the ease of alloying-dealloying combined with the correlation between this phenomenon and the detection/stabilization of formate intermediates that the efficient alloying-dealloying process in this highly dynamic PdGa catalyst could be at the origin of its improved methanol activity and selectivity at higher CO\textsubscript{2} conversion, since it would avoid an accumulation of formate intermediates and increase the rate of methanol formation.

**CONCLUSIONS**

In summary, PdGa@SiO\textsubscript{2}, prepared via SOMC using a tailored traceless Pd molecular precursor and a Ga-doped silica surface, is a highly selective and active catalyst for the hydrogenation of CO\textsubscript{2} to CH\textsubscript{3}OH, displaying activity an order of magnitude greater than the benchmark Cu-based systems. In contrast to previously reported Pd-based systems, the CH\textsubscript{3}OH selectivity is high (ca. 80\%), and it does not decrease markedly at a higher conversion, suggesting that the use of a gallium-doped silica support containing exclusively isolated Ga\textsuperscript{III} sites prevents the formation of larger Ga\textsubscript{2}O\textsubscript{3} domains, which are known to promote RWGS. Analysis of the reduction process by XAS-TPR indicates that the PdGa alloy is formed through a gradual intercalation of Ga to Pd nanoparticles at elevated temperatures.

A study of the material under reaction conditions reveals that, while partial oxidation of Ga\textsuperscript{III} occurs, the Ga\textsuperscript{III} species are
exclusively tetracoordinate Ga sites. IR and NMR experiments allow the detection of surface-stabilized methoxy groups on PdGa@SiO2. An in situ study of PdGa@SiO2 by XAS, indicates that there are facile redox processes enabling the transformation between GaIV/GaIII under CO2 hydrogenation conditions, while the observed reaction intermediates, probed by operando DRIFTS, show a similar dependence on the gas-phase composition. Transient experiments reveal the presence of both methoxy and formate species under reaction conditions, with the two surface species having inversely proportional concentrations. These observations highlight the subtle role of dynamic dealloying/reallyloying processes and how this can be exploited to generate highly active and selective catalytic systems. Further studies into the subtle interplay between the Pd/Ga and Pd/GaIII/O2 are currently underway, with the goal to understand the origin of the observed synergistic behavior between Pd and Ga; other research efforts are directed at exploring the general applicability of this approach toward the formation of oxide-supported PdM nanoparticles and their application in selective hydrogenation reactions.

**EXPERIMENTAL SECTION**

**Synthesis of Pd(COD)Me(OSi(OtBu)3**

Pd(COD)MeCl (1.00 g, 3.77 mmol) was dissolved in toluene (80 mL). To this was added a solution of NaOSi(OtBu)3 (1.08 g, 3.77 mmol) in toluene (20 mL), followed by successive washings of the reaction vessel (2 × 10 mL). The reaction mixture was stirred at room temperature, for 16 h. The solvent was removed under reduced pressure to yield a dark solid. The remaining solid was washed with Et2O (3 × 10 mL), and the combined washings were concentrated under reduced pressure to yield a solid. The solid was dissolved in CH2Cl2 (10 mL) and cooled to −40 °C to yield a small amount of white crystals. The reaction mixture was filtered, and rinsed with CH2Cl2 (3 × 40 mL), overnight, to yield colorless rhombohedral crystals. Successive recrystallizations yielded 1.16 g of product (62% yield).

**Synthesis of Pd(COD)Me@Ga@SiO2-700**

To a suspension of Ga@SiO2 (1.000 g) in C6H6 (20 mL) was added a clear solution of Pd(COD)Me(OSi(OtBu)3 (78.9 mg, 0.16 mmol) in C6H6 (10 mL). The suspension was stirred for 1 h at 25 °C. After it was stirred, the material was filtered, rinsed with C6H6 (3 × 7 mL), and dried under vacuum (10−3 mbar). Isobutene (1.9 equiv) was identified as the side product of the reaction.

**Synthesis of PdGa@SiO2-700**

To a glass flow reactor containing a medium porosity glass frit was added Pd(COD)Me@Ga@SiO2 (0.773 g). The flow reactor was evacuated (10−5 mbar) and then filled with H2. The reactor was subsequently heated to 500 °C (5 °C min−1) while maintaining a flow of H2 (960 mbar a). After 12 h of heating, the reactor was evacuated (10−3 mbar), while still hot, yielding a dark solid material.

**General Considerations**

Unless otherwise indicated, all manipulations were undertaken using conventional air-free techniques (argon). All solvents were purified by a solvent purification system (SPS) or by drying followed by distillation and stored over activated molecular sieves. [Mg-(CH2Ph)2(THF)2]4, Pd(COD)Cl4, Ga(OSi(OtBu)3)4(THF), and HO Si(OtBu)3 (THF = tetrahydrofuran) were synthesized as described in earlier literature.29−42 Silica (Aerosil Degussa, 200 m2 g−1) was compacted with deionized water, dried at 100 °C for 7 d, crushed, and sieved (250−400 μm) for easier handling. Silica-700 (SiO2−700) was calcined at 500 °C in air for 12 h, allowed to return to room temperature, and treated under high vacuum (10−3 mbar) at 500 °C for 12 h (ramp: 5 °C min−1) and then at 700 °C for 24 h (ramp: 1.7 °C min−1).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00021.

Complete experimental procedures, general considerations, spectroscopic methods, and associated data (PDF)

Crystallographic data file for 1 (CCDC Deposition No. 2007107) (CIF)

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Author Contributions
All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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