

Silica-Supported PdGa Nanoparticles

Metal Synergy for Highly Active and Selective CO₂-to-CH₃OH Hydrogenation

Docherty, Scott R.; Phongprueksathat, Nat; Lam, Erwin; Noh, Gina; Safonova, Olga V.; Urakawa, Atsushi; Copéret, Christophe

DOI

[10.1021/jacsau.1c00021](https://doi.org/10.1021/jacsau.1c00021)

Publication date

2021

Document Version

Final published version

Published in

Journal of the American Chemical Society

Citation (APA)

Docherty, S. R., Phongprueksathat, N., Lam, E., Noh, G., Safonova, O. V., Urakawa, A., & Copéret, C. (2021). Silica-Supported PdGa Nanoparticles: Metal Synergy for Highly Active and Selective CO₂-to-CH₃OH Hydrogenation. *Journal of the American Chemical Society*, 1(4), 450-458. <https://doi.org/10.1021/jacsau.1c00021>

Important note

To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

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

Scott R. Docherty, Nat Phongprueksathat, Erwin Lam, Gina Noh, Olga V. Safonova, Atsushi Urakawa, and Christophe Copéret*



Cite This: *JACS Au* 2021, 1, 450–458



Read Online

ACCESS |

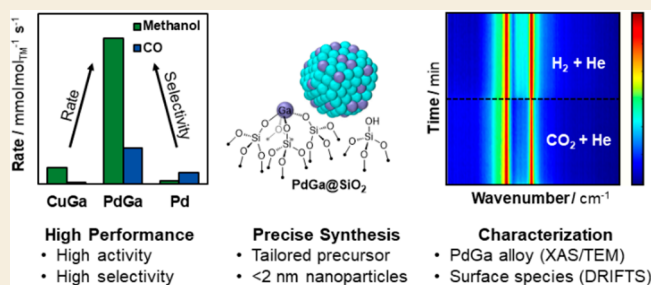
Metrics & More

Article Recommendations

Supporting Information

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 Ga^{III} isolated sites, selectively catalyze the hydrogenation of CO₂ to CH₃OH. At 230 °C and 25 bar, high activity (22.3 mol_{MeOH} mol_{Pd}⁻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/re-alloying 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.

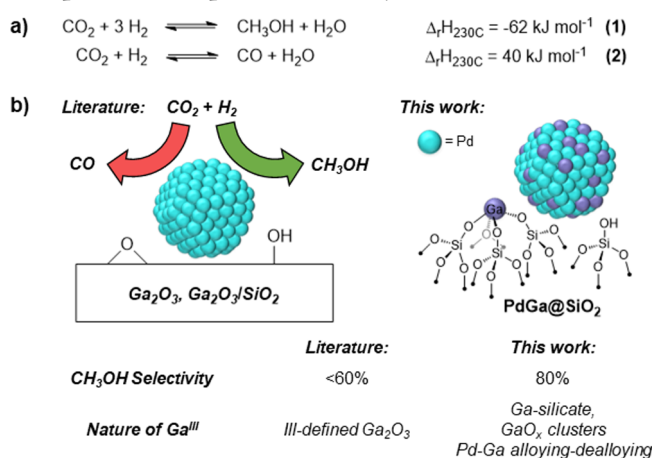
KEYWORDS: CO₂ hydrogenation, Heterogeneous catalysis, Alloys, Nanoparticles, Operando spectroscopy, Hydrogenation



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).^{5,9–11} 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.⁵ In this context, Pd-containing systems (Pd/MO_x)^{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.^{13,14,19–23} 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

Scheme 1. (a) Thermodynamics of CO₂ Hydrogenation. (b) Comparison of Reported Pd/Ga Systems and This Work



Received: January 18, 2021

Published: March 17, 2021

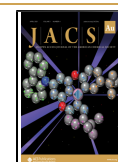


Table 1. Physicochemical Properties of Reduced Materials

material	EA, wt %	particle size, ^a nm	CO chemisorption, ^b mol _{CO} mol _{Pd} ⁻¹ (D_{CO})	H ₂ chemisorption, mol _{H₂} mol _{Pd} ⁻¹	H/CO ratio	terminal CO stretch, cm ⁻¹	bridging CO stretch, cm ⁻¹
PdGa@SiO ₂	Pd: 1.08 Ga: 1.66	1.6 ± 0.4	0.55 (55%)	0.56	2.0	2086	1960
Pd@SiO ₂	Pd: 1.61	1.6 ± 0.3	0.61 (61%)	0.91	3.0	2094	1967

^aParticle size determined by TEM. ^bDispersion assumes 1:1 ratio CO/Pd_{surface}.

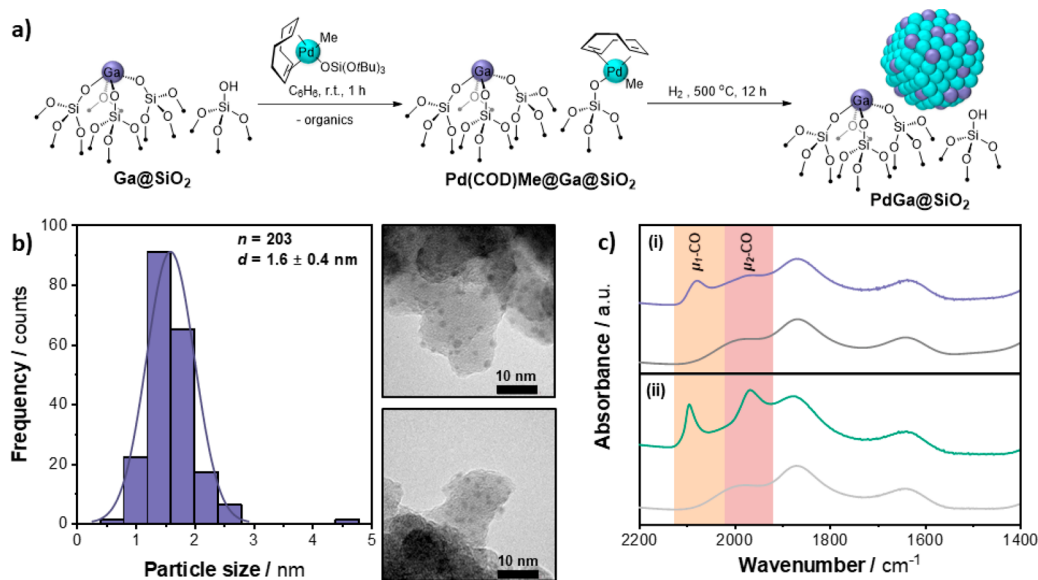


Figure 1. (a) Synthetic procedure for PdGa@SiO₂. (b) Particle size distribution and representative TEM images for PdGa@SiO₂; and (c) CO-adsorption IR for (i) PdGa@SiO₂ exposed (purple, top) and prior to CO adsorption (gray, bottom); (ii) Pd@SiO₂ exposed (green, top) and prior to CO adsorption (gray, bottom). 10 mbar CO.

(<60%, Scheme 1b) due to the competing reverse water gas shift (RWGS) reaction (eq 2).^{13,21} 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.^{24–28} 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(O^tBu)₃) (**1**) (COD = 1,5-cyclooctadiene), on the silanol sites of silica-containing isolated Ga^{III} sites (Ga@SiO₂),²⁹ 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.³⁰ 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(O^tBu)₃), **1** (Supporting Information S2 and S3). We first evaluated the grafting of **1** on silica dehydroxylated at 700 °C (SiO₂₋₇₀₀, 0.26 mmol – OH g⁻¹) that affords a monografted complex, (≡SiO)Pd(COD)Me, with a concomitant liberation of 0.8 equiv of HOSi(O^tBu)₃ per Pd (Supporting Information S4). An IR analysis of the grafted material (Supporting Information S5) reveals the emergence of C–H stretching (3100–2700 cm⁻¹) and bending (1700–1300 cm⁻¹) bands, alongside a decreased intensity for the isolated ≡SiOH band at 3747 cm⁻¹, indicative of grafting through silanol groups. ¹³C cross-polarization magic-angle spinning (CP-MAS) NMR (Support-

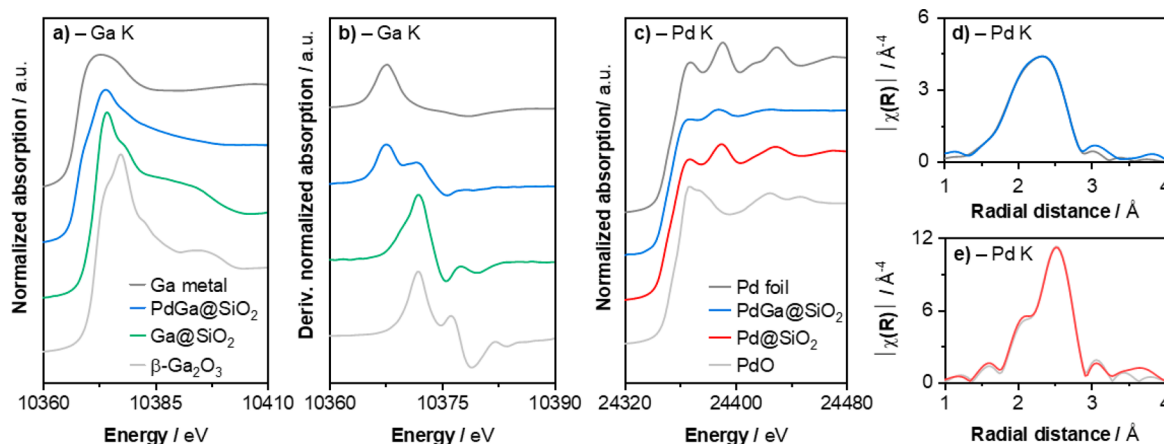


Figure 2. Normalized XANES spectra for (a) Ga K edge, (b) first derivative Ga K edge—Ga metal (dark gray), PdGa@SiO₂ (blue), Ga@SiO₂ (green), and β -Ga₂O₃ (light gray); (c) Pd K edge—Pd foil (dark gray), PdGa@SiO₂ (blue), Pd@SiO₂ (red), and PdO (light gray); and Pd K edge EXAFS fits (d) PdGa@SiO₂ and (e) Pd@SiO₂ (*k*-weight: 3, fit in light gray).

ing Information S5) shows signals at 126, 94, 30, 27, 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 (*t*BuO)₃SiO- 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 mol_{H₂} mol_{Pd}⁻¹ and 0.61 mol_{CO} mol_{Pd}⁻¹, respectively (Table 1, Supporting Information S6). Considering a 1:1 CO/Pd stoichiometry,³² the dispersion from CO chemisorption (\bar{D}_{CO}) equals 61%, in a reasonable agreement with the dispersion from TEM ($\bar{D}_{\text{TEM}} \approx 70\%$; Supporting Information S9).³² 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 \bar{D}_{CO} 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(O*t*Bu)₃ is consistent with the presence of Lewis acid sites, which catalyze the decomposition of HOSi(O*t*Bu)₃.²⁹ An IR analysis of the grafted material reveals the emergence of C–H stretching and bending bands, alongside a decreased intensity for the isolated ≡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 Pd^{II} 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 mol_{H₂} mol_{Pd}⁻¹ and 0.55 mol_{CO} mol_{Pd}⁻¹ ($\bar{D}_{\text{CO}} = 55\%$, 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 than that 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 terminally bound CO on Pd (μ_1 -CO_{Pd}) and bridged CO species (μ_2 -CO_{Pd}), 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 Ga⁰ 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 Ga^{III} with an edge energy typical of tetracoordinate Ga sites.³⁶ The absence of any species with the energy expected for octahedral Ga sites indicates that the material formed does not correspond to bulk Ga₂O₃—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 2c, 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 Pd^{II} 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, Figures S31–S39). Ga K edge XANES (Figures S35–S36) indicates that the formation of a metallic Ga species occurs, while MCR analysis indicates that this is a gradual process (Figure S37). MCR analysis of the corresponding Pd K edge XANES, measured in identical conditions, demonstrates that changes occur simultaneously for Pd (Figure S33), indicating that the reduction and intercalation of Ga occur in unison (see the Supporting Information S8 for an extended discussion).

An analysis of the extended X-ray absorption fine structure (EXAFS) region was also performed. PdGa@SiO₂ was fitted with Pd–Ga scattering path ($N = 2.8 \pm 0.9$, $R = 2.48 \pm 0.02$ Å) and Pd–Pd path ($N = 3.1 \pm 0.9$, $R = 2.73 \pm 0.01$ Å), providing further evidence for the formation of an alloy with 1:1 Pd/Ga stoichiometry (Figure 2d, Supporting Information S8). For comparison, the Pd K edge EXAFS for Pd@SiO₂ was fitted with a Pd–Pd scattering path (Figure 2e, $N = 8.1 \pm 0.4$, $R = 2.73 \pm 0.002$ 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_{MeOH+DME} mol_{Pd}⁻¹ s⁻¹ was observed, while Pd@SiO₂ displays a much lower intrinsic rate for CH₃OH (0.14 mmol_{Pd}⁻¹ s⁻¹). Under the same conditions, Ga@SiO₂ is inactive. The catalyst slowly deactivates (25%) over 36 h on stream. Note also that the CH₃OH formation rate is ca. 1 order of magnitude greater for PdGa@SiO₂ than for Cu-based reference catalysts (Table 2).^{11,27} In addition to an increased rate, the PdGa@SiO₂ system displays a significantly increased CH₃OH selectivity (81% vs 20% for Pd@SiO₂). The large difference in selectivity and activity between PdGa@SiO₂ and the parent monometallic materials highlights the remarkable synergistic effect of Pd and Ga. In addition, the high CH₃OH selectivity with PdGa@SiO₂ does not decrease markedly as conversion increases (ca. 75% selective for methanol at 4%

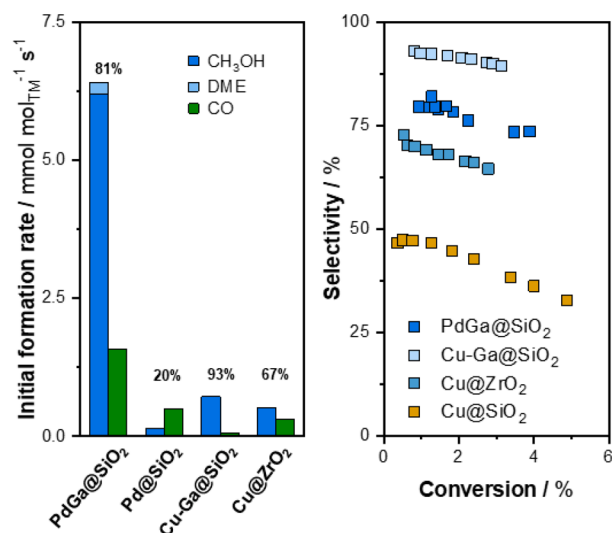


Figure 3. (left) Formation rates for PdGa@SiO₂, Pd@SiO₂, Cu-Ga@SiO₂, and Cu@ZrO₂. (right) Selectivity as a function of conversion for PdGa@SiO₂, Cu-Ga@SiO₂, Cu@ZrO₂, Cu@SiO₂. Conditions: 3:1:1 H₂/CO₂/Ar, 25 bar, 230 °C, 200 mg of catalyst, 5 g of SiC, 6–100 sccm.

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 mol Pd/Cu ⁻¹			selectivity
	CH ₃ OH + DME ^a	CO	CH ₄	S(CH ₃ OH+DME)/ S(CO)/ S(CH ₄)
PdGa@SiO ₂ (1.08)	6.40	1.57	<0.01 ^b	81/19/n/a
Pd@SiO ₂ (1.61)	0.14	0.50	0.03	20/75/5
Ga@SiO ₂ (n/a)	n/a ^b	n/a ^b	n/a ^b	n/a
Cu@SiO ₂ ^c (4.5)	0.23	0.24	<0.01 ^b	49/51/n/a
Cu@ZrO ₂ ^c (2.33)	0.51	0.30	n/a	67/33/n/a
CuGa@SiO ₂ ^c (3.88)	0.72	0.06	n/a	93/7/n/a

^aConditions: 3:1:1 (H₂/CO₂/Ar), 25 bar, 230 °C, 200 mg of catalyst, 5 g of SiC, 6–100 sccm. Normalized by mole carbon. n/a indicates not applicable. ^bBelow the detection limit of the thermal conductivity detector/flame ionization detector. ^cPreviously reported under the same conditions.^{11,27}

conversion, Figure 3), in contrast to Cu/ZrO₂ or Cu/ZnO/Al₂O₃, 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_{MeOH} mol_{Cu}⁻¹ 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 Ga^{III} component (10 367.2 and 10 371.5 eV, Supporting Information S11). The LCF of the Ga K edge gives a Ga⁰/Ga^{III} ratio of 46:54, suggesting that part of the alloyed gallium is oxidized under reaction conditions. Notably, the oxidized Ga appears to be exclusively tetraordinated 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 GaO_x 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 CO, 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 tetraordinate 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/re-alloying 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)

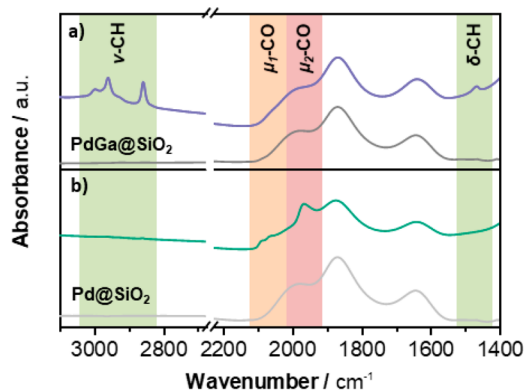


Figure 4. IR analysis after exposure to CO₂/H₂ (3:1) at 230 °C and 5 bar for (a) PdGa@SiO₂ exposed (purple, top) and prior to exposure to reaction gases (gray, bottom); (b) Pd@SiO₂ exposed (green, top) and prior to exposure to reaction gases (gray, bottom). Reaction time: 12 h.

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 1964 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 (μ_1 -CO_{Pd}), bridging CO species bound to Pd (μ_n -CO_{Pd}), 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 Ga⁰ is observed by XAS, with a

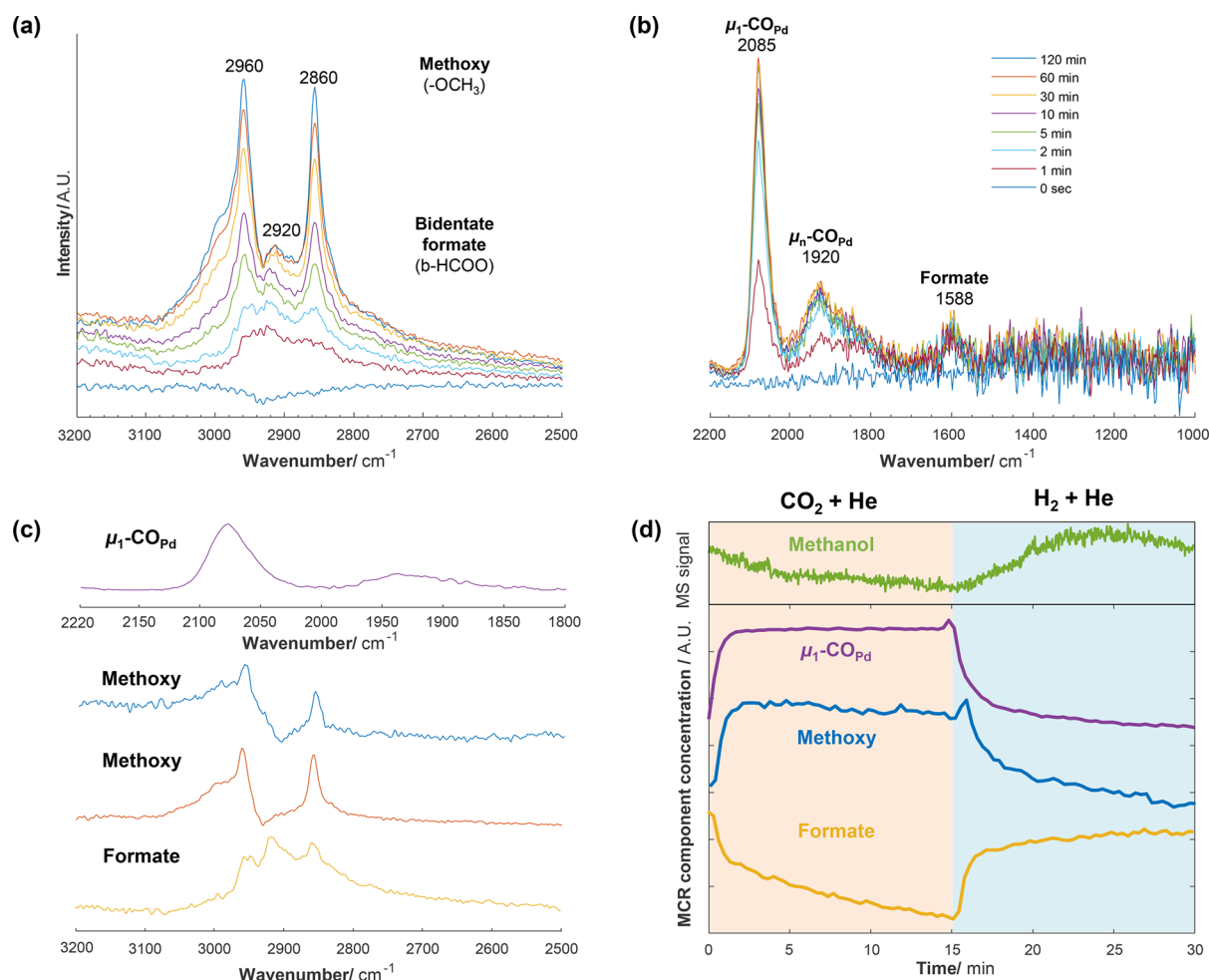


Figure 5. Operando DRIFTS spectra for (a, b) PdGa@SiO₂ under H₂/CO₂ at steady state (3:1, 20 bar, 230 °C); (c) MCR-resolved component profiles, and (d) MCR-resolved concentrations for PdGa@SiO₂ under both CO₂/He (1:3) and H₂/He (3:1). Conditions: 20 bar, 230 °C.

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.³⁸ In contrast, under CO₂-rich conditions, an increased proportion of tetracoordinate Ga^{III} is observed, alongside an increase in surface methoxy species, which are most likely stabilized by the Ga^{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@SiO₂ catalyst contrasts what is observed for Cu/ZrO₂ 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/Al₂O₃, leads to the formation of methyl formate with increasing CO₂ conversion (high methanol concentrations), which has been shown to decompose into methanol and CO under these conditions, thus decreasing the methanol selectivity.³⁹ Hence, the lower stability of formate intermediates is likely linked to the higher observed methanol selectivity at an elevated conversion for PdGa@SiO₂ catalysts. These results support that an efficient methanol synthesis from CO₂ should involve a fast conversion of CO₂ 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 CO₂ conversion, since it would avoid an accumulation of formate intermediates and increase the rate of methanol formation.

CONCLUSIONS

In summary, PdGa@SiO₂, 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 CO₂ to CH₃OH, displaying activity an order of magnitude greater than the benchmark Cu-based systems. In contrast to previously reported Pd-based systems, the CH₃OH 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^{III} sites prevents the formation of larger Ga₂O₃ 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 Ga⁰ occurs, the Ga^{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 Ga⁰/Ga^{III} 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/re alloying 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/Ga^{III}O_x 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 white crystalline 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 over diatomaceous earth, and the supernatant was collected and concentrated under reduced pressure to yield a yellow solid. The solid was dissolved in pentane (3 mL) and cooled to −40 °C 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 high vacuum (10^{−5} 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^{−5} 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], Pd(COD)Cl₂, Ga(OSi(OtBu)₃)₃(THF), and HOSi(OtBu)₃ (THF = tetrahydrofuran) were synthesized as described in earlier literature.^{29,40–42} 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^{−5} 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}).

Attenuated total reflectance (ATR) IR spectra were recorded inside an Ar-filled glovebox on a Bruker FT-IR Alpha spectrometer. Transmission-IR were recorded on Bruker FT-IR Alpha spectrometer or a Nicolet 6700 FTIR spectrophotometer. Spectra are normalized to the Si–O–Si overtone peak maximum at 1868 cm^{−1} for all materials. Solution NMR spectra were obtained on Bruker DRX 300 spectrometer (7.05 T, Larmor Frequency: 300 MHz (¹H), 75.5 MHz (¹³C)). ¹H and ¹³C chemical shifts are referenced relative to residual solvent peaks.⁴³ Solid-state NMR spectra of grafted samples were recorded on a Bruker 400 MHz NMR spectrometer using a double-resonance 4 or 3.2 mm probe. Single-crystal XRD was performed on a Bruker APEX-II CCD diffractometer, and structures were solved with the olex2.solve structure solution program⁴⁴ using Charge Flipping and refined with the ShelXL⁴⁵ refinement package using Least Squares minimization. Particle size estimations were obtained by transmission electron microscopy (JEOL JEM-1400 Plus microscope). Energy-dispersive X-ray mapping was measured on a Talos F200 X microscope. XAS measurements were performed at the Pd and Ga K edges at the SuperXAS beamline at SLS (PSI). The program package Demeter was used for the analysis of EXAFS.⁴⁶ For operando DRIFTS experiments, a custom-made high-pressure reaction cell was mounted in a Harrick Praying Mantis diffuse reflection (DRIFTS) accessory. The spectra were collected using a Thermo Scientific Nicolet 6700 FT-IR spectrometer. The outlet gas stream was analyzed by a Pfeiffer OmniStar GSD 300C mass spectrometer.

CO₂ hydrogenation rates were measured at 230 °C at differential conversions (<10%) on all samples. Samples were loaded in an argon-filled glovebox. Samples were treated at 300 °C in 5:1 H₂/N₂ (60 sccm, 1 bar) for 1 h before being cooled to the reaction temperature (230 °C in N₂ flow (50 sccm, 1 bar)), after which, CO₂, H₂, and Ar (1:3:1) were introduced, and the reactor was pressurized (25 bar). The reactor pressure was maintained by a back-pressure regulator (Bronkhorst EL-PRESS). Gas flow rates were screened in the range from 100 to 6 sccm. Reactant and product concentrations in the reactant and effluent streams were measured by online gas chromatography (Agilent 7890N GC). Product selectivity is defined on a per-carbon basis. Intrinsic formation rates (i.e., rate at zero contact time) are obtained by using a second-order polynomial fit on the experimental data and extrapolating to zero residence time.

Experimental procedures, purification procedures for commercial chemicals, instrument specifications, and characterization data are covered in greater detail in the Supporting Information.

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)

AUTHOR INFORMATION

Corresponding Author

Christophe Copéret – Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland;

orcid.org/0000-0001-9660-3890; Email: ccoperet@ethz.ch

Authors

Scott R. Docherty – Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland; orcid.org/0000-0002-8605-3669

Nat Phongprueksathat – Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, 2629 HZ Delft, The Netherlands; orcid.org/0000-0003-4225-8205

Erwin Lam – Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland

Gina Noh – Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093 Zurich, Switzerland; orcid.org/0000-0003-4717-5767

Olga V. Safonova – Paul Scherrer Institute, CH-5232 Villigen, Switzerland; orcid.org/0000-0002-6772-1414

Atsushi Urakawa – Catalysis Engineering, Department of Chemical Engineering, Delft University of Technology, 2629 HZ Delft, The Netherlands; orcid.org/0000-0001-7778-4008

Complete contact information is available at: <https://pubs.acs.org/10.1021/jacsau.1c00021>

Author Contributions

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

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

S.D., N.P., O.V.S., A.U., and C.C.H. thank the Swiss National Science Foundation (Grant Nos. 200021_169134 and CRSII5_183495) for funding. Part of this research was also funded by the SCCER Heat and Energy Storage program (InnoSuisse). The authors acknowledge J. Alfke, C. P. Gordon, and D. Trummer for assistance with XAS, SS-NMR, and X-ray crystallography, respectively. The authors thank L. Rochlitz and Dr X. Huang for recording TEM carried out at ScopeM. The authors also thank PSI SuperXAS for beamtime and provision of Ga⁰ and Pd⁰ reference materials.

REFERENCES

- (1) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazábal, G. O.; Pérez-Ramírez, J. Status and Perspectives of CO₂ Conversion into Fuels and Chemicals by Catalytic, Photocatalytic and Electrocatalytic Processes. *Energy Environ. Sci.* **2013**, *6* (11), 3112–3135.
- (2) Goepfert, A.; Czaun, M.; Jones, J.-P.; Surya Prakash, G. K.; Olah, G. A. Recycling of Carbon Dioxide to Methanol and Derived Products – Closing the Loop. *Chem. Soc. Rev.* **2014**, *43* (23), 7995–8048.
- (3) Olah, G. A. Towards Oil Independence Through Renewable Methanol Chemistry. *Angew. Chem., Int. Ed.* **2013**, *52* (1), 104–107.
- (4) Álvarez, A.; Bansode, A.; Urakawa, A.; Bavykina, A. V.; Wezendonk, T. A.; Makkee, M.; Gascon, J.; Kapteijn, F. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO₂ Hydrogenation Processes. *Chem. Rev.* **2017**, *117* (14), 9804–9838.
- (5) Jiang, X.; Nie, X.; Guo, X.; Song, C.; Chen, J. G. Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. *Chem. Rev.* **2020**, *120* (15), 7984–8034.
- (6) Kasatkin, I.; Kurr, P.; Kniep, B.; Trunschke, A.; Schlögl, R. Role of Lattice Strain and Defects in Copper Particles on the Activity of Cu/ZnO/Al₂O₃ Catalysts for Methanol Synthesis. *Angew. Chem., Int. Ed.* **2007**, *46* (38), 7324–7327.
- (7) Chinchén, G. C.; Denny, P. J.; Jennings, J. R.; Spencer, M. S.; Waugh, K. C. Synthesis of Methanol: Part 1. Catalysts and Kinetics. *Appl. Catal.* **1988**, *36*, 1–65.
- (8) Bart, J. C. J.; Sneed, R. P. A. Copper-Zinc Oxide-Alumina Methanol Catalysts Revisited. *Catal. Today* **1987**, *2* (1), 1–124.
- (9) Schild, C.; Wokaun, A.; Baiker, A. On the Hydrogenation of CO and CO₂ over Copper/Zirconia and Palladium/Zirconia Catalysts. *Fresenius' J. Anal. Chem.* **1991**, *341* (5), 395–401.
- (10) Fisher, I. A.; Woo, H. C.; Bell, A. T. Effects of Zirconia Promotion on the Activity of Cu/SiO₂ for Methanol Synthesis from CO/H₂ and CO₂/H₂. *Catal. Lett.* **1997**, *44* (1), 11–17.
- (11) Larmier, K.; Liao, W.-C.; Tada, S.; Lam, E.; Verel, R.; Bansode, A.; Urakawa, A.; Comas-Vives, A.; Copéret, C. CO₂-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal-Support Interface. *Angew. Chem., Int. Ed.* **2017**, *56* (9), 2318–2323.
- (12) Sahibzada, M.; Metcalfe, I. S.; Chadwick, D. Methanol Synthesis from CO/CO₂/H₂ over Cu/ZnO/Al₂O₃ at Differential and Finite Conversions. *J. Catal.* **1998**, *174* (2), 111–118.
- (13) Collins, S. E.; Baltanás, M. A.; Bonivardi, A. L. An Infrared Study of the Intermediates of Methanol Synthesis from Carbon Dioxide over Pd/ β -Ga₂O₃. *J. Catal.* **2004**, *226*, 410.
- (14) Collins, S. E.; Delgado, J. J.; Mira, C.; Calvino, J. J.; Bernal, S.; Chiavassa, D. L.; Baltanás, M. A.; Bonivardi, A. L. The Role of Pd–Ga Bimetallic Particles in the Bifunctional Mechanism of Selective Methanol Synthesis via CO₂ Hydrogenation on a Pd/Ga₂O₃ Catalyst. *J. Catal.* **2012**, *292*, 90–98.
- (15) Arana, J.; Homs, N.; Sales, J.; Fierro, J.L.G.; Ramirez de la Piscina, P. CO/CO₂ Hydrogenation and Ethylene Hydroformylation over Silica-Supported PdZn Catalysts. *Catal. Lett.* **2001**, *72* (3), 183–189.
- (16) Ota, A.; Kunkes, E. L.; Kasatkin, I.; Groppo, E.; Ferri, D.; Poceiro, B.; Navarro Yerga, R. M.; Behrens, M. Comparative Study of Hydrotalcite-Derived Supported Pd₂Ga and PdZn Intermetallic Nanoparticles as Methanol Synthesis and Methanol Steam Reforming Catalysts. *J. Catal.* **2012**, *293*, 27–38.
- (17) Fiordaliso, E. M.; Sharafutdinov, I.; Carvalho, H. W. P.; Grunwaldt, J.-D.; Hansen, T. W.; Chorkendorff, I.; Wagner, J. B.; Damsgaard, C. D. Intermetallic GaPd₂ Nanoparticles on SiO₂ for Low-Pressure CO₂ Hydrogenation to Methanol: Catalytic Performance and In Situ Characterization. *ACS Catal.* **2015**, *5* (10), 5827–5836.
- (18) Bowker, M. Methanol Synthesis from CO₂ Hydrogenation. *ChemCatChem* **2019**, *11* (17), 4238–4246.
- (19) Manrique, R.; Rodríguez-Pereira, J.; Rincón-Ortiz, S. A.; Bravo-Suárez, J. J.; Baldovino-Medrano, V. G.; Jiménez, R.; Karelavic, A. The Nature of the Active Sites of Pd–Ga Catalysts in the Hydrogenation of CO₂ to Methanol. *Catal. Sci. Technol.* **2020**, *10* (19), 6644–6658.
- (20) Manrique, R.; Jiménez, R.; Rodríguez-Pereira, J.; Baldovino-Medrano, V. G.; Karelavic, A. Insights into the Role of Zn and Ga in the Hydrogenation of CO₂ to Methanol over Pd. *Int. J. Hydrogen Energy* **2019**, *44* (31), 16526–16536.
- (21) Fujitani, T.; Saito, M.; Kanai, Y.; Watanabe, T.; Nakamura, J.; Uchijima, T. Development of an Active Ga₂O₃ Supported Palladium Catalyst for the Synthesis of Methanol from Carbon Dioxide and Hydrogen. *Appl. Catal., A* **1995**, *125* (2), L199–L202.
- (22) Oyola-Rivera, O.; Baltanás, M. A.; Cardona-Martínez, N. CO₂ Hydrogenation to Methanol and Dimethyl Ether by Pd–Pd₂Ga Catalysts Supported over Ga₂O₃ Polymorphs. *J. CO₂ Util.* **2015**, *9*, 8–15.
- (23) García-Trenco, A.; White, E. R.; Regoutz, A.; Payne, D. J.; Shaffer, M. S. P.; Williams, C. K. Pd₂Ga-Based Colloids as Highly Active Catalysts for the Hydrogenation of CO₂ to Methanol. *ACS Catal.* **2017**, *7* (2), 1186–1196.
- (24) Lam, E.; Larmier, K.; Wolf, P.; Tada, S.; Safonova, O. V.; Copéret, C. Isolated Zr Surface Sites on Silica Promote Hydrogenation of CO₂ to CH₃OH in Supported Cu Catalysts. *J. Am. Chem. Soc.* **2018**, *140* (33), 10530–10535.

- (25) Noh, G.; Docherty, S. R.; Lam, E.; Huang, X.; Mance, D.; Alfke, J. L.; Copéret, C. CO₂ Hydrogenation to CH₃OH on Supported Cu Nanoparticles: Nature and Role of Ti in Bulk Oxides vs Isolated Surface Sites. *J. Phys. Chem. C* **2019**, *123* (51), 31082–31093.
- (26) Noh, G.; Lam, E.; Alfke, J. L.; Larmier, K.; Searles, K.; Wolf, P.; Copéret, C. Selective Hydrogenation of CO₂ to CH₃OH on Supported Cu Nanoparticles Promoted by Isolated Ti^{IV} Surface Sites on SiO₂. *ChemSusChem* **2019**, *12* (5), 968–972.
- (27) Lam, E.; Noh, G.; Chan, K. W.; Larmier, K.; Lebedev, D.; Searles, K.; Wolf, P.; Safonova, O. V.; Copéret, C. Enhanced CH₃OH Selectivity in CO₂ Hydrogenation Using Cu-Based Catalysts Generated via SOMC from Ga^{III} Single-Sites. *Chem. Sci.* **2020**, *11*, 7593–7598.
- (28) Copéret, C. Single-Sites and Nanoparticles at Tailored Interfaces Prepared via Surface Organometallic Chemistry from Thermolytic Molecular Precursors. *Acc. Chem. Res.* **2019**, *52* (6), 1697–1708.
- (29) Searles, K.; Siddiqi, G.; Safonova, O. V.; Copéret, C. Silica-Supported Isolated Gallium Sites as Highly Active, Selective and Stable Propane Dehydrogenation Catalysts. *Chem. Sci.* **2017**, *8* (4), 2661–2666.
- (30) Zhao, B.; Pan, Y.; Liu, C. The Promotion Effect of CeO₂ on CO₂ Adsorption and Hydrogenation over Ga₂O₃. *Catal. Today* **2012**, *194* (1), 60–64.
- (31) Laurent, P.; Veyre, L.; Thieuleux, C.; Donet, S.; Copéret, C. From Well-Defined Pt(II) Surface Species to the Controlled Growth of Silica Supported Pt Nanoparticles. *Dalt. Trans.* **2013**, *42* (1), 238–248.
- (32) Tew, M. W.; Miller, J. T.; van Bokhoven, J. A. Particle Size Effect of Hydride Formation and Surface Hydrogen Adsorption of Nanosized Palladium Catalysts: L₃ Edge vs K Edge X-Ray Absorption Spectroscopy. *J. Phys. Chem. C* **2009**, *113* (34), 15140–15147.
- (33) Sheppard, N.; De La Cruz, C. The Reliability of Vibrational Spectroscopy as a Means of Identification of the Structures of Chemisorbed Species on Metal Surfaces: The Cases of CO, NO and C₂ Hydrocarbon Surface Species. *Catal. Today* **2001**, *70* (1–3), 3–13.
- (34) Kovnir, K.; Armbrüster, M.; Teschner, D.; Venkov, T. V.; Szentmiklósi, L.; Jentoft, F. C.; Knop-Gericke, A.; Grin, Y.; Schlögl, R. In Situ Surface Characterization of the Intermetallic Compound PdGa – A Highly Selective Hydrogenation Catalyst. *Surf. Sci.* **2009**, *603* (10), 1784–1792.
- (35) Su, X.; Lin, W.; Cheng, H.; Zhang, C.; Li, Y.; Liu, T.; Zhang, B.; Wu, Q.; Yu, X.; Zhao, F. PdGa/TiO₂ an Efficient Heterogeneous Catalyst for Direct Methylation of N-Methylaniline with CO₂/H₂. *RSC Adv.* **2016**, *6* (105), 103650–103656.
- (36) Nishi, K.; Shimizu, K.; Takamatsu, M.; Yoshida, H.; Satsuma, A.; Tanaka, T.; Yoshida, S.; Hattori, T. Deconvolution Analysis of Ga K-Edge XANES for Quantification of Gallium Coordinations in Oxide Environments. *J. Phys. Chem. B* **1998**, *102* (50), 10190–10195.
- (37) Sun, Q.; Chen, B. W. J.; Wang, N.; He, Q.; Chang, A.; Yang, C.-M.; Asakura, H.; Tanaka, T.; Hülsey, M. J.; Wang, C.-H.; Yu, J.; Yan, N. Zeolite-Encaged Pd–Mn Nanocatalysts for CO₂ Hydrogenation and Formic Acid Dehydrogenation. *Angew. Chem., Int. Ed.* **2020**, *59* (45), 20183–20191.
- (38) Corral-Pérez, J. J.; Bansode, A.; Praveen, C. S.; Kokalj, A.; Reymond, H.; Comas-Vives, A.; VandeVondele, J.; Copéret, C.; von Rohr, P. R.; Urakawa, A. Decisive Role of Perimeter Sites in Silica-Supported Ag Nanoparticles in Selective Hydrogenation of CO₂ to Methyl Formate in the Presence of Methanol. *J. Am. Chem. Soc.* **2018**, *140* (42), 13884–13891.
- (39) Copéret, C.; Lam, E.; Corral-Pérez, J. J.; Larmier, K.; Noh, G.; Wolf, P.; Comas-Vives, A.; Urakawa, A. CO₂ Hydrogenation on Cu/Al₂O₃: Role of Metal/Support Interface in Driving Activity and Selectivity of a Bifunctional Catalyst. *Angew. Chem., Int. Ed.* **2019**, *58* (39), 13989–13996.
- (40) Drew, D.; Doyle, J. R.; Shaver, A. G. Cyclic Diolefin Complexes of Platinum and Palladium. In *Inorganic Syntheses*; John Wiley & Sons, Ltd, 2007; pp 47–55. DOI: 10.1002/9780470132449.ch11.
- (41) Sandoval, J. J.; Palma, P.; Álvarez, E.; Cámpora, J.; Rodríguez-Delgado, A. Mechanism of Alkyl Migration in Diorganomagnesium 2,6-Bis(Imino)Pyridine Complexes: Formation of Grignard-Type Complexes with Square-Planar Mg(II) Centers. *Organometallics* **2016**, *35* (18), 3197–3204.
- (42) Docherty, S. R.; Estes, D. P.; Copéret, C. Facile Synthesis of Unsymmetrical Trialkoxysilanol: (RO)₂(R'O)SiOH. *Helv. Chim. Acta* **2018**, *101* (3), e1700298 DOI: 10.1002/hlca.201700298.
- (43) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercauw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179.
- (44) Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The Anatomy of a Comprehensive Constrained, Restrained Refinement Program for the Modern Computing Environment - Olex2 Dissected. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, *71* (1), 59–75.
- (45) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *71* (1), 3–8.
- (46) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: Data Analysis for X-Ray Absorption Spectroscopy Using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12* (4), 537–541.