

Reactivity Switch of Platinum with Gallium: From Reverse Water Gas Shift to Methanol Synthesis

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Cite This: *J. Am. Chem. Soc.* 2024, 146, 10806–10811



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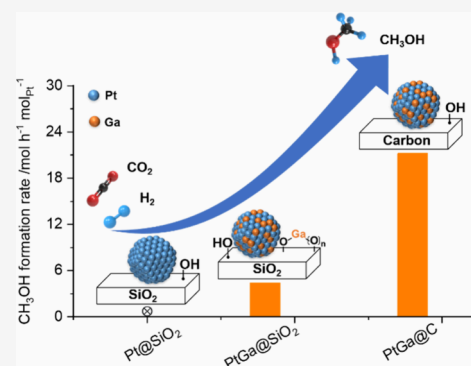


Article Recommendations



Supporting Information

ABSTRACT: The development of efficient catalysts for the hydrogenation of CO₂ to methanol using “green” H₂ is foreseen to be a key step to close the carbon cycle. In this study, we show that small and narrowly distributed alloyed PtGa nanoparticles supported on silica, prepared via a surface organometallic chemistry (SOMC) approach, display notable activity for the hydrogenation of CO₂ to methanol, reaching a 7.2 mol_{CH₃OH} h^{−1} mol_{Pt}^{−1} methanol formation rate with a 54% intrinsic CH₃OH selectivity. This reactivity sharply contrasts with what is expected for Pt, which favors the reverse water gas shift reaction, albeit with poor activity (2.6 mol_{CO₂} h^{−1} mol_{Pt}^{−1}). *In situ* XAS studies indicate that ca. 50% of Ga is reduced to Ga⁰ yielding alloyed PtGa nanoparticles, while the remaining 50% persist as isolated Ga^{III} sites. The PtGa catalyst slightly dealloys under CO₂ hydrogenation conditions and displays redox dynamics with PtGa–GaO_x interfaces responsible for promoting both the CO₂ hydrogenation activity and methanol selectivity. Further tailoring the catalyst interface by using a carbon support in place of silica enables to improve the methanol formation rate by a factor of ~5.



INTRODUCTION

CO₂ hydrogenation to methanol using “green” H₂ offers an attractive route to mitigate CO₂ emissions and store excess electricity obtained from intermittent renewable energy.^{1–3} Extensive efforts have focused on using Cu-based catalysts to convert CO₂ to methanol, since similar catalysts are already commercially implemented in established syngas (CO/H₂)-to-methanol processes.^{4–8} However, when CO₂ is used in place of CO as a C₁ feedstock, the Cu-based catalysts suffer from limited activity, methanol selectivity, and rapid deactivation as a consequence of the additional water produced.⁹ Thus, alternative catalysts have been investigated to address these challenges, by changing the active metal, e.g., from Cu to Ni or Pd for instance,^{10–14} or through including various promoters such as Zn, Ga and In.^{15,16}

In that context, recent reports on Ga-promoted systems have enabled to clarify some structure-performance relationships using tailored materials prepared via Surface Organometallic Chemistry (SOMC).^{17,18} Detailed operando spectroscopic investigations on a series of well-defined Ga-promoted catalysts (M = Cu, Ni, and Pd) supported on silica (CuGa@SiO₂,¹⁹ PdGa@SiO₂,²⁰ and NiGa@SiO₂)²¹ indicate that all systems consist of alloyed MGA nanoparticles under reductive conditions (H₂) and undergo significant dealloying for M = Cu and Pd under CO₂ hydrogenation conditions, generating an interface between metallic Cu or Pd and GaO_x, which is critical for high methanol selectivity.^{19,20} For M = Ni, the system mostly remains alloyed under the same CO₂ hydrogenation conditions, enabling the suppression of the methanation reaction, which is the favored pathway on the

pure Ni catalyst under the same conditions. Nonetheless, the presence of a small fraction of GaO_x at the interface with the NiGa alloy remains key for methanol selectivity.²¹ Overall, both alloying and dealloying, as well as the formation of GaO_x interfaces in dynamic redox processes, likely play an essential role in driving activity and methanol selectivity in these catalytic systems.

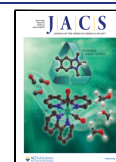
Considering the dramatic change in reactivity of Ni and Pd in the presence of Ga and the role of the interface and dynamic redox processes, we became intrigued to understand how Ga and the support would influence the properties of Pt, a metal well-known to catalyze the reverse water gas shift reaction.^{22,23} Notably, there is only one example of Pt-catalyzed CO₂ hydrogenation to methanol in batch reactor using 1,4-dioxane as a solvent and Mo as a dopant.²⁴ In this work, we develop silica-supported PtGa nanoparticles using SOMC and show that this material catalyzes the selective hydrogenation of CO₂ to methanol and that the PtGa–GaO_x interface plays a vital role in stabilizing key intermediates like formate and methoxy species and promoting methanol formation. We also found that switching the support from silica to carbon enhances the methanol formation rate, further testifying the importance of

Received: January 24, 2024

Revised: March 6, 2024

Accepted: March 19, 2024

Published: April 4, 2024



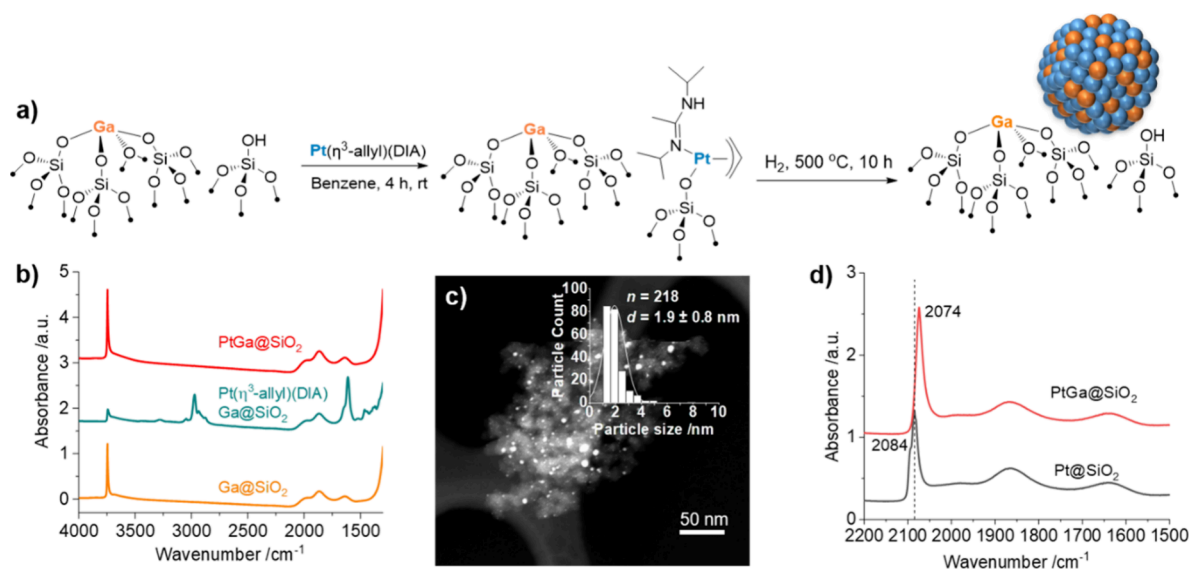


Figure 1. (a) Schematic procedure for grafting of a Pt(η^3 -allyl)(DIA) molecular precursor on Ga^{III}@SiO₂ followed by reduction under H₂ at 500 °C. (b) FTIR spectra throughout the synthesis of PtGa@SiO₂ starting from Ga^{III}@SiO₂. (c) STEM image and particle size distribution of PtGa@SiO₂. (d) FTIR spectra of CO adsorbed on Pt@SiO₂ and PtGa@SiO₂ under 5 mbar of CO at room temperature.

surface and interfaces in controlling the reactivity of supported metal nanoparticles.

RESULTS AND DISCUSSION

We started by preparing silica-supported PtGa nanoparticles (PtGa@SiO₂) via SOMC. An analogous system was developed earlier in the context of propane dehydrogenation.²⁵ Here, we selected Pt allyl-(*N,N'*-diisopropyl)acetamidinate, Pt(η^3 -allyl)(DIA), a siloxide-free molecular precursor, in order to avoid the formation of additional interfaces from the decomposition of the organic ligands.²⁶ The synthesis consists of a two-step process, involving grafting of the molecular Pt precursor on silica decorated with isolated Ga^{III} sites (Ga^{III}@SiO₂, 1.83 wt % corresponding to ca. 0.8 Ga^{III} nm⁻²) (Figure S1),²⁷ followed by a treatment under H₂ to generate supported nanoparticles (Figure 1a). We monitored the preparation process via Fourier transform infrared (FTIR) spectroscopy. Upon grafting Pt(η^3 -allyl)(DIA) on Ga^{III}@SiO₂, the IR band at 3747 cm⁻¹ associated with Si–OH almost disappears (Figure 1b), while new bands appear at ca. 3250 cm⁻¹ (N–H stretching), 3100–2700 cm⁻¹ (C–H stretching), 1700–1600 cm⁻¹ (C=N), and 1500–1300 cm⁻¹ (C–H bending stretching), consistent with grafting via protonation. After reduction under H₂ at 500 °C, the resulting black solid displays only the characteristic Si–OH group in the IR spectrum, with no remaining organic residues. The corresponding monometallic Pt@SiO₂ catalyst was prepared analogously using the same precursor, but a silica support, partially dehydroxylated at 700 °C (SiO₂₋₇₀₀), in place of Ga^{III}@SiO₂ (Figure S2).

Elemental analysis shows that Pt loadings for both materials are similar, in the range of 4.2–4.5 wt %, with Pt/Ga ratio of ca. 1:1 for PtGa@SiO₂ (Table S1). High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images show that the supported nanoparticles on both materials are also similar to a narrow particle size distribution of an average size of ca. 1.9 nm (Figure 1c and Figure S3). Energy-dispersive X-ray (EDX) spectroscopy elemental mapping of PtGa@SiO₂ shows that the profile of Ga overlaps to a great extent with that of Pt, suggesting the

formation of alloyed PtGa nanoparticles after H₂ reduction (Figure S4). This is in line with CO-adsorption IR experiments, which show red-shifted linearly adsorbed CO IR bands by ca. 10 cm⁻¹ for PtGa@SiO₂ vs Pt@SiO₂, further confirming alloying (Figure 1d).^{28,29}

The as-prepared bimetallic PtGa@SiO₂ and monometallic Pt@SiO₂ materials were next evaluated for CO₂ hydrogenation at 230 °C at 25 bar (H₂/CO₂/Ar = 3:1:1). Following controlled exposure to air, the catalysts were reduced at 300 °C under H₂ prior to CO₂ hydrogenation. The effect of the gas flow rate was also studied to obtain kinetic information related to product formation. Under the aforementioned reaction conditions, PtGa@SiO₂ shows a total CO₂ hydrogenation activity reaching 13.5 mol_{CO2} h⁻¹ mol_{Pt}⁻¹, which is around 5 times higher than that for Pt@SiO₂ (2.6 mol_{CO2} h⁻¹ mol_{Pt}⁻¹), while Ga^{III}@SiO₂ is inactive under the same conditions (Figure 2a). More strikingly, the Ga-promoted catalyst displays an unexpectedly high activity toward methanol formation alone (7.2 mol_{CH3OH} h⁻¹ mol_{Pt}⁻¹), with a ca. 50% methanol selectivity, which steadily decreases with increasing CO₂ conversion, the other product being mostly CO as well as a small amount of DME, likely produced from the dehydration of CH₃OH on Ga^{III}@SiO₂ sites (Figure 2b and Figure S6).^{19,20} The PtGa@SiO₂ catalyst performance sharply contrasts with what is observed for the monometallic Pt@SiO₂ catalyst, which does not show any methanol but produces CO (≈67%) along with methane (≈33%) (Figure S5). Overall, these results show that the synergy between Pt and Ga promotes the CO₂ hydrogenation activity and methanol formation.

We next investigated the change of catalyst structure under different conditions (air exposed, reduced under H₂ and post CO₂ hydrogenation) using *in situ* X-ray absorption spectroscopy (XAS) experiments. The evolution of the catalyst structure was first analyzed by Pt L₃-edge spectra (Figure 3). The corresponding best-fitting details are presented in Figures S7–S12 and summarized in Table S2. The Pt L₃-edge X-ray absorption near-edge structure (XANES) spectrum of air-exposed PtGa@SiO₂ is similar to that of the Pt foil. The extended X-ray absorption fine structure (EXAFS) spectrum

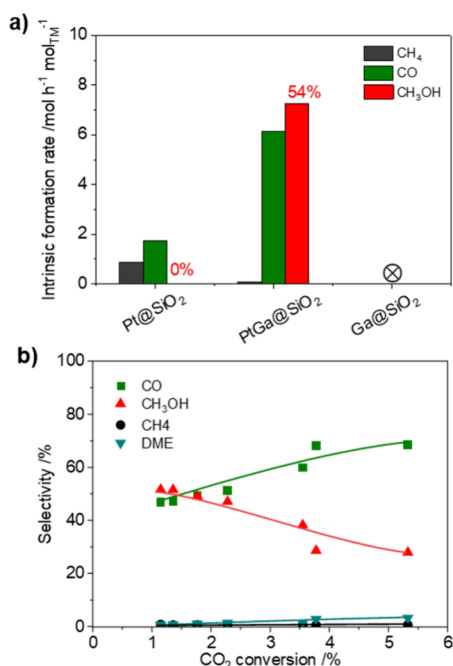


Figure 2. (a) Intrinsic formation rates for different catalysts. (b) Product selectivities vs CO₂ conversion for PtGa@SiO₂. Reaction conditions: $W_{\text{cat}} = 200$ mg, $F = 6\text{--}100$ mL/min, $T = 230$ °C, $P = 25$ bar.

was modeled by using the Pt–Pt scattering path, revealing an average coordination number (CN) of 8.3 for Pt–Pt (Figure S10 and Table S2). After H₂ reduction, Pt L₃-edge XANES indicates a small shift of the edge energy to higher energy along with an increase in the white line intensity (Figure 3a). Meanwhile, the intensity of the first peak at ca. 2.1 Å in R space

became more intense with respect to the second peak at ca. 2.7 Å (Figure 3b), which can be attributed to the interaction between Ga and Pt, consistent with alloying of the two metals.^{30,31} EXAFS fitting reveals the presence of a Pt–Pt scattering path ($\text{CN}_{\text{Pt-Pt}} = 6.1$), as well as a low-degeneracy Pt–Ga path ($\text{CN}_{\text{Pt-Ga}} = 2.0$). In sharp contrast, the XANES spectra of monometallic Pt@SiO₂ closely resemble the spectrum of the Pt foil and are all similar under different conditions (Figure 3c,d). The fitting results reveal an average CN of Pt–Pt of around 10 (Table S2), which is smaller than that for bulk platinum ($\text{CN} = 12$). This is consistent with the presence of small Pt nanoparticles with an expected lower average CN, in line with the observations from STEM measurements.³² After exposure to CO₂ hydrogenation conditions, the XANES spectra and the CN of Pt–Ga remain quite similar compared to the spectrum of the H₂ reduced catalyst (Figure 3a,b), revealing that the PtGa alloy in PtGa@SiO₂ is mostly preserved after reaction, aligning with what is observed for the NiGa system.²¹

We further collected Ga K-edge XANES spectra under identical conditions to gain more insights into the interplay between Pt and Ga in the bimetallic PtGa@SiO₂ system (Figures S13 and S14). The findings show that the Ga K-edge spectrum of the air-exposed PtGa@SiO₂ is similar to that of the Ga₂O₃ reference. Upon H₂ reduction, the edge energy shifts to lower energy along with a significant decrease in the white line intensity, indicating a partial reduction of Ga^{III} into Ga⁰, which is incorporated into PtGa nanoparticles (*vide supra*). Linear combination fitting (LCF) analysis shows that ca. half of Ga is reduced and incorporated into alloyed PtGa nanoparticles, resulting in an average Pt/Ga⁰ ratio of 1.8:1 (Figure S15 and Table S3), while the remaining Ga (50%) is likely in the state of Ga^{III}@SiO₂.

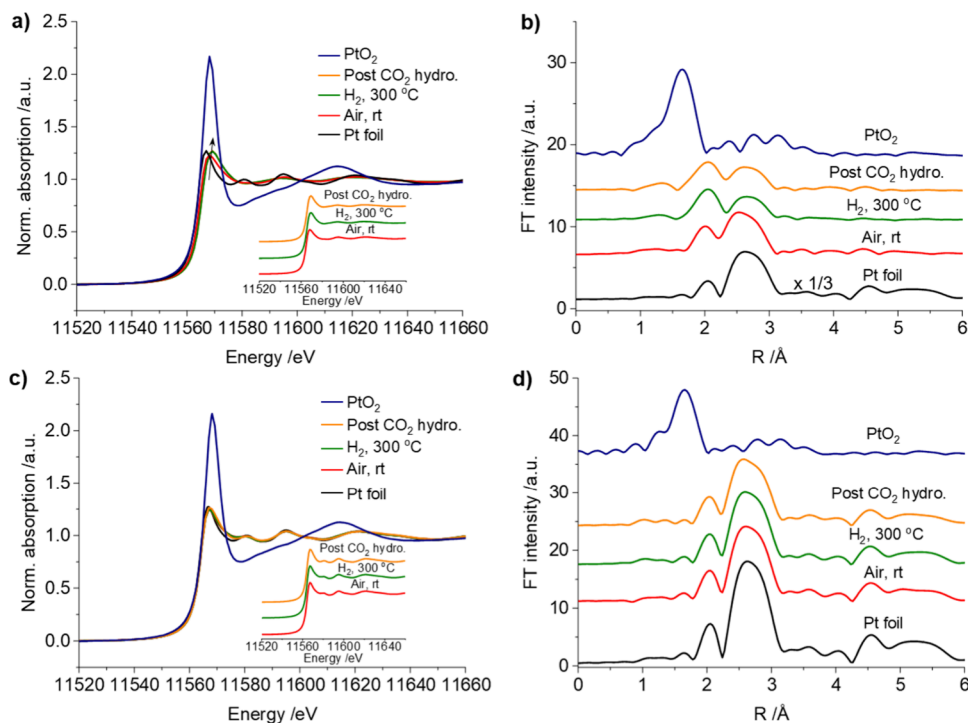


Figure 3. XANES spectra and corresponding k^3 -weighted Fourier transforms of EXAFS spectra of at Pt L₃-edge under different conditions (air exposed, H₂ reduced and post CO₂ hydrogenation): (a) and (b) for PtGa@SiO₂, (c) and (d) for Pt@SiO₂.

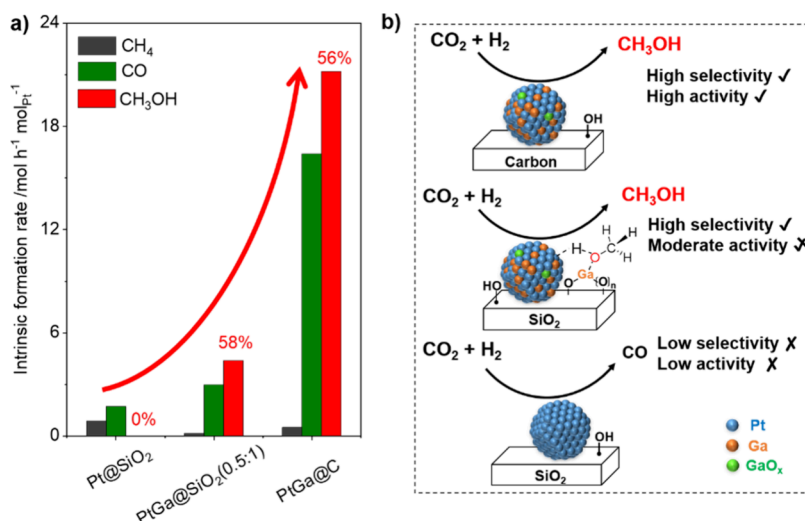


Figure 4. (a) Intrinsic formation rates for different catalysts. Reaction conditions: $W_{\text{cat}} = 180\text{--}200$ mg, $F = 6\text{--}100$ mL/min, $T = 230$ °C, $P = 25$ bar. (b) Scheme summarizing the CO₂ hydrogenation outcome over Pt@SiO₂, PtGa@SiO₂, and PtGa@C catalysts based on the different interfaces.

In addition, both Pt L₃-edge and Ga K-edge *in situ* XANES spectra of PtGa@SiO₂ catalysts were recorded under CO₂ hydrogenation conditions at 230 °C and 20 bar of gas mixture (H₂/CO₂/Ar = 3:1:1), in order to investigate more subtle variations. The spectra before and after 2 h of reaction are shown in Figure S16. Under *in situ* conditions, the edge position at the Ga K-edge slightly shifts to higher energy along with a slight increase in white line intensity, indicating that Ga is slightly oxidized in the course of the reaction to GaO_x species. On the other hand, there are no significant changes in the spectra at the Pt L₃-edge, indicating that the Pt within the PtGa nanoparticles remains metallic. The combined information indicates that the alloyed PtGa nanoparticles slightly dealloy under CO₂ hydrogenation conditions to form a PtGa–GaO_x interface. This is consistent with previous reports on Ga-promoted catalysts such as for silica supported CuGa, PdGa, and NiGa, where redox dynamics involving M(MGa)–GaO_x interfaces play a pivotal role in promoting activity and methanol formation.^{19–21} We thus propose that the redox dynamic at the PtGa–GaO_x interface likely lies at the origin of the promotional effect of Ga in CO₂ hydrogenation toward methanol also in the case of PtGa.

Furthermore, *in situ* DRIFTS were performed to observe possible key intermediates over PtGa@SiO₂ and Pt@SiO₂ during CO₂ hydrogenation at 20 bar. Upon switching to the H₂/CO₂/Ar (1:3:1) gas mixture, two CO IR bands appear over the PtGa@SiO₂ catalyst at ca. 2074 and 2047 cm⁻¹, and their intensity gradually increases with time on stream (Figure S17). These two bands indicate the presence of two types of Pt sites, likely associated with adsorbed CO* on PtGa and PtGa–GaO_x interfaces, which are in line with the *in situ* XAS data. After ca. 4 min, new bands appear, whose intensity gradually increases with time on stream: the two bands at 2940 and 2840 cm⁻¹ correspond to formate, while these at 2956 and 2856 cm⁻¹ are associated with methoxy species.^{33,34} In addition, gaseous CO (2170 cm⁻¹) starts to emerge at about 9 min. Note that in sharp contrast only adsorbed CO* and gaseous CO are observed over Pt@SiO₂. Considering the aforementioned *in situ* XAS results and the literature precedents on Cu-, Ni-, and Pd-based CO₂ hydrogenation catalysts, these findings point to the role of the PtGa–GaO_x interface in

stabilizing formate and methoxy intermediates, and promoting methanol formation under CO₂ hydrogenation.^{19–21}

We next examined the influence of the support on the catalytic performance of the PtGa system. Considering that carbon is a more neutral support and less prompt to interfere with the dynamic at the PtGa–GaO_x interface than silica, we thus prepared carbon-supported PtGa nanoparticles (PtGa@C) via SOMC.³⁵ For this, a mesoporous carbon was first treated in refluxing nitric acid to introduce oxygen functional groups (R–OH),³⁶ followed by sequential grafting of two siloxide-free precursors Ga(Mesityl)₃ and Pt(η³-allyl)(DIA) to avoid the introduction of an additional oxide interface (Figure S18). Finally, treatment under H₂ resulted in the formation of narrowly distributed PtGa nanoparticles supported on carbon with an average size of 1.4 nm (Figure S23) and a Pt/Ga⁰ ratio of ca. 0.9:1 based on elemental analysis and EDX mapping, which is higher than that observed for PtGa@SiO₂ (Figure S26 and Table S4). While the average nanoparticle sizes in PtGa@SiO₂ and PtGa@C are similar, the Pt/Ga⁰ ratios within the nanoparticles are different. We thus also prepared PtGa@SiO₂ catalysts with varying Pt/Ga⁰ ratios, in order to enable a closer comparison (Figures S19–S27). The materials were denoted PtGa@SiO₂(x:1), where x:1 represents the nominal ratio of Pt/Ga. LCF analysis indicates that the Pt/Ga⁰ ratio within the alloyed PtGa nanoparticles in PtGa@SiO₂(0.5:1) are close to the Pt/Ga ratio of PtGa@C, while still displaying a similar average nanoparticle size of 1.7 nm. (Figure S28 and Table S4).

The as-prepared catalysts were then evaluated in CO₂ hydrogenation (Figures S29–S32 and Table S5). As shown in Figure 4a, PtGa@C displays a 21.2 mol_{CH₃OH} h⁻¹ mol_{Pt}⁻¹ intrinsic formation rate for CH₃OH with 56% CH₃OH selectivity, which outperforms most previously reported SOMC based catalysts (Figure S33 and Table S6). In particular, the intrinsic formation rate for CH₃OH on PtGa@C is ca. 5 times higher than that of PtGa@SiO₂(0.5:1) and the total activity is highest among all of the reported SOMC system so far (Figure S33). In addition, no DME is formed over a wide range of CO₂ conversion on the carbon-supported PtGa@C catalyst (Figure S31), sharply contrasting what is observed for all of the prepared PtGa@

SiO₂ catalysts, confirming that DME is formed on Ga^{III}@SiO₂ sites. Notably, the methanol intrinsic formation rate decreases with a lower Pt/Ga ratio in PtGa@SiO₂ catalysts, indicating that larger fractions of Ga inhibit the methanol formation (Figure S32). While XAS is not readily possible for PtGa@C catalysts due to the rather low metal loading, we performed CH₃OH temperature programmed desorption (CH₃OH-TPD) experiments in order to understand further the role of the presence of Lewis acidic Ga^{III} sites. Overall, no CH₃OH is adsorbed on the carbon support or PtGa@C, while two distinct desorption peaks at *m/z* = 31 are observed for Ga^{III}@SiO₂ as well as the silica-supported PtGa catalyst (Figure S34). The peak at a higher temperature can be assigned to the desorption of CH₃OH adsorbed on Lewis acidic Ga^{III}@SiO₂ by using SiO₂ as a reference, indicating that CH₃OH can be strongly adsorbed on Ga^{III}@SiO₂. These observations are consistent with the CO₂ hydrogenation results, where the presence of Ga^{III}@SiO₂ was found to suppress the formation rate of CH₃OH by obstructing the desorption of CH₃OH (Figure 4b)

CONCLUSIONS

To summarize, the silica-supported PtGa@SiO₂ hydrogenates CO₂ with a 13.2 mol_{CO₂} h⁻¹ mol_{Pt}⁻¹ total activity and a 54% intrinsic methanol selectivity, which greatly contrasts the poor CO₂ hydrogenation performance of monometallic Pt@SiO₂, yielding mostly CO and methane under the same reaction conditions. Detailed *in situ* XAS analysis indicates, that alloyed PtGa nanoparticles are formed after H₂ reduction, while 50% of Ga remains as Ga^{III}. Under CO₂ hydrogenation conditions, a small fraction of Ga is oxidized to generate PtGa–GaO_x interfaces, which are likely responsible for promoting CO₂ hydrogenation and methanol formation by stabilizing the formate and methoxy species, as evidenced by *in situ* DRIFTS. Altering the interface by replacing silica by a carbon-support further boosts the methanol formation rate by ca. 5, which is due at least in part to improving methanol desorption as a result of the absence of Lewis acidic Ga^{III} sites. This study shows that altering the surface and interface of metal nanoparticles like Pt by adding promoters and tuning the support can dramatically affect the properties of metal sites, thus opening new opportunities for tailoring efficient catalysts, such as in the case of CO₂ hydrogenation to CH₃OH, where redox dynamics are thought to play an important role.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c01144>.

Detailed experimental procedure, general considerations, microscopy data, spectroscopy data for all methods, and associated data (PDF)

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<https://pubs.acs.org/doi/10.1021/jacs.4c01144>

Funding

W.Z. and C.C. thank bp plc for financial support. This publication was created as part of NCCR Catalysis (grant number 180544), a National Center of Competence in Research funded by the Swiss National Science Foundation. C. E. acknowledges the Swiss National Science Foundation (grant 200020B_192050) and the Scholarship Fund of the Swiss Chemical Industry (SSCI)

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Dr. G. J. Sunley is thanked for scientific discussion. The authors acknowledge Dr. W. V. Beek and Dr. D. Stoian at the Swiss Norwegian Beamlines (SNBL, ESRF) for the provision of beamtime and support with *in situ* XAS experiments via proposal A31-1-197. The authors acknowledge N. Zimmerli for the assistance with CH₃OH-TPD and X. Zhou for the assistance with TEM. The authors acknowledge Dr. Y. Wang and C. Wang (Kunming University of Science and Technology) for the assistance with *in situ* DRIFTS. Furthermore, ScopeM is gratefully acknowledged for their support and assistance in this work through project Nos. 2460 and 2568.

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